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DENITRIFICATION: ITS IMPORTANCE IN A RIVER DRAINING AN INTENSIVELY CROPPED WATERSHED

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ABSTRACT

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Nitrogen transport was studied during summer low flows in a 20-km reach of the Nottawasaga River which drains an intensively cropped sand plain which has an underlying shallow water-table aquifer. Nitrogen inputs to the river were measured on 30 days in May to October of 1977—81. These data indicated that about 38% of the daily nitrate input entered the river through ground water. The magnitude of this input is a consequence of widespread contamination of the shallow aquifer by nitrogen fertilizer. Ground water entering the river from springs and seeps near fertilized fields frequently contained more than 10 mg l^{-1} of NO_3-N. Mass balance studies of nitrogen transport in the river revealed an average daily nitrate loss of 46 ± 23 kg N. This rate of nitrate removal represented about 40% of the ground water input to the river from the sand plain. Analysis of a mass balance for total Kjeldahl nitrogen revealed an essentially balanced budget, whereas chloride showed a small daily gain of about 5%. Laboratory experiments involving the incubation of stream sediment cores and the use of the acetylene block technique suggested that the bulk of the nitrate loss during river transport was caused by denitrification in bottom sediments.

INTRODUCTION

It is generally recognized that non-point agricultural sources can provide a significant contribution to nitrogen levels in ground and surface water. Many studies have revealed strong positive correlations between stream nitrate exports and a variety of land-use variables such as rates of fertilizer application and the percentage of the watershed area cultivated in row crops (Johnson et al., 1976; Commoner, 1977; Hill, 1978; Klepper, 1978; Correll and Dixon, 1980). Detailed studies of individual field plots and small watersheds indicate that subsurface waters underlying heavily fertilized land often contain high NO_3-N concentrations (Logan and Schwab, 1976; Miller, 1979; Baker and Johnson, 1981). In several cases large losses of nitrogen through leaching in subsurface flows contributed 80—90% of the soluble nitrogen exports in streams draining small agricultural watersheds (Jackson et al., 1973; Burwell et al., 1976).

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Despite the evidence that nitrogen from agricultural land may enter streams via surface runoff and subsurface flow, few researchers have examined the subsequent transport and transformation of nitrogen in rivers (Kaushik et al., 1981). Several field observations indicate the loss of considerable quantities of NO_3-N during transport in streams. During 1975 and 1976 about 250 and 450 kg N, respectively, were lost from a 2-km reach of a small spring-fed stream (Robinson et al., 1979). Subsequent laboratory investigations using labelled NO_3-N showed that most of the nitrate removal was caused by denitrification in stream sediments (Chatarpaul and Robinson, 1979; Chatarpaul et al., 1980).

The analysis of a mass balance for the downstream reaches of Duffin Creek, a moderately sized river near Toronto, Ontario, showed consistent losses of nitrate during summer low flows (Hill, 1979). Most of the average daily loss of 45 kg NO_3-N occurred in reaches receiving effluent from a sewage treatment plant. The bulk of the loss was attributed to denitrification, with uptake by benthic algae and nitrogen immobilization accounting for a small portion of the observed removal (Hill, 1981). Denitrification was also assumed to be responsible for the rapid removal of NO_3-N from drainage ditches in an irrigated watershed (Oosterveld and McMullin, 1979). These studies suggest that denitrification may act as an important mechanism for the permanent removal of nitrates in some surface water courses. However, further research is needed to verify the occurrence of denitrification in bottom sediments of streams draining agro-ecosystems, and to evaluate the significance of this process with respect to the removal of nitrates contributed by agriculture.

The purpose of this study is to determine the magnitude of nitrogen loss and the possibility of denitrification during stream transport in relation to the quantity of nitrogen entering a river from agriculture and other land uses. This research focuses on a portion of the Nottawasaga River which flows through one of the most heavily fertilized areas of crop land in Ontario, Canada.

Previous research has produced conflicting evidence regarding the effects of agriculture on stream nitrate levels in this region. Some preliminary observations in 1972 revealed considerable increases in stream NO_3-N concentrations of 5—10 mg l^{-1} adjacent to fertilized fields (Hill and McCague, 1974). However, subsequent research suggests that errors in analysis may account for some of these high concentrations. Further research in 1974 revealed high NO_3-N concentrations (10—34 mg l^{-1}) in ground water under fertilized fields, whereas measurements of nitrate concentration at stream sites showed little evidence of any significant contribution from fertilizers to nitrate levels in the Nottawasaga River (Hill and Wylie, 1977). Clearly, an evaluation of nitrogen inputs to streams requires the construction of a budget involving the measurement of water fluxes and cannot be based solely on the analysis of nutrient concentrations.

