

STREAMFLOW CHEMISTRY AND NUTRIENT YIELDS FROM UPLAND-PEATLAND WATERSHEDS IN MINNESOTA¹

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Abstract. Twenty-two water quality parameters were determined for the streamflow from complex but typical upland-peatland watersheds over a period of 5 yr. Five watersheds with oligotrophic peatlands and one with a minerotrophic peatland were studied. Concentrations of organically derived nutrients are highest in the streamflow from watersheds containing oligotrophic peatlands; while concentrations of nutrients derived from solution of aquifer minerals are higher in streamflow from the watershed containing a minerotrophic peatland. However, flow-weighted concentrations of organically derived nutrients are similar for both watersheds.

Annual nutrient yields (kilogram/hectare per year) calculated for two of the tight upland-oligotrophic peatland watersheds are generally low and are quite similar to values for other forested areas in North America which do not contain peatlands.

Key words: Bogs; fens; forests; nutrient yields; streamflow chemistry; water quality; watershed, upland-peatland.

INTRODUCTION

This paper summarizes 5 yr of streamflow water quality analyses for six forested watersheds in north-central Minnesota. Here, as in much of the Lake States, watersheds are a mixture of low-land organic soils with upland mineral soils. Often a single watershed unit consists of a central peatland surrounded by uplands but drained by a small stream through either organic or mineral soils (Fig. 1).

Water samples were taken from intermittent and perennial streams draining such primary watersheds to provide insight to the chemistry of streamflow, calculate the annual production or losses of water-borne nutrients, and compare watersheds with and without a large groundwater contribution to streamflow.

SITE DESCRIPTION

The six watersheds in this study are located on the Marcell Experimental Forest in central Itasca County ($\approx 47^{\circ}32'N$, $93^{\circ}28'W$). They range in size from 9 to 96 ha of which 11%–30% is composed of peatland (Table 1).

Geology

Bedrock (Ely Greenstone of Precambrian age) lies at depths of 36–120 m. Overlaying the bedrock is a thick layer of compacted till consisting of sand and gravel in a clay matrix with carbonate rock

fragments. On top of the ground moraine is a deposit of sand and gravel ranging from 6–30 m in thickness; it is carbonate free and is still exposed in some places. Finally there is a thick layer of weakly calcareous ground moraine till on top that ranges up to 12 m in depth (Sander 1971).

Soils

Soils developed in the slightly calcareous surface till which is light olive brown, loam to clay-loam textured with cretaceous shale fragments constitute 54% of the Marcell Experimental Forest. Another 20% of the forest contains soils developed in the outwash sands which are noncalcareous, yellowish brown, coarse textured, of granite origin, and ranging up to 30 m in depth. Upland slopes for all watersheds average 10%. Peatlands compose 21% of the forest. Peat deposits are deep (up to 12 m), with the thickness of the deposit feathering out near the uplands. They consist of *Sphagnum* peat at the surface with woody, sedge, and aquatic peats deeper in the solum (Boelter 1962). The remaining 5% of the forest is open water.

The degree of peat decomposition is well correlated with water content and hydraulic conductivity and, consequently, strongly influences the hydrology of peatlands. Surface layers of live *Sphagnum* transmit water readily ($> .04$ cm/s) (Boelter 1970). Lower horizons of the peat profile generally decrease in hydraulic conductivity as they decompose. As a result most water in peatlands moves in the upper 25 cm through horizons of live *Sphagnum* and partially decomposed *Sphagnum* peat (Gorham and Hofstetter 1971).

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FIG. 1. Watershed, WS-2, with an aspen upland and black spruce peatland in center. Arrow indicates a small stream draining the area.

Climite

Itasca County has a continental climate characterized by wide and rapid variations in temperature, low winter precipitation, and normally ample summer rainfall. The Marcell Experimental Forest receives an average annual precipitation of 762 mm. Of this, 75% (572 mm) occurs as rain from mid-April to early November; the remaining 25% is in the form of snow. The average annual temperature is 4°C; the extremes are -46°C and 40°C. Average January and July temperatures are -14°C and 19°C, respectively (Aakre 1966).

Evapotranspiration averages 505 mm from 1 May to 1 November (Bay 1967). This, compared to a rainfall of 546 mm, indicates the dynamic exchange of rainfall input and vapor output of these watersheds.

