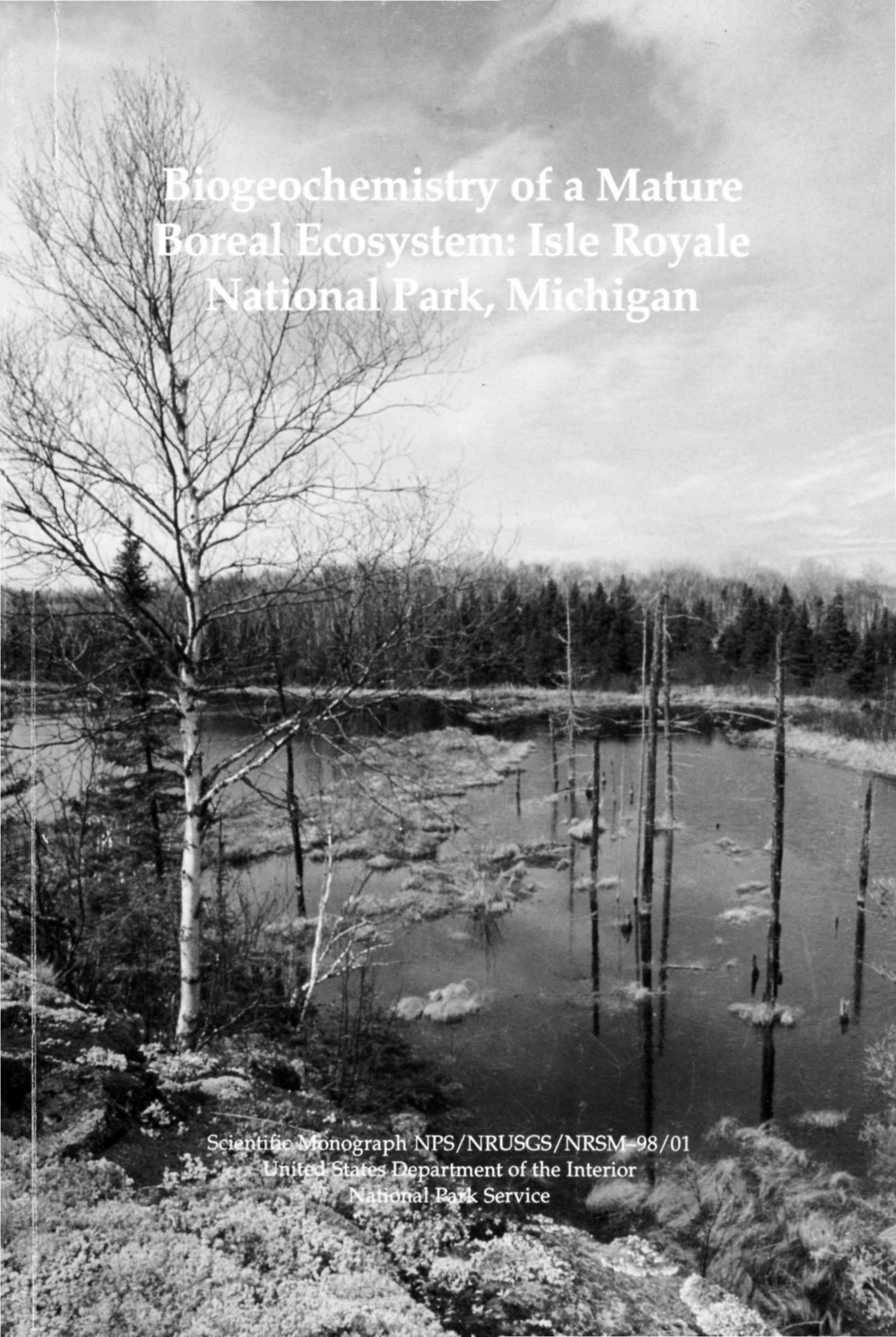
# Biogeochemistry of a Mature Boreal Ecosystem: Isle Royale National Park, Michigan



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*Cover photograph*: Wallace Lake, Isle Royale National Park, Michigan.

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# Preface

The importance of watershed ecosystem research to the management of natural areas such as national parks cannot be overstated. Watershed conditions are affected by uncertain and complex interactive environmental trends, many of global occurrence. Questions about watershed science, although often site specific, thus require answers in a global context. Frequently, input to the highest levels of government decision making is needed if modern society is to mitigate, stop, or reverse the large scale alterations of watershed ecosystems worldwide. However, our ability to sensibly and effectively manage natural resources in today's global environment is often constrained by our lack of knowledge about the hydrologic cycle and its relation with the geosphere and biosphere. We know that the current condition of natural resources in parks and other preserved lands is subject to many widespread anthropogenic changes from acidification, eutrophication, toxic substances, boundary encroachments, overuse, species shifts or extirpation, desertification, loss of biodiversity, land use change, and sea level rise. Long-term watershed research and monitoring of natural and remote areas in the National Park System and in similar reserves provide important data on ecosystem processes and interactions for detecting spatial and temporal changes in environmental conditions. These data collections allow the partitioning of cause-and-effect relations of ecological change in watersheds. They also serve to meet reference and early warning objectives correlative with natural ecosystem change. Accordingly, the scientific and public policy communities can employ watershed ecosystem information as one means of obtaining early indications of the potential effects of anthropogenic stress and an improved assessment of its magnitude. Use of the concept to address several goals of research into *acid precipitation* or biogeochemical cycling demonstrated the utility of these integrated watershed data for inter-ecosystem comparison between preserved and other watersheds. The long-term management strategies of the National Park Service combined with the *protected* nature of park lands placed the service in a unique position among federal agencies and among international conservation organizations to document relations between ecosystem effects and anthropogenic influences.

Studies of watershed ecosystems collect long-term baseline data on the ecosystem health of park and equivalent reserves. Research and monitoring at the watershed level by the U.S.Geological Survey and the National Park Service since 1980 have contributed to the accumulation of important baseline information on deposition, meteorology, hydrology, ecosystem functioning, and biology in selected parks and biosphere reserves. Important information on biological diversity and biogeochemical processes have also been obtained. Activities have ranged from needs identification to reconnaissance or synoptic analyses to long-term monitoring and long-term ecosystem research. Quantification of the hydrologic cycle and chemical flux is a major objective of the watershed program. Such measurements, when combined with other geographic resource data (e.g., geology, land-use, topography, and historic and pre-historic records), provide a better understanding of ecosystem-level processes and of how watershed ecosystems respond to various natural and anthropogenic stimuli. Currently, these data are available for developing, testing, and implementing state-of-the-art methods and procedures for improved management of water and land resources at the national and international levels.

By 1982, the National Park Service had implemented studies in three national parks: Sequoia-Kings Canyon, (California), Rocky Mountain (Colorado), and Isle Royale (Michigan) national parks. Sites were selected to be biogeographically representative of mature ecosystems in relatively remote areas that receive varying levels of atmospheric contaminant inputs. Two years later, the largely pollution-free Olympic National Park (Washington) was added. The sites have several important common attributes including a long-term protected status, a core area (undisturbed watershed), research hypotheses and experimental design for detection of ecosystem change and understanding the mechanisms of change, basic inventory information, research or monitoring capabilities, monitoring techniques that will not change unless calibrated to new techniques, sampling protocols that fit within the time frame of known physical and biologic events, and standardized protocols for data collection, sample storage, sample archival, and data management.

Today, comprehensive watershed ecosystem inventory, monitoring, and research data, a series of publications on ecosystem function and structure, and to some extent management of park resources that span more than 15 years are available from the four original sites and from Shenandoah National Park (Virginia) where watershed studies began in 1979. Shorter or discontinuous records of watershed ecosystems are available from Big Bend (Texas), Denali (Alaska), Glacier (Montana), and Great Smoky Mountains (North Carolina and Tennessee) national parks and from Noatak National Preserve (Alaska). Six parks are now part of the National Park Service-U.S. Geological Survey Global Climate Change Program: Rocky Mountain, Isle Royale, Olympic, Sequoia, Glacier, and Crater Lake national parks. Three watershed sites are included in the cooperative Inventory and Monitoring Program of the service and the survey: Shenandoah, Great Smoky Mountains, and Denali national parks. Sites range from the hot Chihuahuan Desert in the Southwest to the moist boreal forests of Michigan, the eastern deciduous forests of Virginia, Tennessee, and North Carolina, the alpine environment of California and Colorado, and the Alaskan taiga-tundra.

The condition of natural resources within these natural watersheds has often been difficult to ascertain, but gaining this knowledge has provided the key to understanding the nature of ecosystem change. The existence of sites with a commitment to gathering long-term ecosystem level data permits research activities aimed at testing hypotheses relevant to ecosystem processes and structure. These data further make it possible to question existing paradigms and to obtain new understandings about fundamental relationships within and between naturally functioning ecosystems. This applies equally to other areas and is suggested as appropriate for a potential network of long-term global baseline research sites. Potentially significant conclusions, common to most long-term watershed ecosystem programs and studies, are thus emerging.

This monograph presents the results of the first 16 years of watershed research in Isle Royale National Park. It is an example of the value of staying the course to increased understanding of park natural resources and of mature boreal ecosystems.

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# Biogeochemistry of a Mature Boreal Ecosystem:
## Isle Royale National Park, Michigan

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**Abstract.** During 1982–96, a study was conducted of the biogeochemistry of the mature boreal forested Wallace Lake watershed in Isle Royale National Park, Lake Superior basin, Michigan. The research objectives were the quantification of the ecosystem structure and function and the determination of the response of the watershed to atmospheric inputs and climate change. The Lake Superior basin receives moderate atmospheric $H^+$, $NH_4^+$, $NO_3^-$, and $SO_4^{2-}$ inputs. In recent decades, regional temperatures increased and precipitation amount declined. In the Wallace Lake watershed, precipitation averaged 75 cm, 40% of which fell in winter. Canopy interception ranged from 20% to 35% incident precipitation. Snowpack depths were sufficient to keep soils unfrozen except beneath spruce where high interception reduced snowpack depth. Unfrozen soils and mid-winter thaws reduced the peak water equivalent (PWE) of the snowpack and the ion content. Stream flow was dominated by snowmelt and averaged 68% of precipitation. Since 1982, precipitation $H^+$ and $SO_4^{2-}$ concentrations declined. Throughfall $H^+$ and $NO_3^-$ flux were less than precipitation input, but $SO_4^{2-}$ increased. Base cation ($C_B$), $HCO_3^-$, and $SO_4^{2-}$ flux were greater in soil water than in throughfall, but $H^+$, $NH_4^+$, and $NO_3^-$ were less in soil water than in throughfall. Ninety percent of the precipitation entered forest soils where soil processes significantly modified its chemistry. Soil inorganic N pools were more than 5 times the precipitation input and peaked in spring and early summer. Soil net N mineralization occurred throughout the year and peaked in May–June. Net N mineralization rates declined as soil temperature increased. Soil gross mineralization rates were about 25 times the net mineralization and increased with soil temperature, $CO_2$ efflux, and moisture. Microbial N immobilization was greatest beneath alder and increased with soil temperature. Soil net and gross N mineralization rates did not correlate. Soil respiration rates increased with temperature. During snowmelt, the stream water acid neutralization capacity declined more than 475 $\mu$eq $L^{-1}$, 98% from dilution. Watershed $C_B$ output exceeded input 17 times. The watershed retained more than 99% of $H^+$ inputs and 75% of $NO_3^-$ and $NH_4^+$ inputs. $SO_4^{2-}$ output was 1.2 times greater than $SO_4^{2-}$ input. The aboveground living biomass of the boreal forest was 108 t $ha^{-1}$, which was comparable to that in the interior Alaskan taiga. Annual volume-weighted base cation uptake was about 90 and N was 39 kg $ha^{-1}$ $year^{-1}$. The net change in total aboveground biomass with time was small.

**Keywords:** boreal, watershed, biogeochemistry, nutrient cycling, Isle Royale, Michigan.

Since the 1960s, concern and interest in the potential effects of atmospheric $H^+$, $NH_4^+$, $NO_3^-$, and $SO_4^{2-}$ inputs on North American terrestrial and aquatic ecosystem structure and function have been considerable (Bormann and Likens 1967; Bormann 1985; Edmonds et al. 1997). The heightened interest contributed to an expanded use of the watershed ecosystem concept to more fully link terrestrial to aquatic effects (Likens 1983). To better establish linkages between anthropogenic atmospheric inputs and ecosystem health, the National Acid Precipitation Assessment Program (NAPAP) was established in 1980. The program was complemented by similar research in Europe and by the Electric Power Research Institute's Integrated Forest Study in North America (Johnson and Lindberg 1992).

As part of NAPAP, in 1982 the National Park Service established the Watershed Research Program with four ecosystem study sites: Isle Royale National Park, Michigan; Olympic National Park, Washington; Rocky Mountain National Park, Colorado; and Sequoia-Kings Canyon National Parks, California. The program was funded by the National Park Service from 1982 until 1992, by the National Biological Service from 1993 until 1995, and by the Biological Resources Division of the U.S. Geological Survey as of 1996. The research objectives were the quantification of ecosystem structure and function and the determination of the response of the watersheds to atmospheric inputs and climate change (Herrmann and Stottlemyer 1991). Stressor-oriented monitoring was to be emphasized for the detection of change with time.

Isle Royale was selected as a research site for several reasons. First, it is one of the most remote national parks in the 48 contiguous states (Fig. 1a). Second, it has a history of little human land use and no possible conterminous land use. Third, it is representative of a mature southern boreal ecosystem (Fig. 2), a system that despite its expansive global importance has been little studied in a long-term context. Fourth, the Wallace Lake watershed has the highest atmospheric $H^+$, $NH_4^+$, $NO_3^-$, and $SO_4^{2-}$ inputs (NADP 1982–96) of parks and reserves in the Watershed Research Program and, like much of the boreal biome, is in a region that is experiencing climate change (Schindler et al. 1990).

Isle Royale is in the Northern Superior Upland section of the Superior Upland geomorphic province, a glacially scoured peneplain characterized by rolling hills and level uplands with elevations from 180 to 700 m (McNab and Avers 1994). The park is in the transition zone between northern hardwood and southern boreal forests. Such ecotonal regions are intrinsically sensitive (Lavoie and Payette 1994; Risser 1995; Arseneault and Payette 1997). Linked forest productivity and soil-process models suggest this boreal ecosystem fringe may be the most sensitive of the eastern North American forests to climate change (Pastor and Post 1988; Solomon 1988).

Boreal forest ecosystems, like deserts and the tundra, provide good evidence of the importance of functional group diversity in maintaining stability (Tilman et al. 1997). The effect of removal of a single species can be consider-

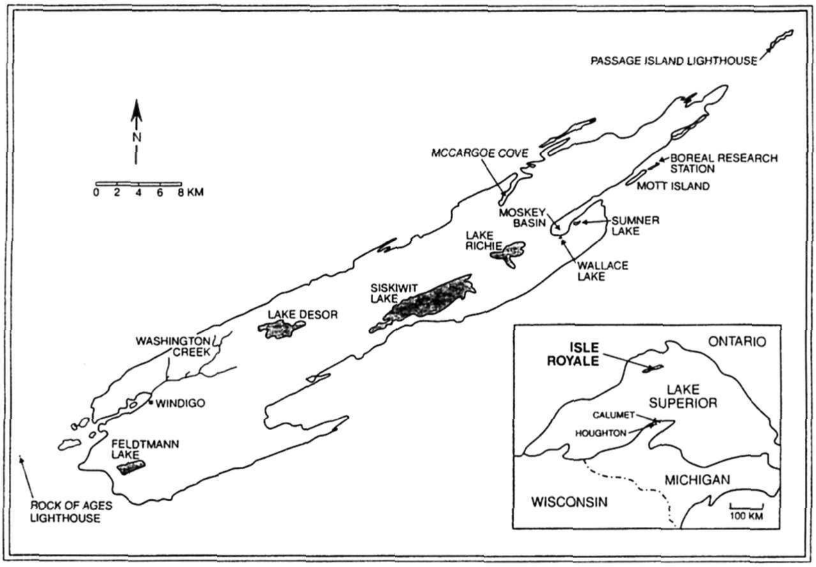


**Figure 1a.** Isle Royale National Park in the Lake Superior Basin of Michigan.

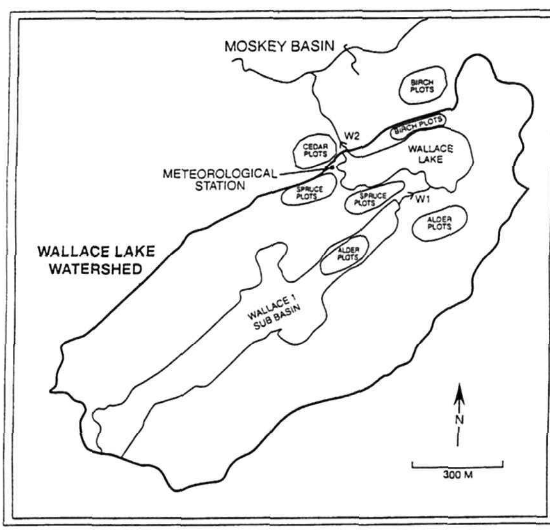


**Figure 1b.** Wallace Lake watershed and the location of major water, soil, and vegetation sampling points, Isle Royale National Park, Michigan.

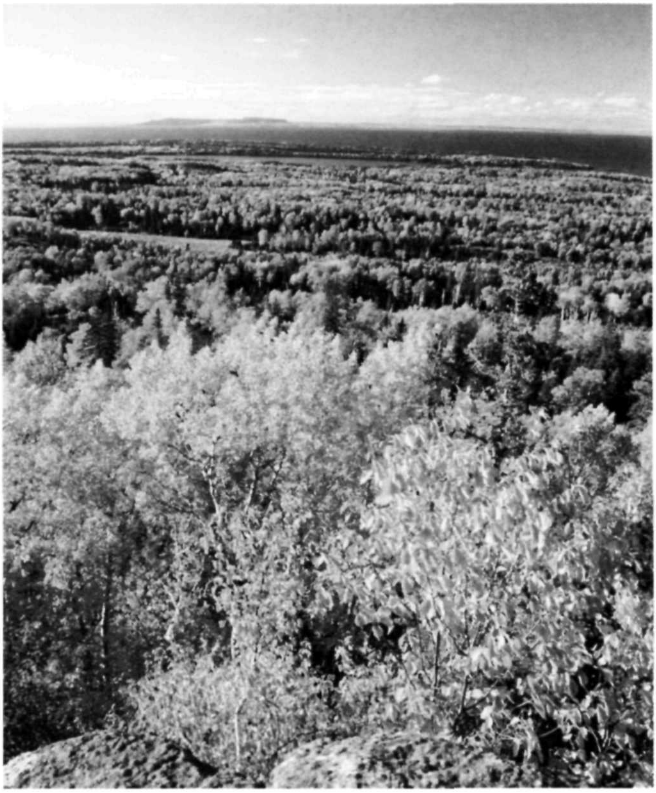

**Figure 2.** Boreal forest of Isle Royale National Park with dominant species of white birch (*Betula papyrifera*), quaking aspen (*Populus tremuloides*), white spruce (*Picea glauca*), balsam fir (*Abies balsamea*), and tag alder (*Alnus rugosa*).

able. Examples of the influence of single species on Isle Royale are the beaver (*Castor canadensis*) and the moose (*Alces alces*). The boom-and-bust cycles of mammalian grazers in this ecosystem are related to the system's simplicity (McLaren and Peterson 1994). Despite this sensitivity (Pastor and Post 1988; Schindler et al. 1990; Lavoie and Payette 1996) and the extensive area covered globally by the boreal forest, this ecosystem has been little studied (Larsen 1980; Van Cleve et al. 1983a, 1983b; Van Cleve et al. 1986; Mooney et al. 1991).

In this paper, we provide (1) a summary of the precipitation and stream water chemistry and flux during 1982–96 in the Wallace Lake watershed, (2) a comparison of the chemical flux of dominant boreal-forest species, (3) a description of the modification of the precipitation chemistry by the forest canopy and the surface mineral soils before entering the stream, and (4) a description of the processes that may account for the observed changes.

# Study Site

Conducting long-term, ecosystem-level research in a national park has a major advantage because of the legal protection against arbitrary land-use changes. Because the value of long-term study increases with time, the selected site can represent a significant investment of funding, time, and personnel. The removal of potential arbitrary and incompatible land use or activity, which are common on public land outside wilderness and parks, on or conterminous to the site is probably the most important site-selection criterion.

Selection of the Wallace Lake watershed on Isle Royale followed an extensive survey of surface-water quality in the park's streams and lakes in 1980–81 (Table 1). The two objectives of the survey were the characterization of surface-water chemistry throughout the park and the determination of whether the increase in glacial till coverage and depth from the northeastern to the southwestern end of the park (Huber 1973) significantly affected surface-water chemistry. Our site-selection criteria were a watershed ecosystem with surface-water-quality characteristic of Isle Royale and a system vegetated exclusively by boreal forest. The latter objective limited our site selection to the northeastern two-thirds of the park because portions of the southwestern end of the park are vegetated by mature northern hardwoods. A final consideration was accessibility. Sites in the interior of the park are especially difficult to reach in fall, winter, and early spring.

At the time of site selection, interest in the response of sensitive (low acid-neutralization capacity or ANC) lakes and streams to acid precipitation was great. The 1980–81 surface water survey revealed that the lakes and streams of Isle Royale were not directly sensitive to acid precipitation. The lower specific conductance and pH waters on Isle Royale are dominated by high concentrations of dissolved organics. The absence of a clear-water, sensitive system was not a limitation because our primary research goal was the long-term study of the structure and function of a southern boreal ecosystem and its response with time to a variety of atmospheric inputs and climate change.

## *Topography*

The 115-ha Wallace Lake watershed (48° 03' N, 88° 38' W) is in the northeastern third of Isle Royale National Park, Michigan, in northwestern Lake Superior, about 130 km north of Houghton in the upper peninsula of Michigan (Fig. 1a). In the watershed is the 5-ha Wallace Lake (Fig. 1b) and the gauged first-order subcatchment W1 (16 ha), the only subcatchment with year-round stream discharge (Fig. 3). This stream flows north-northeast into Wallace Lake, and the Wallace Lake outflow, gauged at Station W2, flows north-northwest into the Moskey basin.

The watershed elevation ranges from 195 m at the lower stream gauging station (W2) to 275 m on a ridge that is the watershed's eastern border. The

**Table 1.** Parameters sampled in a subset of streams and lakes on Isle Royale during 1980–1981 to characterize surface water quality. Lakes and streams are arranged from the northeastern to the southwestern sections of the park. Upstream-downstream stations are numbered with the lowest number at the head of the watershed and the highest number at the mouth of the watershed. Concentrations are in μeq $L^{-1}$.

| Station[a] | pH | Temp | Cond | $HCO_3^-$ | $Ca^{2+}$ | $Mg^{2+}$ | $Na^+$ | $K^+$ | $NH_4^+$ | $NO_3^-$ | $SO_4^{2-}$ | $Cl^-$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Lakes | | | | | | | | | | | | |
| Amygdaloid | 7.0 | | 81 | 620 | 343 | 371 | 34 | 15 | 0 | <0.5 | 104 | 25 |
| Forbes | 7.2 | 13 | 74 | 360 | 287 | 190 | 60 | 4 | 0 | <0.5 | 91 | 7 |
| Newt | 6.6 | 7 | 97 | 500 | 547 | 245 | 37 | 4 | 3 | <0.5 | 67 | 5 |
| John | 7.6 | | 97 | 460 | 342 | 80 | 34 | 2 | 0 | 1.0 | 124 | 4 |
| Epidote | 7.1 | 15 | 73 | 280 | 397 | 162 | 29 | 3 | 0 | <0.5 | 90 | 0 |
| Theresa | 7.5 | 5 | 32 | 120 | 180 | 109 | 20 | 3 | 3 | 0.1 | 54 | 7 |
| Angleworm | 7.3 | 15 | 63 | 240 | 202 | 148 | 54 | 4 | 0 | <0.5 | 128 | 6 |
| Chickenbone | 6.3 | 9 | 69 | 580 | 377 | 289 | 61 | 5 | 0 | 7.0 | 98 | 12 |
| Livermore | 7.7 | | 57 | 980 | 328 | 435 | 93 | 6 | 0 | <0.5 | 88 | 7 |
| Richie | 7.5 | 15 | 77 | 340 | 314 | 214 | 63 | 6 | 0 | <0.5 | 117 | 18 |
| Scholtz | 6.7 | 14 | 58 | 260 | 238 | 149 | 33 | 7 | 0 | 5.0 | 103 | 5 |
| George | 7.0 | 13 | 94 | 520 | 506 | 122 | 20 | 1 | 0 | 11.0 | 77 | 8 |
| Dustin | 6.8 | 13 | 59 | 280 | 256 | 145 | 30 | 14 | 0 | 8.0 | 96 | 6 |
| Whittlesey | 7.8 | 16 | 67 | 300 | 277 | 159 | 41 | 10 | 0 | 0.5 | 96 | 7 |
| Intermediate | 7.3 | 15 | 60 | 220 | 224 | 171 | 44 | 6 | 0 | <0.5 | 132 | 14 |
| Hatchet | 7.2 | | 78 | 700 | 282 | 411 | 91 | 6 | 0 | <0.5 | 91 | 43 |
| Desor | 7.9 | | 88 | 860 | 370 | 452 | 80 | 13 | 0 | <0.5 | 90 | 9 |
| Halloran | 6.6 | | 185 | | 1614 | 223 | 140 | 12 | 14 | 3.0 | 97 | 121 |

**Table 1.** *Continued.*

| Station[a] | pH | Temp | Cond | $HCO_3^-$ | $Ca^{2+}$ | $Mg^{2+}$ | $Na^+$ | $K^+$ | $NH_4^+$ | $NO_3^-$ | $SO_4^{2-}$ | $Cl^-$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Streams | | | | | | | | | | | | |
| Tobin | 7.8 | | 99 | 935 | | | | | | 15.0 | 60 | 33 |
| John | 7.7 | 17 | 146 | 590 | 768 | 213 | 50 | 4 | 0 | 3.0 | 103 | 4 |
| John 2 | 7.7 | | 119 | 476 | 498 | 145 | 32 | 2 | 4 | 0.0 | 33 | 0 |
| Newt | 7.1 | 6 | 106 | 459 | 581 | 246 | 52 | 33 | 34 | 1.0 | 55 | 6 |
| Epidote | 7.0 | 9 | 90 | 312 | 460 | 191 | 34 | 3 | 0 | 2.0 | 79 | 0 |
| Scholtz | 6.6 | 9 | 66 | 262 | 344 | 125 | 23 | 0 | 0 | 0.0 | 78 | 3 |
| Whittlesey t2 | 6.0 | 11 | 56 | 148 | 309 | 177 | 44 | 7 | 5 | 1.0 | 68 | 2 |
| Whittlesey t3 | 6.2 | 11 | 58 | 131 | 318 | 179 | 49 | 9 | 7 | 1.0 | 69 | 3 |
| Whittlesey t4 | 6.2 | 11 | 55 | 180 | 316 | 182 | 41 | 6 | 4 | 2.0 | 70 | 0 |
| L. Siskiwit | 6.2 | | 94 | 213 | 391 | 378 | 57 | 3 | 3 | 14.0 | 458 | 18 |
| Little Todd | 6.9 | | 115 | 820 | 430 | 633 | 100 | 7 | 0 | 1.0 | 142 | 16 |
| Island Mine | 7.4 | | 132 | 918 | 569 | 576 | 117 | 9 | 0 | 16.0 | 153 | 9 |
| Washington | 6.9 | 7 | 115 | | 489 | 370 | 100 | 10 | | 2.0 | 129 | 52 |

**Table 1.** *Continued.*

| Station[a] | pH | Temp | Cond | $HCO_3^-$ | $Ca^{2+}$ | $Mg^{2+}$ | $Na^+$ | $K^+$ | $NH_4^+$ | $NO_3^-$ | $SO_4^{2-}$ | $Cl^-$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Upstream-Downstream | | | | | | | | | | | | |
| Washington 1 | 6.7 | 9 | 100 | | 486 | 354 | 91 | 10 | | 2.0 | 94 | 22 |
| Washington 2 | 7.3 | 19 | 150 | | 789 | 526 | 87 | 18 | | | | |
| Washington 3 | 6.6 | 7 | 105 | | 475 | 362 | 96 | 10 | | 0.0 | 108 | 27 |
| Washington 4 | 6.7 | 7 | 100 | | 468 | 362 | 100 | 10 | | | | |
| Wash Tr1 | 6.5 | 5 | 76 | 525 | 75 | 313 | 65 | 13 | | 8.0 | 72 | 10 |
| Wash Tr2 | 6.8 | 6 | 148 | 1427 | 133 | 1398 | 235 | 16 | | 5.0 | 58 | 10 |
| Wash Tr3 | 7.0 | 5 | 162 | 1542 | 105 | 1069 | 196 | 16 | | 0.0 | 117 | 15 |
| Greenstone 1 | 7.1 | 13 | 64 | 168 | 269 | 218 | 50 | 3 | 0 | 1.0 | 89 | 1 |
| Greenstone 2 | 6.9 | | 63 | 156 | 248 | 208 | 64 | 4 | 4 | 0.0 | 101 | 14 |
| Greenstone 3 | 7.0 | 17 | 64 | 143 | 246 | 204 | 60 | 3 | 4 | 0.0 | 100 | 10 |
| Greenstone 4 | 7.7 | 16 | 64 | 150 | 254 | 210 | 63 | 3 | 0 | 2.0 | 104 | 10 |
| Noname 2 | 7.0 | 12 | 65 | 303 | 320 | 105 | 33 | 8 | 7 | 1.0 | 31 | 6 |
| Noname 3 | 6.9 | 11 | 70 | 310 | 327 | 125 | 39 | 6 | 5 | 1.0 | 29 | 11 |

[a] Station numbers increase downstream.

**Figure 3.** Stream gauging station (W1) at the mouth of the first-order sub-catchment Wallace 1 in the Wallace Lake watershed, Isle Royale National Park, Michigan.

watershed has a northern aspect. Rock outcrops (Fig. 4) are generally vegetated by scattered white spruce (*Picea glauca*) and make up about 40 ha of the watershed, primarily in the western portion. The watershed is characterized by a relatively flat topography, broken by northeast-southwest oriented small (< 5-m elevation change) bedrock ridges, most of which were exposed by glaciation. Such geomorphology is characteristic of the Northern Superior Uplands (McNab and Avers 1994). One of these small ridges dams Wallace Lake.

To provide a reference set of stream water chemistry, the conterminous Sumner Lake watershed east of the Wallace Lake watershed is also gauged

**Figure 4.** Exposed ridge vegetated with white spruce (*Picea glauca*), Wallace Lake watershed, Isle Royale National Park, Michigan.

(Fig. 1a). The Sumner Lake watershed is slightly larger than the Wallace Lake watershed and has a more northeastern aspect, but its elevation is similar. Stream water chemistry is monitored here at two locations: in the year-round stream feeding Sumner Lake (Station S1) and in the Sumner Lake outflow (S3).

## *Climate*

In the Northern Superior Uplands, annual precipitation ranges from 66 to 78 cm and generally increases from north to south (McNab and Avers 1994). Annual precipitation along the southern shore of Lake Superior exceeds this range (Stottlemyer and Toczydlowski 1996a, 1996b). Sixty percent of the annual precipitation in the Northern Superior Uplands falls in the growing season (80–123 days). The mean annual temperature is 2–3°C; the warmer temperatures are near Lake Superior.

During 1982–96, the mean annual temperature in the Wallace Lake watershed was 3°C (standard deviation = 1.8°C; Fig. 5). The mean annual minimum temperature was 0.2° and the mean maximum temperature 5.8°C. The mean annual temperature was 2.4°C lower in the Wallace Lake watershed than at the NOAA (National Oceanographic Atmospheric Administration) station on the Houghton County Airport, 100 km south of the Wallace Lake watershed, and 1.3°C lower than at the NOAA station in Grand Marais, Minnesota, 142 km

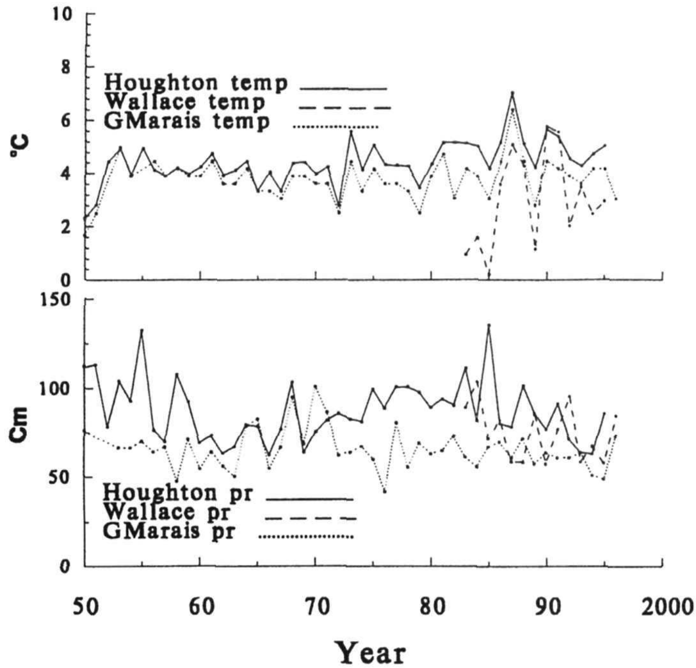


**Figure 5.** Mean annual temperature and precipitation, NOAA station on the Houghton County Airport, Houghton, Michigan, 6 km from the Calumet watershed and 100 km south of Wallace Lake; NOAA station in Grand Marais, Minnesota, 142 km west of Wallace Lake; and Wallace Lake watershed, Isle Royale National Park, Michigan, 1982–1996.

west of the Wallace Lake watershed. We were unable to obtain post–1990 data from Thunder Bay, Ontario, 62 km northwest of Wallace Lake. During 1982–90, when the Thunder Bay and the Wallace Lake watershed records overlap, the annual mean temperatures were similar. In the Wallace Lake watershed, the mean monthly seasonal temperatures ranged from –9°C in January to 15.8°C in July (Fig. 6).

