

**Effect of climate change on C:N pools in a boreal ecosystem,
Isle Royale, Michigan**

**R. Stottlemyer,
U. S. Geological Survey
240 W. Prospect Rd.
Ft. Collins, CO 80526**

**Final Report
Research Rept. #80**

February 10, 1999

Summary

In 1989, the Committee on Earth Sciences, Office of Science and Technology Policy, established an inter-Departmental, external peer reviewed, national climate change research program. Of seven science priorities, the second highest was Biogeochemical Dynamics: Terrestrial Biosphere Nutrient and Carbon Cycling. Our global change research proposed initially in 1991 and began in 1992 on Isle Royale National Park addressed this question.

The 115 ha boreal Wallace Lake watershed, one of six NPS (now USGS-BRD) long-term watershed research sites, is located in Isle Royale National Park, northwestern Lake Superior. Boreal ecosystems have large soil nitrogen and carbon reservoirs. Should climate change increase soil inorganic nitrogen (N) availability, then nutrient cycling, biomass, and below- and above-ground biodiversity will be altered. Our primary climate change research objectives were to 1) compare the relative importance of precipitation N inputs to N from soil processes, 2) quantify the effect of change in soil temperature and moisture on N mineralization, 3) determine the effect of climate change and increased N on the ecosystem carbon (C) budget, and 4) assess whether climate change could make this boreal ecosystem a net C sink or source. The emphasis in this phase of study was on the nitrogen cycle response to climate change. All study was conducted within the Wallace Lake watershed, and experiments repeated in the laboratory. Selected Wallace climate change studies were also initiated in other northern ecosystems (Fraser, CO, Noatak, AK) with additional support.

The Wallace Lake watershed ecosystem strongly retains atmospheric N inputs. Soil N mineralization rates were 10 times precipitation inputs. Soil gross N mineralization rates increased with temperature. Over-winter soil N mineralization was significant because of unfrozen soils. The peak in spring soil N mineralization was concurrent and related to streamwater N concentration and output. The ecosystem C budget appeared near balance. However, soil and fine root respiration (CO_2 efflux) increased with temperature. Streamwater dissolved organic carbon (DOC) export was 16% above-ground C cycling, and appeared to increase with increased soil temperature. The relatively high atmospheric N inputs appear to have little direct effect on surface water chemistry or the aquatic ecosystem. However, the high retention of atmospheric N by the terrestrial system suggests likely changes in below and above-ground biomass and biodiversity have and are occurring.

Introduction

The boreal biome covers 15 M km², 11% of the earth's land area second in extent only to tropical forest (Olson et al. 1983). Molot and Dillon (1996) estimate boreal lakes cover 10% of the biome area. The boreal biome also contains the world's largest wetland expanse. Boreal C pools above-ground are estimated at 64 Gt, in soils 247-286 Gt, peatlands 419 Gt, and in lake sediments 120 Gt for a total of >825 Gt. The boreal forests are a major component of north temperate forests, and may equal oceans as a CO_2 sink, or 50% of the missing sink for excess CO_2 now generated from fossil fuels.

The boreal ecosystem has large, mostly unavailable organic reservoirs of carbon, nitrogen, and phosphorus (Rutkowski and Stottlemeyer 1993). Typically, >95% of total ecosystem nitrogen, phosphorus, and carbon is found in soil organic matter (SOM) (Shaver et al. 1992). The nutrient and C storage in SOM pools is a function of high soil moisture and low temperature which slow decomposition. The percentage of ecosystem organic pools stored in the soil increases with latitude further limiting nutrient availability.

Linked forest productivity/soil process models suggest that the southern boreal ecosystem fringe could be the most sensitive of eastern North American forests to climate change (Pastor and Post, 1988; Solomon, 1988). The rate of climate change in this region may be more significant than its magnitude (Solomon and Bartlein, 1992). Unfortunately, the boreal ecosystem has been little studied outside of Alaska (Botkin and Simpson, 1990; Mooney et al., 1991; Strain and Bazzaz, 1983).