Hydrology

The peatlands within the study watersheds are classed hydrologically as either perched or groundwater peatlands. The water table in perched peatlands is perched above and isolated from the regional groundwater table, and represents an independent hydrologic system. The water table in a groundwater peatland is simply an exposed part of the regional groundwater system. Groundwater peatlands occur in kettle depressions of the sand and gravel outwash plain, while perched peatlands occur in depressions either in the surface till or the outwash plain. Perched peatland bottoms are sealed against seepage by the highly decomposed, nearly impermeable peat deposits, the clay loam till, or by thin layers of lake-deposited silts and clays.

The terms perched and groundwater peatlands correspond to widely accepted Fennoscandia terminology. Perched peatlands correspond to ombrotrophic bogs, meaning their water is derived mostly from ion-poor precipitation, and groundwater peat-

TABLE 1. Total area and peatland area (in hectares) of study watersheds on the Marcell Experimental Forest. Figures in parentheses represent percent of total that is peatland

Area	WS-1	WS-2	WS-3	WS-4	WS-5	WS-6
Total	33	10	96	34	53	9
Peatland	8(24)	3(30)	25(26)	8(24)	6(11)	2(22)

lands correspond to minerotrophic fens, meaning their water is derived mostly from ion-enriched groundwater (Gorham 1966).

Five of the watersheds (WS), 1, 2, 4, 5, and 6, contain perched ombrotrophic bogs, and watershed 3 contains a groundwater fen. Streamflow from the perched bog watersheds is primarily the result of snowmelt and late spring rains; two-thirds of the annual flow occurs before 15 June. Streamflow usually ceases during late summer, and over winter from January to late March. In contrast, streamflow from the groundwater fen watershed is perennial and thus is more evenly distributed throughout the year.

Groundwater entering the fen in WS-3 leaves it as surface streamflow or as evapotranspiration. It is estimated that 86% of the groundwater approaching the fen passes under it in the aquifer and the remaining 14% occurs as surface flow in the fen (Sander 1971). The watersheds with perched ombrotrophic bogs are tight and essentially all of the streamflow leaves through the central bog and exit stream. A detailed discussion of peatland hydrology is included in Bay (1969, 1970) and Verry and Boelter (1975).

Vegetation

Vegetation on the watersheds is dominated by mature stands of aspen, *Populus tremuloides* Michx. on the uplands and black spruce, *Picea mariana* (Mill.) B.S.P. on the peatlands (Table 2).

Brush cover under the aspen stands is dense and composed largely of beaked and American hazel (*Corylus cornuta* Marsh and *Corylus americana* Walt.). Brush cover under black spruce in perched bogs is scant and largely confined to the bog periphery, but in the groundwater fen, brush cover is moderate to heavy. The dominant brush species for both peatland types is speckled alder, *Alnus rugosa* (Du Roi) Spreng.

The most important species regarding water chemistry is *Sphagnum* moss, which forms a nearly continuous carpet throughout all of the peatlands.

METHODS

A water quality monitoring program was initiated in 1967 to provide base-line information on nutrient

TABLE 2. Average vegetation characteristics on the study watersheds

Forest type	Age (yr)	Ht of dominant and codominant (m)	Diam (cm)	Basal area/ha (m ²)	Merchantable vol/ha (m ³)	Crown closure (%)
Upland aspen	51	22	20.8	25	297	76
Peatland black spruce	87	14	14.2	19	109	49

concentrations and yields from small upland-peatland watersheds typical of much of the northern Lake States and largely unaffected by cultural practices. A single summer sample was taken in 1967 because streamflow from the perched peatlands ceased for the year after a prolonged dry period. In 1968–70 samples were taken in the spring, summer, and fall. In 1971 and 1972 about 15 samples were taken each year. Some ion concentrations were not measured until the latter half of the monitoring program.

Field measurements included pH, temperature, and specific conductance adjusted to 25°C. Water samples were stored in a cooler at 5°C and periodically shipped in ice chests to the USDA Forest Service, Water Quality Laboratory at Ely, Minnesota.

The following ions were analyzed by atomic absorption methods: iron, manganese, aluminum, copper, lead, and zinc (all pretreated with HNO₃); calcium and magnesium (both pretreated with lanthanum); and sodium, potassium, and silicon (all untreated).

