Water Quality

Phosphorus and Nitrogen Export from Forested Stream Catchments in Central Ontario

P. J. Dillon,* L. A. Molot, and W. A. Scheider

ABSTRACT

The ability to predict export of algal nutrients from forested stream catchments is essential to estimate background levels of nutrients in lakes and therefore gauge the effects of anthropogenic activities on the trophic status of Ontario lakes. Data from 32 forested stream catchments in the Muskoka-Haliburton area of central Ontario collected during the 8-yr period 1976–1977 to 1983–1984 were used to develop empirical regression models of long-term average NH_4^+, NO_3^-, TON, and TP export employing mathematical transformations of geology, physiography, hydrology, and annual meteorological data. At least 6 consecutive years of sampling were necessary to avoid poor fits due to anomalous years and to produce regression models able to make reliable ($R^2 > 0.70$) long-term average predictions of TP export. Atmospheric deposition of algal nutrients typically exceeded catchment export. Total annual phosphorus (TP) export was variable with outputs from two catchments exceeding atmospheric inputs. Total organic nitrogen (TON) export was also variable with annual export from 22 catchments exceeding atmospheric inputs, although total N (TN) export never exceeded input. Peat deposits or beaver (*Castor canadensis* Kuhl) ponds in most of these catchments were the likely sources of the high TP and TON export. Nitrate retention (defined as the fraction of annual deposition retained by the catchment) was high in most catchments, exceeding 0.74 in 26 of the 32 catchments. Low NO_3^- retention was observed primarily in those catchments with steep grades (>5.9%). Ammonium retention was very high (>0.87) in all catchments.

A CONCERTED EFFORT has been made during the past two decades to predict the effects of changes in total phosphorus (TP) loading and concentration on the trophic status of lakes (Dillon and Rigler, 1975). Development of predictive tools has focused upon steady-state models because paramaterization of steady-state models is limited, making them readily adaptable as management tools.

Two models that have met with some success are those that predict chlorophyll *a* as a function of TP concentration in P-limited lakes (Dillon and Rigler, 1974; Jones and Bachmann, 1976; Canfield, 1983; Prepas and Trew, 1983; Riley and Prepas, 1985; Molot and Dillon, 1991) and those that predict lake TP concentration as a function of annual TP load and hydrologic characteristics (Vollenweider, 1969; Dillon and Rigler, 1975; Dillon, 1975; Kirchner and Dillon, 1975; Larsen and Mercier, 1976; Canfield and Bachmann, 1981; Frisk et al., 1981; Chapra and Reckhow, 1983; Reckhow and Chapra, 1983). Together, these models permit dose/response estimates by linking catchment output or export of TP, which may in turn reflect land use activities, to change in water quality.

Substantial effort has also been expanded on quantifying algal nutrient (TP and N) outputs from a range of land use categories such as forested, pasture, urban, row crop, etc. (Omernik, 1976, 1977; Neilson and Mackenzie, 1977; Hill, 1978, 1981; Kauppi, 1979; Beaulac and Reckhow, 1982; Cootes et al., 1982; Daniel et al., 1982; Clesceri et al., 1986a,b; Harper and Stewart, 1987). However, the output or export values derived from these studies may only be applicable to the regions of origin because too little is understood about the mechanisms and factors underlying variability in nutrient export from catchments to permit extrapolation to other sites.

Detailed studies of nutrient export from catchments in Ontario are lacking, although effects of bedrock geology and drainage density on TP export were reported by Dillon and Kirchner (1975) and Kirchner (1975). In central Ontario, the prediction of P and N export from forested catchments is an essential part of a methodology developed to estimate the effects of shoreline development on lake trophic status. In this paper, we test the hypothesis that export of algal nutrients is a function of catchment geology, physiography, and hydrology. We present empirical models for prediction of annual TP, ammonium (NH_4^+), nitrate (NO_3^-), and total organic nitrogen (TON) export from forested stream catchments as functions of bedrock and surficial geology, catchment physiography, hydrology, and meteorological data.

STUDY AREA

The data were collected from 32 streams/catchments in central Ontario during the 8-yr period 1976 to 1984. All streams are headwater streams, although several of the catchments include small beaver ponds in the drainage pattern.

Geological and physiographic characteristics for the 32 forested stream catchments are listed in Table 1. The catchment are located in the District of Muskoka or Haliburton County, Ontario (Fig. 1). Most of the catchments are underlain by Precambrian metamorphic silicate bedrock. Minor till plains (continuous moraine deposits >1 m thick) and thin till deposits (<1 m thick) interrupted by rock ridges represent the dominant surficial geological characteristics. A few catchments are underlain by Precambrian sedimentary deposits, principally dolomitic marble. Detailed descriptions of the geology and physiography of the catchments can be found in Jeffries and Snyder (1983), Girard et al. (1985), LaZerte and Dillon (1984), Seip

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Abbreviations: TP, total phosphorus; TON, total organic nitrogen; TN, total nitrogen; TKN, total Kjeldahl nitrogen.

Table 1. Geological and physiographical characteristics of the 32 study catchments in central Ontario.