Change in ecosystem C is dependent on nutrient status especially available inorganic N (NO_3^- , NH_4^+). Global climate scenarios for the Upper Great Lakes region fail to take into account present atmospheric contaminant inputs of N ($>6 \text{ kg ha}^{-1} \text{ yr}^{-1}$), a level which exceeds the ecological requirements of all major boreal forest species. Almost half this inorganic N input is high energy NH_4^+ possibly preferred by boreal conifers (Reuss and Johnson, 1986). It has been thought that much of this N would be unavailable to forest species, but $>10 \text{ y}$ of boreal watershed-level study shows strong ($>90\%$) N retention (Stottlemeyer et al., 1984; Stottlemeyer and Hanson, 1989; Stottlemeyer and Toczydlowski, 1991).

The effect of chronic N input to northern forested ecosystems appears nonlinear, and conifers appear more responsive than northern hardwoods (Aber et al., 1993; Gundersen, 1991). Due to its ecotonal nature, the Upper Great Lakes region is characterized by large differences among major forest species in potential N mineralization and nitrification rates (Zak et al., 1986). Species variation in response to climate change in the region appears more important than site variation, and groups of species can be separated based upon growth response to climate over time (Graumlich, 1993). Extreme climate events appear especially important in creating a growth response, and some evidence now exists showing species response to the decline in precipitation and increase in temperature of the past decade (Graumlich, 1993; Jones et al., 1993). The complexity of species interaction with both climate change and increased atmospheric N inputs in an ecotonal region point out the need for additional study of major forest species potential response to both climate change and continued high nitrogen inputs especially in the southern boreal fringe.

The primary research objectives in our 1992 global change proposal for Isle Royale National Park were to 1) quantify, over a multi-year period, the amounts of inorganic nitrogen (N) cycled and available from soil and forest floor organic mineralization, 2) determine how soil N mineralization rates respond to change in temperature and moisture, 3) compare the soil N amounts to atmospheric N inputs, and 4) examine what climate change scenarios might alter the boreal ecosystem from a carbon (C) sink to a source.

Site Description

The Wallace Lake watershed ($48^\circ 03' \text{ N}$, $88^\circ 38' \text{ W}$) is located in Isle Royale National Park, northwestern Lake Superior. The watershed is underlined by metamorphosed ophiitic flood basalts covered by scattered alkaline glacial till originally derived from limestone bedrock immediately south of James Bay. The soils are 3000-5000 y old, Alfic Haplorthods, sandy to coarse loamy, mixed and frigid. They are predominantly of the Michigamme-Arcadian-Rock Outcrop Association (Shetron and Stottlemeyer 1991). The surface O horizons have the highest percentage organic matter content (Stottlemeyer and Hanson, 1989). In mineral soil horizons, the A and Bhs under aspen/birch have the highest organic matter content. Calcium is the most important exchangeable cation.

Isle Royale lies within the vegetational transition zone between the boreal forest found on the north shore of Lake Superior and the northern deciduous forest which predominates the lake's south and eastern shores. The 176 ha Wallace Lake watershed is dominated by the boreal forest formation. The overstory is a mixture of white birch (*Betula papyrifera* Marsh.), quaking aspen (*Populus tremuloides* Michx.), white spruce (*Picea glauca* (Moench) A. Voss) and balsam fir (*Abies balsamea* (L.) Mill.). Scattered stands of white cedar (*Thuja occidentalis*) also exist within the watershed. There has been no known direct human disturbance of the watershed except for a small portion of the drainage burned in 1936.

These boreal forests contain 10 canopy species with an above-ground biomass of 108 t ha^{-1} while nearby mature northern hardwoods have about 15 species and a biomass $>250 \text{ t ha}^{-1}$ (Rutkowski and Stottlemeyer, 1993). The boreal understory has a larger number of saplings and much greater biomass (2275 kg ha^{-1}) than does northern hardwoods (85 kg ha^{-1}). Its vascular ground cover also contains more biomass (1180 to 34 kg ha^{-1} for northern hardwoods). The boreal forest floor contains 21% of the

above-ground biomass, the largest above-ground N pool (390 kg ha^{-1} in Oa), and 68% of above ground N.

It is difficult to show differences in N dynamics unless the study plots occur on relatively similar soils and in a similar climate. Variation in the elevation among all study plots was $<10 \text{ m}$. All plots were located in the Michigamme-Arcadian-Rock Outcrop Association, a combination of scattered rock outcrops and moderately steep, shallow to moderately deep, well drained loamy soils on moraines. All plots were within 300 m of Wallace Lake, a sheltered interior lake.