Methods described in Orland (1965) were used to determine total acidity and alkalinity (potentiometric titration), nitrate (phenoldisulfonic method), nitrite (diazotization), and sulfate (turbidimetric method after oxidation with H₂O₂).

The following were measured with the Technicon Auto-Analyzer²: chloride (thiocyanate-mercuric-ferric-ammonium sulfate method), ammonia (alkaline phenol with hypochlorite), and Kjeldahl nitrogen (acid digestion to ammonia).

Total phosphate was determined by adding ammonium persulfate and 15–20 N H₂SO₄ to unfiltered samples and cooking for 50 min prior to color development with an ascorbic acid mixture. Apparent color was determined with a Hellige Aqua TesterTM with colored glass standards calibrated against platinum-cobalt standards such that one color unit equals 1 mg Pt/l.

Values (milligrams/liter and other standard units) for all the above parameters were averaged arithmetically for all perched bog watersheds taken as a

unit; values from the groundwater fen watershed were averaged separately. Annual yield values (kilogram/hectare per year) were calculated for perched bog WS-2 and WS-4 because they are considered to be tight watersheds. The other perched bog watersheds either had areas not contributing to streamflow or large amounts of underflow not recorded at stream gaging sites. Annual yields were not calculated for the groundwater fen watershed because the contributing area for groundwater inflow is unknown. Comparisons between perched bog and groundwater fen watersheds were made using the annual average grams of nutrient per cubic meter of streamflow.

The amount of streamflow from the watersheds is a major factor in calculating annual yields of nutrients. Flow measurements for the perched bog watersheds are good ($\pm 2\%$). Those from the groundwater fen were based on short-term measurements of flow in relation to water table elevations and are poor ($\pm 25\%$).

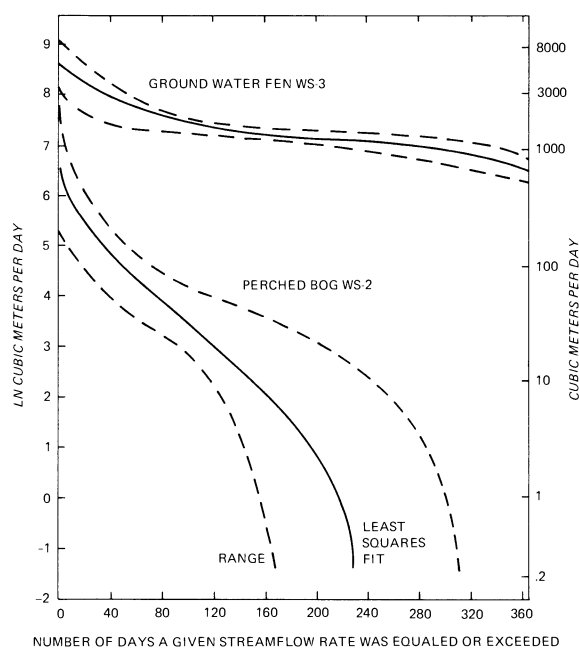


FIG. 2. Flow-duration curves for the groundwater fen and perched bog watersheds.

² Mention of trade names does not constitute endorsement of the products by the USDA Forest Service.

TABLE 3. Average concentration of water quality parameters in the streamflow of perched bog and groundwater fen watersheds. *N* = number of samples; WS-1 = watershed 1, perched bog watershed