A mass balance approach has been used in this paper to quantify the nitrogen inputs to the river from agriculture and other types of land use, as well as to measure the amount of nitrogen lost during stream transport. A chloride mass balance was also examined because this element is a mobile anion similar to NO_3-N but not subject to removal by physical and biological processes during stream transport. This research concentrated mainly on the period of low stream flow during the warm season of the year from May to October. Nutrients have a longer stream residence time and are more likely to be influenced by biogeochemical processes during this period of the year. Research on nitrogen transport in Duffin Creek indicated that nitrate removal occurred primarily in the summer months (Hill, 1979).

METHODS AND MATERIALS

Description of study area

The upper Nottawasaga River basin has an area of 1230 km^2 and is located about 50 km north of Toronto (Fig. 1). Research was restricted to the Alliston sand plain area of the basin which is drained by the Nottawasaga River and its main tributaries, the Boyne River and Innisfil Creek (Fig. 2).

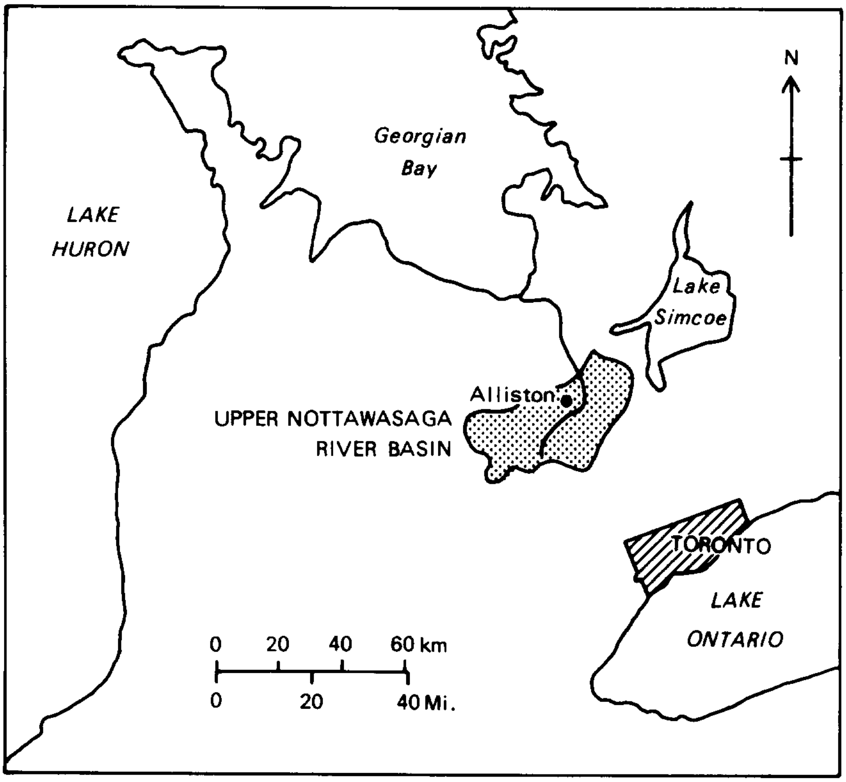

Fig. 1. Location of the upper Nottawasaga River basin.