The mean annual precipitation in the Wallace Lake watershed was 75 (16) cm and ranged from 57 to 104 cm. Annual precipitation in the Wallace Lake watershed was near the upper range of that in the Northern Superior Uplands (McNab and Avers 1994). About 40% of the annual precipitation was snowfall, which is average in this region. The mean monthly precipitation in the Wallace Lake watershed ranged from 3.3 cm in February to 9.0 cm in November (Fig. 6). The annual precipitation was 7 cm less in the Wallace Lake watershed than at the NOAA station on the Houghton County airport and 13 cm greater than in Grand Marais, Minnesota. The differences in precipitation

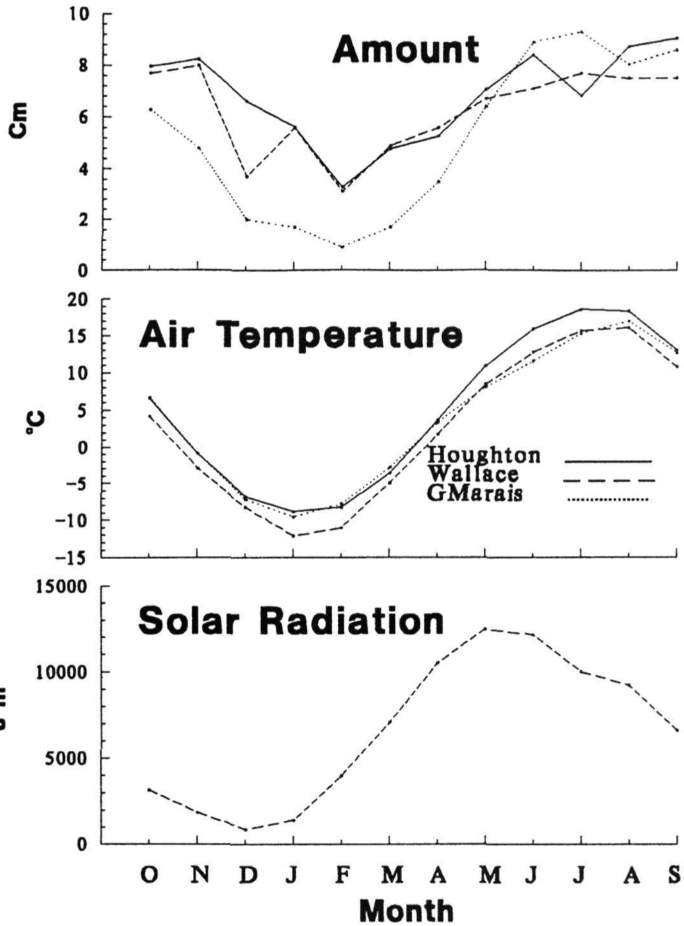


**Figure 6.** Mean monthly precipitation amount and air temperature, NOAA stations on the Houghton County Airport and in Grand Marais, Minnesota, and in the Wallace Lake watershed; and solar radiation, Wallace Lake watershed, Isle Royale National Park, Michigan, 1982–1996.

amounts occurred in winter when there is less lake-effect snowfall at Grand Marais. Only 23% of the annual precipitation at Grand Marais occurred during winter.

Prior to initiation of the study, year-round climate data of Isle Royale were not continuous. The amount of precipitation on Isle Royale is seasonally monitored by the National Park Service at the Windigo Ranger Station (hereafter *Windigo*) and on Mott island (Fig. 1a). Results from the National Park Service stations are summarized to 1984 (Stottlemyer et al. 1985a, 1985b). The National Oceanographic and Atmospheric Administration (NOAA) collects data on wind speed, wind direction, and temperature but not precipitation amount at the Passage Island lighthouse, 5.5 km to the northeast of the main island, and at the Rock of Ages lighthouse, 6 km to the southwest (Fig. 1a). The Rock of Ages lighthouse is on a point of exposed bedrock, and Passage Island is small. Climate data from these stations, except perhaps data on wind direction, are probably not representative of most of Isle Royale.

## *Geology*

The bedrock sequence on Isle Royale consists of a series of lava flows (flood basalts) and sedimentary rock tilted to the southeast (Huber 1973). The sedimentary rocks are sandstones and conglomerates. The linear ridges, generally running northeast to southwest, are the edges of the stacked layers modified by erosion and glaciation. The rock sequence consists of two formations: the lowest and oldest is the Portage Lake Volcanics that includes the lava flows and minor imbedded sedimentary and pyroclastic rocks and the upper more recent formation or Copper Harbor Conglomerate that contains only sedimentary rocks.

Isle Royale was overridden by ice in each of the four major glaciations of the last 2.5 million years (Huber 1973). The last advance in this region was during the Wisconsin Glaciation about 12 000 years ago (McNab and Avers 1994). Because of the resistant nature of Isle Royale's predominantly volcanic substrate, the ridges largely survived the glacial advances. Glacial striations are clearly visible over much of the exposed bedrock in the Wallace Lake watershed (Fig. 4). The glaciation removed most pre-glacial weathered rock from the island (Huber 1973). Glacial till deposits are thin and scattered in the northeastern portion of the park. Southwest of Siskiwit Lake (Fig. 1a), till is extensive and covers most of the bedrock.

The bedrock beneath Wallace Lake is metamorphosed volcanics. Low areas and depressions are filled with glacial debris and beach deposits. Foreign glacial materials consist of granitic pebbles from the Canadian mainland and fossiliferous (Proterozoic) limestone and chert from the Hudson Bay area south of James Bay (McNab and Avers 1994). The resorting and mixing of the glacial till with beach deposits produced a cobbly and sandy mineral-soil parent material (Shetron and Stottlemyer 1991). Weathering of this parent material dominates surface-water chemistry and is an important process that contributes nutrients for vegetation growth (Bailey and Hornbeck 1992).

## *Soils*

Soils in the watershed are primarily sandy to coarse loamy, mixed, and frigid Alfic Haplorthods deposited during the post-glacial Lake Nipissing stage and re-sorted during the post-Lake Duluth stage (Dorr and Eschman 1970). After

**Table 2.** Chemical and physical characteristics of forest soils beneath dominant vegetation types, Wallace Lake watershed, Isle Royale, Michigan. Data from Stottlemyer and Hanson (1989).

| | | | | | Exchangeable Cations mM $kg^{-1}$ | | | |
|---|---|---|---|---|---|---|---|---|
| Horizon | Depth cm | Texture | OM g $kg^{-1}$ | pH | $Ca^{2+}$ | $Mg^{2+}$ | $K^+$ | $Na^+$ |
| | | Spruce (*Picea*) | | | | | | |
| Oi&Oe | 70 | | 660 | 4.5 | 28 | 3 | | |
| E | 0-5 | ls | 23 | 3.8 | 7 | 2 | 0.1 | 1 |
| Bhs | 5-18 | sl | 33 | 4.4 | 9 | 3 | 0.7 | 6 |
| Bs1 | 18-27 | sl | 23 | 4.3 | 8 | 3 | 0.6 | 5 |
| E/Bt | 27-39 | scl | 134 | 4.9 | 22 | 17 | 0.8 | 8 |
| 2Bt | 39-60 | sicl | 132 | 5.1 | 58 | 38 | 0.9 | 12 |
| | | Birch-Aspen (*Betula-Populus*) | | | | | | |
| Oi&Oa | 7-0 | | 560 | 4.6 | 53 | 10 | 3.0 | 8 |
| A | 0-5 | gs | 80 | 4.9 | 63 | 10 | 2.0 | 7 |
| Bhs | 5-21 | gs | 62 | 5.0 | 21 | 3 | 0.4 | 11 |
| 2Bs1 | 21-24 | ls | 44 | 4.9 | 17 | 4 | 0.5 | 6 |
| 2Bs2 | 24–49 | ls | 36 | 5.0 | 19 | 4 | 0.3 | 8 |
| 3E | 49–65 | s & si w/cl lenses | 50 | 5.1 | 15 | 2 | 0.3 | |
| 3E/Bt | 65–85 | s & si w/cl lenses | 27 | 4.9 | 16 | 3 | 0.2 | 10 |
| 3Bt | 85–89 | s & si w/cl lenses | 26 | 5.0 | 16 | 5 | 0.3 | 10 |

deglaciation, Isle Royale rebounded and rose above lake water level. Because of gradual emergence, soils in the Wallace Lake watershed are only between 3000 to 5000 years old. Dating of lake cores from Wallace Lake confirmed this age (Dr. K. Cole, Paleoecologist, University of Northern Arizona, personal communication).

The soils in the Wallace Lake watershed are dominated by two associations, the Histic Humaquepts-Froberg-Rudyard and the Michigamme-Arcadian-Rock Outcrop (Appendix). Mineral-soil horizons are moderately acidic (Table 2). Deeper horizons are stratified clays and sands. The Wallace Bhs horizon is thicker but has the same organic-matter content (3%–6%) as soils beneath mature forests of the McCormick Experimental Forest in the Upper Peninsula of Michigan (Pregitzer 1981; Pregitzer and Barnes 1984). The Bhs has a similar thickness but somewhat higher exchangeable $C_B$ content than soils of the Turkey Lakes watershed in Ontario (Foster et al. 1989). Soils in the Wallace Lake watershed tend to be poorly drained because of low topographic relief and shallow depth to bedrock.

## *Vegetation*

Isle Royale is in the transition zone between the boreal forest on the northern shore of Lake Superior and the eastern deciduous forest that predominates on the southern shore (Larsen 1980). The watershed's overstory is dominated by trembling aspen (*Populus tremuloides*), white birch (*Betula papyrifera*), balsam fir (*Abies balsamea*), and white spruce (*Picea glauca*). The boreal forest is best developed in the lower elevations of Isle Royale (Slavick and Janke 1993). The birch-aspen vegetation type occurs in about 61 ha of the watershed, spruce-fir in 6 ha, tag alder (*Alnus rugosa*) in 3 ha, northern white-cedar (*Thuja occidentalis*) in 1 ha, and wetlands in more than 2 ha.

## *Land Use and Disturbance*

There is no evidence of direct human disturbance of the watershed. In 1971, the National Park Service designated the Wallace Lake watershed as wilderness. Because of the absence of trails, campgrounds, development, and easy boat access, visitor use of the drainage is almost non-existent. There is no archeological evidence of significant early American use in the Wallace Lake watershed (Clark 1995). Periodically in the early part of the twentieth century, scattered northern white-cedar was removed from the shoreline of the Moskey basin for cabins and other construction before the island became a park. But there is no evidence of cutting or human habitation in the late nineteenth or early twentieth century in the Wallace Lake watershed.

A small portion (<10%) of the watershed burned in 1936 in an intense, anthropogenic fire throughout the central one-third of Isle Royale National Park. No evidence exists of other fires in the watershed for at least 125 years. Fire in boreal forests has a significant effect on surface-water chemistry and ecosystem nutrient flux (Schindler et al. 1980). Greater than 80% of the Northern Superior Uplands burns every 300–400 years, and intense canopy fires occur every 150–200 years (McNab and Avers 1994). The frequency of significant fire in boreal forests of Alberta, Canada, ranges from 90 to 180 years (Larsen and MacDonald 1998). But fire frequency in boreal forests is heavily influenced by topography and geography, especially when the forest is near a lake or on an island (Heinselman 1973). The frequency of fire on Isle Royale over the long term is not well documented. One method of determining the long-term frequency of fire disturbance is charcoal deposition. Lake cores have been collected from Wallace Lake and other lakes in the park but have not been fully analyzed (Dr. K. Cole, Northern Arizona University, personal communication).

Other natural processes such as windthrow are important mortality factors, particularly in balsam fir and spruce (Toczydlowski et al. 1993; McNab and Avers 1994). Risenhoover and Maass (1987), Brandner et al. (1990), McInnes et al. (1992), Pastor et al. (1993), and McLaren and Peterson (1994) quantified the significance of herbivory by moose as a natural disturbance of Isle Royale vegetation. However, no specific study of herbivory has been conducted in the Wallace Lake watershed.

# Methods

## *Precipitation*

Precipitation amount and chemistry in the Wallace Lake watershed were quantified to estimate ecosystem inputs. Two meteorological stations were in the Wallace Lake watershed. The primary and fully automated station operated just west of the lake (Figs 1b and 7). This station was equipped with a 3.2-m meteorological tower that monitored wind speed and direction (Met One Instruments), solar radiation (LiCor pyranometer), relative humidity (Met One Instruments), precipitation amount, and air and mineral-soil (5-cm depth) temperatures (LiCor thermisters). Precipitation amount was recorded with two unshielded Belfort rain gages. Early NADP studies did not conclusively demonstrate a significant effect of shielding on precipitation amount (Simmons and Bigelow 1990). One rain gage was attached to the LiCor datalogger, used with the meteorological station. The other was chart-driven and used with the seasonally operated NADP Station MI97. Meteorological sensors were cali-

**Figure 7.** Primary meteorological station, Wallace Lake watershed, Isle Royale National Park, Michigan.

brated annually. The backup meteorological station was in a large natural opening 150 m north of the primary station. This station was chart-operated and until 1987 recorded precipitation amount and chemistry, snowpack amount and chemistry, air temperature, and relative humidity. After 1987, this station only recorded air temperature and relative humidity.

Limited access in winter required the measurement of precipitation chemistry with bulk collectors. In winter, the collector was a 1.5-m long, 20.5-cm diameter tube fitted with custom polyethylene liners. In summer, the collector was a plastic, 10-cm diameter tube fitted with funnel and pre-rinsed ashless filter to reduce evaporation and dust entry. The rain gage was changed weekly, and the filters and rain gage tube were washed in deionized water before use. Samples were collected monthly from January through March and weekly from late April to October. The elevation of the collectors was 210 m or about 20 m above the mean elevation of Lake Superior.

We monitored year-round precipitation amount and chemistry at Windigo from June 1979 to early 1988 when the station closed. The elevation of the station at Windigo was 230 m. In 1986, the National Park Service moved the National Atmospheric Deposition Program (NADP) Station MI97 from Windigo to the Wallace Lake watershed. This station was co-located with the primary meteorological station (Fig. 7) in the watershed. However, because of limited access in winter, the NADP Station MI97 was operated only from May through October.

We also operated the NADP Station MI99 (Chassell, Michigan) on the campus of the Michigan Technological University year-round. This was the closest (107 km) year-round NADP station to the Wallace Lake watershed and provided reference precipitation chemistry for Wallace Lake and our laboratory QA-QC procedures.

## *Throughfall and Stemflow*

We quantified throughfall and stemflow amounts and ion concentrations as part of our estimate of internal nutrient cycling. In 1979 in the Washington Creek drainage at Windigo, maple and cedar plots were established to measure throughfall and stemflow amounts and nutrient concentration and flux. Replicated plots each with at least two trees in each of three diameter classes (15, 30, and 45 cm) were instrumented. During 1979–82, throughfall beneath cedars and maples was sampled with ten randomly located polyethylene containers each fitted with a prerinsed Whatman 42 ashless filter between nested 20-cm diameter funnels. In winter, throughfall was collected with three 38-cm diameter open polyethylene collectors beneath each tree. Throughfall was collected on an event basis or every 2 weeks except in winter when it was collected in the same time intervals as the precipitation at Windigo. Stemflow was measured with collars of foam insulation that were applied around at least six trees (two trees in each diameter class) in each plot. Collars were plumbed to 40-L covered polyethylene containers. Samples were not composited.

An identical protocol was used for sampling throughfall beneath birch-aspen and spruce in the Wallace Lake watershed in 1983–84 (Stottlemyer and Hanson 1989). Throughfall beneath alder in the Wallace Lake watershed was sampled in 1989 with 10-cm diameter, 3.2-m long troughs. Troughs were plumbed to 18-L containers, and throughfall was collected weekly or more frequently if amounts warranted. Stemflow was not measured in the throughfall studies in the Wallace Lake watershed.

## *Snowpack*

In the Wallace Lake watershed, a snow survey transect (five sampling points, each of which was a minimum of 2 m apart) was set up at the secondary meteorological station where monthly (January–March) snow-water equivalent (SWE) and depth were determined with a Mount Rose snow sampler. On each sampling date, a snow sample was retained for chemical analyses. A similar protocol was used at Windigo for snowpack sampling, except sampling dates were more frequent (about every 2 weeks).

About the time of peak snowpack water equivalent (PWE) during the winters of 1987 and 1988, sampling was done at 18 additional snowpack stations throughout the park in openings near inland lakes or bays where foot access or plane landing was possible. The points were located throughout the park and provided a comparison of Wallace Lake SWE and chemistry with those elsewhere in the park. The sites included Island Mine, Todd Harbor, Duncan Bay, Moskey basin, Brady Cove, Huginnin Cove, Robinson Bay, Rock Harbor; and Chicken Bone, Hatchet, Feldtmann, Whittlesey, Halloran, Sergeant, Desor, Richie, Harvey, and Benson lakes. The snowpack sampling protocol was the same as described above. (Additional details on snowpack sampling protocol are provided by Stottlemyer and Toczydlowski 1996a, 1996b.)

## *Soil Processes*

Soil descriptions and process studies beneath the stands studied for throughfall were examined. In each stand, we attempted to dig a 1.25-m deep soil pit (Fig. 8), but bedrock was generally reached at a depth of less than 1 m (Shetron and Stottlemyer 1991). Soil profiles were described with standard terminology (Soil Survey Staff 1975; Shetron and Stottlemyer 1991). Three soil samples were taken from each horizon, composited, air-dried, and passed through a 2-mm sieve for analyses. Organic-matter content of oven-dried samples (65°C for 24 h) was determined by ashing in a muffle furnace at 550°C for 8 h (Nelson and Sommers 1982). Soil bulk density was determined with the core method (Blake and Hartge 1986). Soil pH was determined with 0.01-M $CaCl_2$ with a weight-to-volume ratio of 1:2 for mineral horizons and 1:5 for organic horizons (McLean 1982). Soil texture was estimated by hydrometer (Gee and Bauder 1986). Exchangeable base cations were determined by ex-

**Figure 8.** Soil pit beneath birch-aspen (*Betula-Populus*) forest, Wallace Lake watershed, Isle Royale National Park, Michigan.

traction with 1-M $NH_4Cl$ and by analyzing the filtered (0.45 μm) extract on an atomic absorption spectrophotometer (Perkin-Elmer).

To examine change in chemistry concentration and flux beneath the forest litter layer and in mineral soils, zero tension and tension lysimeters were installed. The objectives for this multi-year study were (1) the quantification of ion concentration and flux of soil solutions in mature boreal conifer and hardwood forests; (2) determination of whether conifer forests, with their year-round foliage for capturing atmospheric aerosols, may be more prone to soil $SO_4^{2-}$

anion mobility; and (3) determination of which cations are associated with mobile anions (Stottlemyer and Hanson 1989). Soil solution was sampled at three depths. In each plot except in alder plots, three zero-tension polyethylene lysimeters (15 × 25 × 5 cm deep), fitted with Nytex screen, were placed just beneath the litter layer. Triplicate-tension lysimeters (PVC tubes, ceramic porous cups, by Soil Moisture Corp.) were placed in each of two mineral-soil horizons at about 15-cm and 30-cm depths. A tension of 0.033 MPa was placed on the lysimeters. Samples were collected from lysimeters at 2-week intervals during summer and (depending on soil freezing) on the same days as precipitation was collected during winter. The alder stands were not sampled in winter. Tension was placed on the lysimeters 24 h before sample collection. Samples were not composited for chemical analyses.

From May 1992 to May 1997, monthly soil inorganic nitrogen (N) pools and net N mineralization-nitrification rates were determined in replicated plots beneath birch, spruce, and alder in the Wallace Lake watershed and beneath maple stands 2 km east of Windigo with methods described in Stottlemyer et al. (1995). The purpose of the 5-year study was to explain some of the processes that account for seasonal trends observed in stream water $NO_3^-$ concentrations in a boreal forested watershed. The study was designed (1) to compare seasonal precipitation N inputs with trends in soil available N pools, net mineralization and nitrification rates, and N in stream water and (2) to relate changes in soil N pools and net mineralization and nitrification rates to soil temperature and moisture. During the last 2 years of the study, field gross N mineralization and immobilization rates were quantified to examine seasonal change in total nitrogen cycled in forest soils. A total of twelve 0.1-ha (20 × 50 m) plots, that is, three plots in each major species, were randomly located along transects. Plots in a given species were about 100 m apart. On each plot, a LiCor datalogger with five temperature sensors (thermisters at 5-cm and 10-m depths beneath the organic layer in the forest litter and 10 cm and 130 cm above the forest floor) was installed during the last week in May and operated each year until the third week of October. Dataloggers were left in place for overwinter monitoring at one of the three plots in each species. Daily mean temperatures were logged throughout the study. For soil temperatures, the mean temperature at 5-cm and 10-cm depths and a composite of both were used when assessing field N mineralization and nitrification response to temperature.

Monthly total inorganic N mineralization and $NO_3^-$ mineralization in each species were estimated with the buried polyethylene bag technique (Eno 1960). In each 0.1-ha plot, three 25-$m^2$ subplots were established. Each month from May to October, a site for soil sampling and incubation was randomly selected in each subplot. After pulling back the surface organic layer or O1 (also called $O_i$ or litter layer), the upper 10 cm consisting of the O2 (litter fragments and humus or $O_a$ and $O_e$) and mineral soil were sampled with a 5-cm diameter soil corer. Paired cores were collected in each subplot. One sample from each pair, representing a nonincubated sample, was placed in a Whirl Pac and returned to the field laboratory at the Boreal Research Station on Davidson Island, 10 km northeast of the Wallace Lake watershed (Fig. 1a). The other was placed in a polyethylene bag and returned to the same hole for incubation, and the surface organic matter was replaced. After 30 days, the field incubated sample was collected for analyses. Because of limited winter access, three sets of incubation samples were placed in each subplot in late October for over-winter sampling. A bag was removed from each subplot in January, February, and late April or early May when monthly incubations resumed.

After collection, soil samples were refrigerated at 2°C for no more than several days to allow time for completion of sample collection. Soil moisture was determined by oven drying (105°C for 24–30 h) a subsample. Bulk density was calculated from the quotient of the total oven dry weight and the total soil volume. A larger subsample was separated in a 2-mm sieve. The greater than 2-mm fraction was weighed. The less than 2-mm material was weighed and divided into two samples; one was extracted for $NO_3^-$ and $NH_4^+$ with 2M KCL, the other was frozen for total N determination.

Soil N mineralization incubations in the laboratory were conducted at the Michigan Technological University following the basic design in Binkley et al. (1994a). In July 1993, three samples from each subplot beneath birch, spruce, and alder were collected for laboratory incubations at 10°C, 15°C, and 20°C (27 samples from each species at each temperature). At each temperature, three moisture treatments on replicated samples for each species were applied: *low moisture* that was field moisture; *medium moisture* that was 15% of the total sample weight; and *high moisture* that was 30% of the total sample weight. The high moisture content was at field capacity. Samples were incubated for 38 days in Percivial growth chambers operating at 75% relative humidity with 16 h of light daily. Following incubation, samples were kept in a dark refrigerator during processing. (Further details on field and laboratory methodology and site descriptions are in Stottlemyer et al. 1995.)

Field gross N mineralization, nitrification, and immobilization rates were studied in 1995–96. This study was confined to the Wallace Lake watershed beneath alder, birch, and spruce stands. The $^{15}N$ isotope dilution method was used to estimate gross rates (Brooks et al. 1989; Davidson et al. 1991; Hart et al. 1994). Field incubations were undertaken in May, June, August, and September of 1995 and in June of 1996.

On each date, the methods described above for the net-mineralization and nitrification study were carried out. Initial soil inorganic N pools were determined and a 30-day net mineralization and nitrification incubation was started. In addition, a separate set of intact soil cores was collected immediately adjacent to the net incubation samples and processed as follows. With a needle (spinal needle, 18 gage, 10-cm length) and syringe, one intact core was administered a 6-ml aliquot of Na $^{15}NO_3$ solution that provided about 2 μg N $g^{-1}$ of dry soil. A separate intact core received 6 ml of $(^{15}NH_4)_2\ SO_4$ again providing about 2 μg N $g^{-1}$ of dry soil. The $^{15}N$ solution injections were 1 ml each, and spaced around the core. The $^{15}N$ enrichment in the Na $^{15}NO_3$ and $(^{15}NH_4)_2$ $SO_4$ solutions was 99%.

After a 24-h incubation period, the cores were collected, taken to the Boreal Research Station, and mixed, and a subsample was extracted with 2M KCl. After a minimum of 1-h mixing, all solutions were filtered through Whatman #1 filters prerinsed with KCl. Ammonium and $NO_3^-$ analyses were done on a Lachat flow-injection autoanalyzer. Nitrogen diffusion (Brooks et al. 1989) was used to prepare the samples for $^{15}N$ analyses, and the glass fiber filter traps were analyzed at Michigan State University.

The isotope dilution method of Kirkham and Bartholomew (1954) was used to calculate gross $NH_4^+$ consumption and mineralization rates of the cores labeled with $^{15}NH_4^+$ and the gross $NO_3^-$ consumption and mineralization rates of the $^{15}NO_3^-$ labeled cores. The assumptions in this method are discussed in Brooks et al. (1989) and Davidson et al. (1991, 1992).

Beginning in May 1993, we measured $CO_2$ evolution from mineral soils in each species. The study was conducted one day each month from May through October 1993–96 on each N incubation plot. Soil $CO_2$ evolution was measured as an index of soil respiration; measured also were the change of soil $CO_2$ with temperature and its relation with nitrogen mineralization rates (Cropper et al. 1985; Ewel et al. 1987). Measured rates of soil $CO_2$ evolution are dependent on the applied method (Cropper et al. 1985; Raisch and Nadelhoffer 1989). We used the static method in this study rather than the dynamic method (IRGA system) because there was no opportunity to charge batteries or repair equipment near the sites. Cropper et al. (1985) found little difference in the static and dynamic methods at soil temperatures up to 15°C. However, more recently, Nay et al. (1994) found some sources of bias in the static chamber method. In the Wallace Lake watershed, three 11-L chambers each of which covered a 0.054-$m^2$ area were placed at random in each plot. At the beginning of each incubation period, a container with 60g KOH and a surface area of 60 $cm^2$ was placed in each incubation chamber. After a 24-h incubation, the KOH containers were removed and immediately capped. Upon return to the laboratory, they were oven dried and re-weighed to determine $CO_2$ absorption. Blanks were also collected on each sampling date to account for any $CO_2$ absorption during storage and handling. The airtight blank containers were opened and immediately closed. For each field incubation, a thermister attached to a Licor datalogger was inserted in the chamber at a 5-cm soil depth to log temperature during the 24-h incubation.

## *Stream water*

Parshall flumes (46 cm wide at W2, 15 cm wide at W1) equipped with Stevens F recorder (1982–90) or Stevens pressure transducer and LiCor model 1000 datalogger (1990–96) were used to measure stream water discharge continuously year-round (Fig. 3). Ice blockage was not a major problem, and the flumes were unheated.

In winter, precipitation, snowpack, and stream samples for chemical analyses were collected monthly except in November and December. From late April to late October, samples were collected weekly. Stream water and precipitation were sampled on the same day. Stream water chemistry was also intensively monitored during major stream-flow events and hourly to assess diurnal change. Above the flumes, stream samples were collected with brown polyethylene 500-ml bottles. Before retaining a sample, the bottles were washed, rinsed three times in deionized water, and rinsed twice with stream water. Stream water temperature and flume-stage height were recorded at the time of sampling.

## *Aboveground Biomass and Nutrient Distribution*

Five randomly located 0.1-ha (20 m × 50 m) permanent plots were established in 1983 (Fig. 1b). The objective was the periodic (every 5–10 year) inventory of change in biomass and its nutrient content. (Details of the methods are described in Rutkowski and Stottlemyer 1993.) Samples were first collected in 1985, and a reinventory of biomass was conducted in 1991. The diameter at breast height (1.4 m) was measured of all trees with a dbh greater than 2.5 cm in each plot, and tree height was estimated with a clinometer. The height and species of saplings (dbh < 2.5 cm, > 0.5 m) were determined in 10-$m^2$ subplots located at the four corners of each 0.1-ha plot, and of seedlings (< 0.5 m tall) in 1-$m^2$ subplots nested in the sapling plots. Herbaceous vascular plant cover (height <0.5 m) was estimated in five 1-$m^2$ subplots randomly located on a transect 5 m to the side of and parallel to the long axis of each 0.1-ha plot. The cover of herbs and shrubs that were taller than 0.5 m was estimated in three 4-$m^2$ subplots randomly located along the same transect. The forest floor was sampled just prior to leaf fall from five 0.1-$m^2$ subplots randomly located along this transect. Because destructive sampling of whole trees to estimate biomass was not permissible, estimates of the overstory biomass of all trees were derived from published species-specific allometric regression equations. A similar approach was used for estimating the biomass of understory seedlings and saplings.

Litterfall quantity and quality were sampled as of 1984 with six 1-$m^2$ traps/plot. The plots were randomly located beneath each major forest species. Litter collections were made in early May, immediately before leaf fall in September, and after leaf fall in mid-October. (For details on pooling of plant tissue samples prior to chemical analyses, see Rutkowski and Stottlemyer 1993.)

## *Windthrow*

In 1989–91, we conducted a study of windthrow as a mortality factor in the boreal forest of the northeastern one-third of the park. Nine 10-m wide transects (first established in 1976 by R. Janke, Department of Biological Sciences, Michigan Technological University) located throughout the northeastern 20 km of the island were selected for sampling. The transects are at right angles to the prevailing slope and were sampled from May to September 1989 and during August and September 1991. The area of the transects varied from 0.5 ha to more than 1.5 ha for a total of 6.73 ha. In 1989, measurements were taken of all trees that were determined to have fallen during the previous year. These determinations were based on (1) condition of the tree (live needles, leaves, or buds present), (2) condition of neighboring trees (recently broken branches, torn or scraped bark), and (3) the break (snap or uproot appeared clean with little or no accumulated debris, fungal growth, or invading herbaceous growth). In 1991, fallen trees with a greater than 5-cm dbh on each transect were measured again to quantify trees fallen during 1989–91.

For each fallen tree, the following data were collected: topographic slope, aspect, and position along slope; elevation and distance from Lake Superior; replicated measurements of soil depth to bedrock; species, dbh; whether the tree was dead or alive; replicated canopy cover readings (spherical densitometer); height, direction, and distance to adjacent vegetation (wedge prism, basal area factor = 10) from fallen tree; presence of other nearby windfalls, condition of windfalls, contribution if any to canopy opening; height of windfall, snapped or uprooted, direction of fall, was tree alive when fell, and height of snap when present. Similar variables except those specifically dealing with downed tree characteristics were measured on 140 randomly selected standing *target trees*. To provide a further basis for comparison of downed-tree and standing-tree environments, the same standing target trees also served as the center point for 140 plots to determine tree density with the point-centered quarter method (Cottam and Curtis 1956). All sampled trees were numbered and tagged for future measurements.

Beginning in 1984, data on wind direction and speed were obtained from the automated NOAA weather station on Passage Island. This station records open-lake conditions or wind conditions that impinge on the northeastern section of Isle Royale. Continuous weather data, recorded during 1984–91, were analyzed.

## *Laboratory Analyses*

### Precipitation, Throughfall, Stemflow, Lysimeter, Snowpack, and Stream Water

In summer, samples were taken immediately to the Boreal Research Station on Davidson Island (Fig. 1a). In winter, samples were flown to Windigo for field processing. For all water samples, pH, specific conductance, and alkalinity (titration with 0.02 N $H_2SO_4$ to pH 4.5, not snowpack or precipitation samples) were determined as soon as samples reached room temperature. Separate, filtered (pre-rinsed, 0.45 μm) subsamples (amber 60-ml linear polyethylene bottles) for ion analyses were refrigerated at 2°C. During 1982–90, the filtered subsamples were shipped in coolers to our laboratory at the Michigan Technological University, Houghton, Michigan. After 1990, refrigerated samples were shipped to the Water Quality Laboratory of the U.S. Forest Service Rocky Mountain Research Station in Fort Collins, Colorado. Calcium, $Mg^{2+}$, $Na^+$, $K^+$, $NH_4^+$, $NO_3^-$, $SO_4^{2-}$, and $Cl^-$ concentrations were determined with a Dionex Model 2020 ion chromatograph (Dionex Corp, Sunnyvale, California; Johnson and Haak 1983). Laboratory and field sampling procedures remained constant during the study.

Snow samples were melted at room temperature in pre-rinsed, covered polyethylene containers. Determination of pH and specific conductance was made as in other water samples. A 60-ml subsample was then filtered (pre-rinsed, 0.45 μm) for major ion analyses.

Whole water subsamples for total N and P (Kjeldahl digestion, Lachat autoanalyzer) and filtered subsamples for DOC (dissolved organic carbon) determinations (Dohrman 80 carbon analyzer, successor models, then Sievers Model 600) were kept frozen until analyzed. Heavy-metal and trace-metal analyses were conducted on acidified ($pH < 2$, Ultrex) samples analyzed by Inductively Coupled Plasma Emission Spectroscopy (ICPE).

**Soil and Plant Tissue Samples**

For determination of soil inorganic N content, 5-g soil subsamples were extracted with 50 ml of 2M KCl, and $NO_3^-$ (cadmium reduction) and $NH_4^+$ (indophenol) were determined on a Lachat autoanalyzer (Lachat Instruments, Milwaukee, Wisconsin). The net total inorganic N mineralized in each incubation period was estimated from the difference between initial and final $NO_3^-$ and $NH_4^+$ content, and net $NO_3^-$ mineralization was estimated by the difference between the initial and final $NO_3^-$ content (Binkley et al. 1994a). Total N was determined from Kjeldahl digestions (Hauck et al. 1994). Quality assurance on the Lachat included running control standards every 10 samples, 10 duplicates in each block of approximately 40 samples, and 10% reruns. In each total N digestion block set, six of the 40 samples were duplicates.

For plant tissue sampling, polyethylene gloves were worn during collection and processing. Tissue samples were oven-dried at 80°C for 48 h. Then the dried samples were ground in a Wiley Mill to pass a 60-mesh stainless steel screen. Ground material was then placed in clean plastic bags and stored at 2°C. Litterfall samples were analyzed for C and N on a Leco CHN analyzer. The N concentration in other plant tissue was determined by Kjeldahl digestion. Calcium, Mg, Na, K, heavy metals, trace metals, P, and S in plant tissue were analyzed by Inductively Coupled Plasma Emission Spectroscopy.