Methods

A few of the key watershed monitoring methods are summarized here since they provided some context for the global change research on soils conducted at Wallace Lake. For an overview of all monitoring methods at Wallace Lake, see Stottlemeyer et al. (1998).

Precipitation

Precipitation amount and its chemistry are quantified for Wallace to estimate ecosystem inputs. Prior to initiation of the Wallace study there were no continuous year-round climate data for Isle Royale. The National Oceanographic and Atmospheric Administration (NOAA) also operates year-round weather stations at Grand Marais, MN, 142 km west of Wallace, and at the Houghton County airport 100 km south of Wallace and 6 km from the USGS-BRD Calumet watershed on Michigan's Keweenaw Peninsula. These stations record precipitation amount. Year-round precipitation data are also available from Thunder Bay, Ontario, 62 km to the northwest. We monitor year-round precipitation amount and chemistry at Wallace Lake, a record which began in June 1982. In 1986, the National Park Service moved the National Atmospheric Deposition Program (NADP) station MI97 from Windigo to the Wallace Lake watershed. This station is co-located with the primary meteorological station in the watershed, but with limited winter access NADP station MI97 is only operated May through October.

There are two meteorological stations in the Wallace Lake watershed. The primary and fully automated station operates just west of the lake. This station is equipped with a 3.2 m meteorological tower which monitors wind speed and direction (Met One Instruments), solar radiation (LiCor pyranometer), relative humidity (Met One), precipitation amount, and air and mineral soil (5 cm depth) temperatures (LiCor thermistors). Precipitation amount is recorded using two unshielded Belfort raingages. One raingage is attached to the LiCor datalogger used with the meteorological station. The other is chart-driven used as backup and for the seasonally operated NADP station MI97. Meteorological sensors are calibrated annually.

Limited winter access requires precipitation chemistry be measured with bulk collectors. In winter, the collector, a 1.5 m long, 20.5 cm diameter tube, is fitted with custom polyethylene liners. In summer, the collector is a plastic, 10 cm diameter tube fitted with funnel and pre-rinsed ashless filter to reduce evaporation and dust entry. The raingage is changed weekly, and filters and raingage tube washed in deionized water before use. Samples are collected monthly January through March, and weekly from late April to October. The elevation of the collectors is 210 m or about 20 m above the mean elevation of Lake Superior. We also operate NADP station MI99 (Chassell, MI) year-round on the campus of Michigan Technological University. This is the closest year-round NADP station to Wallace (distance 107 km), and provides reference precipitation chemistry for Wallace and our laboratory QA/QC procedures.

Streamwater

Streamwater discharge from the watershed is continuously measured year-round using Parshall flumes (46 cm wide at station W2, 15 cm at station W1) equipped with Stevens F recorder (1982-1990) or

Stevens pressure transducer and LiCor model 1000 datalogger (1990 to the present). Ice blockage is not a major problem, and the flumes are unheated.

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

Laboratory Analyses of Precipitation and Streamwater

In summer, samples are brought immediately to the Boreal Research Station on Davidson Island. In winter, samples are 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) are determined as soon as samples reach room temperature. Separate filtered (pre-rinsed, 0.45 μm) subsamples (amber 60-ml linear polyethylene bottles) for ion analyses are refrigerated at 2° C. The filtered subsamples were shipped in coolers to our laboratory at Michigan Technological University, Houghton, MI, from 1982-1990. Since 1990, samples are shipped refrigerated to the U.S. Forest Service Rocky Mountain Research Station Water Quality laboratory, Ft. Collins, CO. Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NH_4^+ , NO_3^- , SO_4^{2-} , and Cl^- concentrations are determined using a Dionex Model 2020 ion chromatograph (Dionex Corp, Sunnyvale, CA; Johnson and Haak 1983). Laboratory and field sampling procedures remained constant during the study.

Whole water subsamples for total N and P are kept frozen until analyzed (autoanalyzer) as are filtered subsamples for DOC determinations (Dohrman 80 carbon analyzer, successor models, now Sievers Model 600). Heavy/trace metal analyses are conducted on acidified (pH <2, Ultrex) samples analyzed by Inductively Coupled Plasma Emission Spectroscopy (ICPE).