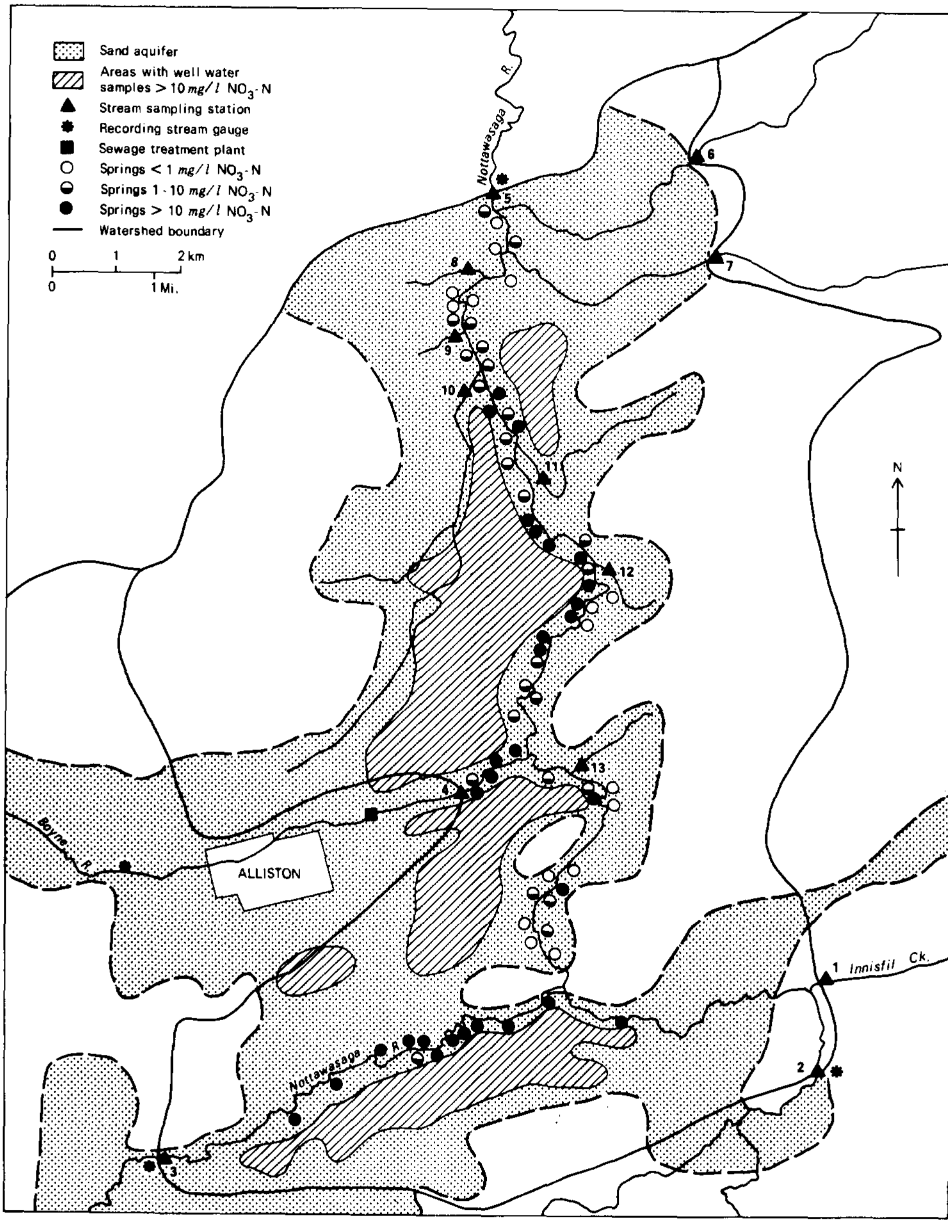

Fig. 2. Location of river sampling stations, recording stream gauges and ground water sampling sites in the Alliston and plain area.

About 45% of the study area is used for the commercial production of potatoes, in some cases under continuous cropping, but more often in an annual rotation with grains (barley, rye or mixed grain). Other crops include corn, soybeans, nursery turf and asparagus. Water pumped from the major rivers is used for sprinkler irrigation of potatoes and turf. Forest and scrub land occurs extensively in the northeast section of the sand plain and along the major river valleys. Potato crops usually receive 168—247 kg ha^{-1} of fertilizer nitrogen usually as ammonium nitrate. Applications of fertilizer for asparagus, corn and turf generally range between 100 and 336 kg N ha^{-1}. The only urban centre in the study area is Alliston, a town of approximately 4500 people served by a sewage treatment plant which discharges effluent into the Boyne River about 2 km upstream from Station 4. An analysis of effluent flow rate and nitrogen concentration data provided by the Ontario Ministry of Environment indicates that the average daily nitrate output from this plant is approximately 40 kg.

The soils of the area are well-drained sandy loams and loamy sands which lie on a thick sequence of fine- to medium-grained sands deposited in glacial Lake Algonquin (Sibul and Choo-Ying, 1971). The sand plain is an area of extremely flat topography, interrupted only by occasional drumlins and the valleys of the Nottawasaga River and its main tributaries, which are incised to a depth of 9—18 m below the plain.

The sand plain deposits form a shallow water-table aquifer, known as the Lake Algonquin Sand Aquifer, throughout the study area (Sibul and Choo-Ying, 1971). Well records and exposures in river valleys indicate that the permeable sand deposits are often greater than 15 m thick, and usually have underlying slowly permeable stratified silts. The depth of the water table usually varies between 3 and 6 m but increases to 12 m in areas adjacent to the Nottawasaga and Boyne Rivers. The ground water flow direction determined from measurements of the water table elevation is towards the major rivers (Hill, 1982). Numerous ground water seepage areas and springs occur in the river valleys at the junction of the sand deposits and the underlying silts. Commercial nitrogen fertilizer is a major source of nitrate in the aquifer and approximately 40% of the study area has underlying ground water with NO_3-N concentrations exceeding 10 mg l^{-1} (Hill, 1982). Three large zones of nitrate contamination are associated with the major potato growing areas of the sand plain (Fig. 2).