Overall quality assurance and quality control procedures in place during the study are described in Stottlemyer (1987a). Samples arrived in the laboratory with field data on disc. Samples were queued for analyses to maintain some control over elapsed time since collection. Samples were analyzed in blocks of 150–350 of similar age since collection. About 12% of the analyses were blanks, standards, or other quality-assurance material. Working-strength standards were of similar age as samples.

For external checks on our laboratory analyses, we had the following procedures in place. Since 1982, we split weekly samples of precipitation from the NADP station MI99. We processed one split in our laboratory. There were no significant differences (Student's t-test) between ion concentrations from the NADP Central Analytical Laboratory and our laboratory (Stottlemyer 1997). To compare chemistry between bulk and NADP event precipitation collectors (Aerochem Metrics), from 1986 to 1996 bulk collectors, as described above, were located 10 m from the Aerochem Metrics collector of NADP Station MI99. Bulk collector and split MI99 samples were analyzed in our laboratory with the same analytical procedures as those used by NADP. During the 10 years the bulk collector was in place, concentrations of $Ca^{2+}$, $Mg^{2+}$, $Na^{+}$, $NO_3^{-}$, $SO_4^{2-}$ and $Cl^{-}$ were significantly higher (Student's t test, $p < 0.05$) in bulk precipitation than in samples from the Aerochem Metrics collector. Other external checks on laboratory results included the use of manufactured certified water and plant tissue samples, sample exchange with a private laboratory, quality-control water samples from the U. S. Geological Survey, and EPA (Environmental Protection Agency) quality-control samples sent to a large number of public and private laboratories.

## *Data Analyses*

In this study, trend analyses focused only on describing trends rather than on hypothesis testing. Systat modules were used for ANOVA analyses of seasonal and annual differences in precipitation and stream water chemistry (Wilkinson 1990). The procedures were as follows. The routine least-squares model was first used to show ion concentration against time, and the residuals were saved to test independence. An autocorrelation plot of regression residuals was then performed. If the autocorrelations were not significant, the time trend was that defined by the regression. Most variables did not exhibit significant autocorrelation. When autocorrelations were significant, i.e., outside the two-standard error confidence band, the independence of observations was suspect. Autocorrelation was then removed by differencing, and the transformed (differenced) variables were checked for autocorrelation. If a significant autocorrelation remained, a cross-correlation function plot of differenced variables was run. Then a lagged regression on the transformed variables was performed, adjusted for the appropriate lag interval. If the lagged regression was significant ($p < 0.05$) and there were no warnings of outliers or other influence, the model was used to explain the trend. If the lagged regression was significant but contained outlier or other influence warnings, a subsequent autocorrelation plot and Runs test (Systat NPAR module) of the residuals from the transformed variables was conducted.

Selected variables of annual precipitation and stream water amounts, ion concentrations, and chemical budgets and cycles are presented. Ion concentrations are generally given as volume-weighted values. We estimated the standard deviation ($S_{y.x}$) of volume-weighted means as follows:

$$\left[ n / n-1 \sum_{i=1}^{n} \left( w_i / \sum w_i \right) \left( C_i - \bar{x} w_i \right)^2 \right]^{\frac{1}{2}}$$

where n is the number of weeks of sampling, $C_i$ is concentration, and $W_i$ is flow.

For estimates of variation in input and output, if the relation between concentration and amount or flow was not high ($r^2 < 0.5$), the estimate of the total input or output for a unit of time (generally 1 week) was the product of the unweighted concentration and the amount, and the estimate of standard deviation of the total was the product of the standard deviation of the mean concentration of weekly samples and the total flow or volume. When there was a good relation between concentration and flow or precipitation amount, the error was estimated with the product of $S_{y.x}$ from the regression relation and the flow or precipitation during the relevant period of time.

For ion budgets, results were from the water year of 1 October–30 September. For precipitation and snowpack, the input amount was the product of concentration and the depth from which monthly or annual amounts were computed. Annual element uptake by vegetation was the sum of litterfall, throughfall, and stemflow minus the precipitation input. Throughfall and stemflow were considered part of the internal ecosystem nutrient cycling and not inputs. For stream water output, the weekly mean ion concentration (number of samples ranged from 1 to 30+ $\text{week}^{-1}$) was weighted by the stream water discharge of the week, and then monthly or annual outputs were computed. When stream water was not sampled weekly in winter, the concentration from the last sample in fall and the first sample in mid-winter were averaged and weighted by the amount of discharge for the elapsed period.

For the determination of soil respiration, net and gross N mineralization or nitrification, or nutrient pools in field studies, the three subplot soil samples from each vegetation plot were averaged, giving an n of three (three plots) for each species on each sample date. When testing for the need to apply repeated measures analyses, each plot was checked for correlation with time (months) for all measured variables. Generally, correlation was not significant with time, and repeated-measure analysis was not used. For monthly analyses among species, results from each incubation period (month) were combined with those from the same month in subsequent years. We used Systat Multivariate General Linear Hypothesis (MGLH) ANOVA routines. To examine the effects of vegetation, month, and plots within vegetation, we used the split plot design (analysis of variance for profile data; Morrison 1967).

For laboratory experiments, results from the three subplot samples were averaged, giving an n of three (three plots) to each species and to each treatment. Temperature-moisture chambers were unreplicated, and residual error from the three factor analysis was used in all tests.

For the nutrient content of aboveground biomass, nutrient pools were estimated by multiplying mean nutrient concentration within a given component by the estimated dry weight of the component for a given unit of area or for the entire watershed.

# Results

## *Temperature*

Since 1950, the mean annual air temperature at the NOAA station on the Houghton County airport increased ($p < 0.001$, $r^2 = 0.26$, b = 0.03°C; Fig. 5). Temperature gains in March, May, June, July, and August ($p < 0.05$, $r^2 > 0.10$) accounted for most of the annual temperature increase. During 1982–96, no significant trends in mean annual air temperature were observed at the NOAA station or Wallace Lake watershed meteorological station. Seasonally, air temperature increased during March, May, June, November, and December.

Under the forest canopy, air temperatures in winter were lowest beneath spruce (Fig. 9; Table 3). The mean snowpack temperature at 10 cm from the forest floor averaged 5°C warmer than air temperature and was warm enough to allow snowpack solute movement. The forest litter layer froze beneath birch-aspen and spruce but not beneath alder. Shallow mineral-soil temperatures remained above freezing except beneath spruce.

## *Wind Speed and Direction*

At the two NOAA lighthouse weather stations (Fig. 1a), the prevailing wind directions were from the west and northwest. Wind speeds exceeded 55 km h$^{-1}$ for more than 300 h annually and exceeded 75 km h$^{-1}$ for more than 30 h. The prevailing direction of high-velocity winds was from the west-northwest (300 °).

Seasonally, the prevailing wind direction and speed varied widely. Average wind speeds were highest from October through January. During January and February, the prevailing wind direction was from the west and northwest.

**Table 3.** Mean temperatures in winter (1 November–30 April) beneath birch-aspen (*Betula-Populus*), white spruce (*Picea glauca*), and tag alder (*Alnus rugosa*) canopies, Wallace Lake watershed,1992–1996.

| Species | Air Temperature °C | Snowpack at 10-cm Depth | Litter Layer | Soil at 5-cm Depth | Soil at 10-cm Depth |
|---|---|---|---|---|---|
| Birch-aspen | –7.4 | –2.0 | –0.4 | 0.4 | 0.6 |
| White spruce | –8.7 | –4.0 | –1.5 | –0.5 | –0.1 |
| Tag alder | –6.0 | –1.4 | 0.7 | 1.2 | 1.8 |

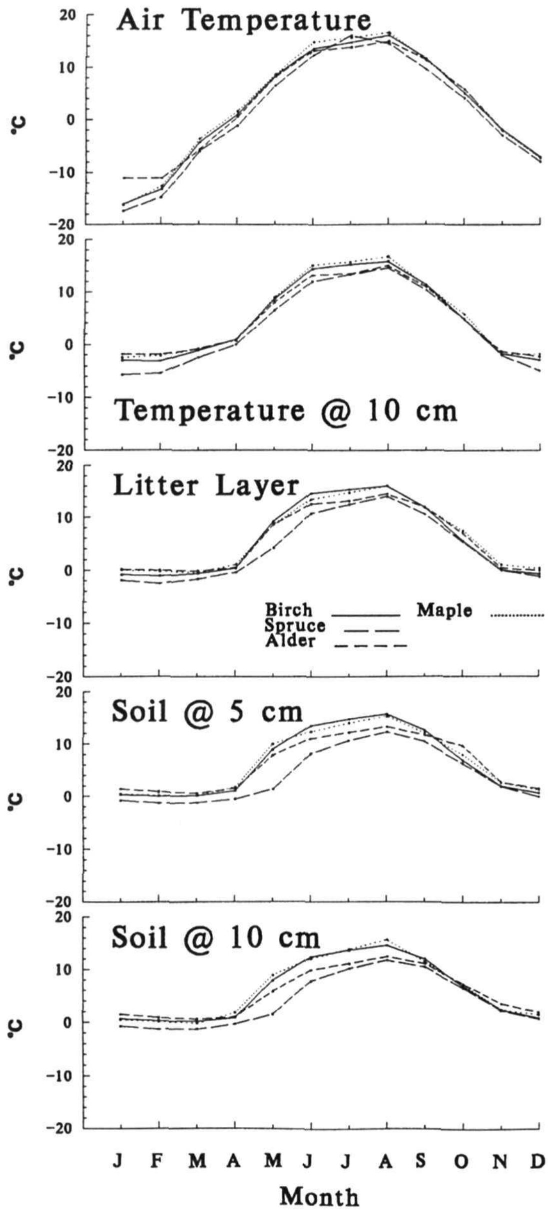


**Figure 9.** Mean seasonal temperatures of air (130 cm and 10 cm above forest floor), litter, and mineral soil (5-cm and 10-cm depths) beneath birch (*Betula papyrifera*), spruce (*Picea glauca*), and alder (*Alnus rugosa*) in the Wallace Lake watershed and beneath sugar maple (*Acer saccharum*) in southwestern Isle Royale, Michigan, 1992–1996. Each point represents the mean of about 120 daily measurements.

In March, the wind direction began to increasingly shift between the southeast and southwest. The shift in wind direction to the south was concurrent with change in precipitation chemistry in the Upper Great Lakes region. From April through August, the prevailing wind direction continued to be from the south. Beginning in September, the prevailing wind direction increasingly shifted to the west. By early December, the direction again prevailed from the west to the northwest.

## *Radiation*

The mean solar radiation above the forest canopy was 6632 (SD = 5787) J $m^{-2}$. Radiation peaked in May and June and was lowest in December (Fig. 6).

## *Hydrologic Cycle*

### Precipitation

During 1950–96, the annual precipitation amount at the NOAA station on the Houghton County airport averaged 87 cm (range 63–136 cm; Fig. 5). Beginning in 1982, the annual precipitation declined ($p < 0.05$, $r^2 = 0.31$, b = –2.6 cm). The decline was most pronounced in November and December. The decrease in December was about 1 cm $year^{-1}$ ($p < 0.05$, $r^2 = 0.32$). During the same period, the annual precipitation amount at Grand Marais, Minnesota, averaged 66 cm (range 42–101 cm). Since 1982, the annual precipitation amount in the Wallace Lake watershed averaged 75 (15) cm (range 57–104 cm). There was no significant trend in annual precipitation amount. Precipitation in winter (November–April) averaged 29 cm or 39% of the annual precipitation. The mean monthly precipitation amount in winter was 77% of the monthly average of the year. Monthly precipitation amount increased from March through November (Fig. 6). Precipitation fell each month, and the greater amounts fell in late summer and fall. In the year with the highest precipitation (1984), precipitation measured more than 11 cm in June and August and more than 16 cm in November. The long-term average precipitation during these months was less than 8 cm.

Precipitation amount in winter increased with small gain in elevation above Lake Superior (Table 4; Stottlemyer 1982). Precipitation amount increased about one-third with a gain of 100 m elevation on Isle Royale, 80% on the Keweenaw Peninsula (Stottlemyer and Rutkowski 1990), and about 60% in Pictured Rocks National Lakeshore. In summer, there was no significant effect of elevation on precipitation amount.

The amount of precipitation also varied spatially, particularly from north to south, around the Lake Superior Basin. During 1967–80, the annual mean precipitation at Thunder Bay, Ontario, was 68 (18) cm, 76 (10) cm at the NOAA station on Passage Island adjacent to Isle Royale (precipitation no longer measured at this station), 88 (12) cm at the NOAA station on the Houghton County

**Table 4.** Change in mean moisture content (cm) of snowpack with elevation on northwestern slope adjacent to Lake Superior in January and February 1979–1982 (Stottlemyer 1982). Standard deviation in parentheses.

| | Elevation | | | |
|---|---|---|---|---|
| Station | 190 m | 225 m | 260 m | 295 m |
| Isle Royale | 10.7 (2.6) | 13.3 (2.8) | 11.9 (2.6) | 14.1 (3.6) |
| Calumet | 13.8 (7.6) | 15.7 (5.2) | 18.5 (4.5) | 24.8 (5.4) |
| Pictured Rocks[a] | 11.8 (3.3) | 14.9 (4.2) | 15.8 (4.4) | 19.0 (4.3) |

[a] Pictured Rocks National Lakeshore, Munising, Michigan.

airport on Michigan's Keweenaw Peninsula, and 78 (14) cm at Pictured Rocks National Lakeshore (Stottlemyer 1982).

In the Wallace Lake watershed, the annual precipitation amount since 1982 followed the trend of precipitation amount at the NOAA station on the Houghton County airport on the southern shore of Lake Superior (Fig. 5). The seasonal pattern of precipitation amount since 1982 closely followed that at the NOAA station on the Houghton County Airport (Fig. 6) but averaged 15% less.

## Throughfall and Stemflow

Annual canopy interception of precipitation was 24% by spruce, 19% by birch-aspen (Stottlemyer and Hanson 1989), 35% by cedar, and 10% by maple (Stottlemyer 1982). During May–October 1989, the alder canopy intercepted 24% of incident precipitation. The cedar and maple data are from the Washington Creek drainage near Windigo (Fig. 1a).

Stemflow amount was related to precipitation amount. In all diameter classes, the relation between precipitation and stemflow amount was weakest in maple ($p < 0.05$, $r^2 = 0.40$) and strongest in cedar ($p < 0.01$, $r^2 = 0.79$). The average stemflow amount of maple was inverse to tree diameter, and the mean ranged from 2407 ml in the 15-cm dbh class to 1155 ml in the 45-cm dbh class. Change in stemflow volume with diameter class in cedar was little. The mean volume was 888 ml in the 15-cm dbh class, 760 ml in the 30-cm dbh class, and 823 ml in the 45-cm dbh class.

## Snowpack

On average, a snowpack formed in the Wallace Lake watershed by mid-November and remained until the end of April. In the open, the mean peak water equivalent (PWE) of snowpack was 15.5 (5) cm, and it occurred in early March. It was 13 (4) cm at Windigo on the southwestern end of Isle Royale (Fig. 10). Snowpack PWE averaged 20% of the annual precipitation, 54% of

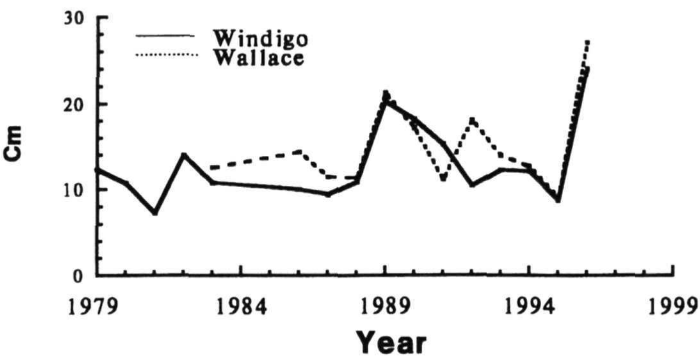


**Figure 10.** Annual peak water content of snowpack at the Wallace and Windigo stations, Isle Royale National Park, Michigan, 1979–1996.

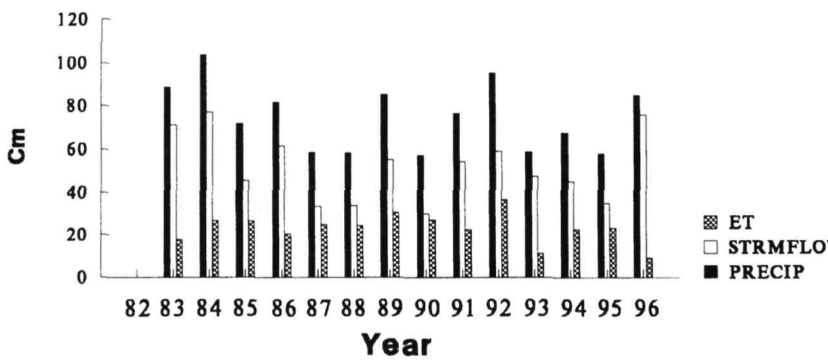


**Figure 11.** Annual precipitation amount, stream flow, and evapotranspiration, Wallace Lake watershed, Isle Royale National Park, Michigan, 1982–1996.

the total precipitation in winter (November–April), and 82% of the precipitation in winter to snowpack PWE in early March.

The mean island-wide snowpack PWE during 1987–88 was 9 (4) cm (range 4–16 cm). The average snowpack PWE in the Wallace Lake watershed and at Windigo during 1987–88 was 10.8 (0.9)cm.

### Stream Flow

Annual stream flow (mean 51 [15] cm, range 30–77 cm; Fig. 11) varied more (S.D. = 30% of mean) than the annual precipitation. The mean ratio of stream flow to precipitation was 0.68 (0.11, range 0.53–0.89; Fig. 12). The relation between annual stream flow and precipitation amount was significant. The ratio of stream flow to precipitation was higher than expected in 1993 and 1996 and lower than expected in 1990 and 1992. The ratio was lowest in 1990,

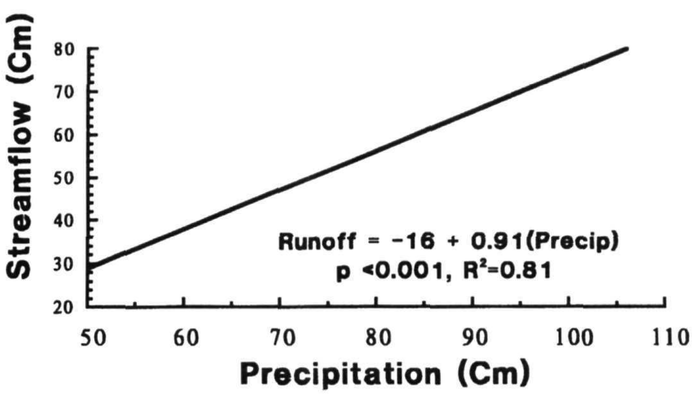


**Figure 12.** Relation between annual precipitation amount and stream flow, Wallace Lake watershed, Isle Royale National Park, Michigan, 1982–1996.

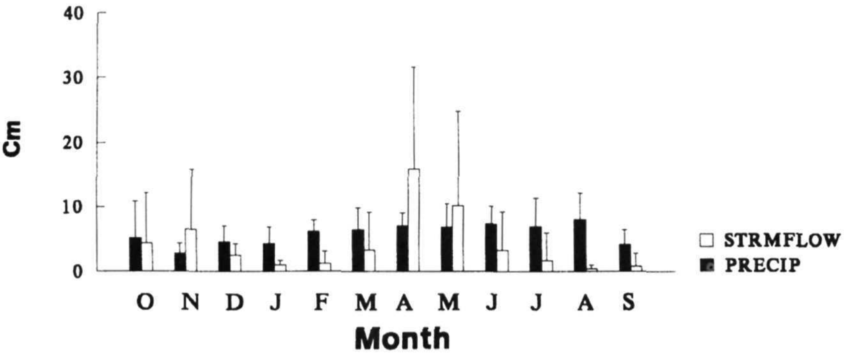


**Figure 13.** Mean monthly precipitation amount and stream flow (Station W2), Wallace Lake watershed, Isle Royale National Park, Michigan, 1982–1996. Bars represent one standard deviation.

the year of least total precipitation. The ratio of stream flow to precipitation was highest in 1996. The highest precipitation input and stream flow was in 1984.

Evapotranspiration increased until 1993 ($p < 0.10$, $r^2 = 0.33$) when it began to decrease. The trend reversal coincided with the pattern of average annual air temperatures in the watershed during the period (Fig. 5). However, there was no correlation between annual temperature and evapotranspiration expressed as a percentage of precipitation or as evapotranspiration during the period of record. A weak ($p < 0.10$) relation existed between the estimated annual evapotranspiration and the precipitation.

Snowmelt dominated the annual hydrograph in the Wallace Lake watershed (Figs 13 and 14). On average, the mean daily stream flow peaked on 26 April.

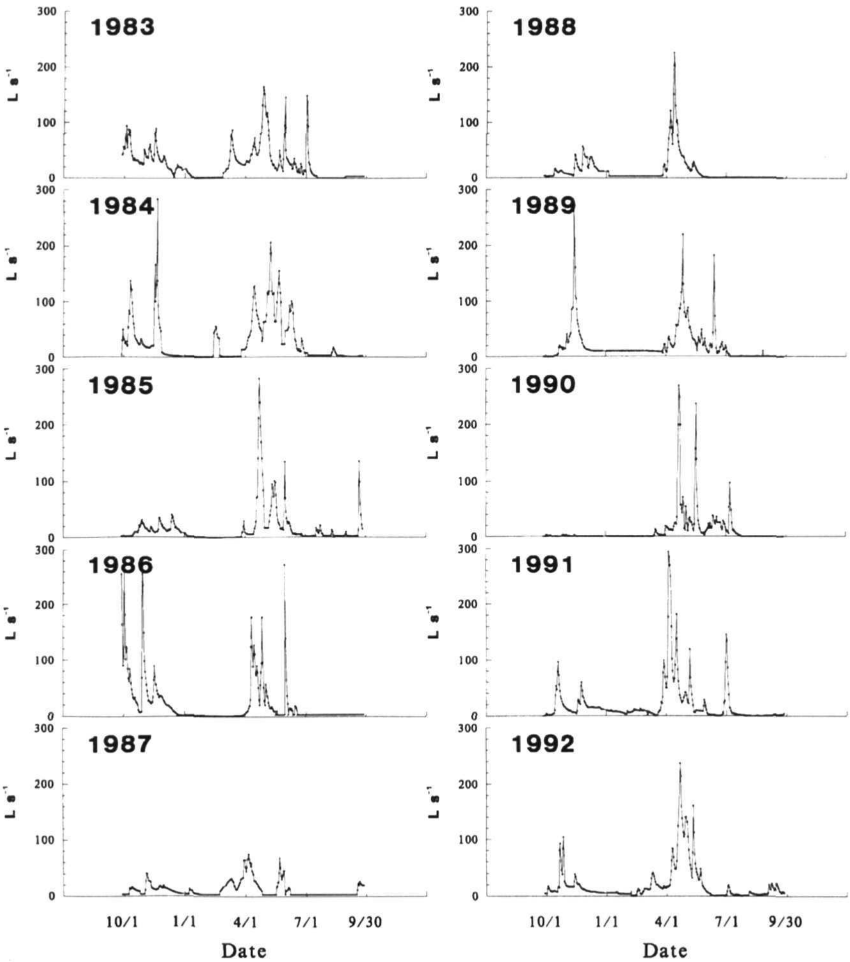


**Figure 14.** Daily stream flow by water year at station W2, Wallace Lake watershed, Isle Royale National Park, Michigan, 1982–1996.

The time range of peak stream flow during snowmelt was from 6 April in 1987 to 20 May in 1984. In 1984 and 1989, daily discharge peaked in late fall. Stream flow in winter (1 November–30 May) was 46 cm or 90% of the annual stream flow. More than 30% of the annual stream flow at Station W2 occurred in April, and more than 50% occurred in April and May combined. A positive relation ($p < 0.001$, $r^2 = 0.74$) existed between stream flow in winter and annual stream flow from the watershed. No relation existed between the date of peak stream flow, its amount, or the sum of precipitation in winter.

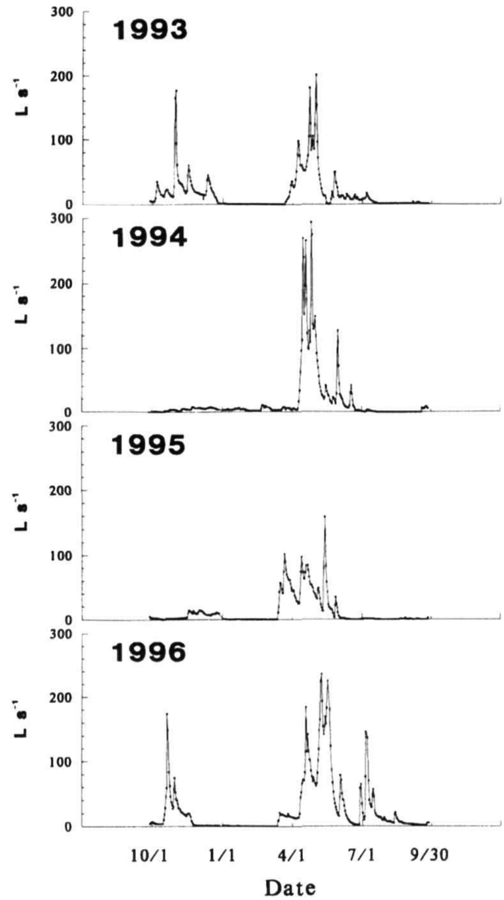


**Figure 14.** *Continued.*

## *Biogeochemistry*

### Precipitation

Annual volume-weighted base cation ($C_B$) concentration in wet precipitation (Aerochem Metrics event collector) at the NADP Station MI99 declined ($p < 0.001$, $r^2 = 0.65$, b = –1.0) beginning in 1982 (Fig. 15). $C_B$ concentration at the adjacent MI99 Bulk Collector increased ($p < 0.05$, $r^2 = 0.54$, b = 4.5) during 1988–96.

Volume-weighted $H^+$ concentration (mean 0.15 $\mu$eq $L^{-1}$, pH = 4.94) in NADP MI99 wet precipitation showed no trend with time. The $H^+$ concentration (mean 28 $\mu$eq $L^{-1}$, pH = 4.55) at the MI99 Bulk Collector declined ($p < 0.01$, $r^2 =$ 0.71, b = –2.0 $\mu$eq $L^{-1}$ $year^{-1}$) since 1988. Volume-weighted $H^+$ concentration

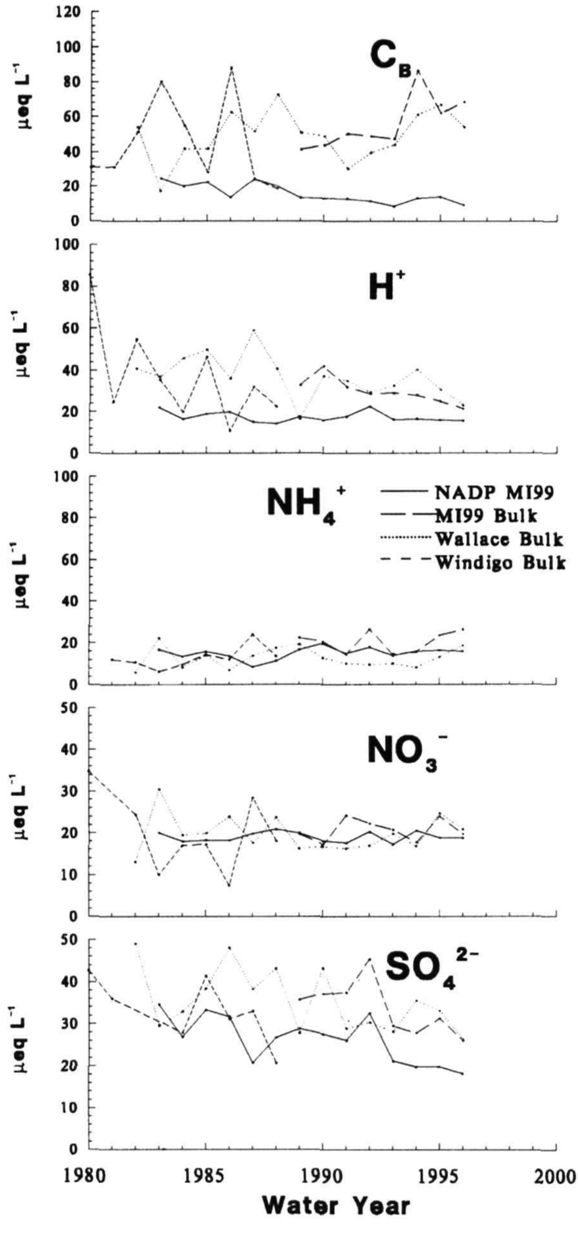


**Figure 15.** Annual volume-weighted ion concentration in precipitation, National Atmospheric Deposition Program Station MI99 (1982–1996), and paired bulk collector at MI99 (1988–1996), Chassell, Michigan, and precipitation bulk collectors at Windigo (1981–1988) and Wallace Lake (1982–1996), Isle Royale National Park, Michigan.

(mean 35 μeq $L^{-1}$, pH = 4.45) also declined in the bulk precipitation collectors in the Wallace Lake watershed ($p < 0.05$, $r^2 = 0.26$, b = –1.2) and at Windigo ($p < 0.10$, $r^2 = 0.32$, b = –4.0; mean 37 μeq $L^{-1}$, pH = 4.43).

The $NH_4^+$ and $NO_3^-$ concentrations in precipitation showed no significant trends at any station. The $NH_4^+$ to $NO_3^-$ and $NO_3^-$ to $SO_4^{2-}$ ratios (equivalent basis) also showed no significant trend during 1982–96.

The annual volume-weighted $SO_4^{2-}$ concentration in wet precipitation at NADP MI99 declined ($p < 0.01$, $r^2 = 0.51$, b = –0.95) during 1982–96. The $SO_4^{2-}$ concentration declined at the MI99 Bulk Collector ($p < 0.08$, $r^2 = 0.43$, b = –1.7) and in the Wallace Lake watershed ($p < 0.05$, $r^2 = 0.25$, b = –0.8) during 1982–96. The $SO_4^{2-}$ concentration declined at Windigo ($p < 0.05$, $r^2 = 0.52$, b = –3.0) during 1980–88.

Cation to anion ratios of precipitation in event and bulk collectors were near balance (Table 5). The $C_B$ concentrations in the MI99 Bulk Collector were four times the levels in the adjacent event collector at NADP Station MI99. The increases in $C_B$ and $HCO_3^-$ concentrations in the bulk collector in the Wallace Lake watershed were similar to the MI99 bulk collector.

The seasonal (monthly) change in ion concentration in precipitation was pronounced (Fig. 16). In general, the volume-weighted concentrations of $C_B$, $NH_4^+$, and $SO_4^{2-}$ in the bulk collectors followed the pattern of the monthly precipitation amount. The amount and trend of ion concentrations in the NADP stations in summer were similar. In bulk collectors, the $C_B$, $H^+$, $NH_4^+$, and $SO_4^{2-}$ concentrations generally increased during spring and peaked in early summer. The $NO_3^-$ to $SO_4^{2-}$ ratio in precipitation was higher in winter (0.78) than in other seasons (0.45) or in annual precipitation (0.57). During summer, the only season the NADP Station MI97 was in operation, the $C_B$ and $H^+$ concentrations were higher in the bulk collectors than in the NADP event collectors. The $NH_4^+$ concentrations were similar or reduced, and the $NO_3^-$ and $SO_4^{2-}$ concentrations were similar.

Except $C_B$, annual ion input from precipitation in the Wallace Lake watershed declined during 1982–96 (Fig. 17). The declines of $H^+$ ($p < 0.01$, $r^2 = 0.49$), $NO_3^-$ ($p < 0.08$, $r^2 = 0.24$), and $SO_4^{2-}$ ($p < 0.05$, $r^2 = 0.37$) were significant. A decrease in precipitation amount primarily accounted for the decline in ions input. However, the decline in $H^+$, $NO_3^-$, and $SO_4^{2-}$ inputs exceeded the decrease in precipitation amount.

Except $NH_4^+$ and $NO_3^-$, the seasonal change in ion input also largely reflected a change in monthly precipitation amount (Fig. 18). Except $NH_4^+$, the monthly input and variation in inputs were less in winter than in summer.

## Throughfall, Stemflow, and Forest-Floor Leachate

As a result of the interaction of precipitation with the boreal canopy, the $C_B$ concentration was greater and the $H^+$ concentration was smaller in throughfall than in precipitation (Tables 6 and 7). The seasonal change in $C_B$ concentra-

**Table 5.** Mean ion concentration ($\mu eq\ L^{-1}$), DOC, and cation/anion (C/A) ratios at the precipitation station MI99 of the National Atmospheric Deposition Program and in the adjacent bulk precipitation collector; in the bulk precipitation collector and in stream water stations 1 and 2 in the Wallace Lake watershed. DOC concentrations in $\mu eq\ L^{-1}$ estimated from Gorham et al. (1984).

| Station | $Ca^{2+}$ | $Mg^{2+}$ | $Na^{+}$ | $K^{+}$ | $H^{+}$ | $NH_4^{+}$ | $NO_3^{-}$ | $SO_4^{2-}$ | $Cl^{-}$ | $HCO_3^{-}$ | DOC | C:A[a] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| NADP MI99 | 9 | 3 | 3 | 1 | 17.0 | 15 | 19 | 27 | 3 | | | 0.98 |
| MI99 Bulk | 37 | 14 | 7 | 2 | 30.0 | 23 | 25 | 39 | 9 | 39[b] | | 1.00 |
| Wall. Bulk | 30 | 10 | 10 | 3 | 36.0 | 12 | 19 | 36 | 10 | 28 | | 1.10 |
| Wall 2 str. | 639 | 316 | 95 | 7 | 0.1 | 3 | 6 | 51 | 81 | 825 | 96 | 1.00 |
| Wall 1 str. | 578 | 385 | 58 | 11 | 0.1 | 3 | 11 | 35 | 11 | 747 | 90 | 1.10 |

[a] Cation:anion ratios (equivalent basis).

[b]Alkalinities determined only on a subset of precipitation samples.