STRM	AREA	GRADE	ROAD	STRML	ASTRML	BHG	DIOR	AS	MIG	MARB	GMAM	TLLCRB	MTLLPL	TTLLRR	PEAT	ROCK	WASH	ESKER	DRUM	SAND	POND
	m²	%	m			%															
BC1	204 300	7.0	15 400	488	419	100.0	0.0	0.0	0.0	0.0	0.0	0.0	94.0	6.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
BE1	5 716 000	1.0	4 300	3 690	1 550	0.0	0.0	0.0	0.0	20.6	79.4	89.3	0.0	0.0	6.9	0.0	0.0	1.5	0.1	0.0	2.2
CB1	596 900	3.0	0	1 070	560	100.0	0.0	0.0	0.0	0.0	0.0	0.0	24.2	72.4	2.8	0.6	0.0	0.0	0.0	0.0	0.0
CB2	1 260 000	2.0	0	1 830	689	100.0	0.0	0.0	0.0	0.0	0.0	0.0	16.7	75.3	8.0	0.0	0.0	0.0	0.0	0.0	0.0
CN1	4 563 000	1.2	0	2 260	2 020	0.0	0.0	0.0	100.0	0.0	0.0	0.0	17.1	67.1	8.6	0.0	0.0	0.0	0.0	0.0	7.2
DE10	788 900	1.0	1 300	975	809	0.0	0.0	0.0	100.0	0.0	0.0	0.0	0.0	82.9	17.1	0.0	0.0	0.0	0.0	0.0	0.0
DE11	762 700	1.0	0	1 980	385	0.0	0.0	0.0	100.0	0.0	0.0	0.0	0.0	79.1	20.9	0.0	0.0	0.0	0.0	0.0	0.0
DE5	2 998 000	1.0	10 100	762	393	0.0	0.0	0.0	100.0	0.0	0.0	0.0	0.0	74.6	25.4	0.0	0.0	0.0	0.0	0.0	0.0
DE6	218 000	1.6	15 600	488	447	0.0	0.0	0.0	100.0	0.0	0.0	0.0	0.0	78.0	22.0	0.0	0.0	0.0	0.0	0.0	0.0
DE8	669 600	1.0	28 000	1 220	549	0.0	0.0	0.0	100.0	0.0	0.0	0.0	13.7	78.1	8.2	0.0	0.0	0.0	0.0	0.0	0.0
DK1	473 000	1.4	31 800	1 650	287	0.0	0.0	0.0	0.0	11.9	88.1	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
HD1	483 000	4.0	0	335	1 440	100.0	0.0	0.0	0.0	0.0	0.0	0.0	13.81	64.2	22.0	0.0	0.0	0.0	0.0	0.0	0.0
HAL12	656 000	9.0	0	914	717	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.0	0.0	0.0	0.0	0.0
HP3	259 900	4.0	19 600	1 010	258	93.0	0.0	7.0	0.0	0.0	0.0	0.0	79.5	11.2	9.3	0.0	0.0	0.0	0.0	0.0	0.0
HP3A	196 500	8.0	8 500	762	258	42.6	0.0	57.4	0.0	0.0	0.0	0.0	97.1	0.0	2.9	0.0	0.0	0.0	0.0	0.0	0.0
HP4	1 195 000	5.0	3 700	2 040	585	13.2	0.0	86.8	0.0	0.0	0.0	0.0	56.1	32.8	0.0	0.9	0.0	0.0	0.0	7.5	2.7
HZP5	1 905 000	3.0	0	1 830	1 040	100.0	0.0	0.0	0.0	0.0	0.0	0.0	34.5	48.6	13.3	0.0	0.0	0.0	0.0	3.6	0.0
HP6	99 700	8.0	11 100	701	142	100.0	0.0	0.0	0.0	0.0	0.0	0.0	45.2	54.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0
HP6A	152 800	10.0	0	610	251	33.3	66.7	0.0	0.0	0.0	0.0	0.0	6.6	84.9	8.5	0.0	0.0	0.0	0.0	0.0	0.0
JY1	73 000	8.0	0	457	160	100.0	0.0	0.0	0.0	0.0	0.0	0.0	77.4	22.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
JY3	6 663 000	2.5	0	3 050	2 190	100.0	0.0	0.0	0.0	0.0	0.0	0.0	13.4	78.4	5.2	0.1	0.0	0.0	0.0	2.5	0.4
JY4	410 000	9.0	0	762	538	100.0	0.0	0.0	0.0	0.0	0.0	0.0	13.7	83.5	0.0	0.0	0.0	0.0	0.0	2.8	0.0
ME1	4 379 000	2.6	7 100	4 180	1 050	5.9	0.0	0.0	0.0	94.1	0.0	97.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.8
PC1	233 400	5.9	0	790	295	99.36	0.0	0.0	0.64	0.0	0.0	0.0	9.6	80.2	7.0	3.2	0.0	0.0	0.0	0.0	0.0
PT1	213 000	8.8	0	1 130	189	100.0	0.0	0.0	0.0	0.0	0.0	0.0	51.7	38.0	0.0	0.0	5.6	0.0	0.0	0.0	4.7
RC1	1 336 000	1.0	3 000	2 900	461	100.0	0.0	0.0	0.0	0.0	0.0	0.0	53.2	41.1	0.0	0.0	0.8	0.0	0.0	0.0	4.9
RC2	269 600	1.5	1 400	732	369	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	67.9	10.5	19.4	0.0	0.0	0.0	0.0	2.2
RC3	704 900	3.5	0	1 280	551	100.0	0.0	0.0	0.0	0.0	0.0	0.0	81.7	2.7	9.9	1.2	0.0	0.0	0.0	0.0	4.5
RC4	454 600	2.5	0	1 010	452	100.0	0.0	0.0	0.0	0.0	0.0	0.0	76.3	16.0	2.9	0.0	0.0	0.0	0.0	0.0	4.8
TBAY1	79 000	24.0	0	381	207	100.0	0.0	0.0	0.0	0.0	0.0	0.0	56.1	35.5	0.0	8.4	0.0	0.0	0.0	0.0	0.0
TWN1	4 267 000	1.8	4 500	2 530	1 690	0.0	0.0	0.0	0.0	11.8	88.2	93.0	0.0	0.0	2.6	0.0	1.4	0.1	0.0	0.0	2.9
TWS1	1 718 000	1.6	1 400	2 800	613	0.0	0.0	0.0	0.0	2.2	97.8	81.0	0.0	0.0	8.6	0.0	6.7	0.0	0.0	0.0	3.7

† Characteristics are defined in Table 2. Definitions of terms are included in Table 2.