Soil Processes

From May 1992 to May 1997, monthly soil inorganic nitrogen (N) pools and net N mineralization/nitrification rates were determined at replicated plots beneath birch, spruce, and alder at Wallace, and beneath maple stands 2 km east of Windigo (Stottlemeyer et al. 1995). The five-year study attempted to explain some of the processes which may account for seasonal trends observed in streamwater NO_3^- concentrations in a boreal forested watershed. The study objectives were 1) to compare seasonal precipitation N inputs to trends observed in soil available N pools, net mineralization and nitrification rates, and N in streamwater, and 2) relate changes in soil N pools and net mineralization and nitrification rates to soil temperature and moisture. During the last two years of study, field gross N mineralization and immobilization rates were quantified to examine seasonal change in total nitrogen cycled in forest soils. Within each major species type, three 0.1 ha (20 X 50 m) plots were randomly located along transects for a total of 12 plots. Plots for a given species type were about 100 m apart. On each plot a LiCor datalogger with five temperature sensors (thermistors at 5 and 10 cm depth beneath the organic layer, in the forest litter, 10 cm and 1.3 m above the forest floor) was installed the last week in May, and operated until the third week of October each year. Dataloggers were left in place for over-winter monitoring at one of the three plots in each species types. Daily mean temperatures were logged throughout the study. For soil temperatures, the mean temperature at 5 cm, 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 type were estimated using the buried polyethylene bag technique (Eno, 1960). Within each 0.1 ha plot, three 25 m² subplots were established. Each month from May to October, a site for soil sampling and incubation was

randomly selected within each subplot. After pulling back the surface organic layer or O1 (also called Oi or litter layer), the upper 10 cm consisting of the O2 (litter fragments and humus or Oa and Oe) and mineral soil was 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 located on Davidson Island 10 km northeast of Wallace. The other was placed in a polyethylene bag and returned to the same hole for incubation, and the surface organic matter replaced. After 30 d, the field incubated sample was collected for analyses. Due to limited winter access, for over-winter sampling three sets of incubation samples were placed in each subplot in late October. 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 20° 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 to 30 h) a subsample. Bulk density was calculated from total oven dry weight/total soil volume. A larger subsample was separated in a 2-mm sieve. The >2-mm fraction was weighed. The <2-mm material was weighed and divided into two samples; one extracted for NO_3^- and NH_4^+ using 2M KCL, the other frozen for total N determination.

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

Field gross N mineralization, nitrification, and immobilization rates were studied in 1995-1996. 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 June of 1996.

On each date, the methods described above for net mineralization and nitrification study were carried out. Initial soil inorganic N pools were determined, and a 30-d net mineralization and nitrification incubation started. In addition, a separate set of intact soil cores was collected immediately adjacent the net incubation samples and processed as follows. Using a needle (spinal needle, 18 gage, 10 cm length) and syringe, one intact core received a 6-ml aliquot of $\text{Na}^{15}\text{NO}_3$ solution providing about $2\mu\text{g N g}^{-1}$ of dry soil. A separate intact core received 6 ml of $(^{15}\text{NH}_4)_2\text{SO}_4$ again providing about $2\mu\text{g N g}^{-1}$ of dry soil. ^{15}N solution injections were one ml each, and spaced around the core. ^{15}N enrichment in the $\text{Na}^{15}\text{NO}_3$ and $(^{15}\text{NH}_4)_2\text{SO}_4$ solutions was 99%.

After a 24-h incubation period, the cores were collected, taken to the Boreal Research Station, mixed, and a subsample extracted using 2M KCl. After a minimum of one-h of mixing, all solutions were filtered through Whatman #1 filters prerinsed with KCl. NH_4^+ 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.