The Nottawasaga River is a hardwater stream which ranges in width from 10 to 25 m and has a mean annual discharge of 7.9×10^5 m^3 day^{-1} at Station 5. The river between Station 3 and the junction with Innisfil Creek consists of alternating riffles and pools. Gravel riffles are generally absent in other reaches and the river bed consists of unstable medium to coarse sand. Benthic algae occur on the gravel riffles between Station 3 and the junction with Innisfil Creek; elsewhere the river channels are largely devoid of benthic algae and macrophytes.

River inputs and exports

The construction of a nutrient mass balance for river reaches involves the measurement of a number of input and output vectors. During low flows the nutrient load of the river as it enters and leaves a particular reach constitutes the major input and output terms in the budget. In some river reaches additional inputs may be represented by tributary streams and ground water entering the main channel.

River discharge and element concentrations were measured at 13 sites in the Nottawasaga basin in the period 1977—81 (Fig. 2). Government streamflow recording gauges provided discharge records at a number of sampling stations. Current meter measurements coupled with cross-sectional areas were used to calculate discharge at times of stream water sampling for the remaining sites. The quantity of river water used for irrigation was estimated from water extraction permits submitted by individual landowners to the Ontario Ministry of Environment.

Ground water inputs

Seepage of ground water through bottom sediments occurs in the upper Nottawasaga River between Station 3 and the junction of Innisfil Creek and in the Boyne River downstream from Station 4. Elsewhere in the study area the Nottawasaga River is incised below the junction of the stratified silts and the permeable sand plain deposits. In these reaches ground water from numerous springs and seeps located at the base of the sands enters the river channel by overland flow from adjacent valley bluffs.

The quantity of ground water entering the major rivers was evaluated by several methods. Discharges from springs which flowed in well-defined channels were measured by current meter or in some cases by complete collection of flow in a bucket. This procedure provided an underestimate of ground water entering the river because flows through bottom sediments and from numerous diffuse valleyside seepage areas were not measured. A second approach employed data from six small streams (Stations 8—13) draining portions of the sand plain. These streams are sustained entirely by ground water during summer low flows and their discharge divided by drainage area provides an estimate of ground water flux per km^2. This estimate was then applied to those areas of the sand plain which drain directly to the Nottawasaga River and its major tributaries, Innisfil Creek and the Boyne River. The input derived using this procedure was about 30% smaller than the ground-water flux which can be calculated as the difference between daily inputs of water from major rivers plus the sand plain tributaries, and the export of water measured at Station 5 together with estimates of withdrawals for irrigation.

The concentrations of major nitrogen forms and chloride were measured in ground water entering the Nottawasaga River from 60 springs and seeps in June 1980 (Fig. 2). Four of these springs, adjacent to fertilized crops, were also sampled at intervals of 1—4 weeks throughout the 1977—82 period. Element concentrations in ground water entering the river through bottom sediments were analyzed at 15 sites in the summer of 1982. Samples were collected by inserting a mini-piezometer to depths of 0.4—0.5 m below the river bed (Lee and Hynes, 1978).

Water chemistry

Water samples were collected in acid-washed polyethylene bottles and were transported to the laboratory on ice. An automated cadmium reduction method was used to measure NO_3 + NO_2-N (APHA, 1976). Tests were also made separately for NO_2-N in the water samples. Since concentration of NO_2-N were very low, the NO_3 + NO_2-N value will henceforth be referred to as NO_3-N. Water samples were analyzed for NH_4-N using an automated indophenol blue method (Technicon, 1975). Total Kjeldahl nitrogen (TKN) was measured on unfiltered water samples (APHA, 1976) and values for organic nitrogen were obtained by subtracting NH_4 from the TKN values. Chloride was analyzed using an automated thiocyanate procedure (Environment Canada, 1979).

Sediment samples

A coring device was used to remove sediment samples (0—10 cm depth) at 10 sites on the Nottawasaga River and its major tributaries. Ammonium-N and NO_3 + NO_2-N were determined by extraction of moist sediment samples with 2M KCl followed by colorimetric analysis using the procedures outlined for water samples. Organic nitrogen in sediments was determined using a block digester followed by determination of the ammonia on the Auto-Analyzer (Issac and Johnson, 1976). Organic carbon was estimated by the Walkley—Black method (Allison, 1965). Sediment pH was measured with a glass electrode on a 1:2 soil and water mixture.