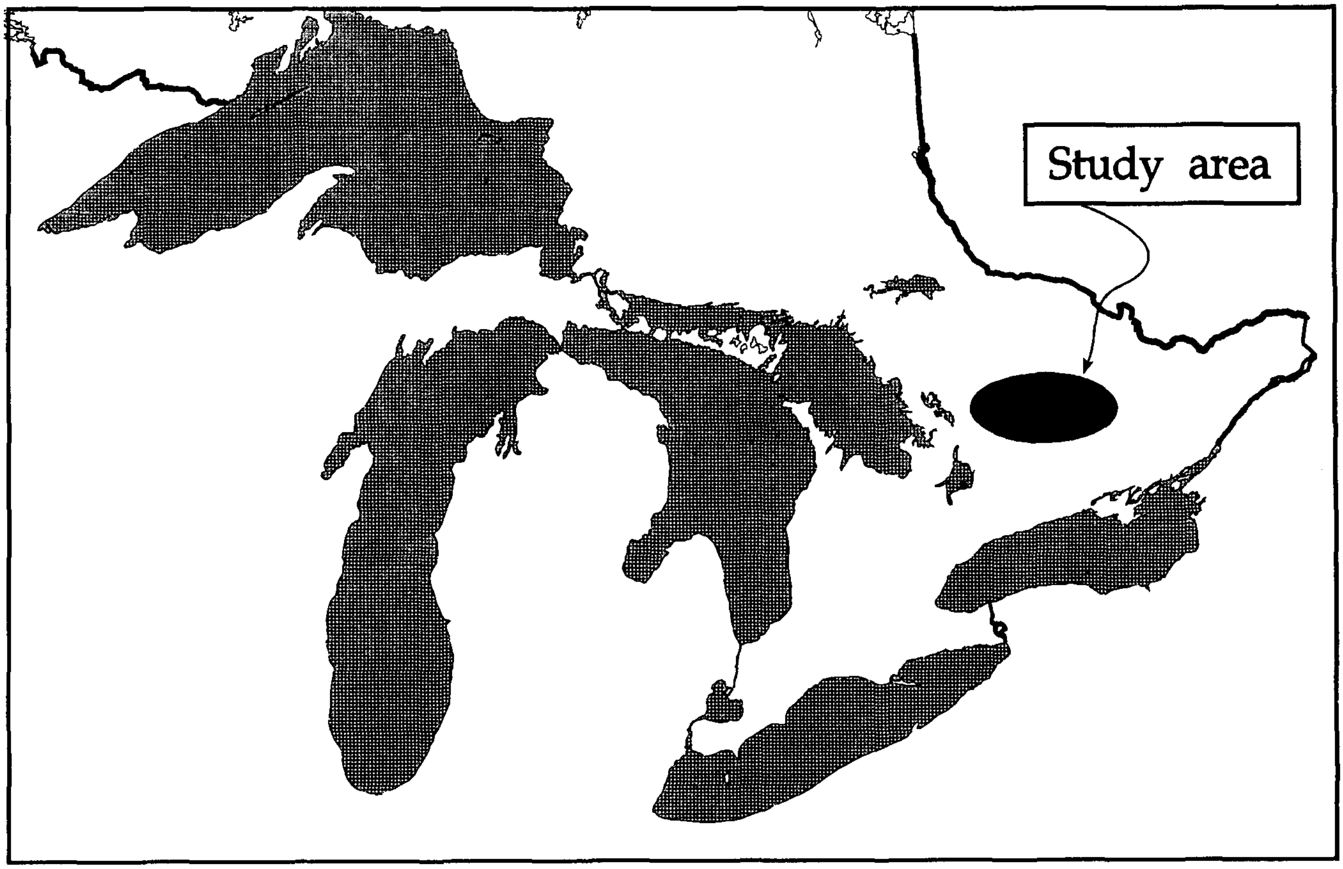

Fig. 1. Map of central Ontario showing location of study area.

et al. (1985), Dillon et al. (1986), Dillon et al. (1987), and Reid et al. (1987).

A large proportion of the surficial deposits are shallow and are composed of sand, silt, and gravel of granitic composition. Soils in the area contain very low proportions of silt and clay-sized particles (Jeffries and Snyder, 1983). The dominant soil types are acidic brunisols and podsols, which form on noncarbonate, moderate to well-drained slopes, generally on coarse-grained parent surficial material with poor soil profile development. Gleysolic soils are generally limited to the moderately or poorly drained valleys in the south east portion of the study area underlain by Precambrian marble with carbonate tills. Organic soils (peat) are common throughout the region in areas with very poor drainage, which are typically saturated with water for a large part of the year. The organic material is supplied primarily by the growth of *Sphagnum* mosses but also by grasses, reeds, rushes, sedges, and conifers (Jeffries and Snyder, 1983).

The study area is in the Great Lakes–St. Lawrence forest region east of Lake Huron and is characterized by secondary growth forests. All of the catchments are primarily forested. The area was selectively logged in the 1800s and early 1900s primarily for eastern white pine (*Pinus strobus* L.) and red pine (*P. resinosa* Ait.); there has been no logging in the study catchments for at least several decades, leaving a predominance of deciduous trees such as sugar maple (*Acer saccharum* Marsh.) and aspen (*Populus tremuloides* Michx. and *P. grandidentata* Michx.). White spruce [*Picea glauca* (Moench) Voss] tamarack [*Larix laricina* (Du Roi) K. Koch], eastern hemlock [*Tsuga canadensis* (L.) Carr.], yellow birch (*Betula alleghaniensis* L.), white birch (*Betula papyrifera* Marsh.), beech (*Fagus grandifolia* Ehrh.), white oak (*Quercus alba* L.), basswood (*Tilia americana* L.), eastern white cedar (*Thuja occidentalis* L.), red maple (*Acer rubum* L.), and red oak (*Quercus rubra* L.) are also common in the area. Black spruce [*Picea mariana* (Mill) B.S.P.] is common in the wetland areas. Well-drained soils generally have deciduous or mixed forests, whereas the poorly drained soils have mixed or coniferous forest.

There are no population centers in the study catchments. Typically, cottages in the region are built close to lake shores rather than inland from the lakes.