Gross NH_4^+ consumption and mineralization rates were calculated for the cores labeled with $^{15}\text{NH}_4^+$ using the isotope dilution method of Kirkham and Bartholomew (1954), and the gross NO_3^- consumption and mineralization rates were calculated for the $^{15}\text{NO}_3^-$ labeled cores using the same method but

replacing NO_3^- values for NH_4^+ . The assumptions used 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 type. The study was conducted one day each month from May through October, 1993-1996, on each N incubation plot in Wallace. Our objective was to use soil CO_2 evolution as an index of soil respiration, its change with temperature, and relationship to nitrogen mineralization rates (Cropper et al. 1985, Ewel et al. 1987). Rates of soil CO_2 evolution are dependent on the method used (Cropper et al. 1985, Raisch and Nadelhoffer 1989). We used the static method in this study rather than the dynamic (IRGA system) method because there is 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. At Wallace, three 11 L chambers each covering 0.054 m^2 area were placed at random in each plot. At the beginning of each incubation period, a container with 60 g KOH and 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 reweighed 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 air-tight 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.

Additional Laboratory Analyses of Soil Samples

For soil inorganic N content (available nitrogen pools), 5 g soil subsamples were extracted with 50 ml of 2M KCl, and NO_3^- (cadmium reduction) and NH_4^+ (indophenol) determined on the Lachat autoanalyzer. The net total inorganic N mineralized for each incubation period was estimated from the difference between initial and final NO_3^- and NH_4^+ content, and net NO_3^- mineralization estimated by the difference between initial and final NO_3^- content (Binkley et al. 1994). Total N was determined using Kjeldahl digestions (Hauck et al. 1994) early in the study. We now use a Leco CHN analyzer. Quality assurance on the Lachat includes running control standards every 10 samples, ten duplicates in each block of approximately 40 samples, and 10% reruns. In each total N digestion block set, six of the 40 samples are duplicates.

Soil Data Analyses

In the field studies to determine soil respiration, net and gross N mineralization or nitrification, or nutrient pools, the three subplot soil samples from each vegetation plot were averaged, giving an n of three (three plots) for each species type each sample date. When testing for the need to apply repeated measures analyses, each plot was checked for correlation with time (months) for all variables measured. Generally, correlation was not significant with time, and repeated measures analysis was not used. For monthly analyses among species types, 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).

Results

Here I summarize the research results primarily related to global change and soil processes. For more specific results, one is referred to the journal papers in particular Stottlemeyer et al. (1995a & b; 1998) and Stottlemeyer and Toczydlowski (1999a & b) (see Literature Cited below).

Precipitation

For the period 1950 to 1996, annual precipitation amount at the Houghton County airport NOAA station averages 87 cm (range 63 - 136 cm). Since 1982, annual precipitation declines ($p < 0.05$, $r^2 = 0.31$, $b = -2.6$ cm). The decline is most pronounced in November and December. The December decrease is about 1 cm yr^{-1} ($p < 0.05$, $r^2 = 0.32$). For the same period, annual precipitation amount at Grand Marais, MN, averages 66 cm (range 42 - 101 cm). Since 1982, annual precipitation amount at Grand Marais declines 0.5 cm yr^{-1} , but the decrease is not significant. Most of the decrease (0.2 cm yr^{-1}) occurs in November. Since 1982, annual precipitation amount at Wallace Lake averages 75 ± 15 cm (standard deviation) (range 57 - 104 cm), and also declines about 1.5 cm yr^{-1} , but the trend is not significant ($p = 0.2$). At Wallace, winter precipitation (Nov. - April) averages 29 cm or 39% of annual. Mean monthly winter precipitation amount is 77% the monthly average for the year. Monthly precipitation amount increases from March through November. There is precipitation each month with the greater amounts in late summer and fall. In the year of highest precipitation (1984) since the study began, precipitation was >11 cm in June and August, and >16 cm in November. The long-term average precipitation for these months is <8 cm.

At Wallace Lake, since 1982 the annual precipitation amount follows the trend seen at the Houghton County airport NOAA station on the south shore. The seasonal pattern of precipitation amount since 1982 closely follows NADP station MI99, but averages 15% less.

Volume-weighted H^+ concentration (mean $0.15 \mu\text{eq L}^{-1}$, $\text{pH} = 4.94$) in NADP MI99 wet precipitation shows no trend with time. H^+ concentration (mean $28 \mu\text{eq L}^{-1}$, $\text{pH} = 4.55$) at the MI99 bulk collector declines ($p < 0.01$, $r^2 = 0.71$, $b = -2.0 \mu\text{eq L}^{-1} \text{yr}^{-1}$) since 1988. Volume-weighted H^+ concentration (mean $35 \mu\text{eq L}^{-1}$, $\text{pH} = 4.45$) also declines in the bulk precipitation collectors at Wallace ($p < 0.05$, $r^2 = 0.26$, $b = -1.2$) and Windigo ($p < 0.10$, $r^2 = 0.32$, $b = -4.0$) (mean $37 \mu\text{eq L}^{-1}$, $\text{pH} = 4.43$).