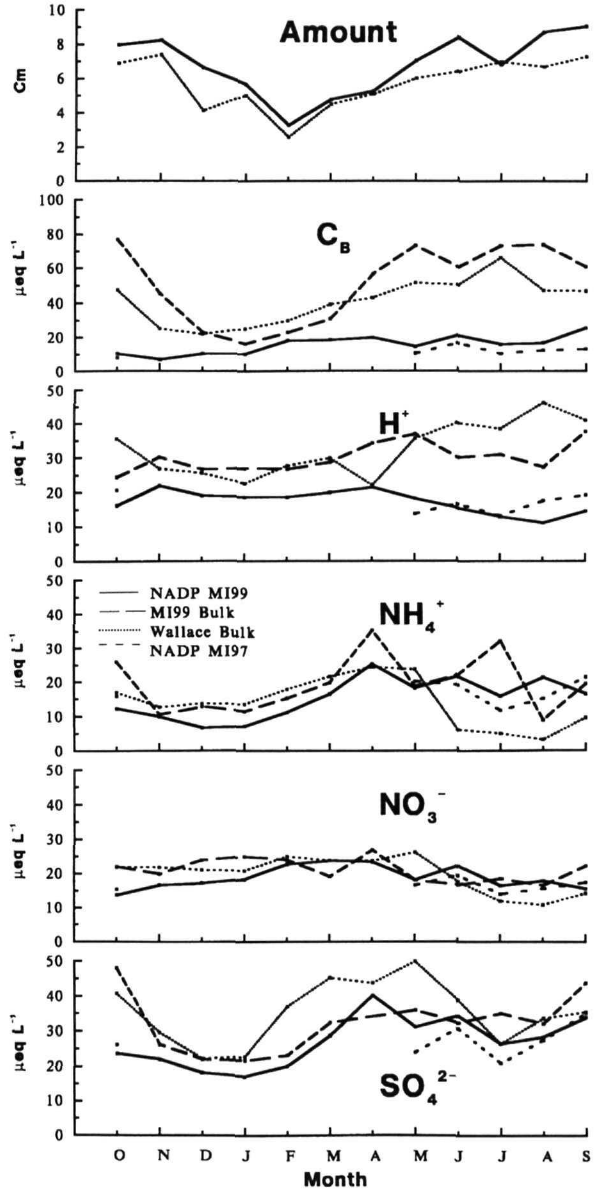


**Figure 16.** Mean monthly precipitation amount and ion concentration at the National Atmospheric Deposition Program (NADP) Station MI99 during 1982–1996 and the paired bulk collector during 1988–1996, Chassell, Michigan; at the Wallace Lake bulk precipitation collector during 1982–1996 and at the seasonally operated NADP Station MI97 in the Wallace Lake watershed during 1986–1996, Isle Royale National Park, Michigan.

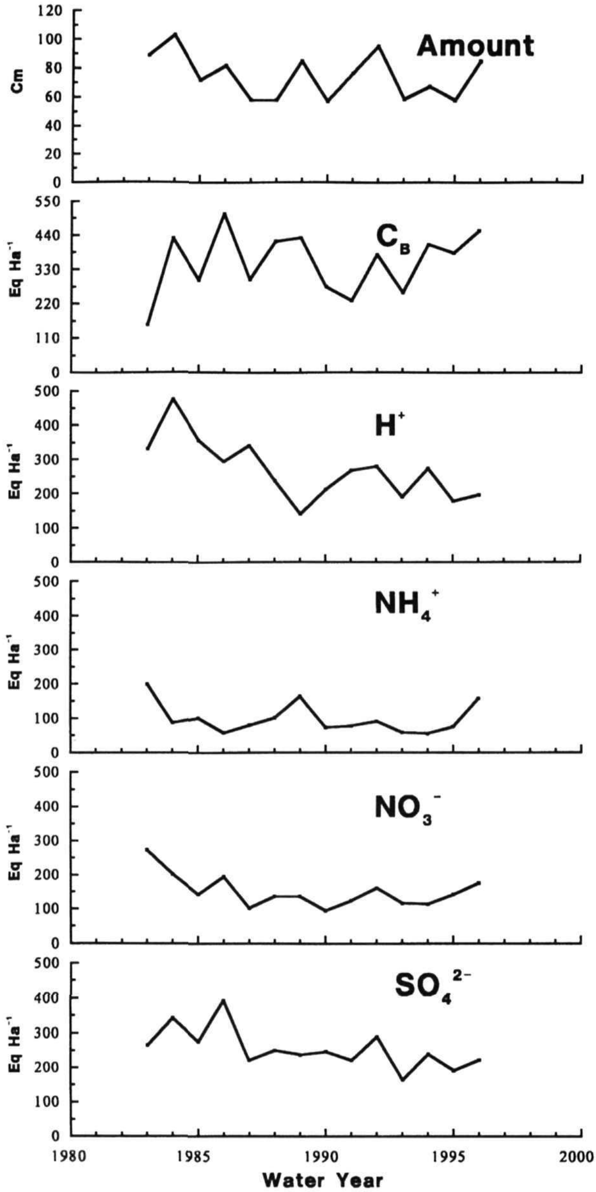


**Figure 17.** Annual precipitation amount (Belfort recording rain gages) and ion (bulk collector) input, Wallace Lake watershed, Isle Royale National Park, Michigan, 1983–1996.

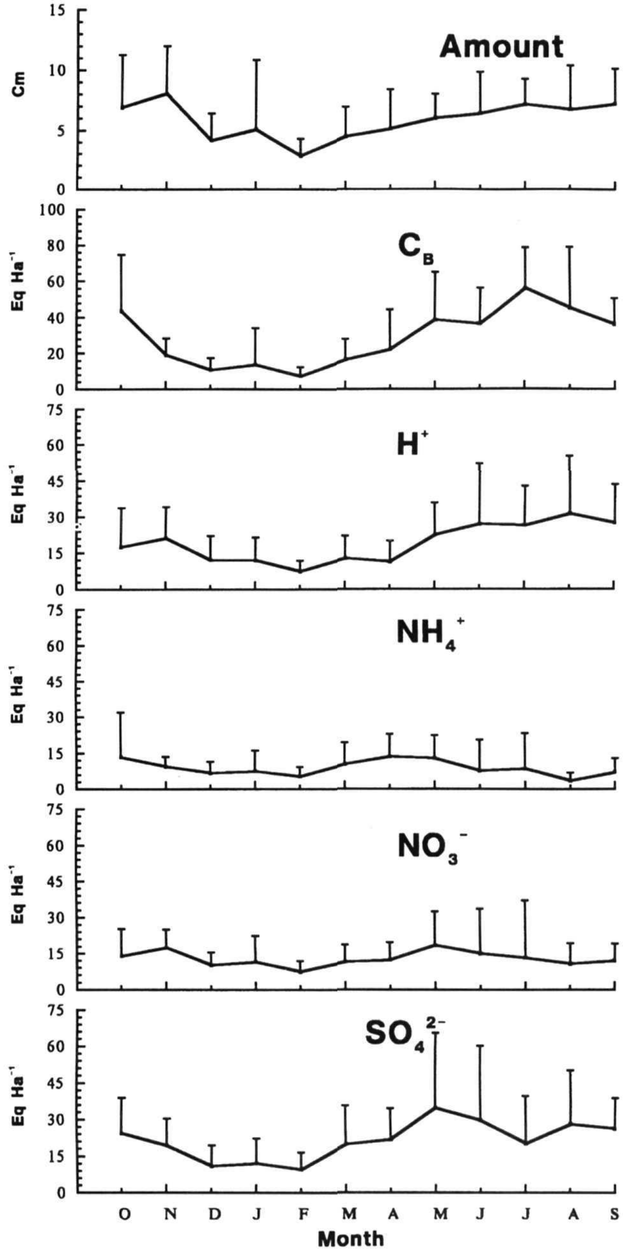


**Figure 18.** Mean monthly precipitation amount and ion input, Wallace Lake watershed, Isle Royale National Park, Michigan, 1982–1996. Bars represent one standard deviation.

**Table 6.** The mean ionic concentration of precipitation, throughfall, litter layers, and soil solution in mineral horizons. Data of spruce (*Picea* spp.) and aspen-birch (*Populus-Betula*) from Stottlemyer and Hanson (1989); data of northern white cedar (*Thuja occidentalis*) from Stottlemyer (1982); and data of alder (*Alnus rugosa*) from Stottlemyer (unpublished), Wallace Lake watershed, 1982–1996.

| Mineral Horizon | $Ca^{2+}$ | $Mg^{2+}$ | $K^{+}$ | $Na^{+}$ | $H^{+}$ | pH | $NH_4^{+}$ | $NO_3^{-}$ | $SO_4^{2-}$ |
|---|---|---|---|---|---|---|---|---|---|
| Spruce | | | | | | | | | |
| PPT[a] | 7d[b] | 2d | 5c | 9b | 22ab | 4.7 | 9a | 18a | 15d |
| TF | 52c | 22c | 87b | 36b | 24a | 4.6 | 43a | 11ab | 38cd |
| Oe/E | 147b | 42b | 131a | 17b | 1ac | 6.0 | 31a | 3c | 49c |
| Bsl | 242a | 95a | 75b | 86a | 6abc | 5.2 | 34a | 1bc | 111ab |
| E/Bt | 160b | 65b | 39bc | 75a | 3abc | 5.4 | 3a | 0.4bc | 87b |
| Aspen-Birch | | | | | | | | | |
| PPT | 7d | 2c | 5c | 9b | 22a | 4.7 | 9b | 18a | 15c |
| TF | 56c | 28b | 79b | 19b | 6b | 5.2 | 8b | 10ab | 30bc |
| A | 166a | 65a | 125a | 20b | 0.6b | 6.2 | 49a | 9ab | 25abc |
| Bhs | 127b | 59a | 26c | 40a | 3b | 5.4 | 3b | 9b | 38ab |
| 2Bs2 | 108b | 45ab | 15c | 47a | 1b | 6.0 | 10b | 6b | 42a |

**Table 6.** *Continued.*

| Mineral Horizon | $Ca^{2+}$ | $Mg^{2+}$ | $K^{+}$ | $Na^{+}$ | $H^{+}$ | pH | $NH_4^{+}$ | $NO_3^{-}$ | $SO_4^{2-}$ |
|---|---|---|---|---|---|---|---|---|---|
| Alder | | | | | | | | | |
| PPT | 29a | 7a | 7a | 21b | 19b | 4.7 | 17b | 18a | 37a |
| TF | 195b | 81b | 105b | 6a | 2a | 5.7 | 30b | 8a | 42a |
| Oa1 | 518c | 222c | 10a | 52c | 1a | 6.0 | 6b | 169b | 73b |
| Oa2 | 713d | 378d | 4a | 91d | 1a | 6.0 | 3a | 56a | 50a |
| Northern White Cedar | | | | | | | | | |
| PPT | 25a | 12a | 4a | 9a | 43b | 4.4 | 10a | 19a | 48a |
| TF | 82b | 43b | 51b | 15a | 39b | 4.4 | 16a | 32a | 87b |
| A | 118b | 39b | 122c | 7a | 2a | 5.7 | 35b | 31a | 111b |

[a] Precipitation (PPT), throughfall (TF).

[b] Mean values within a column followed by the same letter are not significantly different (p = 0.05, Student Newman Keuls test).

**Table 7.** Mean volume-weighted throughfall and stemflow ion concentration ($\mu eq\ L^{-1}$) of spruce (*Picea* spp.), maple (*Acer* spp.), and northern white cedar (*Thuja occidentalis*) in plots in the Washington Creek drainage, 1979–1982.

| Species | $Ca^{2+}$ | $Mg^{2+}$ | $K^+$ | $Na^+$ | $H^+$ | $NH_4^+$ | $NO_3^-$ | $SO_4^{2-}$ | $Cl^-$ |
|---|---|---|---|---|---|---|---|---|---|
| Throughfall | | | | | | | | | |
| Spruce | 126 | 142 | 267 | 18 | 25 | 27 | 36 | 274 | 114 |
| Maple | 135 | 264 | 530 | 9 | 20 | 48 | 137 | 284 | 80 |
| Cedar | 146 | 195 | 199 | 9 | 20 | 27 | 59 | 273 | 55 |
| Stemflow | | | | | | | | | |
| Spruce | 258 | 230 | 451 | 22 | 45 | 16 | 2 | 267 | 16 |
| Maple | 88 | 61 | 408 | 10 | 2 | 18 | 4 | 294 | 14 |
| Cedar | 638 | 268 | 114 | 18 | 6 | 12 | 10 | 311 | 39 |

**Table 8.** Estimated annual flux of major ions ($kM\ ha^{-1}$) in precipitation, throughfall, and mineral soil, Wallace Lake watershed, 1984–1986.

| Stratum | Water (cm) | $H^+$ | Sum of Cations | $SO_4^{2-}$ | $NO_3^-$ |
|---|---|---|---|---|---|
| Beneath Spruce (*Picea* spp.) | | | | | |
| PPT | 75 | 0.16 | 0.32 | 0.11 | 0.13 |
| TF | 57 | 0.14 | 1.49 | 0.22 | 0.05 |
| Oe/E | 45 | 0.03 | 3.31 | 0.49 | 0.01 |
| Bsl | 45 | 0.01 | 3.13 | 0.40 | <0.01 |
| E/Bt | 45 | 0.04 | 1.81 | 0.59 | <0.01 |
| Beneath Birch-Aspen (*Betula-Populus*) | | | | | |
| PPT | 75 | 0.16 | 0.32 | 0.11 | 0.13 |
| TF | 61 | 0.04 | 1.59 | 0.18 | 0.05 |
| A | 45 | 0.02 | 3.18 | 0.17 | 0.04 |
| Bhs | 45 | <0.01 | 2.46 | 0.19 | 0.02 |
| 2Bs2 | 45 | <0.01 | 2.34 | 0.20 | <0.01 |

tion in throughfall from conifer and hardwood and the seasonal change in precipitation were similar (Stottlemyer and Hanson 1989). The $SO_4^{2-}$ concentrations in throughfall from all species and in precipitation were similar except during late summer and early fall when concentrations in throughfall were greater. The $K^+$ concentration in throughfall peaked in September beneath hardwoods and in October beneath conifers. The $NO_3^-$ in throughfall from the conifer canopy was highest in winter, and the $H^+$ concentration was highest in late spring. In summer, the boreal hardwood canopy (birch, aspen, alder) significantly reduced $H^+$ concentration in precipitation. The chemical flux in throughfall from the two dominant forest vegetation types (Table 8) showed N and $H^+$ were retained in the canopy, but $SO_4^{2-}$ increased in throughfall.

In the earlier (1979–82) study of throughfall and stemflow in the Washington Creek watershed (Table 7), concentrations of $Ca^{2+}$, $H^+$, and $SO_4^{2-}$ were higher in stemflow than in throughfall. The $K^+$ and $Na^+$ concentrations were similar, and the $Mg^{2+}$, $NH_4^+$, $NO_3^-$ and $Cl^-$ concentrations were reduced. The total ion concentration was highest in the stemflow of cedar. Except in spruce, the $H^+$ concentrations were lower in stemflow than in throughfall and precipitation. The concentrations of $Ca^{2+}$, $Mg^{2+}$, $K^+$, and $H^+$ in stemflow significantly differed among species (Student Newman-Keuls). The $Ca^{2+}$ and $Mg^{2+}$ concentrations were highest in cedar stemflow, and $K^+$ and $H^+$ were highest in spruce stemflow. The anion deficit was larger in stemflow (cation:anion = 2.4) than in throughfall (cation:anion = 1.7), which indicated the increased importance of organic acids in stemflow.

The $C_B$ concentration was significantly greater in litter leachate beneath the major species than in throughfall (Table 6). Calcium became the dominant cation in litter leachate and $K^+$ the dominant cation in throughfall. The $NO_3^-$ concentrations in litter leachate were reduced beneath spruce, but $SO_4^{2-}$ concentrations remained unchanged.

**Snowpack Chemistry**

Although the snowpack PWE in the Wallace Lake watershed slightly exceeded the PWE at Windigo (Fig. 10), the snowpack PWE or its ion load did not differ between the two locations (Fig. 19). During 1983–96, when sampling was routinely conducted at both stations, the mean $C_B$ load of snowpack PWE was 38 (24) eq $ha^{-1}$, $H^+$ was 20 (10), $NH_4^+$ was 15 (9), $NO_3^-$ was 29 (12), and $SO_4^{2-}$ was 26 (9). Almost two-thirds (63%) of the elemental N in the snowpack at PWE was $NH_4^+$–N. During 1982–96, the snowpack PWE $SO_4^{2-}$ load in the Wallace Lake watershed decreased ($p < 0.08$, $r^2 = 0.28$, b = –1.2 eq $ha^{-1}$). The ratio of cations to anions (equivalent basis) was 1.15.

In surveys of a series of additional snowpack stations along the north to south gradient on Isle Royale in winter, the SWE in 1987 and 1988 was at the low end of the range during 1979–96 (Fig. 10). The snowpack amount and ion load, except $C_B$, were uniform among stations (Fig. 20). The mean $C_B$ content in the snowpack was 29(9) eq $ha^{-1}$, $H^+$ was 18 (4), $NH_4^+$ was 15 (4), $NO_3^-$ was 22 (4), and $SO_4^{2-}$ 21 (4) eq $ha^{-1}$. The snowpack $NH_4^+$– content was more than twice as large as $NO_3^-$. The mean snowpack PWE in 1987–88 was 20% higher at the Windigo and Wallace Lake stations than the island-wide mean of 9 (2) cm. The $C_B$ load was 43% greater, $H^+$ was 20% greater, $NH_4^+$ and $NO_3^-$ were 25% greater, and $SO_4^{2-}$ was 33% greater.

During 1983–96 in the Wallace Lake watershed, there was no significant correlation between cumulative precipitation ion inputs and snowpack content up to snowpack PWE. By PWE, the snowpack lost an average 23% of cumulative $C_B$ input in winter: 39% $H^+$, 48% $NH_4^+$, 34% $NO_3^-$, and 50% $SO_4^{2-}$.

**Soil Characteristics and Soil Processes**

The mean soil moisture was highest ($p < 0.001$, $r^2 = 0.44$) beneath alder (Table 9; Stottlemyer et al. 1995). Soil moisture beneath alder was higher

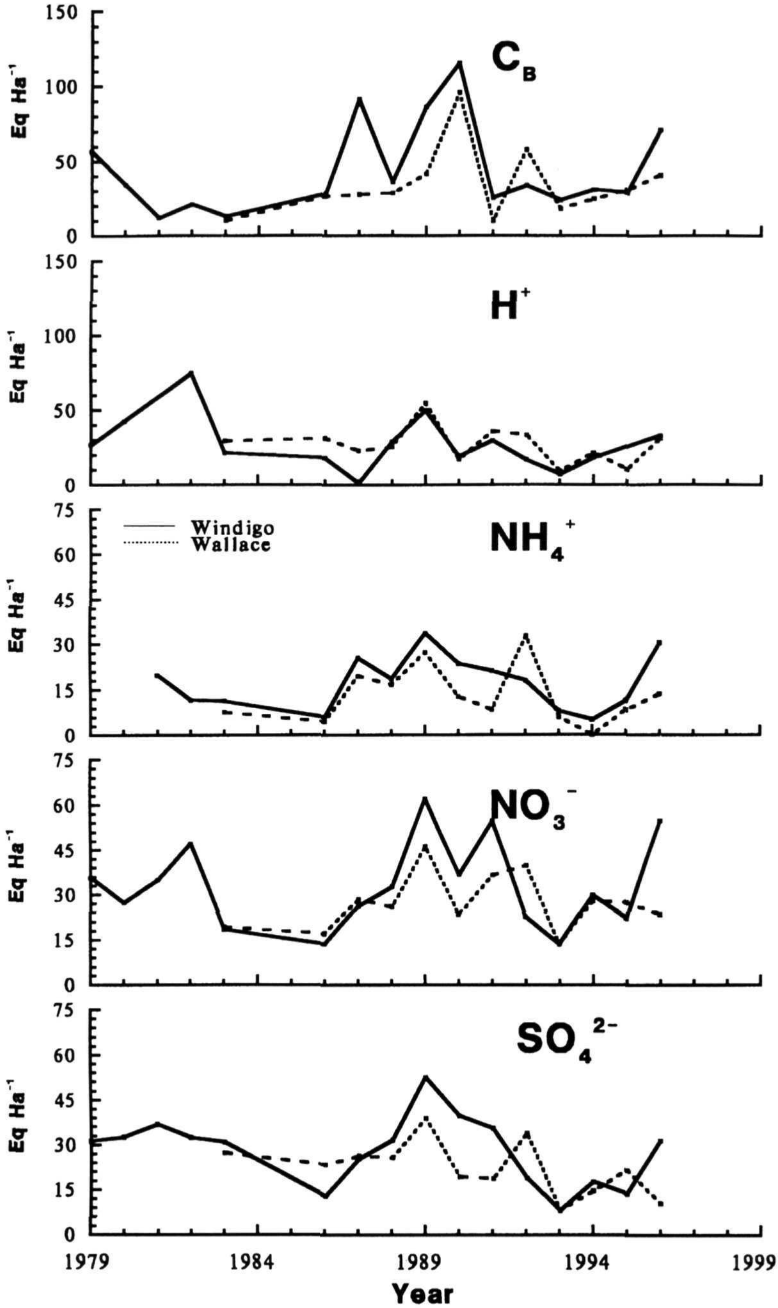


**Figure 19.** Time trend in snowpack ion load, Windigo and Wallace Lake stations, Isle Royale National Park, Michigan, 1979–1996.

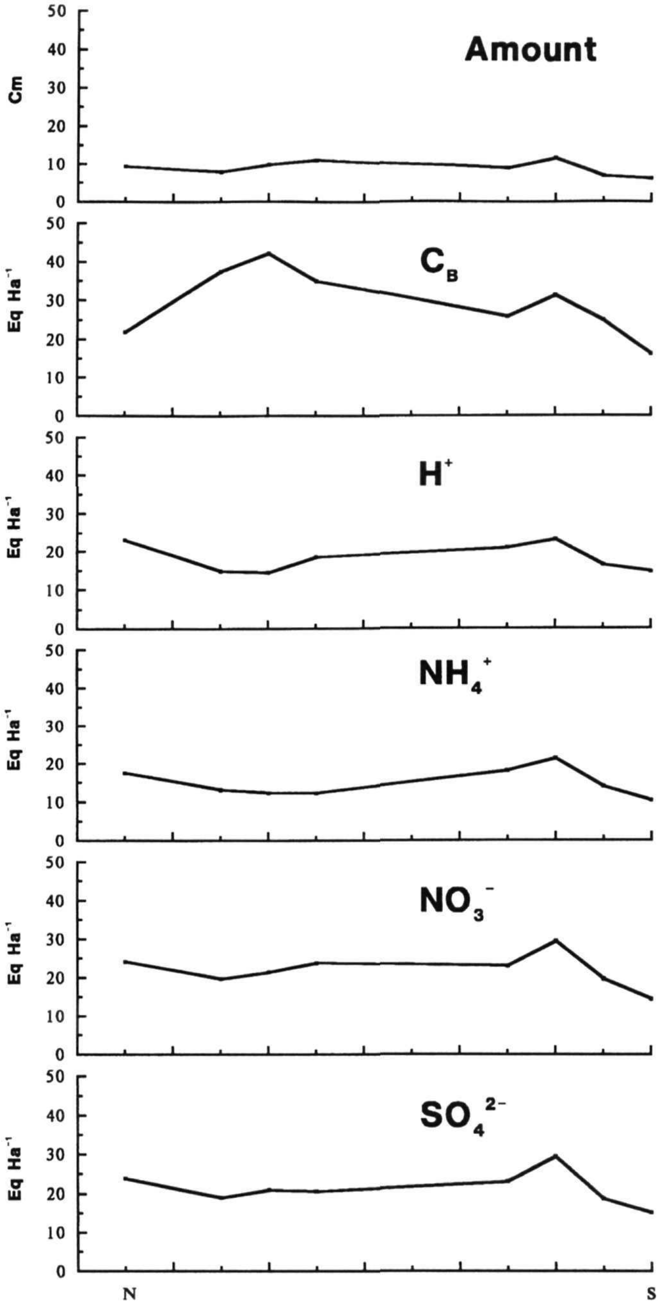


**Figure 20.** Peak snowpack water equivalent (PWE) and ion content along north to south transect in winter, Isle Royale National Park, Michigan, 1987 and 1988.

**Table 9.** Mean field soil characteristics by tree species, Wallace Lake watershed. 1992–1994.

| Species | Percent Moisture[a] | Bulk Density g $cm^{-3}$ | $N0_3^-$ mg N $m^{-2}$ | $NH_4^+$ mg N $m^{-2}$ | Inorganic N $NO_3^- + NH_4^+$ | Total N mg N $m^{-2}$ | Temperature °C |
|---|---|---|---|---|---|---|---|
| Birch[b] | 25 (11) e | 0.6 (0.1) c | 4.0 (8) e | 134 (172) d | 138 (174) d | 189 (22) d | 10.1 (3) c |
| Spruce | 24 (18) e | 0.7 (0.1) c | 9.0 (18) e | 269 (337) c | 278 (345) c | 181 (45) d | 7.3 (3) d |
| Alder | 45 (8) c | 0.5 (0.1) e | 88.0 (63) c | 152 (102) c | 240 (128) c | 267 (58) c | 8.9 (2) c |
| Maple | 31 (4) d | 0.7 (0.1) c | 24.0 (89) d | 257 (361) c | 281 (387) c | 295 (55) c | 9.8 (3) c |

[a] Percent moisture is by weight determined gravimetrically. Standard deviation is in parentheses .
[b] Where letters differ, the differences among means are significant ($p<0.05$).

($p < 0.05$, $r^2 = 0.70$) in all months except in October and was saturated during and after snowmelt. Soil bulk density was lowest in alder ($p < 0.001$, $r^2 = 0.23$). The total N concentration in the soil differed by species ($p < 0.001$, $r^2 = 0.31$) and was higher in soil beneath alder and maple ($p < 0.01$) than in soil beneath spruce and birch. The mean annual soil temperatures (Fig. 9) did not differ by species, but in May soil temperatures beneath spruce were lower ($p < 0.001$, $r^2 = 0.90$). Except beneath spruce, soils did not freeze. Unfrozen soils permitted overwinter processes such as N mineralization and nitrification, which resulted in high net mineralization rates (Fig. 21).

In general, $C_B$ concentrations were greater in soil water than in precipitation and throughfall in all canopy species (Table 6; Stottlemyer and Hanson 1989). The exception was the $K^+$ concentration, which often decreased in shallow (15–20-cm depth) soil water. The $NH_4^+$ concentration beneath birch-aspen litter significantly increased but decreased in deeper (30 cm) soil water beneath alder.The $NO_3^-$ concentrations were significantly less in soil water than in throughfall concentrations except beneath alder and maple (not shown), but $SO_4^{2-}$ concentrations increased except beneath cedar. The ratio of cations to anions was highest in leachate from the forest floor except beneath alder where the ratio was highest in throughfall.

Monthly soil $NO_3^-$ concentrations (extractable) and pools were higher beneath alder (Table 9; $p < 0.05$, $r^2 = 0.70$) and peaked ($p < 0.05$, $r^2 = 0.60$) in October (Fig. 21). Soil $NH_4^+$ concentrations varied by month ($p < 0.001$, $r^2 = 0.85$) and with the interaction of species and month ($p < 0.001$). Concentrations were higher beneath maple ($p < 0.05$) at Windigo than beneath birch or alder in the Wallace Lake watershed and highest ($p < 0.05$) from mid-June to mid-August. Total inorganic N concentration in the soil also varied by month ($p < 0.001$, $r^2 = 0.84$), and the interaction of species with month ($p < 0.001$). Concentrations were higher beneath maple ($p < 0.05$) than beneath birch or alder and highest ($p < 0.01$) from mid-June to mid-August.

Monthly net $NO_3^-$ mineralization rates differed by species ($p < 0.001$ $r^2 = 0.42$, $n = 107$) and were highest ($p < 0.001$) beneath alder (Fig. 21). Monthly net $NO_3^-$ mineralization rates were greater during winter beneath alder, birch, and spruce, but no trends were observed. The net $NH_4^+$ mineralization and total net mineralized inorganic N did not vary by species but by month ($p < 0.05$, $r^2 = 0.16$, $n = 109$). Monthly rates were higher ($p < 0.05$) during October–January than during July and August.

The soil $NO_3^-$ pools and net $NO_3^-$ mineralization rates were inversely related in birch, alder, and maple. Soil $NH_4^+$ pools and net $NH_4^+$ mineralization rates and total inorganic soil N pools and net inorganic N mineralization rates were inverse in birch, spruce, and maple.

The monthly net $NO_3^-$ mineralization rates and mean soil temperature at the 5-cm depth were inverse ($p < 0.05$) in birch, spruce, and alder. The relation between monthly net $NH_4^+$ mineralization, total inorganic N mineralization, and soil temperature was inverse beneath spruce and alder.

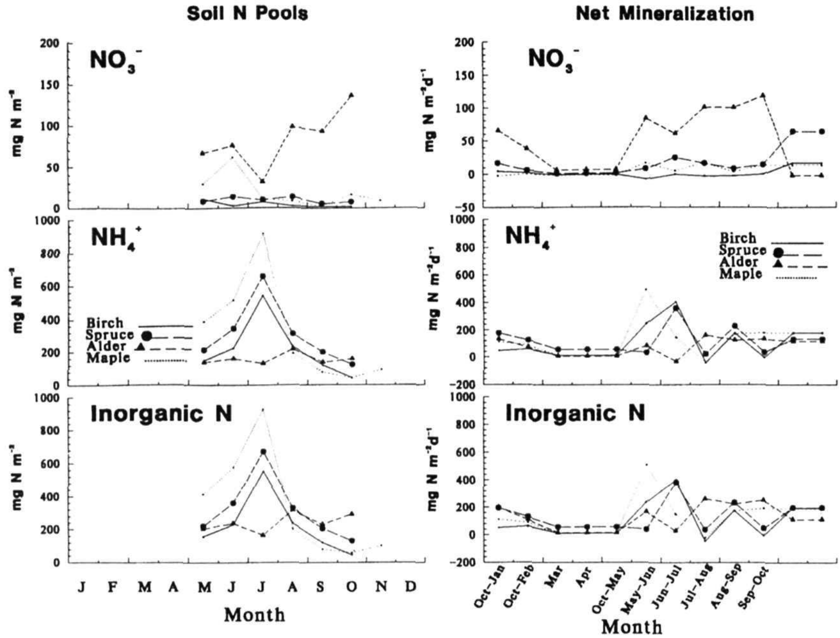


**Figure 21.** Seasonal soil inorganic N pools and net N mineralization rates beneath major canopy species, Wallace Lake watershed, Isle Royale National Park, Michigan, 1992–1997.

The average annual net N mineralization beneath all species was 1.4 g N $m^{-2}$. In the dominant boreal species, birch and spruce, the rate was 1.1 g N $m^{-2}$.

Laboratory incubations, when only temperature and moisture were varied, showed a significant increase in net $NH_4^+$ mineralization in birch, spruce, and maple (equivalent to 18 mg N $m^{-2}$ $day^{-1}$, $p < 0.01$, $r^2 = 0.51$) and in total inorganic N mineralization with temperature (equivalent to 22 mg N $m^{-2}$ $day^{-1}$, $p < 0.01$, $r^2 = 0.32$). There was an increase in net $NO_3^-$ mineralization (12 mg N $m^{-2}$ $day^{-1}$, $p < 0.05$, $r^2 = 0.17$) with increased moisture in spruce and maple (Stottlemyer et al. 1995). Most of the increase in inorganic N mineralization occurred in the mid-temperature range (from 10 to 15°) and at the mid-moisture level. Soil net $NH_4^+$ mineralization increased in birch (24 mg N $m^2$ $day^{-1}$, $p < 0.01$, $r^2 = 0.64$) and spruce (21 mg N $m^2$ $day^{-1}$, $p < 0.05$, $r^2 = 0.45$) with temperature. Net soil inorganic N mineralization increased in birch (23 mg N $m^2$ $day^{-1}$, $p < 0.001$, $r^2 = 0.64$, $n = 27$) with temperature and in spruce with moisture (equivalent of 13 mg N $m^2$ $day^{-1}$, $p < 0.05$, $r^2 = 0.47$).

The gross nitrification rates differed by species ($p < 0.001$, $r^2 = 0.62$; Fig. 22). Nitrification rates were higher beneath alder than beneath birch ($p < 0.001$) or spruce ($p < 0.001$). Among all species, there was no significant seasonal trend (May–October; measurements were not made in winter) in gross nitrification

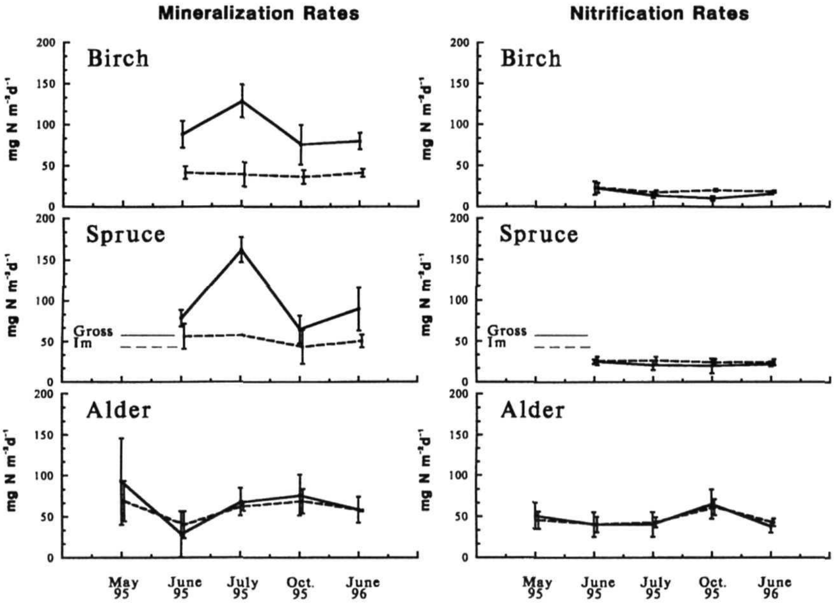


**Figure 22.** Seasonal forest floor and shallow soil gross N mineralization, nitrification, and immobilization rates beneath major canopy species, Wallace Lake watershed, Isle Royale National Park, Michigan, 1995–1996.

rates. Beneath birch, the seasonal change in gross nitrification rates was significant ($p < 0.05$, $r^2 = 0.60$). The rates were higher ($p < 0.05$) in June than in October. No seasonal changes in gross nitrification rates were observed beneath spruce and alder.