METHODS

Definitions of hydrological, meteorological, and geological paramaters are listed in Table 2. Sample collection techniques are described in detail in Locke and Scott (1986). Bulk precipitation, precipitation depth, relative humidity, and air temperature were monitored at up to 12 stations during the study period with never less than four stations in operation. Precipitation samples were removed from collectors when there was sufficient volume for all chemical analyses. Collection periods ranged from 1 to 40 d, although samples were typically removed weekly. Samples were filtered through 76-μm (1977–1982) or 102-μm Nitex mesh (after 1982) to remove coarse particulates. Atmospheric deposition was measured from 1978 for TP and from 1976 for TON, NO_3^-, and NH_4^+.

Water level or stage was recorded continuously and measured instantaneously at regular intervals at weirs or flumes installed on the study streams (Scheider et al., 1983). Stage-discharge relationships were constructed for each stream. Stream samples were collected on average four times per month from June 1976 to May 1984, although samples were usually collected much more frequently during spring snowmelt. Samples were filtered through 76-μm Nitex mesh into prerinsed sample bottles and placed in temperature-controlled containers while in transit to the laboratories. Nutrient export was calculated for each sampling interval (typically $\leq$7 d) by multiplying concentration times the stream discharge for the interval; all results are expressed on an areal basis. Annual data were calculated for the hydrologic year, i.e., 1 June to 31 May.

Table 2. Definitions of geological and physiographical characteristics of the 32 study catchments in central Ontario.

Meteorology and hydrology:
Mean annual air temperature (TEMP, °C)
Relative humidity (HUMID, %)
Annual stream baseflow, defined as the minimum observed flow rate within each month (BASEFLOW, m yr^{-1})
Runoff, defined as annual stream discharge (RUNOFF, m yr^{-1})
Quickflow, defined as runoff-baseflow (QUICKFLOW, m yr^{-1})
Precipitation (PRECIP, m yr^{-1})
Discharge ratio, defined as the ratio of annual daily maximum to annual mean daily stream discharge rate, (MAXM)
Springflow, defined as proportion of total annual runoff occuring 1 February–31 May (SPRINGFLOW)
Yield, defined as ratio of runoff to precipitation (YIELD)

Physiography:
Catchment area (AREA, m^2)
Average catchment grade (GRADE, %)
Stream length (STRML, m)
Stream density, defined as ratio of area to stream length (ASTRML, m)
Road length (ROAD, m)

Bedrock geology: (% area)
Biotite, horneblende and geneiss (BHG)
Diorite (DIOR)
Amphibolite and schist (AS)
Migmatite (MIG)
Marble (MARB)
Gneiss, meta arkose and marble (GMAM)

Surficial geology and physiography: (%area)
Pond, defined as small open waters (POND)
Peat, primarily *Sphagnum* (PEAT)
Exposed bedrock (ROCK)
Esker (ESKER)
Outwash (WASH)
Drumlin, (DRUMLIN)
Carbonate till (TLLCRB)
Minor till plain (MTLLPL)
Thin till with exposed rock ridges (TTLLRR)

There were no strong correlations between stream chemistry (TP, NO_3^-, NH_4^+, or TON concentration) and discharge for any of the sites; thus, we did not attempt to use concentration-discharge relationships to estimate the nutrient fluxes.

Analytical methods for TP, NO_3^-, NH_4^+, and total Kjeldahl nitrogen (TKN) are outlined in detail in Ontario Ministry of the Environment (1983). Total organic N was defined as TKN minus NH_4^+. Study of the 8 streams was discontinued in 1980, at which time two additional streams/catchments were added. There were a total of 208 stream/catchment-years of nutrient export data generated.

Pearson correlation and stepwise (forward) multiple linear regression analyses (with significance levels for entry and staying of 0.15) were performed with PC SAS using each stream-year as an observation (n = 208; referred to as data set A) and then using average values for each stream over the 8-yr period (4-yr in some cases) (n = 32; referred to as data set B).

One objective of the N and TP regression analyses was to derive empirical equations for the prediction of annual nutrient export that were independent of each other, i.e., it was hoped that regression models without nutrient export (TP or any N fraction) as independent variables would have acceptable R^2 (sum of squares due to regression/total sum of squares corrected for mean), arbitrarily defined as $>$0.7. To accomplish this objective, multiple linear regression models were first developed with untransformed variables, with and without nutrients as independent variables, to determine whether linear relationships were strong enough to adequately predict export.

Linear regression analyses were also conducted with an expanded list of both untransformed variables and their reciprocals, squares, and logarithms to search for important nonlinear relationships.

Table 3. Mean annual meteorological, hydrological, and nutrient export values averaged over for 1976 to 1984 for each of the 32 study catchments.†