Water characteristics	Perched bog watersheds		Ground water fen watershed	
	$\bar{x} \pm SD$	<i>N</i>	$\bar{x} \pm SD$	<i>N</i>
Color units				
WS-1	445 $\pm$ 208	39		
Other perched bog WS	303 $\pm$ 120	131	100 $\pm$ 64	22
pH units	3.6 $\pm$ 0.3	93	6.5 $\pm$ 0.28	15
Specific conductance (μ mho at 25°C)	51 $\pm$ 13	104	125 $\pm$ 48	16
	mg/liter			
Total acidity (as CaCO ₃)	48.2 $\pm$ 24	132	---	---
Total alkalinity (as CaCO ₃)	---	---	54.2 $\pm$ 28.0	18
Total-N	1.34 $\pm$ 0.64	167	0.58 $\pm$ 0.29	21
Organic-N	0.69 $\pm$ 0.40	165	0.33 $\pm$ 0.22	21
Ammonia-N	0.45 $\pm$ 0.39	165	0.15 $\pm$ 0.14	21
Nitrate-N	0.20 $\pm$ 0.25	168	0.10 $\pm$ 0.07	21
Nitrite-N	0.003 $\pm$ 0.003	166	0.003 $\pm$ 0.003	21
Total-P (as PO ₄)	0.19 $\pm$ 0.18	136	0.09 $\pm$ 0.04	17
Cl	0.7 $\pm$ 0.8	172	0.4 $\pm$ 0.4	22
SO ₄	4.6 $\pm$ 2.2	73	6.0 $\pm$ 4.2	7
Fe	1.35 $\pm$ 0.8	166	0.98 $\pm$ 0.48	21
Ca	2.4 $\pm$ 1.0	170	16.6 $\pm$ 9.0	22
Na	0.6 $\pm$ 0.3	164	2.0 $\pm$ 1.0	22
Mg	0.97 $\pm$ 0.36	136	2.88 $\pm$ 0.93	15
Mn	0.06 $\pm$ 0.05	136	0.08 $\pm$ 0.06	14
K	1.3 $\pm$ 0.6	128	1.1 $\pm$ 0.4	22
Al	0.79 $\pm$ 0.43	135	0.16 $\pm$ 0.06	14
Cu	0.04 $\pm$ 0.07	121	0.18 $\pm$ 0.36	11
Pb ^a	< 0.05	116	< 0.05	12
Zn	0.08 $\pm$ 0.11	123	0.11 $\pm$ 0.17	12
Si	2.7 $\pm$ 2.1	49	4.9 $\pm$ 4.0	3

^a Usually below detection limit of .05 mg/liter.

Annual nutrient yields were calculated using a 10-yr average flow-duration curve for each of the perched bog watersheds and a 5-yr average flow-duration curve for the groundwater fen watershed (Fig. 2). These curves were arithmetically integrated to obtain the average annual volume of streamflow. Annual nutrient yields were then calculated by multiplying average concentrations times the annual streamflow volume and dividing by the area of the watershed.

For most nutrients, however, concentrations are inversely related to streamflow rate. In these instances small increments of annual streamflow volume from the flow-duration curves were multiplied by the nutrient concentration associated with the average streamflow rate of the increment. Increments of nutrient yield were then summed for

TABLE 4. Milliequivalents (meq/liter) of major anions and cations from perched bog and groundwater fen watersheds

Ion	Perched bog watersheds		Groundwater fen watershed	
	Cations	Anions	Cations	Anions
H ⁺	0.2512		0.0003	
Ca ⁺⁺	0.1198		0.8283	
Mg ⁺⁺	0.0798		0.2369	
Na ⁺⁺	0.0261		0.0870	
K ⁺	0.0322		0.0281	
HCO ₃ ⁻		0.0000		0.5415
SO ₄ ⁻		0.0958		0.1249
Cl ⁻		0.0197		0.0113
NO ₃ ⁻		0.0003		0.0016
NO ₂ ⁻		0.0001		0.0001
TOTAL	0.5091	0.1159	1.1806	0.6794
Difference		0.3932		0.5012

the year and divided by the area of the perched bog watersheds. Concentration-over-streamflow rate relationships were solved with a linear program after natural logarithm (ln) transformations on each axis.

Weighted concentrations are calculated with the average annual flow determined from the integration of flow duration curves, and with the annual weight of nutrient carried in streamflow determined from the multiplication of flow duration curve increments by corresponding increments of the concentration-streamflow rate curves. This process removes much of the variation associated with using instantaneous values of concentration and streamflow rate; thus the unit grams/cubic meter is used to distinguish from other concentration values.

RESULTS AND DISCUSSION

The average concentration of water quality parameters together with their standard deviations and sample size are listed for perched bog watersheds as a group and for the groundwater fen watershed in Table 3. Milliequivalents/liter for the major anion and cation species are listed in Table 4.

Both the perched bog and groundwater fen water samples have an imbalance of anion and cation milliequivalents/liter indicating that many anions are unaccounted for. These unknowns are probably organic acids (Lamar and Goerlitz 1966, Puustjärvi 1968) which can be considered "true solutions of macro-ions or as dilute suspensions of negative hydrophilic colloids" (Ong et al. 1970). Such ion imbalances are common in colored, low pH waters (Hem 1970). Other sources of error include cations measured analytically that were bound to colloids in the undisturbed water (Malmer 1963) and possible failure to detect total amounts of sulfate, a common problem in colored waters that deserves further investigation.