Laboratory systems

The role of sediments in nitrate removal from stream water was investigated in the laboratory. Intact cores of about 10 cm depth were removed from the river bed adjacent to the banks and also in mid-stream at 10 sites on the Nottawasaga River and its major tributaries. The sediment cores were covered with 500 ml of a solution containing 5 mg l^{-1} NO_3-N as KNO_3 and incubated in the laboratory at 20°C. Air bubbles were introduced close to the water—sediment interface to simulate the turbulence and aeration characteristics of river conditions. Nitrate concentrations in the solutions were analyzed at intervals over a period of 6 days. Loss of nitrate from solutions overlying sediment may result from both assimilatory reduction and dissimilatory reduction to ammonia as well as denitrification. In view of this possibility the acetylene block technique which inhibits reduction of N_2O to N_2 was used to provide a direct measure of denitrification activities (Balderston et al., 1976; Yoshinari and Knowles, 1976).

For denitrification assays, 30-g samples of field-moist sediment were added to 125 ml serum bottles and amended with 10 ml of solution containing 2 mg l^{-1} NO_3-N. These amounts of sediment and solution resulted in a 1 cm solution depth overlying a 1 cm sediment layer. The bottles were capped with septum stoppers and left air-filled. A portion of the air was removed by syringe and replaced with acetylene to bring the headspace concentration to 6% by volume. The bottles were incubated at room temperature for 48 h. Gas samples were withdrawn from the bottles and analyzed for N_2O by gas chromatography using a Varian 2740 equipped with a scandium tritide electron capture detector. Nitrous oxide was separated on a Porapak Q column (3.3 m $\times$ 0.25 cm). Temperatures in the injector port, oven and detector were 35, 90 and 240°C, respectively. The carrier gas (N_2) flow rate was 6 ml min^{-1}. Headspace concentrations of N_2O were corrected for N_2O dissolved in the aqueous phase.

Material mass balances

The data used to examine mass balances were collected at irregular time periods between May and October. Measurement of discharge and nutrient concentrations were restricted to periods of low stream flow characterized by discharge fluctuations of less than 10% in the 24—36 h prior to sample collection. The magnitude of diurnal variations in nitrate and chloride concentrations at major stream sampling stations was evaluated by sampling at 2-h intervals on two dates during low flow conditions. A small diurnal variation was observed at Station 4 on the Boyne River. Maximum nitrate and chloride concentrations at this station were about 20% higher than minimum daily values as a result of consistent diurnal fluctuations in the volume of effluent discharge from the upstream sewage treatment plant. In view of this consistent variation Station 4 was sampled at a time period each day when the effluent discharge reaching the station approximated the average daily flow from the treatment plant. The loss of nitrate and chloride calculated for Station 4 therefore provides a measure of the average daily flux at this location rather than maximum or minimum values which would distort the mass balance analysis. Significant diurnal variations in nutrient concentration were absent at the other major stream sampling stations and the analysis of daily fluxes was therefore based on a single sample at these locations.

A mass balance for water and NO_3-N was calculated for the Alliston sand plain area of the Nottawasaga River using data for a total of 30 days of observation in the period 1977—81. Mass balances for total Kjeldahl nitrogen and chloride were constructed from 13 days of observation during the same time period. The daily input for each day was derived from the individual fluxes at Stations 1, 2, 3, 4, 6 and 7 on the major streams, the sand plain tributaries (Stations 8—13) and the ground water contribution. The daily output from the study area consisted of the flux at Station 5 and the estimated removal of water and nitrogen for irrigation (Fig. 2).

RESULTS AND DISCUSSION

Nitrogen and chloride budgets

Low concentrations of NH_4-N (< 0.08 mg l^{-1}) and trace levels of NO_2-N occurred at all stream sampling stations during low summer flows. Concentrations of NO_3-N were usually less than 0.3 mg l^{-1} at Stations 1 and 2, 0.4—0.6 mg l^{-1} at Station 3 and 0.8—1.0 mg l^{-1} at Station 5. Nitrate-N levels ranged between 1 and 2.0 mg l^{-1} at Station 4 downstream from the Alliston sewage treatment plant and similar concentrations also occurred during low summer flows at Stations 6 and 7. The small sand plain streams exhibited considerable contrasts in nitrate concentration. Streams at Stations 9 and 11—13, draining forest and pastures, had NO_3-N levels of less than 0.5 mg l^{-1}, whereas streams flowing through potato growing areas (Stations 8 and 10) had concentrations varying between 3 and 8.0 mg l^{-1}. Organic nitrogen concentrations were considerably less variable ranging from levels of about 0.2 to 0.4 mg l^{-1} at Stations 3, 6 and 7 to 0.6—0.8 mg l^{-1} at Stations 1 and 4. Chloride concentrations were less than 10 mg l^{-1} at Stations 3 and 7, whereas Stations 1, 4 and 10 varied between 20 and 30 mg l^{-1} and the remaining stream stations had levels of 15—20 mg l^{-1}.