CATCHMENT	TEMP	PREC	HUMID	BASE	QICK	RUN	MAXM	SPFL	YILD	NH_4	NO_3	TON	TP
	°C	m/yr	%	m yr^{-1}						µmoL/m^2 per yr		µg-at m^2 per yr	
BC1	4.44	1.05	63.1	0.20	0.22	0.42	16.23	0.57	0.40	347	2 630	5 770	80.2
	0.64	0.09	18.6	0.06	0.14	0.11	6.22	0.19	0.09	295	1 030	2 670	33.5
BE1	4.43	1.05	65.2	0.37	0.16	0.53	10.50	0.52	0.50	993	4 840	14 300	244
	0.61	0.12	15.1	0.03	0.15	0.14	2.27	0.14	0.09	253	1 100	5 250	68.8
CB1	4.38	1.11	63.2	0.26	0.30	0.57	15.33	0.57	0.51	380	1 390	7 640	125
	0.65	0.15	18.5	0.06	0.17	0.16	5.28	0.18	0.13	260	727	2 000	27.3
CB2	4.38	1.11	63.2	0.28	0.24	0.52	13.38	0.54	0.47	1 298	3 040	15 900	397
	0.65	0.15	18.5	0.07	0.09	0.10	4.34	0.17	0.06	1 140	4 800	2 910	95.9
CN1	4.50	1.05	65.7	0.32	0.28	0.60	11.34	0.47	0.53	2 120	1 980	14 600	277
	0.68	0.12	14.0	0.03	0.14	0.11	4.88	0.12	0.05	264	504	2 640	46.8
DE10	4.34	1.10	65.6	0.25	0.32	0.57	13.46	0.55	0.51	659	4 230	15 800	402
	0.66	0.14	14.5	0.05	0.12	0.10	3.09	0.14	0.05	530	5 910	3 420	120
DE11	4.34	1.10	65.6	0.24	0.35	0.59	14.16	0.55	0.54	720	1 760	18 100	475
	0.66	0.14	14.5	0.04	0.12	0.12	4.72	1.06	0.08	320	1 730	5 470	217
DE5	4.34	1.10	65.6	0.25	0.38	0.62	12.52	0.56	0.57	1 510	583	20 100	929
	0.66	0.14	14.5	0.05	0.14	0.12	3.69	0.15	0.09	567	278	4 570	467
DE6	4.34	1.10	65.6	0.26	0.36	0.62	13.47	0.55	0.56	3 720	918	22 200	1 130
	0.66	0.14	14.5	0.05	0.09	0.11	4.01	0.15	0.05	2 030	645	5 560	659
DE8	4.34	1.10	65.6	0.26	0.27	0.53	11.23	0.52	0.47	858	1 040	16 700	233
	0.66	0.14	14.5	0.07	0.20	0.19	5.02	0.15	0.14	453	517	6 390	87.6
DK1	4.47	0.97	59.6	0.46	0.07	0.52	8.46	0.60	0.51	484	3 560	10 100	119
	0.60	0.10	17.6	0.03	0.03	0.00	2.81	0.13	0.02	106	1 160	2 730	32.3
HAL 12	4.42	0.99	58.4	0.37	0.18	0.55	11.57	0.60	0.53	540	17 000	13 100	293
	0.62	0.12	18.3	0.05	0.05	0.08	1.71	0.10	0.06	58	3 820	4 000	64.0
HD1	4.41	0.96	59.2	0.24	0.29	0.54	13.63	0.68	0.54	1 280	7 900	19 500	363
	0.65	0.10	17.8	0.08	0.07	0.06	1.01	0.15	0.04	697	4 550	5 240	163
HP3	4.95	1.06	62.9	0.28	0.30	0.58	14.64	0.51	0.55	1 030	8 790	14 000	420
	0.56	0.12	18.8	0.02	0.12	0.12	3.89	0.11	0.08	733	5 820	3 650	110
HP3A	4.95	1.06	62.9	0.26	0.35	0.61	16.91	0.54	0.58	530.4	20 700	9 400	149
	0.56	0.12	18.8	0.03	0.11	0.14	3.79	0.14	0.13	410.3	16 500	3 240	50.4
HP4	4.95	1.06	62.9	0.30	0.27	0.57	11.53	0.51	0.54	1 821.4	4 060	12 000	297
	0.56	0.12	18.8	0.04	0.11	0.12	3.91	0.13	0.10	795.7	1 340	4 180	56.6
HP5	4.95	1.06	62.9	0.24	0.37	0.61	14.23	0.53	0.58	1 410	5 380	16 000	326
	0.56	0.12	18.8	0.08	0.13	0.12	4.63	0.15	0.11	615	2 540	3 180	58.3
HP6	4.95	1.06	62.9	0.25	0.39	0.65	14.28	0.53	0.61	1 420	10 400	12 300	278
	0.56	0.12	18.8	0.04	0.10	0.12	4.98	0.15	0.10	838	3 870	3 290	45.7
HP6A	4.95	1.06	62.9	0.22	0.29	0.51	18.38	0.60	0.48	377	1 080	10000	201
	0.56	0.12	18.8	0.06	0.08	0.11	5.83	0.18	0.08	294	548	3 420	110
JY1	4.07	1.05	57.4	0.24	0.20	0.44	12.60	0.57	0.42	678	33 600	8 200	147
	0.63	0.11	19.5	0.03	0.07	0.10	2.37	0.05	0.06	385	27 100	3 060	23.0
JY3	4.07	1.05	57.4	0.43	0.05	0.48	10.36	0.58	0.46	2 680	6 580	12 900	312
	0.63	0.11	19.5	0.09	0.10	0.09	4.67	0.10	0.06	585	3 900	5 010	50.0
JY4	4.07	1.05	57.4	0.27	0.14	0.41	11.57	0.69	0.39	727	14 100	8 800	133
	0.63	0.11	19.5	0.12	0.09	0.11	1.69	0.09	0.08	118	1 780	4 480	31.7
ME1	4.61	1.02	55.9	0.40	0.12	0.52	8.27	0.58	0.52	1 190	7 970	12 800	226
	0.67	0.16	19.9	0.07	0.12	0.13	1.05	0.10	0.07	506	3 670	4 770	23.3
PC1	4.45	1.12	72.6	0.18	0.44	0.62	14.43	0.49	0.55	1 670	17 100	49 100	175
	0.65	0.10	1.28	0.06	0.20	0.14	4.76	0.17	0.08	1 860	22 800	12 700	36.7
PT1	4.45	1.10	72.6	0.26	0.29	0.55	15.71	0.54	0.50	465	53 800	6 800	65.5
	0.64	0.12	1.28	0.04	0.07	0.09	5.87	0.17	0.08	321	3 030	3 510	21.5
RC1	4.47	1.10	63.0	0.23	0.33	0.56	14.18	0.55	0.51	3 140	5 510	9 550	197
	0.63	0.15	18.7	0.08	0.15	0.11	2.35	0.18	0.07	2 190	5 300	3 460	61.6
RC2	4.47	1.10	63.0	0.19	0.35	0.54	13.92	0.54	0.49	853	1 000	14 800	186
	0.63	0.15	18.7	0.05	0.12	0.12	5.27	0.15	0.05	498	397	3 420	38.0
RC3	4.47	1.10	63.0	0.38	0.27	0.64	10.74	0.51	0.59	1 900	9 880	13 900	255
	0.63	0.15	18.7	0.09	0.10	0.12	2.22	0.14	0.09	1 220	11 100	4 100	57.9
RC4	4.47	1.10	63.0	0.34	0.20	0.54	10.87	0.49	0.49	3 730	5 070	13 200	360
	0.63	0.15	18.7	0.08	0.10	0.10	3.15	0.12	0.06	1 860	1 930	3 600	56.0
TBAY1	4.49	1.13	72.6	0.12	0.49	0.61	22.98	0.68	0.55	587	25 500	10 000	128
	0.59	0.10	1.38	0.04	0.25	0.27	7.14	0.18	0.24	351	32 900	5 360	52.9
TWNI1	4.55	1.05	65.7	0.40	0.16	0.57	9.56	0.48	0.52	1 930	3 830	14 900	265
	0.60	0.12	14.1	0.02	0.12	0.11	2.50	0.12	0.07	727	1 080	4 240	66.0
TWS1	4.55	1.06	65.7	0.40	0.14	0.54	9.62	0.49	0.50	3 100	2 740	14 900	267
	0.60	0.12	14.0	0.04	0.13	0.11	3.51	0.14	0.07	1 160	729	3 800	43.6