Gross N mineralization rates did not differ by species. Seasonally, gross mineralization rates varied ($p < 0.05$, $r^2 = 0.70$) beneath spruce. The rates were higher ($p < 0.05$) in July than in June. The $NH_4^+$ immobilization rates differed by species ($p < 0.01$, $r^2 = 0.30$, $n = 37$). The rates were higher ($p < 0.01$) beneath alder than beneath spruce and birch. There were no seasonal trends in $NH_4^+$ immobilization rates in any species.

Soil respiration, as indicated by daily $CO_2$ efflux (Fig. 23), correlated (Pearson, $p < 0.001$) with mean soil temperature at the 5-cm depth. Gross $NH_4^+$ mineralization rates correlated with soil temperature ($p < 0.08$) and with $NH_4^+$ immobilization rates ($p = 0.05$). Soil respiration correlated with gross $NH_4^+$ mineralization ($p < 0.05$) and inversely with $NO_3^-$ immobilization ($p < 0.10$). Ammonium immobilization rates correlated with gross nitrification rates ($p < 0.01$) and $NO_3^-$ immobilization ($p < 0.05$). Gross nitrification rates correlated with $NO_3^-$ immobilization ($p < 0.001$).

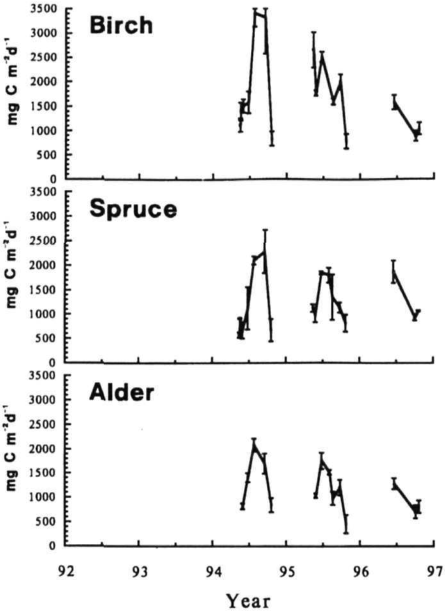


**Figure 23.** Seasonal trends in soil $CO_2$ (as C) emissions beneath birch (*Betula papyrifera*), spruce (*Picea glauca*), and alder (*Alnus rugosa*), Wallace Lake watershed, 1994–1996.

## Stream Water

***Concentration.*** In the Wallace Lake watershed, volume-weighted stream water ion concentrations showed no significant trends during 1982–96 (Fig. 24). The $NO_3^-$ concentration in stream water showed the least change of any ion with time. The bicarbonate alkalinity concentrations followed a similar general pattern as $C_B$ but significantly increased ($p < 0.01$, $r^2 = 0.60$) only at the lower Sumner Lake station (Sumner 3).

Through 1995, the annual volume-weighted DOC concentrations at W2 declined ($p < 0.01$, $r^2 = 0.68$, b = –0.6). Unlike $C_B$ concentrations, DOC concentrations increased with stream discharge ($p < 0.001$, $r^2 = 0.89$). Similarly, the total N concentrations in stream water ($p < 0.001$, $r^2 = 0.21$) and total metal concentrations such as Al ($p < 0.001$, $r^2 = 0.42$, b = 0.26) increased with discharge (Table 10). Total P concentration in stream water did not increase with discharge.

Stream water cation to anion ratios were nearly balanced (Table 5). DOC was about 10% of the stream water anion charge.

Seasonal variation of the ion concentration in stream water reflected the hydrology and biological activity. Snowmelt changed the stream water con-

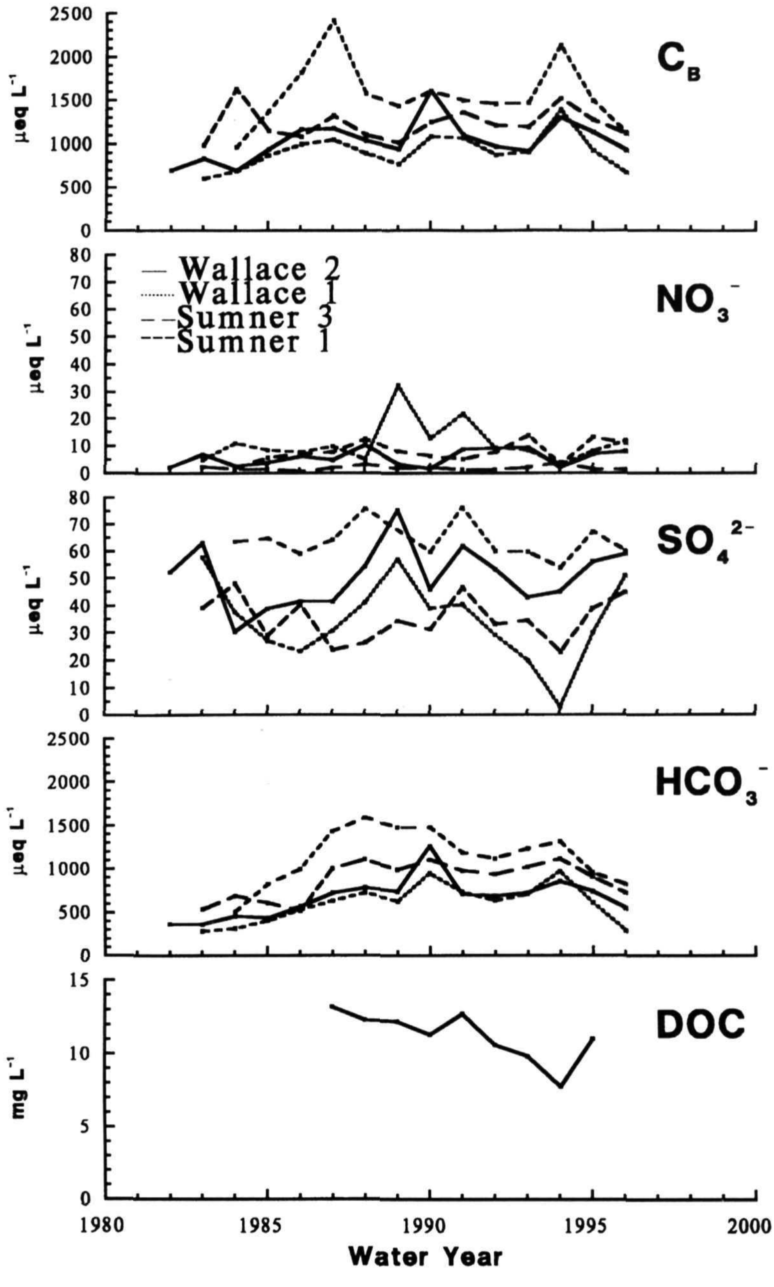


**Figure 24.** Annual stream water ion concentrations at upstream and downstream stations, conterminous Wallace Lake and Sumner Lake watersheds, Isle Royale National Park, Michigan, 1982–1996.

**Table 10.** Weighted average heavy metal and trace metal concentrations (ppb) in stream water, Station W2, Wallace Lake watershed, 1984–1990. SD equals one standard deviation.

| Element | Mean | SD | Element | Mean | SD |
|---|---|---|---|---|---|
| Fe | 245 | 403 | Ag | 10 | 14 |
| Cr | 30 | 11 | Si | 2175 | 3351 |
| Cu | 20 | 5 | B | 156 | 250 |
| Mn | 9 | 24 | Co | 30 | 34 |
| Al | 270 | 324 | Mo | 345 | 580 |
| Cd | 15 | 52 | Li | 15 | 21 |
| Ni | 8 | 13 | Sr | 31 | 73 |
| Be | 80 | 160 | As | 45 | 71 |
| V | 18 | 26 | Se | 41 | 64 |
| Ti | 3 | 1 | Pb | 81 | 123 |
| Zn | 5 | 9 | Ba | <1 | |

centrations of most ions (Fig. 25). The $C_B$ concentration declined 20% and the $HCO_3^-$ concentration declined 31% from means in March. During snowmelt, the average acid neutralization capacity (ANC) decreased 490 μeq $L^{-1}$, 98% from dilution of stream water $C_B$ and $HCO_3^-$ concentrations. The $NH_4^+$ concentration rose about 0.1 mg $L^{-1}$ from December to March. The $NH_4^+$ concentration sharply declined with snowmelt and increased stream flow. At Station W2, $NO_3^-$ concentration increased just before snowmelt peaked, and $SO_4^{2-}$ concentrations at W2 and W1 increased during peak snowmelt and stream flow. Stream water DOC concentrations declined slightly in April but were at the highest concentrations during May and June (Fig. 25), the months of relatively high stream water discharge (Fig. 13).

***Output.*** Annual $C_B$ output from Wallace stations W1 and W2 showed no time trend (Fig. 26). The $C_B$ output at W1 correlated with annual stream water discharge ($p < 0.01$, $r^2 = 0.55$), and the $C_B$ output at W2 correlated with annual precipitation amount ($p < 0.05$, $r^2 = 0.39$). Like annual precipitation (Fig. 11), $C_B$ output at W1 also decreased with time (Fig. 26), but there was no correlation. Watershed $C_B$ output was highest in 1996 when SWE was largest and the ratio of stream flow to precipitation was greatest (Figs 10 and 11). The annual watershed $C_B$ output exceeded input 17 times (Table 11).

Annual watershed $H^+$ output declined during the study ($p < 0.05$, $r^2 = 0.25$, b = –0.07). The decrease was most pronounced at W1 ($p < 0.05$, $r^2 = 0.40$, b = –0.13). At Station W2, the $H^+$ discharge correlated ($p < 0.01$, $r^2 = 0.57$) with annual precipitation amount. Annually, the watershed retained more than 99% of the $H^+$ from precipitation (268 eq $ha^{-1}$).

There was no trend in stream water $NH_4^+$ output with time. Stream water $NH_4^+$ output correlated with annual precipitation amount ($p < 0.01$, $r^2 = 0.53$),

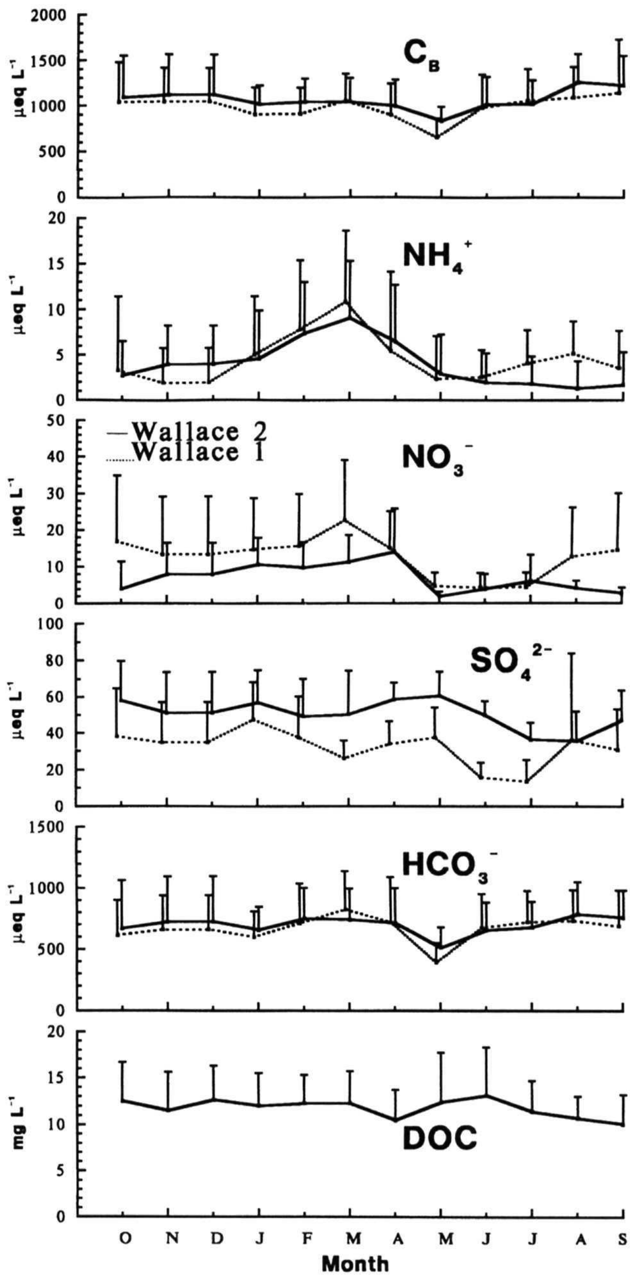


**Figure 25.** Mean monthly stream water ion concentrations at upstream (W1) and downstream (W2) stations, Wallace Lake watershed, Isle Royale National Park, Michigan, 1982–1996. Bars represent one standard deviation.

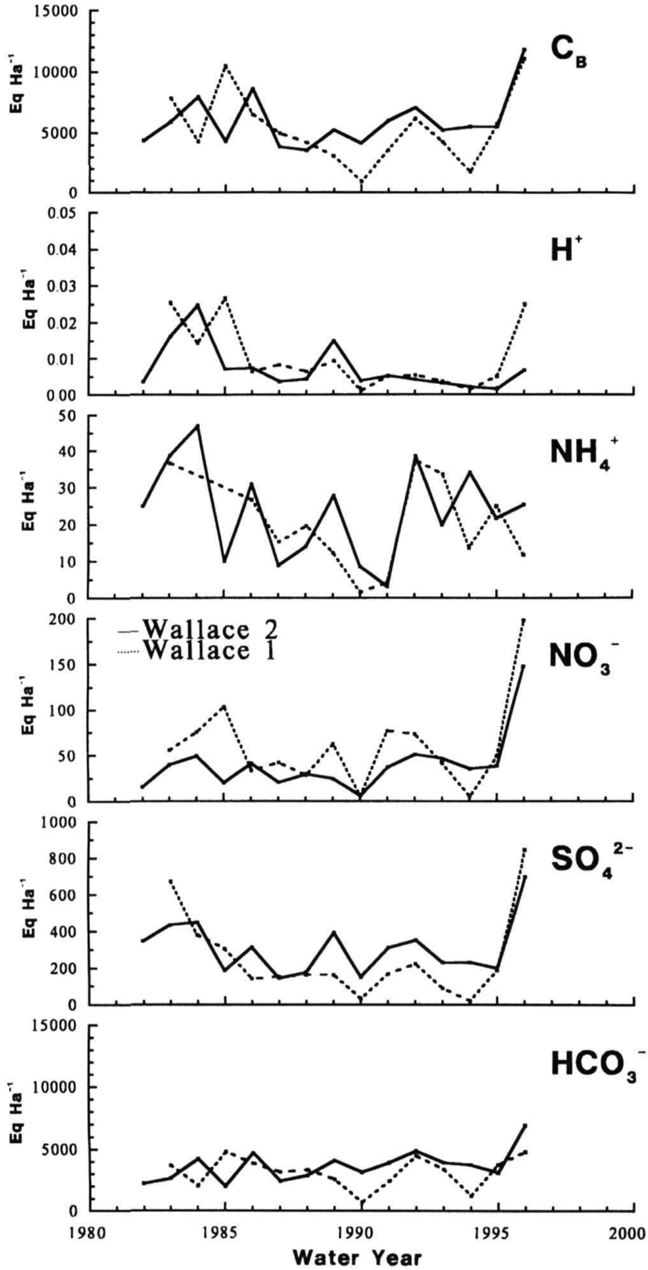


**Figure 26.** Annual stream water ion output at upstream (W1) and downstream (W2) stations, Wallace Lake watershed, Isle Royale National Park, Michigan, 1982–1996.

**Table 11.** Annual biogeochemical flux (kg $ha^{-1}$ $year^{-1}$) and element content of aboveground biomass (kg $ha^{-1}$), Wallace Lake watershed,1982–1996.

| Component | Ca | Mg | Na | K | H | $NH_4$ | $NO_3$ | N | S | Cl | $HCO_3$ | P | Tot N | DOC | C |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Bulk pr | 4.2 | 0.9 | 1.8 | 0.9 | 0.30 | 1.7 | 9.2 | 3.5 | 4.0 | 2.8 | | | | | |
| Aerosol | | | | | | | | | 0.6 | | | | | | |
| Stream | | | | | | | | | | | | | | | |
| W1 | 52 | 21 | 6 | 2.0 | <0.01 | 0.5 | 3.0 | 1.1 | 3.2 | 1.5 | 143 | | | | |
| W2 | 71 | 21 | 12 | 1.5 | <0.01 | 0.4 | 2.0 | 0.8 | 4.9 | 13.0 | 182 | | 34 | 606 | |
| Vegetation uptake | | | | | | | | | | | | | | | |
| spruce | 64 | 7 | 5.2 | 22 | | | | | 8.7 | | | | 27 | | |
| birch | 54 | 10 | 3.2 | 23 | | | | | 7.6 | | | | 26 | | |
| alder | 61 | 11 | 1.9 | 18 | | | | | 6.4 | | | | 65 | | |
| mean | 56 | 9 | 3.5 | 21 | | | | | 7.6 | | | | 39 | | |
| Litterfall | | | | | | | | | | | | | | | |
| spruce | 52 | 4 | 0.5 | 3.0 | | | | | 1.7 | | | 0.9 | 23 | | 1346 |
| birch | 40 | 6 | 0.5 | 4.0 | | | | | 1.8 | | | 1.3 | 24 | | 1203 |
| alder | 51 | 8 | 0.7 | 9.0 | | | | | 3.0 | | | 2.9 | 62 | | 1771 |
| mean | 44 | 6 | 0.6 | 5.3 | | | | | 2.2 | | | 1.7 | 36 | | 1440 |

**Table 11.** *Continued.*

| Component | Ca | Mg | Na | K | H | $NH_4$ | $NO_3$ | N | S | Cl | $HCO_3$ | P | Tot N | DOC | C |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Throughfall | | | | | | | | | | | | | | | |
| spruce | 12 | 3.0 | 4.7 | 19 | 0.10 | 4.4 | 3.9 | 4.3 | 7.0 | | | | | | |
| birch | 14 | 4.0 | 2.7 | 19 | <0.10 | 0.9 | 3.8 | 1.6 | 5.8 | | | | | | |
| alder | 10 | 2.5 | 1.2 | 9 | <0.10 | 1.9 | 5.6 | 2.7 | 3.4 | | | | | | |
| mean | 12 | 3.2 | 2.9 | 16 | <0.10 | 2.4 | 4.4 | 2.9 | 5.4 | | | | | | |
| Soil water at 30 cm | | | | | | | | | | | | | | | |
| spruce | 29 | 7 | 7.8 | 6.8 | 0.02 | 0.2 | 0.1 | 0.2 | 12.0 | | | | | | |
| birch | 19 | 5 | 4.8 | 1.8 | <0.01 | 0.7 | 1.6 | 0.9 | 6.0 | | | | | | |
| alder | 27 | 9 | 4.0 | 0.3 | 0.11 | 0.1 | 6.6 | 1.6 | 1.5 | | | | | | |
| mean | 25 | 7 | 5.5 | 3.0 | 0.06 | 0.3 | 2.8 | 0.9 | 6.5 | | | | | | |
| Soil net mineralization | | | | | | | | 14.0 | | | | | | | |
| Soil gross mineralization | | | | | | | | 80.0[a] | | | | | | | |
| Aboveground biomass | 430 | 39 | | 134 | | | | | 23.0 | | | 25 | 254 | | |
| Forest floor | 460 | 68 | | 40 | | | | | 53.0 | | | 35 | 530 | | |

[a] Gross mineralization rates are in mg N $m^{-2}$ $day^{-1}$.

but there was no correlation between annual $NH_4^+$ inputs and stream water outputs. The watershed retained more than 75% $NH_4^+$ inputs (75 eq $ha^{-1}$).

During 1982–95, there was no trend in stream water $NO_3^-$ output from the Wallace Lake watershed. The increase was slight when data from 1996 were included ($p < 0.1$, $r^2 = 0.24$, b = 3.5 eq $ha^{-1}$). Annual watershed $NO_3^-$ output did not correlate with precipitation amount but correlated with stream water discharge ($p < 0.01$, $r^2 = 0.54$). The $NO_3^-$ output from W1 correlated with precipitation amount ($p = 0.05$, $r^2 = 0.32$) but not with precipitation $NO_3^-$ concentration (Fig. 15) or inputs, which declined (Fig. 17). Precipitation $NO_3^-$ input in 1996 was about average for the Wallace Lake watershed, but stream water output was 3 times higher than the previous annual peak and about equaled the input in 1996. Net annual watershed $NO_3^-$ retention was 110 eq $ha^{-1}$ or 75% of the precipitation input.

During 1982–95, annual stream water $SO_4^{2-}$ output declined at W2 ($p <$ 0.01, $r^2 = 0.23$, b = –17) and W1 ($p < 0.05$, $r^2 = 0.39$, b = –28). When data from 1996 were included, there was no trend. The $SO_4^{2-}$ output correlated with annual precipitation amount ($p < 0.01$, $r^2 = 0.56$) and stream water discharge ($p =$ 0.001, $r^2 = 0.86$). The trend in stream water $SO_4^{2-}$ output followed precipitation $SO_4^{2-}$ loading and concentration, but none correlated. The mean stream water $SO_4^{2-}$ output from W2 was 1.2 times the precipitation input, and W1 output was 0.8 of the precipitation input (Figs 17 and 26). The net annual watershed $SO_4^{2-}$ output was 53 eq $ha^{-1}$.

The annual stream water $HCO_3^-$ outputs at W1 and W2 correlated ($p < 0.001$, $r^2 = 0.80$) with $C_B$ output. At W2, $HCO_3^-$ output weakly correlated with precipitation amount ($p < 0.08$, $r^2 = 0.23$). The $HCO_3^-$ output correlated with stream water discharge at W2 ($p < 0.01$, $r^2 = 0.54$) and W1 ($p < 0.01$, $r^2 =$ 0.50). Bicarbonate alkalinity was the dominant stream water anion in the Wallace Lake watershed; the mean concentration was 1 order-of-magnitude greater than the $SO_4^{2-}$ concentration. As in stream water $C_B$ output, there was no trend in $HCO_3^-$ output with time.

In the Wallace Lake watershed, the snowpack existed on average from mid-November to the end of April. Snowmelt had the most pronounced effect on seasonal ion output from the Wallace Lake watershed (Fig. 27). Ammonium and $NO_3^-$ were the only ions where the seasonal concentration pattern approximated that of ion output (Figs 25 and 27). Only in August did $C_B$ input almost equal stream water output (Figs 18 and 27).

In contrast to $C_B$, inputs of $H^+$ and $NH_4^+$ considerably exceeded stream water outputs each month. The $H^+$ outputs from the Wallace Lake watershed also increased sharply with peak snowmelt, but the net output was smaller than snowpack or winter and spring precipitation inputs. Cumulative precipitation $H^+$ in the Wallace Lake watershed during the snow season averaged 76 eq $ha^{-1}$ (Fig. 18). Mean snowpack PWE $H^+$ content was 26 eq $ha^{-1}$ (Fig. 19). The $H^+$ output from the watershed in April was less than 0.5% of the cumulative inputs and less than 1% of the mean snowpack content at PWE.

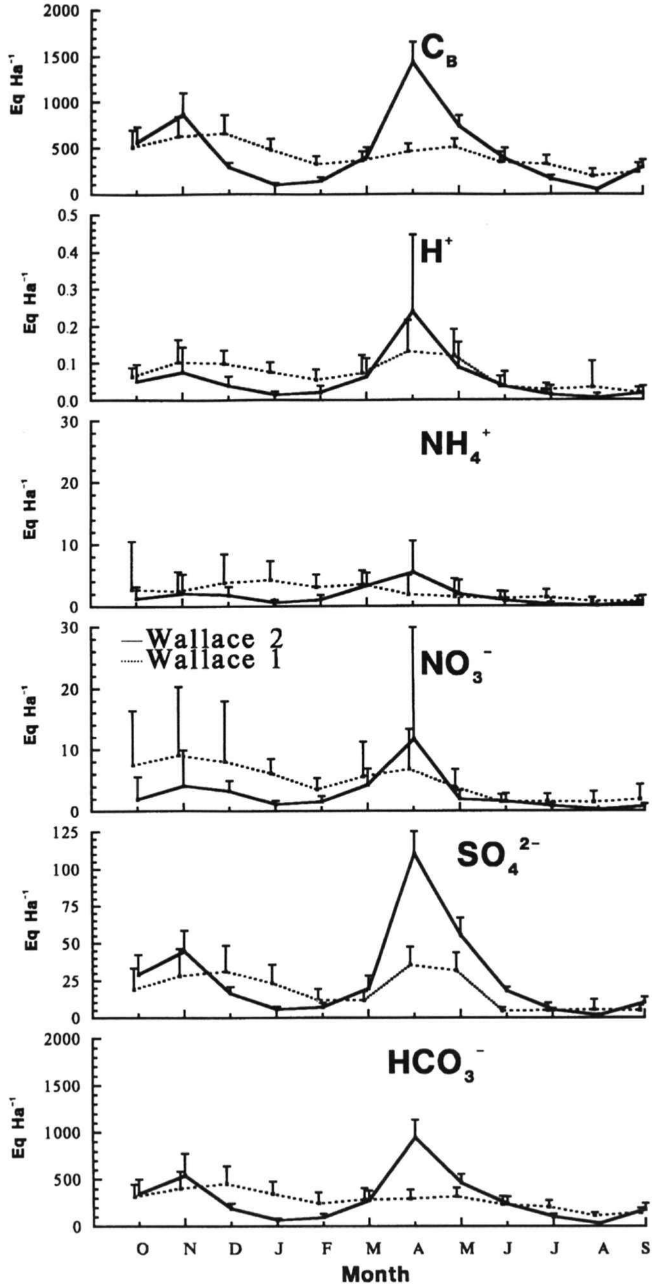


**Figure 27.** Mean monthly stream water ion output at upstream (W1) and downstream (W2) stations, Wallace Lake watershed, Isle Royale National Park, Michigan, 1984–1996. Bars represent one standard deviation.

The $NH_4^+$ retention was similar (Figs 18, 19, and 27). Cumulative $NH_4^+$ inputs from precipitation in winter averaged 52 eq $ha^{-1}$, whereas snowpack PWE content averaged just 18 eq $ha^{-1}$. The $NH_4^+$ output from the Wallace Lake watershed in April was less than 30% of the peak snowpack content and less than 10% of the cumulative precipitation in winter.

Seasonal stream water $NO_3^-$ output from the Wallace Lake watershed peaked in April at about 11 eq $ha^{-1}$, which was less than 20% of the cumulative input from precipitation in winter (Fig. 18) and less than 40% of the average snowpack PWE $NO_3^-$ content (Fig. 19). Stream water $NO_3^-$ output almost equaled input only in April.

The greatest relative range of any ion in the Wallace Lake watershed was that of the monthly stream water $SO_4^{2-}$ output (Fig. 27). The large outputs in April were the product of increased stream water discharge and increase in $SO_4^{2-}$ concentration with discharge. Monthly $SO_4^{2-}$ output exceeded input in November, April, and May (Figs 17 and 27). The $SO_4^{2-}$ output in April and May (165 eq $ha^{-1}$) considerably exceeded cumulative precipitation inputs (93 eq $ha^{-1}$) in winter and the average peak snowpack $SO_4^{2-}$ content (28 eq $ha^{-1}$; Fig. 19). Monthly $HCO_3^-$ outputs followed a similar pattern as $SO_4^{2-}$ and $C_B$.

## *Nutrient Cycles*

Here we summarize the nutrient cycles of two $C_B$ elements, $Ca^{2+}$ and $K^+$, and two elements (N and S) that probably have significant gaseous phases and inputs into the ecosystem. For ready comparison with other published datasets, all values are expressed as kg $ha^{-1}$ (Table 11).

The mean annual bulk precipitation $Ca^{2+}$ input into the Wallace Lake watershed during 1982–96 was 208 eq $ha^{-1}$ (4.2 kg $ha^{-1}$). The forest canopy added about 8 kg $Ca^{2+}$ $ha^{-1}$ $year^{-1}$, the average loss in throughfall $Ca^{2+}$ flux in the dominant species alder, spruce, and birch-aspen. However, the ion gains in throughfall flux were not considered ecosystem inputs but changes in internal nutrient cycling. Because the net change in biomass with time in the watershed was small, we estimated aboveground $Ca^{2+}$ uptake as the sum of throughfall, stemflow, and litterfall, which averaged 56 kg $Ca^{2+}$ $ha^{-1}$ $year^{-1}$. Calcium flux at the 30-cm depth in mineral soil beneath the canopy averaged 25 kg $ha^{-1}$ $year^{-1}$, a net loss of 21 kg $Ca^{2+}$ above precipitation input. This indicated substantial removal of soil exchangeable $Ca^{2+}$ (pool size was 343 kg $ha^{-1}$ beneath spruce, 1515 kg $ha^{-1}$ in top 10 cm mineral soil beneath birch-aspen) and weathering products. Watershed $Ca^{2+}$ output was 71 kg $ha^{-1}$ $year^{-1}$, a net loss of 67 kg $ha^{-1}$ above bulk precipitation inputs.

Annual bulk precipitation $K^+$ input was 0.9 kg $ha^{-1}$. Net leaching of canopy $K^+$, albeit variable (Table 11), was about 15 kg $ha^{-1}$ $year^{-1}$. The estimated annual aboveground plant uptake was 21 kg $ha^{-1}$. Soil water $K^+$ flux at the 30-cm depth beneath the forest canopy was only 3 kg $ha^{-1}$ $year^{-1}$ (mineral soil exchangeable pool size in the top 10 cm was 65 kg $ha^{-1}$ beneath spruce and

142 kg $ha^{-1}$ beneath birch-aspen), and watershed output was 1.5 kg $ha^{-1}$ $year^{-1}$ or 0.6 kg $K^+$ $ha^{-1}$ $year^{-1}$ above bulk precipitation inputs. Because the measurements of precipitation inputs do not fully account for dry deposition, $K^+$ input and output in the watershed seemed to be in near equilibrium.

Bulk precipitation nitrogen (N) input was 3.5 kg $ha^{-1}$ $year^{-1}$. About 60% of the elemental N came from $NO_3^-$ and 40% from $NH_4^+$, but the proportion from $NH_4^+$ increased during the study. Annual $NH_4^+$ flux in throughfall beneath spruce exceeded precipitation inputs, the birch canopy retained some precipitation $NH_4^+$, and the alder canopy altered $NH_4^+$ flux little.

Conversely, $NO_3^-$ was strongly retained by the canopies of spruce and birch (5.4 kg $ha^{-1}$ $year^{-1}$) and alder (3.6 kg $ha^{-1}$ $year^{-1}$). On average, the canopy retained about 0.5 kg of precipitation N $ha^{-1}$ $year^{-1}$. The estimated aboveground N uptake was 33 kg $ha^{-1}$ $year^{-1}$. Soil water inorganic N flux at the 30-cm depth was 0.9 kg $ha^{-1}$ $year^{-1}$. The extractable inorganic N from the top 10 cm of forest floor and mineral soil averaged 26.7 kg N $ha^{-1}$ (Stottlemyer et al. 1995). Watershed $NH_4^+$ output was 0.3 kg N $ha^{-1}$ $year^{-1}$ and $NO_3^-$ 0.5 kg N $ha^{-1}$ or a total of 0.8 kg N $ha^{-1}$ $year^{-1}$. The watershed retained about 77% of the bulk precipitation N input.

Bulk precipitation S averaged 4 kg $ha^{-1}$ $year^{-1}$ (12 kg $SO_4^{2-}$ $ha^{-1}$). Aerosol and gas S deposition were 0.6 kg $ha^{-1}$ (Stottlemyer et al. 1989), but this deposition and wet precipitation inputs cannot be separated in bulk samples. On average, throughfall S flux was 1.4 times the bulk precipitation inputs and 1.6 times the precipitation input at the 30-cm mineral-soil depth (Table 11). Water soluble $SO_4^{2-}$– S in soil beneath birch-aspen averaged about 5 kg $ha^{-1}$ and adsorbed $SO_4^{2-}$ ($NaH_2PO^{4-}$ extractable) 63 kg S $ha^{-1}$ in the top 10 cm of mineral soil (Stottlemyer et al. 1989). Annual aboveground plant uptake was 7.6 kg S $ha^{-1}$. Watershed S output was 4.9 kg $ha^{-1}$ $year^{-1}$, 25% above bulk precipitation input.

## *Aboveground Biomass Distribution and Nutrient Content*

The boreal forest in the Wallace Lake watershed contained 10 canopy species with an aboveground living biomass of 108 t $ha^{-1}$ (Rutkowski and Stottlemyer 1993). The understory contained more than 10 000 stems $ha^{-1}$ with a biomass of 2300 kg $ha^{-1}$. The vascular ground cover also had a relatively large biomass (1180 kg $ha^{-1}$). The forest floor contained almost 25% of the aboveground biomass. Calcium was the most abundant nutrient in the aboveground biomass (900 kg $ha^{-1}$). In descending order of abundance, the remaining nutrients were N (820 kg $ha^{-1}$), K (190 kg $ha^{-1}$), Mg (110 kg $ha^{-1}$), S (80 kg $ha^{-1}$), and P (60 kg $ha^{-1}$). Overall, the forest floor contained the largest aboveground nutrient pools, particularly Mg, S, N, and P.