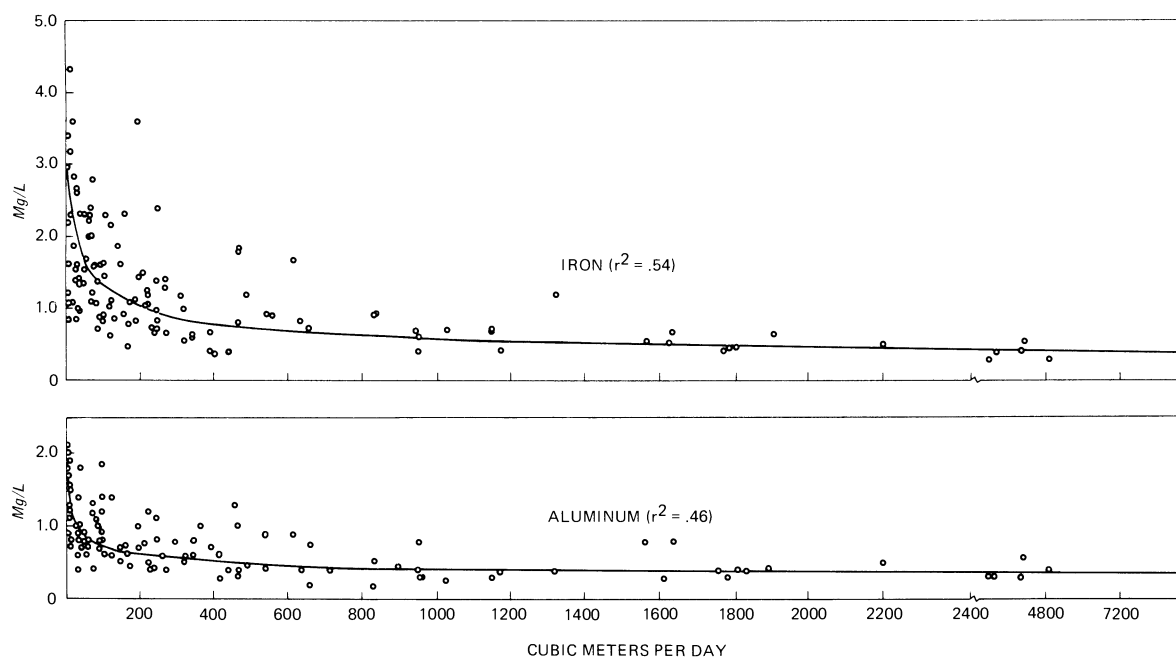


FIG. 3. Relationship of Fe and Al concentration to streamflow rate.

Sulfate and chloride are the major known anions in the perched bog and follow bicarbonate in the groundwater fen; Ca, Al, Mg, Fe, K, and Na are the most important cations in streamflow of each watershed type.

Perched bog watersheds

Color is the most apparent characteristic and ranges from 75–890 color units. It is related to streamflow rate, becoming darker (higher values) as streamflow decreases. High color values in natural waters indicate decomposing organic matter (Kaufman 1969) or a dissolved mineral such as Fe or Mn (Christman et al. 1967). Since Mn and Fe concentrations are low and similar concentrations occur across a wide range of color values, it is likely that the primary cause of color is decomposing organic matter (Lamar 1968).

One of the perched bog watersheds consistently had higher color values than the others (WS-1, Table 3). The higher values are probably related to a zone of well decomposed peat closer to the surface than in the other perched bog watersheds. Even though there is a rather large difference in color values, concentrations of other water quality parameters were not significantly different from those of the other perched bog watersheds.

After color, the most striking characteristic of perched bog water is the low pH (3.1–4.2) which is totally independent of streamflow rate. The most likely major sources of hydrogen ions are dissociation of H_2SO_4 derived from H_2S (Gorham 1956,

1957), and cation exchange in the cell walls of *Sphagnum* plants (Clymo 1964). Levels of pH are important because they control the availability of nutrients to plants and hence are associated with different bog flora (Hofstetter 1969, Heinselman 1970).