† Abbreviations and units are described in the text and in Table 2. Standard deviations are shown beneath the means. Detailed annual results are available on request.

RESULTS

Deposition

Mean long-term deposition rates for TP and N species in the central Ontario study area were 645 μg-at P m^{-2} yr^{-1}, 40.2 mmol NO_3^- m^{-2} yr^{-1}, 28.2 mmol NH_4^+ m^{-2} yr^{-1}, and 11.9 mg-at TON-N m^{-2} yr^{-1}. These NH_4^+ and NO_3^- deposition rates are comparable to those reported (Dillon et al., 1988) for the same study area over a shorter time span. The molar TN/TP ratio was 124. The TON accounted for only 15% of total N deposition.

Export

Long-term average P and N export values are summarized in Table 3.

Atmospheric deposition of TP, NO_3^-, NH_4^+, TON, and TN typically exceeded catchment export. Export of TP from two catchments, DE5 and DE6, however, exceeded atmospheric inputs; these catchments also had the lowest TN/TP export ratios. The TON export from 22 catchments exceeded atmospheric inputs, although TN export never exceeded input. Peat deposits or beaver ponds in these catchments (except HP6) were the likely sources of the extra TON as well as higher TP exports (Devito et al., 1989). In all other catchments, TP and TON export rates were low.

Mean annual export of TP and TN was highly variable, ranging from 66 μg-at P m^{-2} yr^{-1} in PT1 to 1.1 mg-at P m^{-2} yr^{-1} in DE6 and 8.7 mg-at N m^{-2} yr^{-1} in BC1 to 67.8 mg-at N m^{-2} yr^{-1} in PC1 (Table 3).

The ratios (molar) of mean annual export of TN/TP ranged from 24 to 389 with a mean (± 1 SD) of 108 (±82). All TN/TP export ratios were greater than 43 except DE5 and DE6, which were both 24.

Nitrate retention (defined as the fraction of deposition retained by the catchment on an annual basis) was high in most catchments, exceeding 0.74 in 26 of the 32 catchments. Low retention was observed in HAL12, HP3A, JY1, JY4, PC1, and TBAY1 (0.17-0.65), all of which had steep grades >5.9% (Table 1). Grades were also steep in BC1 and PT1, but NO_3^- retention was high (0.93 and 0.87, respectively). Ammonium retention was very high (>0.87) in all catchments.

Correlation Analysis

Specific bedrock types were associated with different morphological features. For example, catchments that had predominately biotite bedrock were steep (correlation with grade was 0.42), migmatite catchments were gently sloping (correlation with GRADE was −0.36) and were therefore more likely to have peat deposits (r = 0.64), amphibolite catchments were likely to have sand deposits (r = 0.66), and gneiss and marble catchments were likely to have carbonated till deposits (r = 0.86 and 0.64, respectively).

Total P export was best correlated with proportion of the catchment that was PEAT and MIGMATITE using both individual catchment-years (data set A; Table 4) and the long-term average annual data (data set B; Table 5).

The highest correlation with NO_3^- export in data set A was only 0.41 (with GRADE). Correlations increased when annual average data were used and the correlation with GRADE increased to 0.66.

Table 4. Pearson correlation coefficients of nutrient export vs. untransformed variables using annual data (208 catchment-years).

Variables	TP	NO_3^-	NH_4^+	TON
TP		−0.14	0.45	0.41
NO_3^-			0.03	−0.07
NH_4^+				0.24
Yield	0.24	0.19	0.18	0.47
Baseflow	0.04	0.01	0.31	0.03
Quickflow	0.20	0.05	−0.08	0.46
Runoff	0.26	0.07	0.12	0.55
Peat	0.62	−0.22	0.08	0.40
Pond	−0.18	−0.10	0.37	−0.16
Minor till plain	−0.28	0.30	−0.01	−0.35
Grade	−0.30	0.41	−0.28	−0.22
Biotite	−0.33	0.24	−0.06	−0.14
Migmatite	0.53	−0.24	0.05	0.27

Table 5. Pearson correlation coefficients of nutrient export vs. untransformed variables using 8-yr (or 4-yr) averages for each stream (n=32 for all parameters).