Precipitation NH_4^+ and NO_3^- concentrations show no significant trends at any monitoring station. NH_4^+ concentrations at most stations show a slight, but non-significant, increase since the early 1980's. At Wallace, the $\text{NH}_4^+/\text{NO}_3^-$ and $\text{NO}_3^-/\text{SO}_4^{2-}$ ratios (equivalent basis) increase since 1982, but the trends are not significant.

Annual volume-weighted wet precipitation SO_4^{2-} concentration at NADP MI99 declines ($p < 0.01$, $r^2 = 0.51$, $b = -0.95$) since 1982. At the MI99 bulk collector, SO_4^{2-} concentration also declines ($p < 0.08$, $r^2 = 0.43$, $b = -1.7$) as it does at Wallace ($p < 0.05$, $r^2 = 0.25$, $b = -0.8$) for the period 1982-1996, and at Windigo ($p < 0.05$, $r^2 = 0.52$, $b = -3.0$) for the period 1980-1988.

Seasonal (monthly) change in precipitation ion concentration is pronounced. In bulk collectors, base cation (C_B), H^+ , NH_4^+ , and SO_4^{2-} concentrations generally increase during spring and peak in early summer. Winter precipitation has a higher $\text{NO}_3^-/\text{SO}_4^{2-}$ ratio (0.78) than non-winter (0.45) or annual precipitation (0.57). During summer months, the only season the Wallace NADP station MI97 is in operation, bulk collectors show much higher C_B and H^+ concentrations than do the NADP event collectors, similar or reduced NH_4^+ concentrations, and similar NO_3^- and SO_4^{2-} concentrations.

Except for C_B , annual precipitation ion input at Wallace declines during 1982-1996. The declines are significant for H^+ ($p < 0.01$, $r^2 = 0.49$), NO_3^- ($p < 0.08$, $r^2 = 0.24$), and SO_4^{2-} ($p < 0.05$, $r^2 = 0.37$). A decrease in precipitation amount primarily accounts for the decline in ion input. However, the decline in H^+ , NO_3^- , and SO_4^{2-} inputs exceeds the decrease in precipitation amount.

Except for NH_4^+ and NO_3^- inputs, seasonal change in ion input also largely reflects change in monthly precipitation amount. Except for NH_4^+ , monthly input and variation in inputs are less in winter than summer.

Streamwater

Annual streamflow (mean 51(15) cm, range 30 - 77 cm) varies more (S.D. = 30% of mean) than annual precipitation. The mean ratio of streamflow to precipitation is 0.68(0.11) (range 0.53 - 0.89). There is a significant relationship between annual streamflow and precipitation amount. Outlier years are 1990, 1992, 1993, and 1996. Two years (1993, 1996) had higher than expected streamflow relative to precipitation inputs, and two (1990, 1992) had lower. The lowest ratio was in 1990, the year of least total precipitation. The highest ratio of streamflow to precipitation was in 1996. The year of highest precipitation input and streamflow (1984) plotted on the regression line.

At Wallace, volume-weighted streamwater C_B concentrations increase during the period 1982-96, but no trend is significant. Streamwater NO_3^- concentration shows the least change of any ion with time. SO_4^{2-} concentrations decline, but no trends are significant.

Up through 1995, annual volume-weighted DOC concentrations at gauging station W2 declined ($p < 0.01$, $r^2 = 0.68$, $b = -0.6$). Unlike C_B concentrations, DOC concentrations increase with stream discharge ($p < 0.001$, $r^2 = 0.89$). Similarly, streamwater total N concentration increases with discharge ($p < 0.001$, $r^2 = 0.21$) as does total metal concentrations such as Al ($p < 0.001$, $r^2 = 0.42$, $b = 0.26$).