Specific conductance is a useful indicator of the source of water entering a bog; that is, whether it is primarily rain and shallow mineral soil inflow or groundwater. Specific conductance is related to streamflow and becomes less after heavy rains or snowmelt. Values $< 80 \mu\text{mho}$ are indicative of a perched water table, and those $> 80 \mu\text{mho}$ of a groundwater table. An exception to this general rule occurs during peak snowmelt runoff when the volumes of water draining both perched bog and groundwater fen watersheds are largely made up of snow water. Values in the 25–45 μmho range are common for both watershed types at this time.

The concentration of other ions, with the exception of some metals, is generally higher in streamflow from the perched bog watersheds than in streamflow from the groundwater fen watershed. Most ion concentrations are inversely related to streamflow rate (Fig. 3, 4); therefore, the higher concentrations primarily result from the lower streamflow rates of perched bog watersheds.

The low pH in perched bogs is another factor which contributes to the higher concentrations of some metal ions. Aluminum and iron tend to remain in solution at low pH levels (Hem 1970), particularly when they are bound under anaerobic conditions

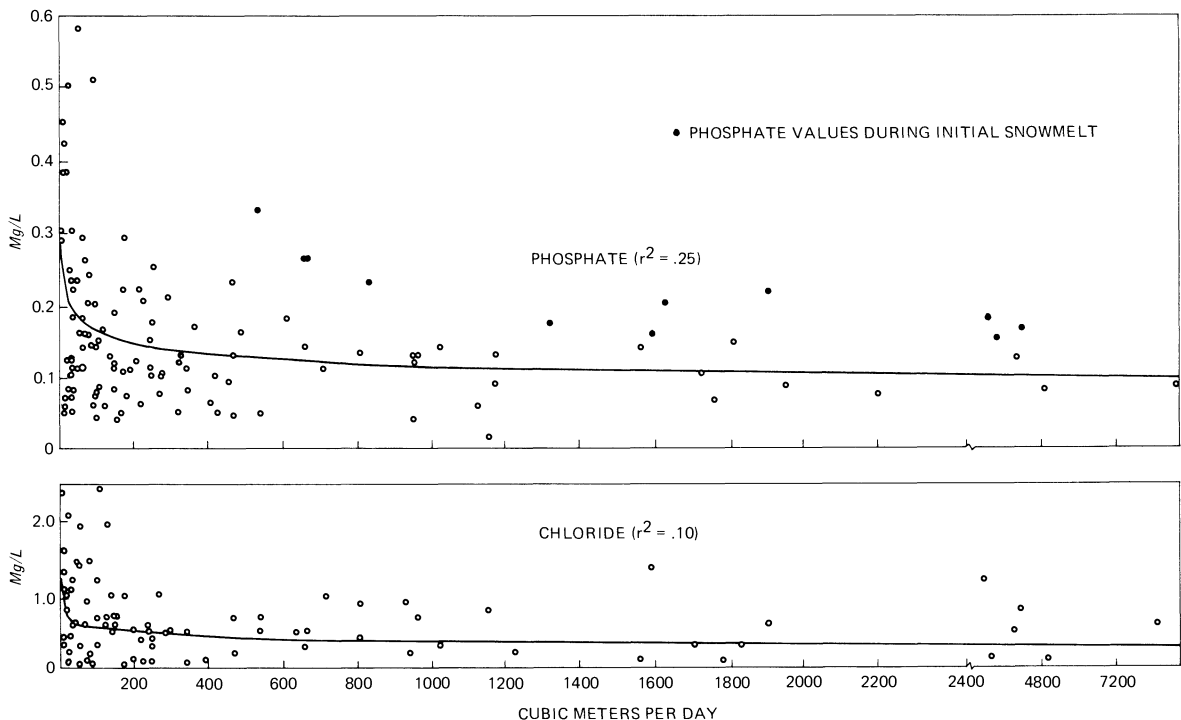


FIG. 4. Relationship of total P (as phosphate) and chloride concentration to streamflow rate.

to organic colloids (Okura and Goto 1955, Hem 1961, Kovalev and Generalova 1967).

Sulfate, Na, and H are not related to streamflow rate. This may be due to the active production of H_2SO_4 in bog waters (Gorham 1956) and the fact that Na is easily removed from cation exchange sites and has no major precipitation reactions (Malmer and Sjors 1955, Gorham and Cragg 1960, Malmer 1962, and Hem 1970).