Ground water entering the Nottawasaga River from springs and seeps contained less than 0.05 mg l^{-1} NH_4-N and low levels of organic nitrogen (< 0.20 mg l^{-1}). Nitrate-N concentrations were extremely variable ranging from 0.02 to 65.0 mg l^{-1}. Very high NO_3-N concentrations ranging between 20 and 65.0 mg l^{-1} were recorded for most ground water sampling sites on the Nottawasaga River between Station 3 and the junction of Innisfil Creek (Fig. 2). Many springs and seeps on the Boyne River downstream from Station 4 and along the west bank of the Nottawasaga River for about 7 km north of the Boyne River junction also exceeded 10 mg l^{-1} NO_3-N. These river reaches were adjacent to extensive areas of heavily fertilized crops. Ground water entering the river from areas of forest and permanent pasture generally contained less than 1.0 mg l^{-1} NO_3-N. Chloride concentrations exhibited a similar pattern with levels varying from 20 to 40 mg l^{-1} in springs down-gradient from fertilized fields, to less than 10 mg l^{-1} in other reaches of the river.

The four springs adjacent to fertilized fields which were sampled throughout the 1977—82 period had moderate seasonal and annual variations in nitrate concentration. Similar nitrate levels were observed during the summers of 1978 to 1982, but concentrations were approximately 25% lower during the period May—October 1977. Ground water samples from 40 wells located in potato growing areas of the sand plain also revealed a similar trend with lower nitrate concentrations in the summer of 1977 in comparison with later years (Hill, 1983).

The water budget for the Nottawasaga River showed that average daily inputs and outputs of water were approximately in balance (Table I). Most

TABLE I

Mean (±SD) daily input and output of water and NO_3-N in the Nottawasaga River during low flows on 30 days between May and October 1977—81

	Input	Output	Net gain or loss	Gain or loss as a percentage of input
Flow ($l\ s^{-1}$)				
Major streams	3326 ±645			
Sand plain streams	142 ±20			
Ground water	127			
Total	3595 ±662	3649 ±776	+54 ±190	2
NO_3-N (kg day^{-1})				
Major streams	189 ±41			
Sand plain streams	22 ±6			
Ground water	93			
Total	305 ±52	259 ±63	−46 ±23[a]	15

[a]Gain or loss significantly different from zero at the 1% level using a pair comparison *t* test

of the daily water input was contributed by Station 3 (45%) and Station 4 (25%), and the other major streams accounted for an additional 21%. Approximately 4% of the daily input was derived from ground water contributed by the sand plain streams (Stations 8—13). Several estimates are available for the ground water component which flows directly to the study reaches. Measurements of discharge from well-defined springs adjacent to the river indicated a daily input of 42 $l\ s^{-1}$ which represents an underestimate of the actual ground water contribution. The ground water flux based on the difference between total stream inputs and the output at Station 5 plus the water used for irrigation was 187 $l\ s^{-1}$, whereas the estimate using the ground water flux per unit area based on the discharges of the sand plain streams was 127 $l\ s^{-1}$. It is this latter estimate which has been used in the water budget calculation (Table I).

Daily inputs of NO_3-N entering the sand plain region through major streams averaged 189 ±41 kg for the 30 observation dates (Table I). Of this total approximately 52 and 33% were contributed by the Boyne River (Station 4) and the upper Nottawasaga River (Station 3), respectively. The average daily flux of NO_3-N contributed to the study reaches by ground water from springs and seeps was about 93 kg. This estimate was based on the quantity of ground water contributed by areas of the sand plain which drain directly into the Nottawasaga River and the average nitrate concentrations of springs and seeps flowing into individual river reaches. The daily nitrate flux from springs and seeps was reduced for observation days in 1977 in order to reflect the evidence from the four continuously monitored springs that nitrate inputs in ground water from fertilized fields were probably 25% lower in this year.

It is impossible to provide an accurate measurement of the NO_3-N input to the Nottawasaga River and its major tributaries from ground water, and the estimate of 93 kg day^{-1} must be regarded as approximate. However, the measurement of water flux and element concentrations for the well-defined springs indicated that at least 35 kg day^{-1} NO_3-N entered the study reaches. This quantity is a considerable underestimate of the actual daily input because it excludes numerous diffuse seepage areas and reaches where ground water enters through the river bed. Consequently, the input of 93 kg used in Table I does not appear unreasonable.