During 1984–96, litter fall beneath spruce, birch-aspen, and alder averaged about 2800 kg $ha^{-1}$ $year^{-1}$ (Fig. 28). However, the range in annual amount was large (Table 12). Annual litterfall generally increased beneath spruce and de-

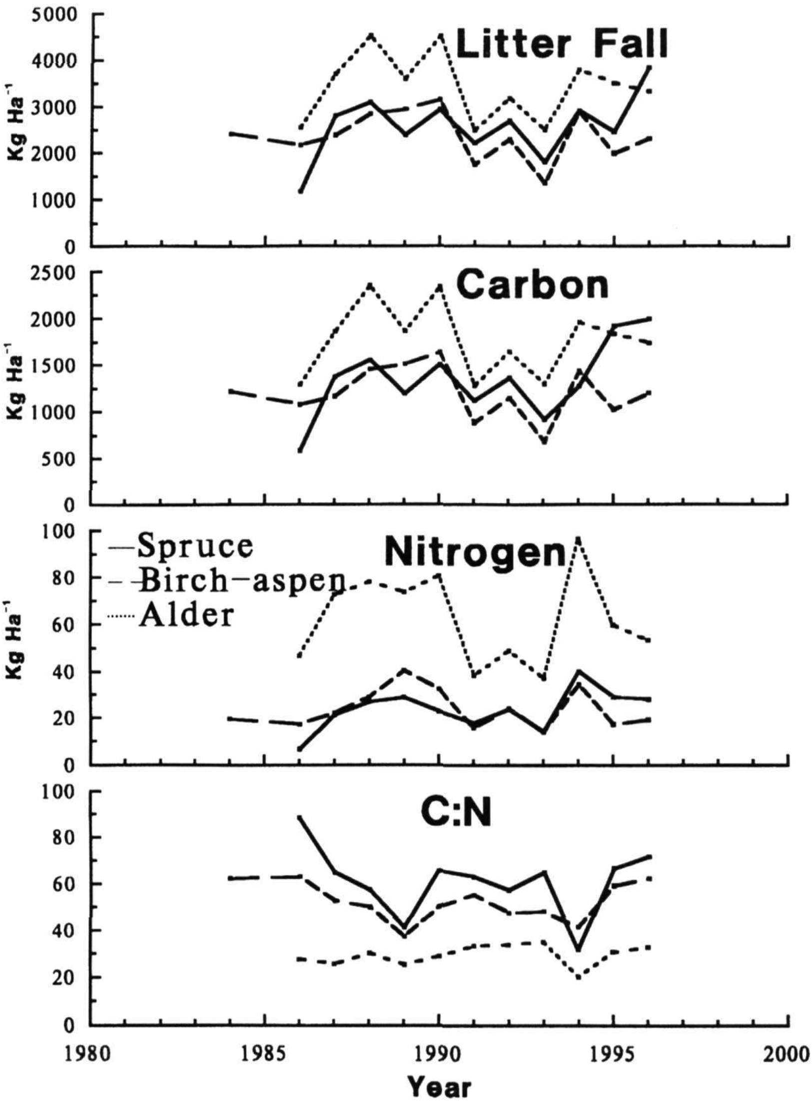


**Figure 28.** Annual litterfall, carbon and nitrogen content in litterfall, and C:N ratio of dominant canopy species, Wallace Lake watershed, Isle Royale National Park, Michigan, 1984–1996.

clined beneath birch-aspen and alder, but a trend in time did not exist. Litterfall sharply decreased beneath birch-aspen and alder for 3 years (1991–93).

For $C_B$, the aboveground Ca content (about 900 kg ha$^{-1}$) was almost evenly divided between the living biomass and the forest floor (Table 11; Rutkowski

**Table 12**. Annual litterfall amount and nutrient content beneath white spruce (*Picea glauca*), paper birch-quaking aspen (*Betula papyrifera-Populus tremuloides*), and tag alder (*Alnus rugosa*), Wallace Lake watershed, 1984–1996.

| | White Spruce | | Paper Birch | | Tag Alder | |
|---|---|---|---|---|---|---|
| | mean | range | mean | range | mean | range |
| Litterfall | 2580 (705)[a] | 1170–3840 | 2377 (531) | 1340–3160 | 3430 (720) | 2500–4530 |
| Carbon | 1346 (408) | 587–1997 | 1203 (275) | 678–1638 | 1771 (378) | 1278–2355 |
| Nitrogen | 23 (9) | 7–40 | 24 (8) | 14–40 | 62 (19) | 37–96 |
| C:N | 61 (14) | 32–88 | 53 (8) | 37–63 | 29 (4) | 20–35 |

[a] Value in parentheses is one standard deviation.

and Stottlemyer 1993). Calcium in annual litterfall averaged 44 kg ha$^{-1}$. The K content of aboveground biomass was about 170 kg ha$^{-1}$; 25% was in the forest floor. Annual K content in litterfall was more than 5 kg ha$^{-1}$, but the year-to-year variation was considerable, primarily because of litterfall amounts.

The N pool in aboveground biomass was 780 kg ha$^{-1}$. Two-thirds of it was in the forest floor. The deeper organic horizons (Oa) contained about twice the N content of living aboveground biomass. Litterfall N content averaged 36 kg ha$^{-1}$ year$^{-1}$ among all species but varied from 23 kg ha$^{-1}$ year$^{-1}$ beneath spruce to 62 kg ha$^{-1}$ year$^{-1}$ beneath alder (Table 12). The range in annual litterfall N content in a species was greater.

Annual C content in litterfall of the dominant vegetation types was 1440 kg ha$^{-1}$. Beneath spruce, C content in litterfall increased ($p < 0.07$, $r^2 = 0.32$) during 1986–96. Since 1986, the mean C:N ratio in litterfall varied considerably among species and was lowest beneath alder and highest beneath spruce (Fig. 28; Table 12).

The S content of aboveground biomass was 76 kg ha$^{-1}$; about two-thirds were in the forest floor. The S content in litterfall averaged about 2 kg ha$^{-1}$ year$^{-1}$. Like Mg and N content, the S content in deeper soil organic layers (Oa) exceeded the aboveground content in living biomass.

## *Growth and Mortality*

There was little net change in total aboveground biomass with time in the Wallace Lake watershed (Table 13). But there was some change among com-

**Table 13**. Change in average basal area of major canopy species on five 0.1-ha plots, Wallace Lake watershed,1986–1991.

| | 1986 | | 1991 | |
|---|---|---|---|---|
| Species | basal area ($m^2$ ha$^{-1}$) | count (n) | basal area ($m^2$ ha$^{-1}$) | count (n) |
| *Abies balsamea* | 1.70 | 100 | 1.40 | 270 |
| *Alnus rugosa* | 1.50 | 574 | 2.50 | 844 |
| *Picea glauca* | 3.90 | 234 | 6.40 | 620 |
| *Sorbus americana* | 0.02 | 2 | 0.03 | 2 |
| *Betula papyrifera* | 8.70 | 256 | 7.20 | 184 |
| *Picea mariana* | 0.09 | 24 | 0.00 | 0 |
| *Populus tremuloides* | 4.10 | 56 | 5.00 | 58 |
| *Thuja occidentalis* | 2.40 | 94 | 1.50 | 104 |
| Number of stems ha$^{-1}$ | | 1340 | | 2082 |
| Total basal area | 22.20 | | 24.10 | |

ponents. During 1986–91, the major declines in basal area were in black spruce (*Picea mariana*), cedar, white birch, and balsam fir. White birch was the dominant species in aboveground biomass in the Wallace Lake watershed (Rutkowski and Stottlemyer 1993). It accounted for almost 50% of the aboveground biomass in 1986 but for only about 30% by 1991. The decline reflected the low reproduction in small-diameter trees and low recruitment into the upper-diameter classes. Basal area and biomass increased mainly in tag alder, white spruce, and aspen. However, the net increase in basal area during 1986–91 was less than 2% $year^{-1}$.

Mortality from blowdown in the vicinity of the Wallace Lake watershed was most pervasive in balsam fir, the species that accounted for 65% of felled live trees (Table 14). White spruce was second, constituting 23% of downed live trees. Among species, an inverse relation existed between the percentages of downed and standing trees in immediate vicinities (Table 15). Specific site variables associated with standing and fallen trees showed little relation to presence of standing or downed trees (Table 16).

**Table 14**. Ranking of downed trees. Wallace Lake watershed and vicinity, 1989–1991.

| Species | Alive or Dead | %[a] |
|---|---|---|
| *Abies balsamea* | alive | 45.0 |
| *Betula papyrifera* | dead | 17.3 |
| *Picea glauca* | alive | 15.6 |
| *Abies balsamea* | dead | 6.8 |
| *Picea glauca* | dead | 5.3 |
| *Betula papyrifera* | alive | 6.4 |
| *Populus tremuloides* | dead | 0.6 |
| *Populus tremuloides* | alive | 1.2 |
| *Thuja occidentalis* | dead | 0.6 |
| *Sorbus americana* | alive | 0.6 |
| *Sorbus americana* | dead | 0.6 |

[a] Percentage of total downed stems.

**Table 15**. Percentage of standing and downed trees of major canopy species, Wallace Lake watershed and vicinity, 1989–1991.

| Species | Standing (%) | Downed (%) |
|---|---|---|
| *Abies balsamea* | 16.3 | 43.9 |
| *Picea glauca* | 33.3 | 21.4 |
| *Betula papyrifera* | 15.6 | 30.6 |
| *Populus tremuloides* | 22.7 | 1.0 |

More than 50% of the windthrown trees fell to the south-southeast and south-southwest, indicating winds from the north-northeast and north-northwest had a major influence on tree mortality. About 21% of all winds in excess of 10 m $s^{-1}$ occurred in October, 19% in November, 19% in December, and 15% in January. Wind felled about 1200 kg $ha^{-1}$ $year^{-1}$ of live aboveground biomass with a nitrogen content of 9 kg N $ha^{-1}$.

# Discussion

## *Temperature*

Since 1950, the mean annual temperature increase at the NOAA station on the Houghton County Airport has been about 2°C. The increase is comparable to the temperature change at the Experimental Lakes Area in western Ontario (Schindler et al. 1990). In the Wallace Lake watershed, the lack of a significant trend in the mean annual temperature may have been due to the mitigating effect of the surrounding Lake Superior or the relatively short record. The temperatures at the NOAA station in Grand Marais, Minnesota, also have not increased since 1950. The mean annual temperatures at the NOAA station on the Houghton County airport peaked in 1987 and again in 1990. The temperatures in the Wallace Lake watershed peaked in 1990 and then declined more than the temperatures at the NOAA station on the Houghton airport (Fig. 5).

**Table 16**. Site variables of standing and fallen trees, Wallace Lake watershed and vicinity,1989–1991.

| Variable | Standing Trees | Downed Trees |
|---|---|---|
| Slope (%) | 13 (52)[a] | 12 (10) |
| Elevation (m) | 217 (17) | 209 (15) |
| Distance from Lake Superior (m) | 289 (221) | 225 (215) |
| Soil depth (cm) | 29 (20) | 29 (18)[b] |
| Topographic position | | |
| top of slope | 18 | 22 |
| midslope | 67 | 63 |
| bottom of slope | 15 | 14 |
| Aspect | | |
| north | 38[c] | 59 |
| south | 62 | 40 |

[a] Value in parentheses is one standard deviation.
[b] Values of snapped trees. At uprooted trees, soil depth was 35 (28) cm.
[c] Percentage of measured trees.

The mean annual temperatures in the Wallace Lake watershed during 1992–94 were 3°C lower than the 1990–91 mean. The data suggest the increased temperature in the region was a random fluctuation and not consistent among stations since 1950.

The greatest differences between mean monthly temperatures in the Wallace Lake watershed and the mean monthly temperatures on the Houghton County airport were in mid-winter and mid-summer (Fig. 6). In late fall and early winter, the ice that gradually forms on northern Lake Superior between the Canadian mainland and Isle Royale, an average distance of about 33 km, reduces the mitigating effect of open lake water on air temperature. By mid-winter, the climate in the Wallace Lake watershed becomes more like that in southern Canada and less like that in sites adjacent or immediately south of Wallace Lake. In mid-summer, cool open Lake Superior water keeps temperatures on Isle Royale and Grand Marais below the averages in locations more distant from the lake.

The combination of reduced air, snowpack, and soil temperatures beneath the spruce canopy coupled with canopy interception of snow resulted in a smaller and colder snowpack. The cooler temperatures and reduced insulation from the snowpack kept soils frozen even after snowmelt. The freezing and generally lower soil temperatures have a significant effect on soil processes such as respiration and nitrogen mineralization. The high N mineralization rates beneath spruce suggested low temperatures inhibited microbial N immobilization more than N mineralization (Stottlemyer et al. 1995).

## *Wind Speed and Direction*

The shift in wind direction from the northwest-southwest to south-southeast in late winter (March) is pervasive in the region (Stottlemyer and Toczydlowski 1991; Semkin and Jeffries 1988) and is associated with an increased frequency of low-pressure systems across the Upper Great Lakes. In most winters of 1982–96, a significant portion of Lake Superior was ice-free especially south of Isle Royale. The shift in wind direction to the south-southeast in late winter seems to have increased the air moisture content and may have accounted for the seasonal increase in precipitation amount beginning in March. The shift also increased atmospheric concentrations and loading, especially of $SO_4^{2-}$ (Figs 16 and 18) from urban sources south of the Upper Great Lakes region.

## *Radiation*

Dense lake fog, commonly lasting for days, occurred on Isle Royale particularly in June when still cold Lake Superior surface water met regional moist air moving over the lake. Fog probably caused the solar radiation to be lower in June than in May. The radiation input was only slightly lower in July than in May.

In the Calumet watershed about 6 km from the NOAA station on the Houghton County Airport and 21 km from Houghton on the southern shore of Lake Superior, Michigan (Fig. 1 a; Stottlemyer and Toczydlowski 1996a, 1996b), radiation inputs in winter have been monitored since 1987. Seasonal solar input in the Wallace Lake watershed was higher in November (8%), February (14%), March (16%), April (26%), and May (6%) and lower in December (34%) and January (6%). The trend reflected the high degree of cloudiness in the Wallace Lake watershed before ice formation on the lake peaks, generally in January or February, and the increased cloudiness along the southern shore from lake effect especially in late fall and early spring.

The amount of total aboveground biomass is greater in the understory (2275 kg $ha^{-1}$) and in the shrub-herb layers (1180 kg $ha^{-1}$) of the boreal forest in the Wallace Lake watershed than beneath mature northern hardwoods south of Lake Superior (Rutkowski and Stottlemyer 1993). The large amount of understory biomass was especially evident beneath the mixed birch-aspen vegetation type. In studies of pure old and young aspen and mixed aspen-white spruce in boreal forests of Alberta (Constabel and Lieffers 1996), only about 6% of incident light reached the forest floor. In mixed stands there, the understory intercepted more than 50% of the above-canopy light. The greatest light transmission through the canopy was during the spring leaf-off period when the solar elevation angle is relatively high. In the Wallace Lake watershed, the mean date of leaf-out of birch-aspen is 11 May, and light transmission to the understory, herb layer, and forest floor is probably maximum in late spring. The understory vegetation, especially vernals and conifer seedlings, probably obtains a large amount of their annual carbon gain during this time.

## *Hydrologic Cycle*

### Precipitation

During the study, annual precipitation was about 30% less and winter precipitation 25% greater than in the region south of Lake Superior (Eichenlaub et al. 1990; NADP 1982–96). The percentage of annual precipitation in winter is similar to that in the Calumet watershed on Lake Superior's southern shore (Stottlemyer and Toczydlowski 1996b) and is average for the Northern Superior Uplands (McNab and Avers 1994).

Precipitation in the Upper Great Lakes region has declined since 1980 (Schindler et al. 1990; Stottlemyer and Toczydlowski 1996b). The decline in annual precipitation amount since 1982 is not as pronounced in the Wallace Lake watershed as in the Calumet watershed. Most of the decline has been in winter snowfall. The combined effect of declining winter precipitation and increased temperature could have a significant effect on SWE and snowpack duration. With a shortened snowpack season, future forest soil temperatures will probably increase earlier in the year. Because soil processes such as N mineralization generally increase with soil temperature in the Wallace Lake watershed, any factor that reduces the duration of a snowpack could have significant effects on nutrient cycling and loss. The increase in temperature and decrease in precipitation amount are already factors in the decline of some regional forest canopy species such as white birch (Jones et al. 1993).

**Throughfall and Stemflow**

Canopy interception of incident precipitation, expressed as a percentage, in the Wallace Lake watershed was similar to values at Hubbard Brook (Likens and Bormann 1995) and interception by lodgepole pine (*Pinus contorta*) forests in the Rocky Mountains where precipitation is dominated by snowfall (Fahey et al. 1988). Interception was less than observed in a mature coastal mixed-conifer forest in Olympic National Park (Edmonds et al. 1997) where total precipitation amount is four times the amount in the Wallace Lake watershed. Factors responsible for differences in the amount of canopy interception can be fog, size of precipitation event (Lovett et al. 1996), amount of annual snowfall and its physical character (Schmidt and Gluns 1991), tree crown shape, and the degree of conifer dominance in the canopy. On Isle Royale, fog is present mainly in late May or June and probably does not significantly affect annual throughfall amounts. However, this has not been specifically measured. In the Wallace Lake watershed, hardwoods dominate more than half the forested area, and rock outcrops with scattered conifers and wetlands cover another 35%. Such factors reduce the importance of canopy interception. The relatively long period hardwoods are without leaves further reduces annual canopy interception in the Wallace Lake watershed.

Where conifers occur, canopy interception of snowfall is especially important. In the study of year-round throughfall and stemflow near Windigo in 1981 and 1982 (Stottlemyer 1982), monthly readings beneath the canopy and in the open nearby showed the SWE was reduced 52% (SWE = 6.5 [1] cm) beneath cedar and 48% (6 [2] cm) beneath spruce. Monthly SWE beneath birch and maple was 96% of SWE in the open.

The larger the precipitation amount is, the greater is the percentage as throughfall. But on Isle Royale during studies of throughfall and stemflow, the largest amount of precipitation in one event was only slightly above 3 cm. The decline or lack of change in stemflow amount with increasing tree diameter class probably reflects the canopy structure and the small amount of precipitation per event that fails to saturate the canopy and bole.

**Snowpack**

The snowpack PWE in the Wallace Lake watershed was two-thirds the average at the Calumet watershed on the south shore of Lake Superior (Stottlemyer and Toczydlowski 1996b). Most of the snowpack PWE difference at the two sites was accounted for by variation in cumulative precipitation amount (Calumet: 37 cm, Wallace: 30.5 cm) in winter. The small remaining SWE difference was probably from variation in mid-winter thaws or snowpack sublimation rates at the two sites. In the Wallace Lake watershed, the mean snowpack temperature at 10 cm above the forest floor (Table 3) was warm enough to permit downward movement of solutes during much of winter. Soils beneath birch-aspen and alder remained unfrozen throughout winter, which provided further energy for snowmelt. Such physical conditions made the snowpack vulnerable to major change from relatively minor thaws especially in mid-winter. Only beneath spruce, where canopy interception of snow significantly reduced snowpack depth and its insulation capacity, were surface mineral soils at or slightly below freezing.

In the Calumet watershed, we intensively studied change in snowpack, snowmelt, and soil solution amounts and chemistry for 15 winters (Stottlemyer 1987b; Stottlemyer and Toczydlowski 1996a, 1996b). In the Calumet watershed, cumulative precipitation amount and SWE steadily diverge until snowpack PWE. Snow lysimeters in the Calumet watershed show steady snowmelt throughout winter. Until snowpack PWE, cumulative snowmelt amounted to 15% of the total winter snowmelt. The relatively warm snowpack temperatures coupled with unfrozen soils may effect a similar pattern of snowmelt loss in the Wallace Lake watershed.

The duration of the permanent snowpack is 3 or 4 weeks longer in the Wallace Lake watershed than in the Calumet watershed. This reflects the lower winter temperatures in the Wallace Lake watershed (Fig. 6).

The regional gradient of increased precipitation amount from north to south across Lake Superior is primarily caused by increased snowfall from lake effect along the southern shore. As already discussed, evidence of this was seen in the winter radiation inputs into the Calumet and Wallace watersheds. The variation in snowpack PWE was identical between the two watersheds. The uniformity of snowpack PWE throughout Isle Royale, at least during years with relatively low snowfall (1987–88), probably was due to sampling near lakes with little difference in elevation. As stated earlier, frozen inland lakes are the only landing places on Isle Royale, and the lakes are at similar elevations. Although precipitation and SWE change with elevation on Isle Royale (Table 4; Stottlemyer 1982), without elevation as a variable, snowfall at least until early March is relatively uniform throughout the park.

**Stream Flow**

The percentage of annual precipitation, which occurs as stream flow (68%) in the Wallace Lake watershed, was in the upper range for this region. Stream flow from 20 basins in the Turkey Lakes watershed ranged from 28% to 63% of precipitation (Nicolson 1988). The long-term average stream flow in the Calumet watershed is 43% of precipitation amount (Stottlemyer and Toczydlowski 1996b). Like the Wallace Lake watershed, the Calumet watershed has a north aspect but steeper slope. The mean daily stream flow with snowmelt peaked on average 24 days later in the Wallace Lake watershed than in the Calumet watershed. The later peak probably reflected the cooler temperatures and the low topographic relief in the Wallace Lake watershed. At the hydrologic benchmark station of the U.S. Geological Survey on Washington Creek at Windigo (Fig. 1a), the daily stream flow peaked on average on 22 April (range 25 March in 1987 to 18 May in 1996), four days earlier than in the Wallace Lake watershed. The Washington Creek watershed and the Wallace Lake watershed have a similar low topographic relief, but the former is considerably larger and has a southwest aspect. In the Wallace Lake watershed, above-average late snowmelt in 1996 accounted for the high stream flow to precipitation ratio. The high snowmelt resulted from a combination of factors including lower than average winter temperatures, a high SWE in late winter (Fig. 10), and a rapid stream flow concurrent with increasing temperatures. The U.S. Geological Survey also measured a record spring stream flow on Washington Creek in 1996.

Like some other investigators in northern watersheds (Likens and Bormann 1995), we found a strong relation between annual stream flow and precipitation inputs in the Wallace Lake watershed. The relation was especially strong during 1983–93 ($p < 0.001$, $r^2 = 0.91$). However, unlike researchers at Hubbard Brook and many other sites, we did not find evapotranspiration independent of precipitation amount. Evapotranspiration and precipitation also correlated in the Calumet watershed (Stottlemyer and Toczydlowski 1996b). Part of the reason for the relation between estimates of annual evapotranspiration and precipitation came from the calculation method for evapotranspiration. Annually, evapotranspiration in the Wallace Lake watershed varied (Fig. 11). It was not a relatively constant amount that is often found in other forested ecosystems. During the leaf-out season in the Wallace Lake watershed, stream flow from June through August declined, precipitation amount was relatively steady (Fig. 13), and evapotranspiration increased exponentially, about matching precipitation amount in August and September. Precipitation amount in late summer seemed to limit evapotranspiration especially in drier years. This constraint may have accounted for much of the annual variation in evapotranspiration. The average evapotranspiration during June–September was 17 cm or 22% of the annual precipitation amount.

Although declines of precipitation amounts on the southern shore of Lake Superior and in the Wallace Lake watershed were similar during 1982–96 (Fig. 5), the annual stream flow in the Wallace Lake watershed declined only about 30% of the decrease (1 cm year$^{-1}$) in the Calumet watershed. We attributed the reduced decline of annual stream flow in the Wallace Lake watershed to overall lower temperatures, the recent drop in mean annual temperatures, and the absence of a decreased stream-flow amount in winter and spring. Stream flow in spring dominated the annual stream flow.

In the Wallace Lake watershed, the percentage of annual stream flow in winter was similar to values from the long-term record at Hubbard Brook, New Hampshire (Federer et al. 1990) and the Turkey Lakes watershed. Stream flow in winter was somewhat higher in the Wallace Lake watershed than in the Calumet watershed.

## *Biogeochemistry*

### Precipitation

The trends in annual precipitation amount in the Upper Great Lakes region illustrate the importance of natural variation in atmospheric $H^+$, $NH_4^+$, $NO_3^-$, and $SO_4^{2-}$ input. Variation in annual precipitation input was less in the Wallace Lake watershed (20% of annual mean) than on the southern shore of Lake Superior. This suggests that more stable continental air masses and reduced upwind $H^+$, $NH_4^+$, $NO_3^-$, and $SO_4^{2-}$ on Isle Royale had a greater effect on annual precipitation ion input than the variation associated with lake-effect snowfall and more frequent penetrations of southern air masses on the southern side of the Lake Superior basin.

The trends in annual precipitation chemistry at the NADP Station MI99 were consistent with the findings of Lynch et al. (1995) in a nationwide assessment of all NADP data. Lynch et al. (1995) found, especially in recent years (1985–93), an increase ($p < 0.05$) in $NH_4^+$ concentration in most stations in the Upper Great Lakes region. The significant declines in $H^+$ and $SO_4^{2-}$ concentration in the Wallace Lake watershed and at Windigo were consistent with regional trends.

We attributed the lack of a decline in precipitation $C_B$ concentration in the Wallace Lake watershed and at Windigo to the use of bulk collectors that increased variance in precipitation chemistry, particularly $C_B$ concentrations, because of local dust (Glass and Loucks 1986). In summer when the regional snowpack is absent and dust inputs are greatest, the bulk collectors in the Wallace Lake watershed and at Station MI99 retained about 3 times the $C_B$ inputs of the two NADP event collectors (Fig. 16). In the Wallace Lake watershed, annual $C_B$ inputs were about twice as high as those at Hubbard Brook where the precipitation amount was greater (Table 17). However, $C_B$ deposition, especially $Ca^{2+}$, is generally twice as high at the NADP stations in the Upper Great Lakes than in the New England region (NADP 1982–96). There was no surface disturbance in the Wallace Lake watershed to increase $C_B$ inputs. Inputs reflect ambient levels in the Upper Great Lakes region and are probably the result of calcareous debris left by glaciers and the increased anthropogenic land disturbance in the region.

In the Upper Great Lakes, $K^+$, $Mg^{2+}$, and $Na^+$ were about 3 times higher in bulk collectors than in NADP event collectors. Conversely, in the Wallace Lake watershed, $NH_4^+$ and $NO_3^-$ in bulk collectors were average for NADP stations in the Lake Superior basin and Upper Great Lakes region. Sulfate inputs in the Wallace Lake watershed are slightly above sulfate inputs in the NADP stations in the Lake Superior basin and below annual inputs just south of Lake Superior (NADP 1982–96).

In the Upper Great Lakes region, the precipitation $NO_3^-$ in 1955–56 was about two-thirds and the $NH_4^+$ concentration was one-third of the concentrations during 1980–96 (Junge 1958). Regional nitrogen emissions then increased

**Table 17**. Nutrients (kg ha$^{-1}$ year$^{-1}$) in input, output, uptake, litterfall, and throughfall and biomass (kg ha$^{-1}$) in litterfall on the forest floor and aboveground at the Hubbard Brook, New Hampshire (Bormann and Likens 1995) and in the interior Alaskan taiga (van Cleve et al. 1983). HB=Hubbard Brook. AK=interior Alaskan taiga.

| | $Ca^{2+}$ | $Mg^{2+}$ | $Na^{+}$ | $K^{+}$ | $H^{+}$ | $NH_4^{+}$ | N | S | $Cl^{-}$ | $HCO_3^{-}$ | Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Input | | | | | | | | | | | |
| HB | 2.2 | 0.6 | 1.6 | 0.9 | | | 6.5 | 12.7 | 6.2 | | |
| AK | | | | | | | | | | | |
| Output | | | | | | | | | | | |
| HB | 13.7 | 3.1 | 7.2 | 1.9 | | | 3.9 | 17.6 | 4.6 | | |
| AK | | | | | | | | | | | |
| Uptake | | | | | | | | | | | |
| HB | 62.0 | 9.0 | 35.0 | 64.0 | | | 80.0 | 24.0 | | | |
| AK | | | | | | | | | | | |
| Conifer | | | | | | | | | | | |
| AK | 13.0 | 1.4 | | 5.0 | | | 7.6 | | | | |
| Hardwood | | | | | | | | | | | |
| AK | 63.0 | 9.5 | | 17.4 | | | 22.3 | | | | |
| Litterfall | | | | | | | | | | | |
| HB | 41.0 | 6.0 | 0.1 | 18.0 | | | 54.0 | 5.8 | | | |
| AK | 28.0 | 5.0 | | 6.5 | | | 14.3 | | | | 1873 |
| Throughfall and stemflow | | | | | | | | | | | |
| HB | 6.7 | 2.0 | 0.3 | 30.0 | | | 9.3 | 21.0 | 4.4 | | |
| AK | 4.2 | 0.7 | | 3.3 | | | 3.3 | | | | |
| Forest floor | | | | | | | | | | | |
| HB | 372.0 | 38.0 | 3.6 | 66.0 | | | 1256.0 | 124.0 | 78.0 | | |
| AK | 430.0 | 70.0 | | 200.0 | | | 706.0 | | | | 50420 |
| Aboveground biomass | | | | | | | | | | | |
| HB | 383.0 | 36.0 | 1.6 | 155.0 | | | 351.0 | 42.0 | 34.0 | | |
| AK | 773.0 | 701.0 | | 218.0 | | | 267.0 | | | | 134700 |

and began to level off in the early 1980s and remained unchanged at least until 1990 (NAPAP 1990). The absence of change in emissions probably accounted for the lack of trend in precipitation N concentration in the Wallace Lake watershed. Except on the southern shore of Lake Superior, $NH_4^+$ and $NO_3^-$ concentrations in the NADP stations in the immediate vicinity of the Lake Superior basin generally decreased during 1985–95 (Lynch et al. 1995). However, $NH_4^+$ increased and trends in $NO_3^-$ concentration were mixed or absent in most stations just beyond the basin. Regionally, $NH_4^+$ is generally the dominant form of N in precipitation. The $NO_3^-$ and $NH_4^+$ concentrations in precipitation, which were lower in the Wallace Lake watershed than in NADP Station MI99, were consistent with regional NADP data from the Lake Superior basin (NADP 1982–96). Volume-weighted $NO_3^-$ and $NH_4^+$ concentrations decreased northward across the Upper Great Lakes region. The increased precipitation ion concentration ratio of $NH_4^+$:$NO_3^-$ (equivalent basis) in the Wallace Lake watershed, albeit slight, reflected the national trends of increased $NH_4^+$ emissions from agriculture and changes in land use (Vitousek et al. 1997).

The significant decline of annual $SO_4^{2-}$ concentration in precipitation probably reflected reduced regional and national sulfur emissions (Likens 1992; NAPAP 1990). The decline of sulfur emissions in the United States began in the early 1970s in response to passage of the Clean Air Act (P.L. 101–549) but was not detectable in precipitation chemistry until the 1980s. The decrease in annual $SO_4^{2-}$ input during this study was smaller (120 eq ha$^{-1}$) than recent declines in the Calumet watershed (Stottlemyer and Toczydlowski 1996b). The difference reflected primarily a greater decline in annual precipitation amount in the Calumet watershed. But the decrease in the Wallace Lake watershed is important when compared to input levels around the Lake Superior basin. Annual $SO_4^{2-}$ deposition was about 200 eq ha$^{-1}$ west of Lake Superior and 400 eq ha$^{-1}$ at the Turkey Lakes east of Lake Superior (Jeffries et al. 1988; NADP 1982–96). The slight increase in the $NO_3^-$ to $SO_4^{2-}$ ratio reflected the little change in regional $NO_3^-$ emissions and the continued decline in $SO_4^{2-}$ concentrations during this and other studies (Stottlemyer and Toczydlowski 1996b).

Seasonally, the increases in the precipitation $NO_3^-$ to $SO_4^{2-}$ ratio in the Calumet watershed and on the south shore of Lake Superior in winter were similar (Stottlemyer and Toczydlowski 1996b). The higher ratio may have represented differences in scavenging efficiencies of $HNO_3^-$ by snow and rain (Topol 1986), reduced oxidation rates of $SO_2$ during winter, or the change in air-mass source during winter. The increase in precipitation $SO_4^{2-}$ concentration beginning in March coincided with an increased frequency of southerly winds and an increase in the percent of precipitation that was rain. Similar shifts in late winter precipitation chemistry have been observed in other studies in the region (Semkin and Jeffries 1988; Stottlemyer and Toczydlowski 1991, 1996a, 1996b).

The decline in $H^+$, $NO_3^-$, and $SO_4^{2-}$ inputs exceeded the decrease in precipitation amount during the study and reflected the general decline in ion concentrations independent of precipitation amount. The decline of $H^+$ and

$SO_4^{2-}$ was significant in the Wallace Lake watershed and at Windigo. A similar decline in $SO_4^{2-}$ deposition was seen in the Calumet watershed (Stottlemyer and Toczydlowski 1996b). From 1970 to 1985, sulfur emissions in the eastern United States declined about 3% year$^{-1}$. The average decline in precipitation $SO_4^{2-}$ concentration in the Wallace Lake watershed was 2.5% year$^{-1}$ and inputs were 3.0% year$^{-1}$. This agreement between precipitation and emissions chemistry was probably chance. For a given region, especially the Upper Great Lakes, sulfur emissions and $SO_4^{2-}$ deposition generally have not correlated (NAPAP 1990).

**Throughfall, Stemflow, and Forest Floor Leachate**

Typically, conifer canopies lightly acidify precipitation inputs (Cronan and Reiners 1983; Edmonds et al. 1995). Canopy processes that acidify incident precipitation include $NH_4^+$ uptake, nitrification, and leaching of organic acids. Throughfall can add more than 20 kg C ha$^{-1}$ year$^{-1}$ to precipitation inputs (Likens and Bormann 1995). Conversely, hardwood canopies with foliage reduce $H^+$ concentrations and significantly increase $C_B$ concentrations. In the Wallace Lake watershed, the increase in throughfall $C_B$ concentration, especially $K^+$, in late summer and early fall reflected abscission-layer formation and leaf breakdown.

Although foliar uptake of precipitation $NH_4^+$ has been observed in some studies (Parker 1983; Stottlemyer et al. 1997), our research into hardwoods and conifers on Isle Royale and other studies (Stottlemyer 1982; Edmonds et al. 1995; Likens and Bormann 1995) revealed no change between precipitation and throughfall $NH_4^+$ concentrations.

On Isle Royale, $K^+$ is the dominant cation in throughfall and stemflow of all species except in cedar stemflow. The high $K^+$ concentration indicates how easily $K^+$ is leached from the forest canopy, a finding in many other studies (Eaton et al. 1973; Likens et al. 1994; Edmonds et al. 1995; Lovett et al. 1996). Unlike $Ca^{2+}$, which is a more permanent constituent of plant cell walls, most aboveground plant $K^+$ is in cell plasma and is easily lost with leaf decadence. The ease with which $K^+$ is lost from decomposing plant debris also results in large increases in available $K^+$ in the snowpack especially in late winter or early spring when plant debris in the snowpack begins to leach (Hornbeck and Likens 1974; Stottlemyer and Toczydlowski 1996b).