Variables	TP	NO_3^-	NH_4^+	TON
TP		−0.33	0.47	0.33
NO_3^-			−0.24	−0.01
NH_4^+				0.26
Humidity	0.05	−0.09	0.03	0.38
Quickflow	0.23	0.13	−0.09	0.35
Runoff	0.39	−0.07	0.23	0.40
Springflow	−0.11	0.32	−0.42	−0.29
Discharge ratio	−0.12	0.28	−0.37	−0.08
Yield	0.35	−0.02	0.18	0.33
Peat	0.73	−0.32	0.15	0.42
Pond	−0.16	−0.23	0.49	−0.15
Minor till plain	−0.30	0.42	−0.03	−0.30
Grade	−0.36	0.66	−0.39	−0.21
Biotite	−0.36	0.42	−0.09	−0.09
Migmatite	0.62	−0.36	0.11	0.24

Ammonium export (data set A) was best correlated with TP export (r = 0.45). This increased slightly to 0.47 in data set B. There were two other strong correlates with NH_4^+ in the long-term data set—SPRINGFLOW and POND (Table 2).

The TON export in data set A was best correlated with RUNOFF, YIELD, QUICKFLOW, TP, and PEAT (r > 0.4). In data set B, these correlations decreased except with PEAT. In general, correlations with TP, NH_4^+, and NO_3^- export increased and correlations with TON export decreased when average annual means were used.

Regression Analysis

Regression analysis of data set A (each catchment year used as a separate observation) using only untransformed variables resulted in R^2 less than 0.7 for prediction models of TP, TON, NH_4^+, and NO_3^- export with and without nutrients as independent variables. The highest R^2 in data set A was for TP export (0.68), but NH_4^+ and NO_3^- were included as independent variables. A model including other chemical parameters as independent variables is, or course, less useful as a predictive tool since it requires very substantial measurement effort.

Using data set B (long-term averages) with untransformed independent variables only, adequate R^2

Table 6. Regression equations for the prediction of long-term mean annual nutrient export from central Ontario study catchments ($n = 32$).

log TP	$= -3.64 \times 10^{-4}$ humidity^2 + 1.57 /springflow + 1.36×10^3 grade^2 + 1.34×10^3 peat^2 − 2.97×10^{-5} minor till − 1.5×10^{-3} carbonate till 1.25×10^{-2} rock -3.48×10^{-3} pond^2 + 0.91 $R^2 = 0.88$, MSE = 0.0115, $F = 20.56$
log NH_4^+	= 1.11 log TP + 7.75×10^{-2} pond − 3.00×10^{-5} migmatite^2 − 9.96×10^{-5} diorite^2 − 3.70×10^{-5} outwash^2 + 2.56×10^{-5} thin till^2 -1.03×10^{-2}peat + 7.45×10^{-2} $R^2 = 0.83$, MSE = 0.0208, $F = 16.18$
NO_3^-	= 1530 grade + 5.18×10^6/humidity + 4.07×10^5 / temperature + 1.02×10^5 quickflow^2 − 73.1 thin till + 5.4×10^4 /precipitation − 9.92×10^4 springflow − 1.73×10^5 $R^2 = 0.81$, MSE = 1.478×10^7, $F = 14.74$
TON	= −1330 pond + 1.12×10^5 quickflow^2 − 1.44×10^2 discharge ratio + 8.17 humidity^2 + 1.96×10^2 diorite + 3.64×10^3/baseflow − 1.09×10^4/grade − 1.89×10^6/ stream density $-1/10 \times 10^3$ sand −4100 $R^2 = 0.85$, MSE = 1.201×10^7, $F = 13.47$

† MSE is the mean square error.

Table 7. Stepwise regression of $\log_{10}$ TP export using averages of annual values for 32 forested stream catchments. R^2 (range), number of consecutive year subsets (n) and number of independent variables selected by stepwise regression are presented. The set of independent variables selected from included all untransformed variables and their reciprocals and squares (except N species).

No. of consecutive years	R^2 range	n	No. of ind. var.
1	0.68–1.00	8	4–17
2	0.60–0.95	7	3–10
3	0.61–1.00	6	3–18
4	0.62–0.95	5	3–7
5	0.60–0.89	4	3–7
6	0.71–0.76	3	4–7
7	0.71–0.82	2	4–8
8	0.90	1	10

(>0.7) was achieved for prediction of NO_3^- export ($R^2 = 0.76$), with or without N species and TP export as independent variables, and prediction of TP export with NH_4^+ export as an independent variable ($R^2 = 0.79$). Neither TON nor NH_4^+ export could be reliably predicted from average annual means, with or without other nutrient export as independent variables. It appears from the regression analysis of untransformed variables that NH_4^+ and TP export are apparently codependent (i.e., NH_4^+ export is an independent variable in the TP export regression model and TP export is an independent variable in the NH_4^+ export regression model although goodness of fit for NH_4^+ export was too low [0.62] to be useful).

Clearly, simple multivariate regression analysis using only untransformed variables was not satisfactory because only TP (with NH_4^+) and NO_3^- export regression models were adequate ($R^2 > 0.70$ using average annual means [data set B]). Therefore, transformed variables (reciprocals, squares, and logarithms) were added to the independent variable list in the hope that goodness of fit might increase. Achieving adequate goodness of fit might then be attributed to nonlinear relationships.

Including transformed as well as untransformed independent variables using data set A increased all R^2, but only R^2 for TON was greater than 0.70 ($R^2 = 0.75$) when N and TP were excluded as independent variables. However, too many independent variables were required to achieve $R^2 = 0.75$ (18 variables) or even to achieve $R^2 = 0.70$ (11 variables). Hence, it was concluded that acceptable regression models could not be developed using annual data as separate observations.

Including transformed as well as untransformed independent variables using data set B increased R^2 for TON and NO_3^- export without N or TP as independent variables to 0.91 and 0.97, respectively. Log_{10} transformations of TP and NH_4^+ export greatly improved R^2 with the expanded list of independent variables (0.90 and 0.80, respectively). Hence, mathematical transformations permitted prediction of long-term, average nutrient export with reasonable confidence.

These models were further refined by eliminating repetitious variables. This satisfied the argument that only the strongest relationship between export and an independent variable should be considered to better approximate physical reality. Furthermore, runoff was considered a repetitious independent variable when either baseflow or quickflow was selected first. Likewise, stream density was removed when stream length was selected first and vice versa. The final regression models are presented in Table 6. The NH_4^+ export model required TP as an independent variable but the final TP, NO_3^-, and TON export models using mathematically transformed variables did not require nutrients as independent variables.