Potassium is the only ion that is positively correlated with streamflow rate. This may be due to the fact that K is easily leached from plant tissue. Potassium concentrations were increased 33% compared to rain in the open under Scots pine stands on undrained peatland in Finland (Päivänen 1974).

Total phosphorus concentrations (as phosphate) may deviate from their normal relationship to streamflow rate for short periods of 1 or 2 weeks during melting of the snowpack. At this time concentrations may increase up to 350% over the average concentrations (Fig. 4). This may be due to a process whereby phosphorus is liberated from the solid peat during freezing and thawing (Saebø 1969), liberated from the rupture of living cells during freezing and thawing as occurs with some agricultural plants (Timmons et al. 1970), and/or due to phosphorus in the snow derived from overwinter dust and litter fall.

Groundwater fen watershed

Concentrations of organically derived ions in streamflow from the groundwater fen watershed are generally lower than in streamflow from the perched bog watersheds, while ions derived primarily from solution of aquifer materials are higher (Table 3). The exception to these relationships is the unknown anion component which is higher in the fen watershed (Table 4). This may be due to errors in sulfate analysis or the leaching of colored and colorless organic acids in sufficient quantities to balance the high Ca input.

Calcium concentrations are seven times greater than in perched bogs. The source of Ca is probably solution of the carbonate rock fragments in the saturated, compacted till overlaying the bedrock. Sodium, Mg, Mn, Cu, Zn, Si, and sulfate also have higher concentrations derived from solution of minerals in the compacted till and coarse outwash.

Color values are lower than in perched bogs, and pH approaches neutral at an average of 6.5. The higher pH is due to the large inflow of calcium and presumably bicarbonate ions. Iron and aluminum tend to precipitate at near neutral pH levels. Armstrong (1967) has shown that iron will precipitate as ferric hydroxide on the roots of fen plants where respiration maintains an oxidizing environment. Iron will also precipitate as ferrous hydroxides and ferrous carbonate under reducing

TABLE 5. Annual yield (kg/ha·yr) of nutrients and other chemicals for perched bog watersheds, WS-2 and WS-4

Chemical constituent	WS-2	WS-4
Total-N	1.91	1.97
Organic-N	0.99	1.02
Ammonia-N	0.64	0.66
Nitrate-N	0.28	0.29
Nitrite-N	0.01	0.01
Total-P	0.08	0.08
Cl	0.87	0.87
SO ₄	7.75	9.17
Fe	1.81	1.66
Ca	3.46	3.55
Na	1.06	1.25
Mg	1.46	1.52
Mn	0.08	0.08
K	1.26	1.41
Al	1.12	1.04
Zn	0.08	0.09
Si	1.71	1.21
Total acidity (as CaCO ₃)	72.01	74.19

conditions at the bottom of hollows in oily, metallic, rust-gray or gold colored films called *rimpis* (Puustjärvi 1952). These *rimpis* are widely scattered over the fen.

The concentrations of chemical constituents in the streamflow from the groundwater fen watershed do not appear to be inversely related to streamflow rate; such a relationship may be masked by concentration variation and the more uniform flow rates from the groundwater fen. Nutrient concentrations at peak snowmelt are slightly lower than at other times and specific conductivity is as much as 50 μ mho lower.

Chemical yields from perched bog watersheds

The annual yield of chemicals (kilogram/hectare per year) is listed for WS-2 and WS-4 (Table 5). These average values should be used with the realization that they may vary by $\pm 25\%$ – $\pm 35\%$, due primarily to variation in annual streamflow (Fig. 2).

Variation in the relationship between chemical

concentration and streamflow rate can also cause variation in annual yield values. The measures of color, specific conductance, total acidity, total-N, total-P, chloride, total Fe, Ca, Na, Mg, Mn, Al, Zn, and Si are inversely related to streamflow rate. These relationships have coefficients of correlation (r^2) ranging from 0.1 to 0.5; however, all have negative slopes significant at the 99% level. Some of the better and poorer relationships are shown in Fig. 3 and 4.

The chemical yields from WS-2 and WS-4 are quite consistent even though watershed areas and annual flow volumes differ by factors of 3 and 4, respectively (Table 1, 5, 7). These watersheds are typical of much of the forested areas of the northern Lake States where medium textured mineral and organic soils predominate. Therefore these chemical yields can be used as inputs to downstream wetlands and lakes or as losses for chemical budgets in this area.