The seasonal changes in throughfall chemistry in the Wallace Lake watershed indicated increased canopy evaporation or change in aerosol and dust deposition. Seasonal change in the chemistry of precipitation in bulk collectors suggested a concurrent change in dry deposition, but the direct measurement of dry deposition in the Upper Great Lakes region is limited.

The relations accounting for change in ion concentration and flux in throughfall and stemflow are more complicated than considered here. Microflora on the bark and leaves probably metabolize dissolved substances in precipitation, use the more labile compounds in deposited aerosols, and in turn release other compounds that further alter the chemistry of throughfall and stemflow. Nutrients, which are normally in a gas phase, are incorporated into the plant, and canopy reactions with $NH_3$ or $SO_2$ are reflected in the chemical composition of throughfall and stemflow. Products from these processes and nutrients from meteorologic inputs and other compounds leached by precipitation from the canopy are primarily part of plant nutrient cycling. Separation of these pathways in the Wallace Lake watershed has yet to be made.

The boreal forest in the Wallace Lake watershed seems to be in a near-steady state (Table 13). We consider throughfall and stemflow to be part of this ecosystem's internal nutrient cycling and not input. Reasonable estimates of vegetation uptake can be determined by summing net throughfall (throughfall minus precipitation input), stemflow, and litterfall element amounts. However, except for S (Table 11), we have no direct measurements of atmospheric aerosol and dry deposition inputs in this site. Bulk precipitation collectors capture some but not all aerosol and dry deposition. Therefore, throughfall probably contained a significant fraction of precipitation inputs that would cause an over-estimation of plant uptake.

**Snowpack Chemistry**

The loss of snowpack ions from mid-winter snowmelt in the Wallace Lake watershed was similar to percentages lost up to snowpack PWE in the Calumet watershed (Stottlemyer and Toczydlowski 1996b). In the Calumet watershed, a decade of intensive study showed that the loss of ions in snowmelt up to snowpack PWE, expressed as a percent of cumulative precipitation inputs, is 37% $Ca^{2+}$, 46% $H^+$, 58% $NH_4^+$, 37% $NO_3^-$, and 45% $SO_4^{2-}$. Overall, ion retention by the snowpack was about 8% higher in the Wallace Lake watershed than in the Calumet watershed. Cooler winter temperatures probably accounted for the higher retention of ions in the snowpack in the Wallace Lake watershed.

The studies in the Wallace Lake watershed were not sufficiently comprehensive to estimate dry deposition in the snowpack. In the Calumet watershed, where such instrumentation exists (Stottlemyer and Toczydlowski 1996a), the snowpack seems to gain about 10% of its ion input up to PWE from dry deposition or aerosol adsorption.

Unfrozen soils and mid-winter thaws are the rule in the Wallace Lake watershed and in the Upper Great Lakes region (Jeffries 1990; Stottlemyer et al. 1995; Stottlemyer and Toczydlowski 1996a, 1996b), although there are exceptions outside the Great Lakes snow belts (Cadle et al. 1984, 1986). In the Wallace Lake watershed, unfrozen soils provided convective heat flux to the base of the snowpack that metamorphosed snow crystals and caused a steady loss of SWE well before peak snowmelt (English et al. 1986). Freeze-thaw cycles are also common in the Upper Great Lakes region (Stottlemyer and Toczydlowski 1996a, 1996b), and, in addition to the movement of meltwater along ice lenses in the snowpack (English et al. 1986), contributed to variation in snowmelt rates throughout winter (Colbeck 1981). In the Calumet watershed, rain and rain mixed with snow, especially during the last month of snowpack (April), increase snowmelt rates and often reduce the chemical content of the snowpack (Jones 1987; Stottlemyer 1987b).

Differential snowpack ion loss has been observed for years (Johannessen and Henriksen 1978; Bales et al. 1989; Bowman 1992; Stottlemyer and Toczydlowski 1996a). The data from the Wallace Lake watershed suggest that $NH_4^+$ and $SO_4^{2-}$ were the ions first lost in the elution sequence. This is consistent with results from previous studies in the Calumet watershed and other sites in the Upper Great Lakes region. The large loss of N in the snowpack as $NH_4^+$ and the loss of one-third of the $NO_3^-$ load by snowpack PWE reduced the probability that N species in the snowpack reached the stream during peak snowmelt. The alteration of surface-water chemistry and ecosystem saturation by N from precipitation and snowmelt is a topic of considerable concern in many regions (Stoddard 1994).

The presence or absence of frozen soils also regulates the flowpath and chemical composition of snowmelt. When soils are frozen, the amount and timing of snowmelt are altered (Cadle et al. 1984, 1986; Semkin and Jeffries 1988), and watershed ion export may change as snowmelt is isolated from interacting with soils (Pierson and Taylor 1985). Frozen soils can increase watershed export of limiting nutrients as $NO_3^-$ from enhanced soil nitrification (Likens et al. 1977) or reduced biological immobilization (Lewis and Grant 1980; Stottlemyer et al. 1995). Conversely, unfrozen soils permit percolating snowmelt to chemically interact and increase biological activity such as microbial nitrogen immobilization in the soil that account for the strong ecosystem retention of snowmelt $NH_4^+$ and $NO_3^-$ in the Calumet watershed and probably in the Wallace Lake watershed. Unfrozen soils also permit greater desorption and mineralization rates that can increase ecosystem export of ions as $SO_4^{2-}$ in amounts well above snowpack content (Foster et al. 1989; Hazlett et al. 1992).

### Soil Characteristics and Soil Processes

Soil water concentrations of the divalents $Ca^{2+}$ and $Mg^{2+}$ in the Wallace Lake watershed were high considering the moderately resistant Precambrian bedrock beneath the watershed (Mollitor and Raynal 1982; Edmonds et al. 1995). The high $C_B$ concentrations reflected readily weathered substrates, which is additional evidence that soils were not derived in place but deposited by glacial activity.

We attributed the lesser $K^+$ concentration in shallow mineral soil water than in throughfall to plant uptake or differences in soil release. The decline of $K^+$ concentration in soil water was most evident beneath hardwoods. Beneath conifers, the decline was reduced or not present, a finding similar in other studies (Likens et al. 1994; Edmonds et al. 1995).

Concentrations of $HCO_3^-$ in soil solution in a subset of soil water samples decreased with depth beneath spruce but increased beneath birch-aspen

(Stottlemyer and Hanson 1989). In this same sample subset, soil water $SO_4^{2-}$ concentrations increased with depth beneath spruce. Beneath spruce, $SO_4^{2-}$ concentrations exceeded $HCO_3^-$ (equivalent basis) fourfold or fivefold. Beneath birch-aspen, $SO_4^{2-}$ and $HCO_3^-$ concentrations were similar. The high $SO_4^{2-}$ concentration in soil water beneath spruce may have been due to reduced $SO_4^{2-}$ adsorption. We found that $SO_4^{2-}$ and DOC concentrations significantly correlated in forest floor leachate and surface soils in northern hardwoods in the Calumet watershed (Stottlemyer and Toczydlowski 1996a). Organics may have contributed to reduced soil $SO_4^{2-}$ adsorption and high soil water concentrations in the Calumet and Wallace Lake watersheds. In the Wallace Lake watershed, the highest cation to anion ratios (equivalent basis) were in the forest floor and the surface-soil organic layers. The ratios indicated the presence of organic acids, but they were not measured. In the Calumet watershed, a 10-year study of forest-floor leachate and soil water chemistry revealed that DOC concentrations were highest in forest-floor leachate and in soil water that percolated through the organic layers of the surface soil (Stottlemyer and Toczydlowski 1996a).

The complexity of species interaction with weather and climate change in an ecotonal region, where atmospheric N inputs are moderate to high, indicates a need for additional study of major forest-species responses. This is especially so in assessing long-term responses to nitrogen availability. Because of its ecotonal nature, the potential N mineralization and nitrification rates in the Upper Great Lakes region are characterized by large differences among forest ecosystems (Zak et al. 1986). The need for this information led to our intensive studies of soil N mineralization rates and their response to change in temperature and moisture in situ and in the laboratory.

In the Wallace Lake watershed, the higher surface-soil moisture content in mid-May and June reflected snowmelt, an increase in seasonal rain (Fig. 6), and low evapotranspiration because of the absence of leaves. Site topography and low soil bulk density contributed to the high soil moisture beneath alder. Alder stands in the Wallace Lake watershed usually occur at low elevation in relatively flat sites once flooded by beaver dams. The increase in general soil moisture in fall reflected increased precipitation, reduced evapotranspiration, and lowering temperatures. Soil moisture was most variable beneath birch. Birch was characterized by a patchy canopy that caused high variation in radiation input and greater spatial variation in distribution of understory biomass (Rutkowski and Stottlemyer 1993).

Beneath hardwoods, the rapid soil-temperature increase in May was in response to the loss of snowpack and the absence of canopy shading. The increase in temperature beneath alder was less and reflected the high soil moisture and lowland topography that permits seasonal pooling of cool air.

In the Wallace Lake watershed, the seasonal trend in inorganic N concentration in the soil was similar to that in other unmanipulated forests (Nadelhoffer et al. 1984; Pastor et al. 1984). Soil $NH_4^+$ concentrations were larger and more variable than $NO_3^-$concentrations. The total inorganic N content was highest in spring and early summer and lowest in mid-summer.

Data on net N mineralization in soil provided a useful index of N supply because they primarily represent the cumulative difference between N immobilization and mineralization. The inverse correlation of monthly soil inorganic N concentrations with mineralization beneath alder and maple indicated the potential importance of microbial immobilization especially in late summer, fall, and early winter. After 1 month or so, high mineralization generally was followed by increased inorganic N concentrations in the soil.

Low soil temperatures in winter seemed to inhibit microbial immobilization more than mineralization. This was most evident beneath alder. With warming soil temperatures beneath alder, net inorganic N mineralization declined during May, June, and early July. This suggested soil microbial immobilization exceeded mineralization with warming temperatures, and readily mineralized organic N became limiting. Net N mineralization rates declined beneath maple after mid-May and beneath birch and spruce after mid-June, concurrent with warming soils and declines in soil moisture. The release of snowpack inorganic N solutes in spring (Stottlemyer and Hanson 1989), which can be as high as 150 mg N $m^{-2}$, added to available soil inorganic N. Much of this was $NO_3^-$, and soil $NO_3^-$ concentrations slightly increased by mid-May in the Wallace Lake watershed.

Nitrogen fixation may have accounted for the higher soil $NO_3^-$ levels beneath alder. When annual N fixation by alder was estimated with the approach of Binkley (1994b), based on alder foliage biomass in this watershed (Rutkowski and Stottlemyer 1993), fixation would be approximately 1.5 g N $m^{-2}$. This was in the low range of fixation rates by this species.

Annual net N mineralization rates in northern temperate forests range from 2 to 12 g N $m^{-2}$ (Nadelhoffer et al. 1983; Pastor et al. 1984). In the Wallace Lake watershed, the annual net N mineralization rate, composited among forest species, was at the low end of this range as may be expected in a boreal system. The composite rate of the two dominant boreal forest species, birch-aspen and spruce, was slightly below rates in low-productivity sites in another study on Isle Royale (Pastor et al. 1993) and more similar to that observed in sites in the inland Alaskan taiga (Hart and Gunther 1989; Stottlemyer 1992).

In dominant forest species in the Wallace Lake watershed, net mineralization rates were a small fraction of the gross mineralization rates, indicating a higher internal cycling of N than suggested by the net mineralization and nitrification rates. The small $NO_3^-$ pool size and low net-nitrification rates in soils beneath spruce may indicate $NO_3^-$ cycling was not important for this species. However, gross nitrification rates were more similar among species. Our results indicated large seasonal responses in gross mineralization and nitrification rates that were probably due to temperature. Small increases in soil temperatures from warming air temperatures could shorten the snowpack season or directly increase the soil temperature, especially in late spring and early summer, and may increase the internal cycling rates of N in the Wallace Lake watershed.

## Stream Water

***Chemical Concentration.*** In the early 1980s, our survey of surface-water chemistry in the park did not show a significant gradient of increasing ion concentrations from the northeast to the southwest. A spatial trend may be expected because of the pronounced increase in till depth and extent of coverage southwest of Siskiwit Lake (Fig. 1a; Huber 1973).

We attributed the general increasing mean annual $C_B$ and $HCO_3^-$ concentrations in stream water in the Wallace Lake watershed to trends in the annual precipitation amount. Annual and winter precipitation amounts in the Wallace Lake watershed declined during the study, and there was a significant relation between annual precipitation amount and stream flow. In addition, stream flow decreased as a percentage of precipitation as precipitation decreased. Such relations suggest deeper soil water or ground water became more important contributors to stream flow as precipitation amount declined (Rice and Bricker 1995). Deeper soil water had higher $C_B$ and $HCO_3^-$ concentrations, and their increase in stream water concentration with time probably reflected the decline in precipitation amount.

Although precipitation inputs of $H^+$, $NO_3^-$, and $SO_4^{2-}$ significantly declined during the study, ion concentrations in stream water had no trend. The lack of trend in stream water $H^+$ (not shown) and $NO_3^-$ concentrations we attributed in part to the strong watershed retention of these ion inputs as seen in canopy throughfall and surface soil fluxes (Tables 6 and 7). Although stream water $SO_4^{2-}$ concentrations generally decline with time (Fig. 24), no trend was present despite significant declines in precipitation $SO_4^{2-}$ concentrations. The absence of a significant decrease in stream water $SO_4^{2-}$ concentration was probably due to increases in $SO_4^{2-}$ flux in mineral soils (Table 8) from desorption (Stottlemyer and Toczydlowski 1996a) and some weathering of deeper mineral soils. Stream water $SO_4^{2-}$ concentrations were an order of magnitude greater than $NO_3^-$ in the Wallace Lake, Sumner Lake, and Calumet watersheds.

The changes in stream water ion concentration during snowmelt also followed seasonal patterns in the Calumet watershed during a similar study period (Stottlemyer and Toczydlowski 1996a, 1996b). The average ANC reduction during peak snowmelt was somewhat greater in the Wallace Lake watershed than in the Calumet watershed (difference of 130 $\mu$eq $L^{-1}$), but the relative importance of dilution in seasonal ANC reduction was the same. Dilution and movement of ions from soil exchange sites resulted in rapid change in stream water ion concentration. Overland flow amount during snowmelt in the Calumet watershed is a small (< 10%) component of total winter stream discharge (Stottlemyer and Toczydlowski 1991). However, during peak snowmelt, soil water levels were near or at the soil surface for as long as 1 week. The more rapid movement of snowmelt through near-surface organic soils and its reduced residence time probably were the primary processes that diluted stream water $C_B$ concentration. In other studies (Barry and Price 1987), dilution accounted for similar reductions (> 90%) in ANC as in the Wallace Lake and Calumet watersheds. Although stream water ANC was reduced during peak stream flow in the Calumet watershed, turbidity and concentrations of dissolved organic carbon (DOC) and total organic N and P increased (Stottlemyer and Toczydlowski 1991). Similarly, in the Wallace Lake watershed, stream water DOC, N, and total metal concentrations increased with spring stream discharge.

The increase in stream water ion concentration with initiation of significant spring snowmelt in the Wallace Lake watershed was also observed of $C_B$, $HCO_3^-$, and $NO_3^-$ in the Calumet watershed. But stream water $SO_4^{2-}$ concentrations declined less than 10% throughout the spring snowmelt. In the Wallace Lake watershed, stream water ion concentrations were usually highest during late winter just prior to peak snowmelt, a temporal pattern also seen in the Calumet watershed and at Hubbard Brook (Likens and Bormann 1995). The high ion concentrations in soil water in winter were probably due to the long contact period with the soil matrix, unfrozen soils that permit overwinter mineralization, and limited soil and aboveground biological uptake (Stottlemyer et al. 1995). At Hubbard Brook, the increase in stream water $NO_3^-$ concentrations associated with snowmelt was attributed to the seasonal increase in nitrification rates (Johnson et al. 1969). When snowmelt begins, the older soil water can be forced out (Abrahams et al. 1989; Campbell et al. 1995; Rascher et al. 1987), resulting in a small pulse or increase in stream water ion concentration, as observed in means of $NO_3^-$ in the Wallace Lake watershed in late spring (Fig. 25). In the long-term watershed study in the Calumet watershed, we found that patterns in stream water $NH_4^+$ concentrations during winter and early spring follow snowmelt changes but at much reduced concentration (Stottlemyer and Toczydlowski 1996b). (The $H^+$ concentration in stream water during snowmelt in the Wallace Lake watershed is not shown in Figs 24 and 25 because concentrations were so low.)

The $SO_4^{2-}$ concentration in stream water had a unique seasonal pattern (Fig. 25). Sulfate is the only ion that increases concentration through the snowmelt season, although the increase from March through May is slight (10 $\mu$eq $L^{-1}$). During June–July, the $SO_4^{2-}$ concentration was about two-thirds of the stream water concentration in mid-winter at W2 and about one-third at W1. The lack of a decline in stream water $SO_4^{2-}$ concentration during peak stream flow probably reflected soil desorption (Harrison et al. 1989; Jeffries 1990; MacDonald et al. 1994). Studies in a variety of forest soils revealed as much as two-thirds of adsorbed $SO_4^{2-}$ can be desorbed by percolating water (Harrison et al. 1989). In regions such as the Lake Superior basin with historically high levels of $SO_4^{2-}$ deposition, large $SO_4^{2-}$ reservoirs probably exist in forest soils. As earlier stated, in the Wallace Lake watershed, the forest-soil adsorbed $SO_4^{2-}$ pool was larger than $SO_4^{2-}$ from precipitation or $SO_4^{2-}$ peaks in snowpack. Soil

$SO_4^{2-}$ desorption seems to have been the only process with the capacity to buffer change in stream water $SO_4^{2-}$ concentration with rapidly increasing discharge during snowmelt.

Station W2 gauged stream flow from the entire watershed, including the 5-ha Wallace Lake (Fig. 1b). The similarity in seasonal pattern and variation of the mean monthly ion concentration, except possibly $NO_3^-$ and $SO_4^{2-}$, in stream water at stations W2 and W1 indicated the presence of this small lake altered stream flow chemistry little.

We attributed the decline in annual stream water DOC concentration to the reduced precipitation input and stream flow. The relative decline in stream flow was greater than the decrease in precipitation. Because DOC, total N, and some trace-metal and heavy-metal concentrations remained the same or increased with stream water discharge, the decline in average stream flow decreased their concentration. With reduced stream flow, there was disproportionately more deep soil water in stream flow and less lateral flow from shallow, more organic soils. The increase in DOC, total N, and metal concentrations with stream flow, as during snowmelt, reflected the higher percentage of soil water moving through shallow soils. In the Wallace Lake watershed, the existence of unfrozen soils throughout winter also promoted decomposition that further contributed to the high concentration and output of organics during and after spring stream flow (Stottlemyer and Toczydlowski 1996b).

***Chemical Outputs.*** The metamorphosed volcanic bedrock in the Wallace watershed (Huber 1973) suggests stream water ion output would be more in line with other sites on resistant bedrock (Table 17; Likens and Bormann 1995). However, the mean annual $C_B$ output from the Wallace watershed was 7 times the output from Hubbard Brook but well within the range of outputs in New England watersheds (Hornbeck et al. 1997). The range in annual $C_B$ output was 3 times the minimum output, the same relative variation as at the Hubbard Brook. The high $C_B$ output in the Wallace Lake watershed reflected the calcareous nature of the soils derived from alkaline till deposited on Isle Royale and along the southern shore of Lake Superior (Shetron and Stottlemyer 1991). The $C_B$ output in the Wallace Lake watershed and in the Calumet watershed, which has a Cambrian sedimentary bedrock, was similar (Stottlemyer and Toczydlowski 1996b).

Conversely, annual $H^+$ output from the Wallace Lake watershed was about 1% of the outputs at the Hubbard Brook where $H^+$ input was about 4 times the inputs into the Wallace Lake watershed. Greater than 90% of the $H^+$ input into the Wallace Lake watershed was retained by the forest floor and shallow mineral soils (Table 8). This pattern was also present in the Calumet watershed (Stottlemyer and Toczydlowski 1996a). The decline in $H^+$ output from the Wallace Lake watershed was significant and probably reflected the trend in annual stream flow and precipitation amount (Figs 5, 11, and 26). Less precipitation and stream flow indicated reduced soil water moving laterally in shallow surface soils where dissolved organics were most abundant in the

Wallace Lake watershed. The decline in annual watershed $H^+$ output and stream water DOC concentration and output were similar.

Annual $NH_4^+$ output from the Wallace Lake watershed exceeded levels from the Hubbard Brook by about 50% (Likens and Bormann 1995) and was about 3 times the annual output in the Calumet watershed where inputs were twice as high as in the Wallace Lake watershed (Stottlemyer and Toczydlowski 1996b). However, stream water output in the Wallace Lake watershed was much less than precipitation $NH_4^+$ input. During 1991–96, $NH_4^+$ concentrations from precipitation increased sharply in the Upper Great Lakes region (Lynch et al. 1995). However, in the Wallace Lake watershed, neither annual precipitation concentration (Fig. 15) nor input (Fig. 17) increased except in 1996. The significant correlations between stream water $H^+$ and $NH_4^+$ outputs and precipitation amount indicated the potential importance of precipitation amount, as opposed to precipitation ion concentration or input, for determining long-term trends in watershed ion losses. The $NH_4^+$ output from W1 peaked in mid-winter, a finding consistent with our results from the Calumet watershed. Output at W2 peaked during snowmelt. In the Wallace Lake watershed, soil inorganic N concentration and net mineralization were also at or near peak during winter and spring as were soil inorganic N reservoirs, which were larger than snowpack $NH_4^+$ content. The seasonal pattern in stream $NH_4^+$ output reflected trends in soil inorganic N pools.

Similar to $NH_4^+$, trends in annual stream water $NO_3^-$ output suggested outputs were regulated by processes independent of trends in $NO_3^-$ levels from precipitation or in the snowpack. The large watershed $NO_3^-$ output in 1996 (108 eq $ha^{-1}$ greater than output in 1995) was much greater than the increase in precipitation input (40 eq $ha^{-1}$; Fig. 17) or snowpack PWE content, which declined 3 eq $ha^{-1}$ (Fig. 19) and was more pronounced than the increase in precipitation amount (12 cm) in 1996. On average, the Wallace Lake watershed retained 75% of $NO_3^-$ inputs, but the watershed $NO_3^-$ output (147 eq $ha^{-1}$) in 1996 was 84% of the input (176 eq $ha^{-1}$). In 1996, the snowpack PWE but not the $NO_3^-$ load (about 20 eq $ha^{-1}$; Fig. 19) was maximum. Cumulative precipitation $NO_3^-$ inputs from November 1995 to May 1996 were 76 eq $ha^{-1}$, and stream water $NO_3^-$ output was 126 eq $ha^{-1}$.

In 1996, the stream flow pattern during snowmelt was unique during this study (Fig. 14). The time of peak stream flow was the latest (19 May) recorded. High stream flow began on 22 April and was sustained until peak stream flow, after which it declined rapidly during the following week. This combination of hydrologic factors produced the maximum ratio of stream flow to precipitation amount (89%) during 1982–96 and was quite unusual in relation to the mean (68%). We hypothesized that the high watershed $NO_3^-$ output was the result of large amounts of late-season snowmelt entering the forest floor and removing highly mobile $NO_3^-$ produced by over-winter soil mineralization and nitrification and the low seasonal microbial immobilization. We suspect that even in years with such high snowmelt and stream flow, precipitation $NO_3^-$ input accounted for less than 20% stream water $NO_3^-$ output. In studies with the natural isotope ratios of $^{18}O$ and $^{15}N$ in precipitation and stream water $NO_3^-$ in watersheds where atmospheric $NO_3^-$ inputs considerably exceed those in the Wallace Lake watershed, stream water $NO_3^-$ is principally the product of soil processes (Kendall et al. 1995).

Annual stream water $SO_4^{2-}$ output showed no trend despite an input decline of more than 40% during the study (Figs 17 and 26). The decline in precipitation $SO_4^{2-}$ input was similar to trends in the Calumet watershed (Stottlemyer and Toczydlowski 1996b). Through 1994, $SO_4^{2-}$ output at Station W1 declined ($p < 0.05$, $r^2 = 0.39$, b = –28), but there was no change during 1982–96. As earlier discussed in explaining the lack of change in stream water $SO_4^{2-}$ concentration during snowmelt, we attributed the lack of a significant decline in stream water $SO_4^{2-}$ output primarily to soil desorption (Harrison et al. 1989; Jeffries 1990). The increases in throughfall and mineral soil $SO_4^{2-}$ concentrations and flux beneath major canopy species in the Wallace Lake watershed suggest desorption, some mineralization, and perhaps release of aerosol deposition from the previous snowfree season accounted for the increase in $SO_4^{2-}$ (Lindberg et al. 1986). Elevated soil water DOC concentrations may in part also explain the increased percolate $SO_4^{2-}$ concentration because DOC reduces soil $SO_4^{2-}$ adsorption capacity (Vance and David 1992). As earlier mentioned, in our studies of the Calumet watershed, forest floor percolate DOC concentrations increased with $SO_4^{2-}$, and there was a correlation between $SO_4^{2-}$ and DOC concentrations. In the Wallace Lake watershed, the average volume-weighted stream water DOC concentration was about 12 mg $L^{-1}$ at Station W2, much greater than the more than 1 mg $L^{-1}$ at the Hubbard Brook, in streams draining old growth western conifer watersheds (Edmonds et al. 1995), and in watersheds of Denali National Park, Alaska (Stottlemyer 1992). The relatively high stream water DOC concentrations in the Wallace Lake watershed suggested elevated soil water DOC concentrations could promote soil $SO_4^{2-}$ desorption at the watershed level. The decline in stream water $SO_4^{2-}$ output was also consistent with the decline in annual volume-weighted stream water DOC concentration.

Unlike in some other northern watershed study sites where atmospheric $SO_4^{2-}$ inputs remained high, $SO_4^{2-}$ in the Wallace Lake watershed was not retained at the watershed level (Likens and Bormann 1995). In the Wallace Lake watershed, some S seems to have been retained at the sub-basin level (Station W1). The small Wallace Lake did not seem to be a sulfur sink like other lakes in the Upper Great Lakes region (Schindler et al. 1986).

The high stream water $HCO_3^-$ concentrations and output in the Wallace Lake watershed again reflected the dominating effect of alkaline till weathering on surface-water chemistry. The high correlation of stream water $HCO_3^-$ concentrations and output with $C_B$ suggested common weathering processes. As in patterns of $C_B$ output, the $HCO_3^-$ output patterns showed the dominating influence of watershed hydrology. The correlation of $HCO_3^-$ output with precipitation amount again showed the potential importance of precipitation amount rather than its chemistry in regulating stream water ion concentration and output.

The largest net losses of dissolved inorganic substances from the Wallace Lake watershed were in wet years or in years with high stream flow to precipitation ratios (1996). The net watershed loss of dissolved inorganic substances was lowest in the driest year (1990) when the stream flow to precipitation ratio was low (Fig. 11). Chemical weathering of the alkaline till and related processes accounted for most of the overall net losses.

The general increase in DOC and the total N concentrations and flux in stream water with increased discharge again indicated the importance of hydrologic flowpath on stream water chemistry. Periods of high stream flow increased the percentage of soil water that moves laterally through shallow mineral and organic soils and the removal of products from decomposition and soil exchange processes. The large DOC and total N fluxes concurrent with snowmelt (not plotted) supported this. Such change in flux also could account for seasonal trends in ion output (Fig. 27), particularly in view of the large size of the soil reservoirs. This linkage of stream water chemistry to soil processes probably accounted for the general lack of seasonal or annual relations between precipitation chemistry or snowpack chemistry and stream water ion concentration and flux.

Monthly $C_B$ inputs approximated outputs in the Wallace Lake watershed only in August, when the ratio of precipitation to stream flow amount was greatest (Fig. 13) and stream flow was at baseflow through September. Precipitation $C_B$ concentration peaked in summer, which probably reflected regional increases in dust input since winter when the regional snowpack minimized dust. In all other months, $C_B$ output considerably exceeded input (Figs 18 and 27).

The difference between cumulative seasonal $H^+$ input and snowpack content in the Wallace Lake watershed indicated how much snowpack $H^+$ was lost prior to peak snowmelt. In the Calumet watershed, where access permits intensive sampling in winter, direct measurement of snowmelt with lysimeters throughout winter for 10 years revealed a loss of $H^+$ in snowmelt (average 65%) from the snowpack through mid-March (Stottlemyer and Toczydlowski 1996a). We attributed this loss to periodic thaws and the constant but small daily snowpack ion losses associated with unfrozen soils in the Wallace Lake and Calumet watersheds (Stottlemyer et al. 1995).

The cumulative loss of snowpack $NH_4^+$ prior to peak snowmelt was also similar to directly measured amounts in the Calumet watershed. In the Calumet watershed, the snowpack loses an average 71% of its total losses of $NH_4^+$ in snowmelt by mid-March. The $NH_4^+$ output from the Wallace Lake watershed in April was similar to seasonal $NH_4^+$ outputs from uncut watersheds at Hubbard Brook (Likens and Bormann 1995). Seasonal stream water $NH_4^+$ output in the Wallace Lake watershed was relatively constant and low throughout the year.

The loss of $NO_3^-$ from the snowpack prior to peak snowmelt in April was also similar to directly measured losses in the Calumet watershed. In both watersheds, stream water $NO_3^-$ output increased in fall, which we attributed to breakdown of fresh litterfall, continued N mineralization and nitrification, and reduced above-ground and below-ground biological uptake. The $NO_3^-$ discharge from the Wallace Lake watershed in April was about one-tenth of the amount at the Hubbard Brook. The total loss of inorganic N from the watershed was less than 1 kg $ha^{-1}$ $year^{-1}$. The same amount was lost at Findley Lake, Washington, where atmospheric N inputs were less than half those in the Wallace Lake watershed (Johnson and Lindberg 1992).

The large pools of water-soluble and adsorbed S in mineral soils, almost 70 kg $ha^{-1}$, in the Wallace Lake watershed could have easily accounted for the lack of decline in stream water $SO_4^{2-}$ concentration during peak snowmelt (Fig. 25). The total S in stream water discharge during and after snowmelt was less than 4 kg $ha^{-1}$ (Fig. 27), a small fraction of the S easily removed from surface forest soils by percolating snowmelt. Stream water $SO_4^{2-}$ output in winter averaged 345 eq $ha^{-1}$ or more than 3 times the cumulative precipitation input. The higher $SO_4^{2-}$ output than $SO_4^{2-}$ input was similar to winter budgets in the Calumet watershed. The peak $SO_4^{2-}$ output in stream flow during snowmelt was about 3 times higher in the Hubbard Brook than in the Wallace Lake watershed, but inputs were also considerably higher into the Hubbard Brook than into the Wallace Lake watershed.

## *Nutrient Cycles*

A comparison of the magnitude and rates of nutrient cycling among sites must be approached with caution. One major variable is the length of the study. For example, we studied biomass and its nutrient content in the Wallace Lake watershed in the mid- 1980s (Rutkowski and Stottlemyer 1993) when the mean litterfall amounts were relatively low. Such data by themselves would significantly affect estimates of nutrient cycling.

Base cation cycling in the Wallace Lake watershed was primarily affected by hydrologic and biologic factors. Unlike carbon, nitrogen, and sulfur, $C_B$ had no significant gaseous phase. The presence of a significant gaseous phase complicates estimating nutrient cycles.

Throughfall $Ca^{2+}$ flux in the canopy was larger in the boreal forest than at Hubbard Brook and in the mid-range of conifer-dominated sites of the Integrated Forest Study (IFS; Johnson and Lindberg 1992). It was more than twice the $Ca^{2+}$ flux in Alaskan taiga sites, which receive half the precipitation amount that the Wallace Lake watershed received (Van Cleve et al. 1983b, 1986). Throughfall $Ca^{2+}$ flux in mature maple at Windigo and at Hubbard Brook were similar (Table 17), even though annual precipitation amount at Windigo was only about half the amount at the Hubbard Brook. Coarse-particle $Ca^{2+}$ in dry deposition to the canopy was an unquantified component of net throughfall

$Ca^{2+}$ flux in this study. Some indication of the importance of coarse-particle $Ca^{2+}$ deposition can be seen in comparisons of differences in $Ca^{2+}$ concentration in wet-only and in bulk precipitation samplers (Fig. 15). Calcium is the ion with the greatest concentration difference. The collection of $Ca^{2+}$ input with bulk collectors accounted for part of the coarse-particle $Ca^{2+}$ input from dry deposition. However, on a unit-area basis, a bulk collector cannot retain as much coarse-particle $Ca^{2+}$ as a tree canopy, especially when one considers the leaf area per unit of ground area beneath the canopy. This process overestimates the throughfall ion flux as part of internal ecosystem nutrient cycling. Another reason for differences in flux was the amount of aboveground biomass, which in the Wallace Lake watershed was above the average in 36 studies of other forests (Cole and Rapp 1981), similar to Alaskan boreal ecosystems (Van Cleve et al. 1983b), but only about 35–40% of the biomass in mature northern hardwoods in the Upper Great Lakes region (Mroz et al. 1985; Rutkowski and Stottlemyer 1993). In mature maple at Trout Lake in the upper peninsula of Michigan, the aboveground living biomass Ca content was almost 1500 kg $ha^{-1}$ or more than 3 times the content of the boreal forest in the Wallace Lake watershed.