The effects of annual variation were investigated by a stepwise regression analysis of log(TP) export using data subsets consisting of different consecutive years (Table 7). At least 6 consecutive years of sampling were necessary to avoid the possibility of a low R^2 (< 0.70). For example, a stepwise regression using mean values for the 5-yr period 1976–1977 to 1980–1981 yielded $R^2 = 0.60$, whereas mean values for the 5-yr period 1979–1980 to 1983–1984 yielded $R^2 = 0.89$. The maximum number of independent variables selected was sometimes large (as high as 18) when the number of consecutive years of sampling was small (≤3) but when the number of consecutive years was 4 or greater, the maximum number of independent variables never exceeded 10.

DISCUSSION

The average TP deposition rate of 645 µg-at m^{-2} yr^{-1} in the central Ontario study area was slightly lower than deposition rates reported for remote northwestern Ontario, whereas the average N deposition rate of 80.3 mg-at N m^{-2} yr^{-1} in central Ontario was about twofold higher (Linsey et al., 1987). Ahl (1988) suggested that annual background deposition rates for TP, which would occur in the absence of significant human activity are likely 3 to 10 kg km^{-2} (97–323 µg-at m^{-2}). These background rates are lower than rates observed in central and northwestern Ontario. However, the estimated background rates are deposition rates for remote northern areas with long winters and extensive snow cover. Presumably, winter limits windblown loss of terrestrial TP, which is considered the major source of atmospheric deposition. Therefore, background deposition rates are likely a function of latitude in temperate and arctic areas.

The principal objective of this exercise was to develop regression models capable of predicting long-term, average annual algal nutrient export from forested catchments in the Precambrian Shield area of central Ontario with a minimum of labor-intensive field and laboratory work. Some parameters indentified by the regression models, such as peat area in the TP export model or grade in the NO_3^- model, may prove to be important causative as opposed to empirical factors.

The regression models are functions of parameters, some of which are readily available from maps, air photos, and weather records. Only hydrological data (quickflow, baseflow, springflow, and discharge ratio) are not readily available for small catchments. When hydrological variables were removed from the independent variable lists, only log(NH_4^+) goodness of fit exceeded 0.70 ($R^2 = 0.83$). However, the NH_4^+ model required TP as an independent variable which, in turn, required hydrological data to increase its goodness of fit from 0.70 to 0.88. Hence, hydrological variables are necessary for reliable prediction of algal nutrient export from these catchments.

There were not many variables, transformed or untransformed, that correlated well with nutrient export. Hence, either important factors are missing from this analysis or nutrient export is a complex process defying simple empirical descriptions with only a few independent variables. Complex regression models with seven to nine independent variables, some of them transformed, were necessary.

The use of transformed and untransformed independent variables was strictly empirical and had no *a priori* theoretical rationale based on hypotheses of cause and effect. Stepwise selection of transformed and untransformed variables resulted in nutrient export regression models with much higher R^2 values than regression models based on untransformed variables only implying that processes dominating export are not always described by linear relationships. It is not known whether the transformed variables are causally related to nutrient export; nevertheless, their inclusion is operationally justified.

Correlations and regression goodness of fit were much higher for 8-yr means (data set B) than when annual means were used as separate observations (data set A), which suggests that these regression models are best considered as steady-state models incapable of accurately predicting annual variation. At least 6 consecutive years of data were necessary to avoid the possibility of $R^2 < 0.70$ for average, long-term log(TP) export. A minimum of 6 years was also found to be necessary for reliable prediction of the average, long-term response of chlorophyll *a* as a function of TP in lakes in the same area (Molot and Dillon, 1991).

The relative areal extent of peat and pond were important factors in regression models of TP, NH_4^+, and TON export. Surprisingly, peat was eliminated from the TON regression by the stepwise regression although TON's highest correlation was with peat.

The type of bedrock geology was not a very important factor in regression models of TP and NO_3^- export from forested stream catchments in the Precambrian Shield area of central Ontario. The TON export model used diorite and the NH_4^+ export model used diorite^2 and migmatite^2 as independent variables. The absence of bedrock geology in the TP export model probably reflects the importance of organically stored TP or atmospheric TP in these catchments.

The importance of grade in the regression model of NO_3^- export is consistent with the hypothesis that NO_3^- is a mobile anion readily affected by leaching (Szperlinski and Badowska, 1977a,b; Johnson and Cole, 1980; Dillon and Molot, 1990). Most of the NO_3^- was exported during spring melt (Molot et al., 1989).

Kirchner (1975) found a significant correlation of 0.94 between drainage density and TP export from catchments in the Precambrian Shield with the highest export value being 274 μg-at m^{-2} yr^{-1}. In data set B using the reciprocal of ASTRML, the correlation was −0.19, but for catchments with long-term average export <300 μg-at m^{-2} yr^{-1}, the correlation was −0.41. Although drainage density appears to be an important factor at very low TP export, the slopes are reversed in the two data sets.

Beaver ponds and other wetlands (classified as PEAT) were probably major sources of the large amounts of TP and TON exported from those catchments in which export exceeded deposition rates. Devito et al. (1989) found that TP retention rates in several wetlands in central Ontario were less than 20% of inputs, although budget uncertainties were equal to or greater than retention rates. Similarly, TON export rates were greater than inputs, whereas TN export rates were generally equal to inputs.

Regression models were presented, which are useful for predicting long-term, average algal nutrient export from forested stream catchments in the Precambrian Shield area of central Ontario. The empirical techniques employed in this report resulted in models considered adequate (Table 6) because (i) $R^2 > 0.8$, the number of independent variables in each model was not unwieldy (7–9), the independent variables were not repetitious; and (ii) only the NH_4^+ export model required a nutrient (TP) as an independent variable.

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