It is somewhat surprising to see that nutrient yields from these watersheds compare quite favorably to other forested areas within a restricted latitude range in North America; even though organic soils compose 24%–30% of the watershed (Table 6).

Comparison of flow-weighted concentrations

Chemical yields from the groundwater fen watershed cannot be calculated on a kilogram/hectare per year basis because the contributing area of the groundwater inflow is unknown. However, some insight to the leaching process can be gained by examining nutrient concentrations data weighted by flow rate.

In the perched bog watersheds most chemical constituents are inversely related to streamflow rate and thus their average annual weighted concentrations are different from the average of sample concentrations. In the groundwater fen watershed chemical constituents are not related to flow rate in a statistically significant sense, thus the average

TABLE 6. Nutrient yields (in metric tons per square kilometer per year) from forested areas in North America. 43°N–48°N latitude. Values other than Minnesota adapted from Likens and Bormann 1974

Area	Vegetation type	Nutrient yield in streamflow		
		N	P	K
Minnesota	Deciduous-coniferous (<i>Populus</i> , <i>Picea</i>) Marcell Experimental Forest	0.20	0.008	0.14
New Hampshire	Deciduous (<i>Acer</i> , <i>Betula</i> , <i>Fagus</i>) Hubbard Brook Experimental Forest	0.23	0.001	0.17
Ontario	Deciduous (<i>Acer</i> , <i>Fagus</i> , <i>Quercus</i>) Clear Lake watershed	0.23	0.016	0.15
Washington	Coniferous Cedar River watershed	0.12–0.27	0.007–0.008	---
Oregon	Coniferous (<i>Pseudotsuga</i> , <i>Tsuga</i>) H. J. Andrews Experimental Forest	0.05	0.052	0.18

TABLE 7. Average annual flow weighted concentrations for perched bog and groundwater fen watersheds (g/m^3). Annual streamflow averages for WS-2, WS-4 and WS-3 are 16,278; 67,429; and 574,954 m^3 , respectively

Chemical constituent	Perched bog watersheds		Groundwater fen WS-3
	WS-2	WS-4	
Total-P	0.05	0.04	0.03
Total-N	1.1	1.0	0.6
Total-Fe	1.1	0.8	1.0
Cl	0.5	0.4	0.4
K	0.8	0.7	1.1
Al	0.67	0.53	0.16
SO_4	3.6	3.5	6.0
Na	0.6	0.6	2.0
Mg	0.9	0.8	2.9
Ca	2.1	1.8	16.6
Mn	0.05	0.04	0.09
Zn	0.05	0.04	0.11
Si	1.0	0.6	4.9

sample concentrations are identical to the weighted concentrations.

Weighted concentrations for the two watershed types are similar for organically derived ions (total-P, total-N, and total-Fe) and for chloride which moves freely in the environment and is not found in large concentrations in the inflowing groundwater. Potassium values are also similar but are probably influenced by significant concentrations in the groundwater (Table 7).

In general, nearly equal amounts of organically derived nutrients are leached from both watershed types in an equal volume of water leaving the watershed as streamflow. The total yield (kilogram/year) of all chemical constituents is primarily a function of the annual volume of streamflow. Precipitation reactions such as aluminum in the groundwater fen watershed and dissolution reactions also play a lesser role in the yield of annual nutrients.

Peatland development

The peatlands in the perched bog and groundwater fen watersheds represent extremes in the development of peatlands (Heinselman 1970). The floristics and water chemistry of the perched peatlands are similar to other ombrotrophic peatlands world-wide, even though they are surrounded by mineral soils and receive subsurface flow from them (Moore and Bellamy 1974). Cation exchange reactions are the most probable mechanism for maintaining the low pH conditions necessary for *Sphagnum* development.

The groundwater fen peatland is apparently building with time since it already is acting as a partial dam to groundwater flow in the area (Sander 1971). These groundwater fens commonly occur upstream from the fingers of a perennial stream

network. In such a location they represent exceptions to the geologic principle that stream channels tend to extend themselves through channel-head cutting. Only in disturbed peatlands does channel-head cutting proceed rapidly (Crisp 1966). In north-central Minnesota, under stable climatic conditions, peat building is the dominant process.

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