Our estimate of annual $Ca^{2+}$ uptake by birch-aspen in the Wallace Lake watershed was quite similar to the uptake by the same or similar species in the Alaskan taiga (52 kg $ha^{-1}$ $year^{-1}$; Van Cleve et al. 1983b). However, $Ca^{2+}$ uptake by white spruce was about 3 times higher in the Wallace Lake watershed than in Alaska. The average annual aboveground $Ca^{2+}$ uptake in the Wallace Lake watershed by all species exceeded the higher ranges in Alaska by about 50% (36 versus 56 kg $ha^{-1}$ $year^{-1}$). However, unlike the studies in the Wallace Lake watershed, the studies in Alaska did not include estimates of understory uptake. Overall, aboveground $Ca^{2+}$ uptake in the Wallace Lake watershed seems to have slightly exceeded the mean uptake by the same species in interior Alaska. The $Ca^{2+}$ uptake by conifers was about two or three times higher in the Wallace Lake watershed than in the IFS study (Johnson and Lindberg 1992) and about 90% of the amount in northern hardwoods at the Hubbard Brook, which is consistent with the larger northern hardwood biomass and an aggrading ecosystem (Likens and Bormann 1995). Failure to fully account for dry deposition of coarse-particle $Ca^{2+}$ or other $C_B$s in throughfall somewhat increased our estimates of uptake.

The exchangeable $Ca^{2+}$ pool in the soil was larger in the Wallace Lake watershed than at the Hubbard Brook. It was in the low range of that in the IFS study and about twice as high (1400 g $m^{-2}$) as that in the Alaskan taiga (0–70 cm depth; Van Cleve et al. 1983b). The larger exchangeable $Ca^{2+}$ pool in the Wallace Lake watershed reflected the relatively recent deposition of alkaline till in the Upper Great Lakes region. The exchangeable $Ca^{2+}$ pool was much larger than the $Ca^{2+}$ flux in mineral-soil solution at the 30-cm depth.

The $SO_4^{2-}$ anion accounted for about 25% of the $C_B$ flux in deeper soil. Sulfate was the dominant inorganic anion in soil water beneath spruce and its concentration was similar to the concentration of $HCO_3^-$ beneath birch-aspen (Stottlemyer and Hanson 1989). In the Calumet watershed, $SO_4^{2-}$ was the dominant anion in soil water beneath immature maple and birch (Stottlemyer and Toczydlowski 1996a), whereas $NO_3^-$ was the dominant anion in soil water beneath mature maple in the Turkey Lakes watershed east of Lake Superior (Foster et al. 1989). In the Turkey Lakes watershed, the high inorganic N concentrations in soil water primarily reflected soil processes. But at the watershed level, the stream water $NO_3^-$ concentration in the Turkey Lakes watershed accounted for considerably less of the cation flux than $SO_4^{2-}$ or $HCO_3^-$. In the Wallace Lake watershed, $HCO_3^-$ accounted for 86% and $SO_4^{2-}$ for 7% of the inorganic anion loss in stream water.

The average loss of $K^+$ from the Wallace Lake watershed was about 75% of the long-term average amount from the undisturbed Watershed 6 at the Hubbard Brook (Table 17; Likens et al. 1994), and it was near the lower range in a series of New England watersheds (Hornbeck et al. 1997). In the Wallace Lake watershed, $K^+$ flux at the 30-cm mineral-soil depth was less than throughfall flux and indicated strong ecosystem retention of $K^+$. The reduction of $K^+$ flux in surface mineral soils was most evident beneath birch-aspen (Stottlemyer and Hanson 1989). Such results suggested that $K^+$ was the most limiting $C_B$. The exchangeable $K^+$ pool size in the soil (520 kg $ha^{-1}$) was larger than $K^+$ flux in mineral surface soils. The net $K^+$ outputs in the Wallace Lake watershed, at Turkey Lakes (Nicolson 1988), and in the Calumet watershed were similar (Stottlemyer and Toczydlowski 1996a).

The annual uptake of $K^+$ was similar between the Wallace Lake watershed (21 kg $ha^{-1}$) and the Alaskan taiga (26 kg $ha^{-1}$ $year^{-1}$; Van Cleve et al. 1983b). Like the uptake of $Ca^{2+}$, the $K^+$ uptake by white spruce and paper birch was greater (50%) in the Wallace Lake watershed than in Alaska. However, the $K^+$ uptake by aspen in Alaska was 50% greater. The amount of $K^+$ uptake was similar between the Wallace Lake watershed and the conifers at lower elevations in the IFS study (Johnson and Lindberg 1992). It was one-third of the levels at the Hubbard Brook (Likens and Bormann 1995). The exchangeable $K^+$ pool in soil was larger in the Wallace Lake watershed than at the Hubbard Brook, above the average amount in the IFS conifer sites, and slightly greater than the amount in the Alaskan taiga (52 to 30 g $m^{-2}$; Van Cleve et al. 1983b).

The strong N retention in the Wallace Lake watershed was consistent with data from the nearby Calumet (Stottlemyer and Toczydlowski 1996a, 1996b) and Turkey Lakes watersheds (Nicolson 1988). The retention of inorganic N relative to precipitation N inputs was higher than at Turkey Lakes. It was higher in the Calumet watershed than in the Wallace Lake watershed. The retention of atmospheric N in watersheds in New England, where N inputs are more than twice as high as in the Wallace Lake watershed, was even greater (Hornbeck et al. 1997). Retention of N from precipitation by the forest canopy was one factor, especially in conifer-dominated ecosystems (Edmonds et al. 1995). Uptake of inorganic N, especially $NO_3^-$, by arboreal lichens has been found in the canopy of fir (*Abies*) forests (Olson et al. 1981). Uptake of $NH_4^+$ by the canopy can reduce the concentration in throughfall (Parker 1983). However, in our and other studies (Edmonds et al. 1995) and in contrast to $NO_3^-$ retention, $NH_4^+$ concentration and flux in precipitation were little altered or increased beneath the conifer canopy.

In the Wallace Lake watershed, aboveground annual N uptake was about half of the uptake at the Hubbard Brook (Tables 11 and 17). Again, this difference probably reflected the aboveground biomass, which is smaller in this boreal ecosystem than in northern hardwoods (Mroz et al. 1985; Rutkowski and Stottlemyer 1993; Likens and Bormann 1995). At Findley Lake in Washington, which is a conifer-dominated IFS site, atmospheric N inputs were the same and N uptake was close to the average uptake in the Wallace Lake watershed. The annual N uptake by white spruce was identical between Alaskan taiga sites (Van Cleve et al. 1983b) and the Wallace Lake watershed. However, the uptake by white birch was 3 times greater in the Alaskan taiga sites than in the Wallace Lake watershed.

If it were assumed that the net change in the aboveground biomass in the Wallace Lake watershed was relatively stable over time, the input-output budgets, which did not include dry deposition, indicated the ecosystem was still retaining almost 3 kg N $ha^{-1}$ $year^{-1}$. Some N (0.5–1.0 kg $ha^{-1}$ $year^{-1}$) was retained by the forest canopy. Another factor that could have accounted for relatively short-term trends in aboveground ecosystem biomass and nutrient content on Isle Royale was herbivory by moose (McInnes et al. 1992; McLaren and Peterson 1994; McLaren and Janke 1996). On Isle Royale, plant growth rates are regulated by cycles in herbivore density (McLaren and Peterson 1994). Growth rates respond to annual changes in primary production only when released from heavy herbivory by predators such as wolves (*Canis lupus*). In the absence of herbivory, tree production increases and the rate of change can be rapid. Herbivory can remove as much as 21 kg $ha^{-1}$ $year^{-1}$ of biomass in these systems, but its effect on nutrient status in poorer sites on Isle Royale is less clear (McInnes et al. 1992). Short-term trends in aboveground biomass change—not detected by our periodic inventories—could also have accounted for some of the retained N. However, when we used annual litterfall (Fig. 28) as an index of ecosystem production, the absence of any significant trend supported our finding of little change in aboveground biomass during the study. The exception was white spruce whose litterfall increased by about 90 kg $ha^{-1}$ $year^{-1}$ with an N content of about 1 kg $ha^{-1}$ during the study. This suggested an increase in biomass production by this species at least over the short term.

Another, more probable accounting for the excess N are belowground processes (Stottlemyer et al. 1995). In the Wallace Lake watershed, surface soils had inorganic N pools that averaged more than 2 kg N $ha^{-1}$. Net N mineralization rates beneath spruce, birch, and alder averaged 14 kg N $ha^{-1}$ $year^{-1}$ or more than 3 times the inputs from precipitation in bulk collectors. The gross N mineralization rates in these species averaged about 80 mg N $m^2$ $day^{-1}$ (0.8 kg

$ha^{-1}$ $day^{-1}$) during the snow-free season (Fig. 22). Because mineralization rates were larger than precipitation inputs, any slight seasonal change in microbial immobilization of N (Fig. 22) could have accounted for the difference between N inputs and outputs. The net N mineralization rates in the Wallace Lake watershed were also sensitive to temperature change, which could have easily raised the ecosystem N budgets to higher levels than the mean differences in N input and output. Evidence for this was provided by the similarity between the seasonal pattern in net N mineralization in the watershed with stream water $NO_3^-$ concentration, a similarity also found in other studies (Johnson and Lindberg 1992; Stottlemyer 1997).

In contrast to the strong N retention in the Wallace Lake watershed, watershed S output exceeded inputs by 25%, depending on the accuracy of the estimated inputs. Sulfur outputs exceeded inputs by almost this amount in the Calumet watershed (Stottlemyer and Toczydlowski 1996a, 1996b). Sulfur input about balanced output in the Turkey Lakes watersheds (Nicolson 1988). A review of results from North American and northern European watershed studies revealed that $SO_4^{2-}$ output in the Wallace Lake watershed was in the low range of the forested ecosystems with conifer or evergreen components (Likens and Bormann 1995). Similarly, net $SO_4^{2-}$ output was lower in the Wallace Lake watershed than in New England watersheds where past and present sulfur inputs were higher (Hornbeck et al. 1997). Watershed $SO_4^{2-}$ output can exceed input by orders of magnitude where precipitation inputs are minimal, but bedrock is easily mineralized (Stottlemyer 1992). Sulfate, $K^+$, and carbon (DOC) are generally the solutes that increase the most in throughfall and stemflow concentration (Mollitor and Raynal 1982; Richter et al. 1983; Lindberg et al. 1986; Likens and Bormann 1995). These and other investigators (Johnson et al. 1982) suggest that throughfall gain in $SO_4^{2-}$ is derived from foliar leaching and atmospheric deposition. Where atmospheric $SO_4^{2-}$ concentrations are low, throughfall and stemflow $SO_4^{2-}$ concentrations seem little altered (Johnson and Lindberg 1992; Edmonds et al. 1995). Few studies have revealed canopy $SO_4^{2-}$ retention.

Our estimated annual aboveground S uptake was about one-third of the amount at Hubbard Brook (Tables 11 and 17), but the living aboveground biomass is only about half as large in the Wallace Lake watershed (Rutkowski and Stottlemyer 1993; Likens and Bormann 1995). At the Findley Lake IFS site, uptake of S by conifers was the same as the uptake by spruce in the Wallace Lake watershed and close to the mean by all species in the Wallace Lake watershed (Johnson and Lindberg 1992). The forest floor in the Wallace Lake watershed contained the largest aboveground pools of S and other major elements except K.

## *Biomass Distribution*

Our estimate of total aboveground biomass (108 t $ha^{-1}$) in the Wallace Lake watershed was much lower than estimates of aboveground biomass in mature northern hardwoods. It was near the low range of those in second-growth hardwoods in the Upper Great Lakes region. Mature boreal forests seem to have lower biomass than most other forests. The biomass in the Wallace Lake watershed was similar to amounts in northern British Columbia (108 t $ha^{-1}$) and Manitoba (102 t $ha^{-1}$). Results from a range of 20 Alaskan taiga sites revealed biomass amounts that were comparable or somewhat above the amounts in the Wallace Lake watershed (Van Cleve et al. 1983b).

The patchy nature of boreal forests on Isle Royale and in the Wallace Lake watershed explained the high amount of biomass in the understory. In the Wallace Lake watershed, surface bedrock, shallow soils, and wetlands break up the canopy and, except beneath spruce, light is not a limiting factor as it often is in northern hardwoods.

The large organic pool in surface soils in the Wallace Lake watershed suggested slow decomposition rates. Such are expected in this cool and moist site with relatively flat terrain. The large organic pool could also reflect the recalcitrant nature of conifer litter. The amount of organic matter in the forest floor was about half as large as the levels in Alaskan taiga sites (Table 17; Van Cleve et al. 1983b). The percentage of total aboveground organic matter was less in the forest floor (21%) than in the Alaskan sites, which probably reflected even slower decomposition rates on the cooler and poorly drained Alaskan sites.

Unlike northern hardwood forests that typically have most of the aboveground nutrient content in the canopy, only about one-third the nutrient content in the Wallace Lake watershed was in the overstory. The remainder was in the forest floor, even though the forest floor contained only 21% of the aboveground biomass.

Because of the high nutrient concentration in forest floor horizons and herbs and shrubs, these ecosystem components contained a disproportionately larger amount of the aboveground nutrient pool. Because of the low nutrient content of tree boles, the overstory in the Wallace Lake watershed had a much lower ratio of nutrient content to biomass. Alban et al. (1978) found a similar aboveground biomass and nutrient distribution pattern in northern Minnesota.

The changes in annual N content in litterfall over time probably indicated relative trends in productivity of ecosystem components (Braswell et al. 1997; Reich et al. 1997). The decline of N in birch-aspen litterfall probably reflected the decadent nature of these species in the Wallace Lake watershed, on Isle Royale in general, and in the Upper Great Lakes region (Jones et al. 1993). The reproduction rates of white birch in the 1–20-cm diameter range sharply declined, and the reproduction rates of white spruce were highest (Rutkowski and Stottlemyer 1993). The losses in birch-aspen may have reflected normal succession patterns, a decline associated with weather trends in the region (Jones et al. 1993), or the absence of disturbance beyond windthrow mortality (Toczydlowski et al. 1993). The increase in the reproduction and biomass of younger spruce probably reflected the balance of similar controls, perhaps coupled with the resistance of spruce to browsing by moose.

In 1991, annual litterfall and its N and C contents in the Wallace Lake watershed sharply declined beneath alder and birch-aspen (Fig. 28). The decline was not evident in spruce with its longer-lived needles. Litterfall and its N and C contents rebounded in 1994. By 1996, litterfall and the N and C contents beneath spruce were highest during the study. This apparent short-term response in litterfall at least beneath hardwoods was consistent with the lagged response and possible indirect effects of weather change on net carbon exchange in the ecosystem (Braswell et al. 1997).

## *Growth and Mortality*

During this study, blowdown was the major disturbance in forest vegetation of the Wallace Lake watershed. Wind seemed to discriminate against larger spruce and fir, and taller and thinner trees were the most vulnerable. A single event of 36 h of 56–81 km $h^{-1}$ (16–23 m $s^{-1}$) north-northeast winds and wet snow on 17–18 October 1990 accounted for high blowdown to the south-southwest (D. Toczydlowski, personal observation). However, wind speed alone did not account for the relatively high conifer loss. The season when high wind occurs could be as or more important. High winds in late fall and winter could select against conifers in part because of loss of buffering from adjacent hardwood foliage. Also in the Lake Superior region, relatively warm lake water delays the onset of winter, and wet snows with high winds during late fall and early winter may further select against conifers. The degree to which this fallen biomass contributes to overall ecosystem nutrient budgets, especially N fixation (Jurgensen et al. 1987) has not been assessed.

Except windthrow, which seems to have affected primarily white spruce and balsam fir, major disturbances of the boreal forests on Isle Royale were infrequent. However, the average life span of dominant canopy species, except those of white spruce and cedar, is short. This causes a dynamic community composition and biomass over relatively short time periods. Study of mortality and growth patterns in northern hardwoods in the Upper Great Lakes region has been considerable (Mroz et al. 1985), but study of southern boreal forests and associated long-term datasets has been limited (Janke et al. 1978). The exceptions are the effects of herbivory by moose on Isle Royale (Risenhoover and Maass 1987; Brandner et al. 1990; McInnes et al. 1992; McLaren and Peterson 1994; McLaren and Janke 1996). Whereas studies in the Wallace Lake watershed suggested a decline in balsam fir, other studies in and about the Wallace Lake watershed indicated a long-term gain in balsam fir regeneration in this portion of Isle Royale National Park (Rutkowski and Stottlemyer 1993; McLaren and Janke 1996).

Annual forest mortality in the Wallace Lake watershed seemed relatively low ($< 2\%$) and characteristic of other mature and stable forest types (Edmonds et al. 1995). Growth is usually little in old-growth forests. However, the Wallace Lake watershed seemed to be accumulating live biomass at less than 2% $year^{-1}$.

But the net live biomass accumulation could have been a relatively short-term phenomenon. Similar short-term gains in net growth have been observed in 500-year old conifer forests in the Cascades (Franklin and DeBell 1988).

## *Management and Policy Implications*

Isle Royale is a remote site without conterminous land use. This attribute renders the park especially attractive for long-term monitoring, inventory, and hypothesis testing. For example, few, if any, of the common anthropogenic chemicals were ever used in or immediately adjacent to the park. Thus, the presence of polychlorinated compounds in the lake sediments indicates atmospheric inputs, the only mechanism by which such compounds can reach an inland lake (Czuczwa et al. 1984). The park's value is enhanced by the additional legal protection from its status as a unit of the National Park System, its status as a wilderness, and its status as a Biosphere Preserve. The level of protection provided by geography and legal mandates makes Isle Royale a unique reserve in the lower 48 states. The park's scientific value is demonstrated by the long-term predator-prey studies conducted there. Because of the rapid changes from global land use, such research cannot be repeated. The sum of these attributes weighed heavily in the designation of Isle Royale as an International Biosphere Reserve in 1982. In addition, Isle Royale is located in the ecotone between the northern hardwood and boreal forests. Ecotones are especially sensitive indicators of change from anthropogenic and other stress.

The surface waters of Isle Royale seem to be representative of the region despite the park's generally resistance bedrock. Much of this region has well buffered soils and surface water, especially in streams (Overton et al. 1986; Wiener and Eilers 1987; Stottlemyer and Toczydlowski 1991). Such streams respond little to atmospheric $H^+$ inputs but can be altered by snowmelt dilution and atmospheric inputs of $NO_3^-$ and $SO_4^{2-}$. The park's surface waters are not sensitive to change from atmospheric $H^+$ inputs, and detection of longer-term ecosystem response to the present moderate $H^+$ input levels would be difficult if not impossible.

The $SO_4^{2-}$ output from the Wallace Lake watershed exceeded precipitation inputs. The excess output was seemingly caused by past and present atmospheric $SO_4^{2-}$ inputs passing through forest soils (Stottlemyer and Hanson 1989). The two soil associations in the Wallace Lake watershed cover 31% of Isle Royale's land area (Shetron and Stottlemyer 1991). The Michigamme-Arcadian-Rock Outcrop Association, the most extensive soil association in the Wallace Lake watershed and the park, is the more sensitive of the two associations to chemical change from atmospheric inputs and global change. Research in the Wallace Lake watershed during the late 1980s revealed excess atmospheric $SO_4^{2-}$ inputs annually leach a small percentage (0.3%) of exchangeable base cations ($C_B$) from surface forest soils (Stottlemyer and Hanson 1989). Based on studies in other regions, this chemical alteration of the ecosystem was smaller than an alteration after fire. This albeit small leaching from the $C_B$ pool is anthropogenic.

Unlike $SO_4^{2-}$ inputs, atmospheric N inputs to the Wallace Lake watershed were strongly retained. Nitrogen is a limiting nutrient in most ecosystems. On Isle Royale, 60% of the atmospheric N input was from $NO_3^-$. In the Wallace Lake watershed, greater than 90% of precipitation $NO_3^-$ input was retained in the forest canopy and surface organic layers. In time, this retention should alter canopy biomass, C:N ratios and N content of litterfall, and the forest floor. However, we did not detect a statistically significant trend in litterfall or forest-floor chemistry. Another probable indicator is change in annual soil net N mineralization rates, but we only monitored this process for 5 years.

Two studies in the Upper Midwest have revealed ecosystem change in response to atmospheric N deposition. A long-term study at the Cedar Creek Long-Term Ecological Research (LTER) site showed a non-linear response of grasslands to chronic N inputs. Non-linearity occurs when soil microbial N immobilization shifts to N mineralization after a threshold is reached where microbial resource needs are met (Wedin and Tilman 1996). In a separate study (K. Pregitzer, School of Forestry and Wood Products, Michigan Technological University, Houghton, Michigan, personal communication), chronic atmospheric N inputs have increased soil DOC production. DOC is relatively labile, can be used by soil organisms, and is an important energy source for aquatic ecosystems. Increases in soil DOC production, generally accompanied by increased dissolved organic nitrogen (DON), alter terrestrial and aquatic biodiversity.

Our research in the Wallace Lake watershed also revealed that year-to-year warming weather or long-term temperature gains (climate change) increase available N in the ecosystem in greater than projected amounts of atmospheric inputs. A warming climate complements atmospheric N inputs and further changes ecosystem biomass and biodiversity (Vitousek et al. 1997; Schindler 1998).

In sum, from a policy perspective, present atmospheric $SO_4^{2-}$ inputs and mineralization and desorption of past S inputs have put into place a process that removes some nutrients from the rooting zone in the Wallace Lake watershed. This effect should decrease with time because of reduced S emissions. Conversely, atmospheric N inputs will probably increase. The present strong N retention by the ecosystem probably is changing below- and aboveground biomass, species diversity, and ecosystem production.

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# Appendix

Detailed descriptions of the two dominant soil associations, Histic Humaquepts-Froberg-Rudyard and Michigamme-Arcadian-Rock Outcrop associations, Wallace Lake watershed, Isle Royale National Park, Michigan (from Shetron and Stottlemyer 1991).

LESS INTENSIVE SOIL MAP UNIT CODE: MAR

COMPONENTS: Michigamme - Arcadian - Rock Outcrop Association. Moderately steep to steep

SLOPES: 5 to > 35% and vertical cliffs; level to hilly.

DRAINAGE: Excessively, well, and moderately well drained.

PARENT MATERIALS: Eolian and lake terrace sediments (sandy loams to silt loams).

LANDSCAPE: Bedrock ridge.

GEOMORPHIC RELATIONS: Michigamme on upper and mid foot slopes 50–100 cm inches to bedrock; Arcadian on back slopes and terraces 25–50 cm to bedrock; Rock Outcrop on steeper slopes and erosional surfaces with < 25 cm of mineral materials.

MAP UNIT COMPOSITION: Michigamme 40%, Arcadian 15%, Rock Outcrop 30%, minor soils 30%.

MINOR SOILS: Nipissing along shorelines; Ishpeming in sandy spots shallow to bedrock, Gravaraet on deeper soils.

REFER TO SOIL DESCRIPTIONS: Michigamme, Arcadian, Rockland.

NOTE: MAR is an extensive unit common to landforms associated with post glacial lake terraces below the Lake Duluth water plane throughout the island. Tree species range from aspen-birch to spruce-fir.

LESS INTENSIVE SOIL MAPPING UNIT: HFR.

COMPONENTS: Histic Humaquepts - Froberg - Rock Outcrop Association; Nearly level to moderately steep.

SLOPES: 0 to 18% (majority are 0 to < 10%). Level to moderately steep.

DRAINAGE: Somewhat poorly drained to poorly drained soils.

PARENT MATERIALS: Sandy-gravelly, loamy tills, and lacustrine sediments (silty clay and clay).

LANDSCAPE: Old post-glacial lake basins and backwater areas; side slopes (moraines) with clayey ablation till or lacustrine clay over till.

GEOMORPHIC RELATIONS: Topographic lows on outwash plains or glacial drainage ways and abandoned post-glacial lake basins (shoreline materials and lake bed materials over till materials below Minong shoreline elevations).

MAP UNIT COMPOSITION: Histic Humaquepts 40%, Froberg 30%, Rock Outcrop 10%, minor soils 20%.

MINOR SOILS: Hettinger; Nunica, Rudyard; Pickford; Froberg, Bowers.

REFER TO SERIES DESCRIPTIONS: Bowers; Froberg; Rudyard.

NOTES: This unit is of limited extent on Isle Royale, but it includes soils on the island that have a fine-loamy, fine, or very fine particle size class. They are generally wet most of the year.

### Rudyard Series

The Rudyard series consists of very deep, somewhat poorly drained soils formed in clayey deposits on lake plains. These soils have very slow permeability. Slopes range from 0 to 4%.

Typical pedon of Rudyard silt loam, 0 to 4% slopes, NE 1/4, NE 1/4, SE 1/4 of section 5, T 65 N, R 34 W in Isle Royale National Park.

A = 0–10 cm, dark reddish gray (5YR 4/2) silt loam, reddish brown (5YR 5/3) dry, moderate medium granular structure, friable, many rounded worm casts, common fine and medium roots, strongly acid, abrupt smooth boundary.

Bt1 = 10–20 cm, reddish brown (5YR 4/4) clay, common medium distinct strong brown (7.5YR 5/6) mottles, weak fine subangular blocky structure parting to weak fine angular blocky, friable, common continuous distinct yellowish red (5YR 4/6) clay films on faces of pedons, common fine and medium roots, medium acid, gradual irregular boundary.

Bt2 = 20–50 cm, reddish brown (2.5YR 4/4) clay, common medium prominent strong brown (7.5YR 5/6) mottles, weak fine subangular blocky structure parting to weak fine angular blocky, firm, few fine roots, neutral, gradual wavy boundary.

C = 50–150 cm, reddish brown (2.5YR 4/4) clay, common medium prominent strong brown (7.5YR 5/6) mottles, greenish gray (5GY 6/1) coatings on faces of pedons, massive, firm, mildly alkaline.

The solum depth ranges from 40 to 100 cm. The A horizon has hue of 5YR or 7.5YR, value of 2 to 4 and chroma of 1 or 2.

The Bt horizons have hue of 5YR or 2.5YR; and value of 3 or 4.

The C horizon has hue of 2.5YR or 5YR; value of 4 or 5 and chroma of 3 or 4.

**Michigamme Series**

The Michigamme series consists of moderately deep, moderately well drained and well drained soils formed in a silty or loamy mantle over loamy glacial till underlain by igneous or metamorphic bedrock on ground moraines. Permeability is moderate. Slopes range from 1 to 60%.

Typical pedon of Michigamme cobbly sandy loam, 15 to 35% slopes, N 1/4, SE 1/4, of sec. 6, T. 66 N., R. 33 W.

Oa = 10–0 cm, very dark gray (5YR 3/ 1) well decomposed forest litter, weak coarse platy structure, friable, many fine and medium roots, slightly acid, abrupt smooth boundary.

A = 0–3 cm, dark gray (5YR 4/1) cobbly sandy loam, weak fine subangular blocky structure, very friable, many fine and medium roots, about 20% cobbles moderately acid, abrupt broken boundary.

Bhs = 3–20 cm, dark brown (5YR 3/3) sandy loam, weak medium subangular blocky structure, very friable, many fine and medium roots, about 10% gravel and 5% cobbles, slightly acid, clear wavy boundary.

Bs1 = 20–45 cm, dark brown (7.5YR 4/4) fine sandy loam, weak coarse subangular blocky structure, friable, common medium and coarse roots, about 10% gravel and 5% cobbles, slightly acid, clear wavy boundary.

Bs2 = 45–60 cm, dark brown (7.5YR 4/4) gravelly fine sandy loam, weak medium subangular blocky structure parting to moderate medium platy, firm, few fine and medium roots, few fine vesicular pores, about 15% gravel and 5% cobbles, slightly acid, abrupt wavy boundary.

2C1 = 60–70cm, dark brown (7.5YR 4/4) gravelly loamy sand, weak medium subangular blocky structure parting to moderate fine platy, firm, few fine vesicular pores, about 25% gravel and 5% cobbles, slightly acid, clear wavy boundary.

2C2 = 70–90 cm, dark yellowish brown (1OYR 4/4) very gravelly sandy loam, massive, firm, about 40% gravel and 5% cobbles, slightly acid, abrupt smooth boundary.

3R = 90 cm, unweathered bedrock.

Solum thickness ranges from 50 to 100 cm. Texture of the solum is sandy loam, fine sandy loam, silt loam or the gravelly or cobbly analogues of these textures. Gravel content ranges from 0 to 25% and cobble content ranges from 0 to 10% throughout. The A horizon has hue of 5YR or 7.5YR, value of 2 or 4, and chroma of 1 to 3. Some pedons have E horizons. The Bhs horizon has value and chroma of 2 or 3. The 2C horizon has hue of 7.5YR or 1OYR; and value of 3 or 4, It is loamy sand, sandy loam, or the gravelly analogues of these textures

**Froberg Series**

The Froberg series consists of very deep, moderately well drained soils formed in clayey and loamy material on lake plains. Permeability is very slow in the clayey material and moderate or moderately slow in the loamy material. Slopes range from 1 to 35%.

Typical pedon of Froberg silt loam, 1 to 6% slopes, NW 1/4, SE 1/4, SE 1/4 of S 29, T 64 N, R 38 W on Isle Royale National Park.

Oe = 2.5–0 cm, dark reddish brown (5YR 3/3) partially decomposed forest litter, weak medium subangular blocky structure, very friable, very strongly acid, abrupt wavy boundary.

A = 0–15 cm, black (N 2/0) silt loam mixed with pockets of pinkish gray (7.5YR 6/2) silt loam (E), moderate medium granular structure, very friable, many fine and medium roots, many medium rounded worm casts, very strongly acid, abrupt wavy boundary.

E = 15–28 cm, pinkish gray (7.5YR 6/2) silt loam, moderate medium granular structure, very friable, many fine and medium roots, very strongly acid, diffuse wavy boundary.

Bt1 = 28–45 cm, yellowish red (5YR 5/6) clay loam, moderate medium granular structure, firm, many fine and medium roots, very strongly acid, abrupt wavy boundary.

Bt2 = 45–60 cm, reddish brown (5YR 5/3) silty clay, common fine and medium distinct reddish brown (2.5YR 5/4) mottles, moderate medium subangular blocky structure, firm, few faint reddish gray (5YR 5/3) discontinuous clay films on pedon faces and in pores, strongly acid, clear wavy boundary.

Bt = 60–75 cm, reddish brown (5YR 4/4) silty clay, moderate medium subangular blocky structure, firm, few faint reddish gray (5YR 5/3) discontinuous clay films on pedon faces and in pores, neutral, clear wavy boundary.

2C = 75–150 cm, reddish brown (5YR 4/4) sandy loam, massive, firm, about 2% gravel, strongly alkaline.

The thickness of the clayey sediments ranges from 40 to 90 cm. The A horizon has hue of 5YR, 7.5YR or is neutral, value of 2 to 5 and chroma of 0 to 3. The E horizon has hue of 5YR or 7.5YR, and value of 5 or 6. The Bt horizon has chroma of 3–6. The 2C horizon is sandy loam, fine sandy loam, or sandy clay loam.

**Appendix Table 1.** Checklist of Soil Map Unit Michigamme – Arcadian – Rock Outcrop in Isle Royale National Park.

| Soil | Percent of Association | Depth Class | Drainage Class | Percent Slope | Texture | Parent Material | Landscape Position | Major Use | Management Concerns |
|---|---|---|---|---|---|---|---|---|---|
| Michigamme | ~40 | moderately deep | well, moderately well | 5–65 | silt loam/bedrock | bedrock <40 | hillsides, tow and foot slopes | forested | campsites, erosion, and compaction on steep slopes |
| Arcadian | ~15 | shallow | well, moderately well | 5–65 | very cobbly fine sandy loam/bedrock | bedrock <20 | hillsides, tow and foot slopes | forested | campsites, trails |
| Rock outcrop | ~30 | very shallow | well | 5–>65 | bedrock | bedrock <10 | ridges | barren | campsites, trails |

**Appendix Table 1.** *Continued.*

| Soil | Percent of Association | Depth Class | Drainage Class | Percent Slope | Texture |
|---|---|---|---|---|---|
| Minor soils | | | | | |
| Nipissing | <15 | moderately deep | well | 5–12 | very cobbly fine sandy loam/bedrock |
| Ishpeming | <15 | shallow | well | 5–35 | loamy sand/bedrock |
| Champion | <10 | very deep | well to moderately well | 3–20 | fine sandy loam/loamy sand till |

| | Parent Material | Landscape Position | Major Use | Management Concerns |
|---|---|---|---|---|
| Nipissing | bedrock <40 | flats, terraces | forested | campsites, trails |
| Ishpeming | bedrock <20 | toe slopes, upland | forested | campsites, erosion and compaction on steeper slopes |
| Champion | gr. loamy sandy till | uplands, footslopes | forested | none; erosion and compaction on steeper slopes |

**Appendix Table 2.** Checklist of Soil Map Unit Histic Humaquepts – Froberg –Rudyard in Isle Royale National Park.

| Soil | Percent of Association | Depth Class | Drainage Class | Percent Slope | Texture |
|---|---|---|---|---|---|
| Histic Humaquepts | ~50 | very deep | very poorly drained | 0–3 | organic/loamy |
| Froberg | ~20 | very deep | well to moderately well | 0–6 | clay/sandy/loam |
| Rudyard | ~10 | very deep | somewhat poorly | 0–6 | clay |

| | Parent Material | Landscape Position | Major Use | Management Concerns |
|---|---|---|---|---|
| Histic | sand, loams, clay | swales, low uplands | forested | campsites, trail locations |
| Froberg | sandy loam | flats, lake benches | forested | campsites, trail compaction/erosion on steep slopes |
| Rudyard | clay | flats, lake benches | forested | campsites, trail location and maintenance |

**Appendix Table 2.** *Continued.*

| Soil | Percent of Association | Depth Class | Drainage Class | Percent Slope | Texture |
|---|---|---|---|---|---|
| Minor soils | | | | | |
| Nipissing | <10 | moderately deep | well | 3–8 | cobbly sandy loam/ bedrock |
| Michigamme | <10 | moderately deep | well to moderately well | 3–10 | fine sandy loam/ bedrock |
| Minong | <15 | shallow | well | 5–14 | organic |
| Peshekee | <10 | shallow | well | 3–6 | fine sandy loam/ bedrock |
| Arcadian | Same as Peshekee except for a very cobbly surface <5% | | | | |

| | Parent Material | Landscape Position | Major Use | Management Concerns |
|---|---|---|---|---|
| Nipissing | cobbles | beach terraces | forested | campsites, trail on steep slopes |
| Michigamme | bedrock <102 cm | toe slopes | forested | campsites, compaction and erosion on steep slopes |
| Minong | bedrock <51 cm | ridges | forested | fragile, fire |
| Peshekee | bedrock <51 cm | shoulder | forested | campsites, trail location |