This nitrate budget for the Nottawasaga River indicates that ground water entering the study reaches, either directly or in the small sand plain streams, represents about 38% of the daily nitrate input during summer low flows. This substantial contribution reflects the contamination of the shallow aquifer by fertilizer nitrogen particularly from potato growing areas (Hill, 1982).

The nitrate mass balance for the Alliston study area showed that inputs from major streams and ground water exceeded outputs at Station 5 on all 30 days of observation. Individual daily deficits ranged from approximately 3 kg to a maximum of 88 kg and the average daily loss was 46 ±23 kg which is equivalent to about 80 mg N m^{-2} of stream bed (Table I). Analysis of total Kjeldahl nitrogen transport indicated no consistent pattern of gains or losses and the average daily difference between inputs and outputs was less than 1% (Table II). Average daily fluxes at Stations 3 and 4 accounted for about 17 and 34%, respectively, of the total chloride input to the Nottawasaga River. In contrast to nitrates considerable quantities of chloride enter the study area at Stations 1 and 2. The chloride mass balance showed a small chloride gain of about 5% which is in contrast to the consistent pattern

TABLE II

Mean (±SD) daily input and output of total Kjeldahl nitrogen and chloride in the Nottawasaga River during low flows on 13 days between May and October 1977—81

	Input	Output	Net gain or loss	Gain or loss as a percentage of input
Total Kjeldahl nitrogen (kg day^{-1})				
Major streams	94 ± 23			
Sand plain streams	5 ±1			
Ground water	2			
Total	101 ±23	102 ±25	+1 ±9	1
Chloride (kg day^{-1})				
Major streams	4401 ±1307			
Sand plain streams	219 ±37			
Ground water	400			
Total	5020 ±1380	5262 ±1391	+242 ±187 [a]	5

[a] Gain or loss significantly different from zero at the 1% level using a pair comparison t test.

of nitrate removal during stream transport (Table II). The relatively small difference between chloride inputs and outputs provides support for the validity of the nitrogen budget and suggests that the procedures and measurements used in the mass balance analysis are reasonable.

Nitrate removal processes in river reaches

A variety of processes may be responsible for the occurrence of nitrate losses during river transport. Several studies indicate that nitrate uptake by water plants may remove less than 5% of the nitrogen transported in streams (Kaushik et al., 1981). However, Vincent and Downes (1980) have suggested that watercress growth in late summer accounted for 72% of the nitrogen loss measured in a small New Zealand stream. Since aquatic macrophytes and benthic algae are generally absent from the Nottawasaga River, this nitrate sink process is probably unimportant in the study area. Nitrate removal as a result of temporary immobilization during decomposition of organic matter is also of minor significance during the summer in southern Ontario streams (Kaushik and Hynes, 1971; Kaushik et al., 1975). The two-way exchange of water between a stream and a subsurface ground water reservoir can cause element losses from river reaches (Rigler, 1979). However, the chloride mass balance and hydrogeologic data indicate an absence of such water exchanges in the Nottawasaga River.

The laboratory incubation experiments revealed disappearance of nitrate from solutions overlying sediment cores with almost total loss occurring in some samples within 6 days despite the presence of high dissolved oxygen levels in the solutions. Control cylinders containing no sediment did not exhibit any change in nitrate concentration during the experimental period. Less than 5% of the nitrate disappeared from solution overlying sediment samples which had been sterilized with formaldehyde, indicating that nitrate removal was caused by biological mechanisms.

High rates of N_2O accumulation were observed in river sediment samples amended with 10 ml of 2 mg l^{-1} NO_3-N in which N_2O reduction was blocked by acetylene. Approximately 80—94% of the nitrate lost from the solutions was recovered as N_2O indicating that assimilatory nitrate reduction was relatively unimportant during the 48-h incubation period. The acetylene blockage technique therefore indicates that most of the nitrate removed from solutions overlying intact sediment cores can be attributed to denitrification.

The 10 sediment cores removed from slackwater areas of the Nottawasaga River exhibited a daily NO_3-N loss varying from 60 to 190 mg m^{-2} of sediment surface over a 6-day laboratory incubation period (Table III). In contrast, 10 cores taken from areas of higher stream velocity in mid-channel had considerably lower NO_3-N losses of 10—59 mg m^{-2} day^{-1}. These differences in denitrification rates may be influenced by sediment characteristics. Bottom sediments generally had a very high sand content throughout

TABLE III

Nitrate-N losses from solutions overlying sediment cores incubated at 20°C for 6 days

Site	Bank margin sediments			Mid-stream sediments		
	NO_3-N in solution[a] ($mg\ l^{-1}$)		NO_3-N loss ($mg\ m^{-2}\ day^{-1}$)	NO_3-N in solution[a] ($mg\ l^{-1}$)		NO_3-N loss ($mg\ m^{-2}\ day^{-1}$)
	Day 3	Day 6		Day 3	Day 6	
Innisfil Ck. (Station 1)	1.16	0.88	121.5	4.17	4.23	22.6
Bailey Ck. (Station 2)	3.93	2.94	60.6	4.31	3.59	41.5
Nottawasaga R. (Station 3)	3.22	1.93	90.5	4.40	4.04	28.3
Boyne R. (Station 4)	2.58	1.29	109.4	3.82	2.97	59.0
Nottawasaga R. north of Innisfil Ck. junction	0.25	0.03	190.0	4.13	3.71	38.0
Nottawasaga R. near Station 13	2.19	0.86	130.0	4.05	3.40	47.1
Nottawasaga R. north of Boyne R. junction	3.55	2.72	67.2	4.71	4.54	14.5
Nottawasaga R. near Station 12	3.29	2.62	70.1	4.73	4.66	10.0
Nottawasaga R. near Station 11	3.44	2.73	66.9	4.15	3.63	40.4
Nottawasaga R. (Station 5)	0.76	0.27	139.0	4.40	4.39	18.0

[a]Initial NO_3-N concentration in the solution was 5 $mg\ l^{-1}$.

the channel cross section. Nevertheless, sediments adjacent to the river banks tended to contain more organic carbon, nitrogen and silt than mid-stream sites (Table IV).

This analysis of various nitrate sink mechanisms suggests that denitrification in river sediments is the major process accounting for nitrate removal in the rivers draining the Alliston sand plain. The average daily removal of approximately 46 kg NO_3-N from the Nottawasaga River represents 40% of the ground water nitrate input to the river from the sand plain. These data, therefore, suggest that this river and its major tributaries have a considerable capacity to assimilate agricultural inputs of nitrogen. The nitrate removal rate of 80 mg N m^{-2} day^{-1} measured by mass balance in the Nottawasaga River is relatively low compared with the nitrate losses of 160—913 mg m^{-2} day^{-1} recorded in other stream studies (Kaushik et al., 1975; Van Kessel, 1977; Robinson et al., 1978; Hill, 1981). It is, therefore, likely that many streams draining agro-ecosystems may have much greater capacities for nitrate removal than occur in the relatively coarse organically poor sediments of the Nottawasaga River.

TABLE IV

Some characteristics of the sediment 0—10 cm depth taken from 10 sites on the Nottawasaga River (Mean ±SD; air-dry basis)

	Bank margin sediments	Mid-stream sediments
pH	7.8 ± 0.3	8.1 ± 0.3
NH_4-N ($\mu g\ g^{-1}$)	3.5 ± 2.8	0.6 ± 1.4
NO_3 + NO_2-N ($\mu g\ g^{-1}$)	0.07 ± 0.07	0.2 ± 0.14
Organic-N (%)	0.018 ± 0.007	0.008 ± 0.004
Organic-carbon (%)	0.23 ± 0.11	0.08 ± 0.05
C/N ratio	12.8:1	10:1
Gravel (%)	2.6 ± 3.0	4.8 ± 8.9
Sand (%)	89.3 ± 5.7	93.2 ± 7.8
Silt (%)	6.2 ± 4.0	1.3 ± 0.8
Clay (%)	1.8 ± 0.8	1.0 ± 0.6

The removal of nitrate from rivers during transport is probably of greatest importance during low summer flows. Evidence derived from laboratory and field studies suggest that denitrification rates decline during the low temperatures which occur in the November to April period in southern Ontario (Hill, 1979). Denitrification is also probably inhibited during major storm flows as a result of the disturbance and aeration of bottom sediments.

A relatively small percentage of the annual nitrogen load of most rivers is transported during low discharges. Nevertheless, the considerable time duration of low-flow regimes must be considered in assessing the significance of denitrification in reducing the environmental impacts of agricultural inputs of nitrate to rivers. In southern Ontario low flows usually occur on 130—150 days between May and October. In other areas of the world which lack a cold season denitrification may act as an important nitrate sink mechanism during low flows throughout the year.

Future research should focus not only on agricultural activities as a source of nitrogen inputs to rivers but also on the capacity of rivers to transform and assimilate nitrogen during downstream transport.

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