Seasonal variation in Wallace streamwater ion concentration reflects hydrology and biological activity. Snowmelt brings major change in streamwater concentrations of most ions. C_B and HCO_3^- concentrations decline 20% and 31% from March means. During snowmelt, the average acid neutralization capacity (ANC) decreases 490 $\mu eq\ l^{-1}$, 98% from dilution of streamwater C_B and HCO_3^- concentrations. NH_4^+ concentration increases slightly gaining about 0.1 $mg\ l^{-1}$ from December to March. NH_4^+ concentration sharply declines with snowmelt and increased streamflow. At station W2, NO_3^- concentration increases just before peak snowmelt, and SO_4^{2-} concentrations increase at both W2 and W1 during peak snowmelt and streamflow. Streamwater DOC concentrations decline slightly in April, but are at the highest concentrations during May and June, months of relatively high streamwater discharge.

There is no significant trend in streamwater NH_4^+ output with time. Watershed output declines from 1982 to 1991 then increases. The trend in streamwater NH_4^+ output is correlated to annual precipitation amount ($p < 0.01$, $r^2 = 0.53$). There is no significant correlation between annual NH_4^+ inputs and streamwater outputs. The watershed retains >75% NH_4^+ inputs (75 $eq\ ha^{-1}$).

For the period 1982-1995, there is no significant trend in streamwater NO_3^- output from Wallace. Including 1996, there is a slight increase ($p < 0.1$, $r^2 = 0.24$, $b = 3.5\ eq\ ha^{-1}$). Annual watershed NO_3^- output is not correlated to precipitation amount, but is correlated to streamwater discharge ($p < 0.01$, $r^2 = 0.54$). NO_3^- output from W1 is correlated to precipitation amount ($p = 0.05$, $r^2 = 0.32$), but not precipitation NO_3^- concentration or inputs which decline. Precipitation NO_3^- input in 1996 is about average for Wallace, but streamwater output is 3 times the previous annual peak and about equals 1996 input. Net annual watershed NO_3^- retention is 110 $eq\ ha^{-1}$ or 75% of precipitation input.

Snowmelt has the most pronounced effect on seasonal ion output from Wallace. NH_4^+ and NO_3^- are the only ions where the annual concentration pattern approximates monthly ion output. Cumulative winter precipitation NH_4^+ inputs average 52 $eq\ ha^{-1}$, while snowpack PWE content averages just 18 $eq\ ha^{-1}$. April NH_4^+ output from Wallace is <30% peak snowpack content and <10% of cumulative winter precipitation inputs.

Seasonal streamwater NO_3^- output from Wallace peaks in April at about 11 $eq\ ha^{-1}$ which is <20% of cumulative winter precipitation inputs and <40% of average snowpack PWE NO_3^- content. April is the only month where streamwater NO_3^- output almost equals input.

Soil Processes

Mean soil moisture is highest ($p < 0.001$, $r^2 = 0.44$) beneath alder (Stottlemeyer et al. 1995). Soil moisture beneath alder is higher ($p < 0.05$, $r^2 = 0.70$) all months except October, and is saturated during and following snowmelt. Soil bulk density is lowest in alder ($p < 0.001$, $r^2 = 0.23$). Total soil N concentration differs by species type ($p < 0.001$, $r^2 = 0.31$) with values higher in alder and maple ($p < 0.01$) than spruce and birch. Mean annual soil temperatures do not significantly differ by species type, but in May soil temperatures beneath spruce are lower ($p < 0.001$, $r^2 = 0.90$). Except beneath spruce, soils do not freeze. Unfrozen soils permit overwinter processes as N mineralization and nitrification to occur which result in high net mineralization rates.

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

Monthly net NO_3^- mineralization rates differ by species type ($p < 0.001$, $R^2 = 0.42$, $n = 107$), and are highest ($p < 0.001$) beneath alder. Monthly net NO_3^- mineralization rates are greater during winter beneath alder, birch, and spruce, but no trends are significant. Net NH_4^+ mineralization and total net inorganic N mineralized do not significantly vary by species type, but do by month ($p < 0.05$, $R^2 = 0.16$, $n = 109$). Monthly rates are higher ($p < 0.05$) October-January than July and August.

Soil NO_3^- pools and net NO_3^- mineralization rates are inversely related for all species types. The relationship is significant for birch, alder, and maple. Soil NH_4^+ pools and net NH_4^+ mineralization rates are inverse for birch, spruce, and maple as are total inorganic soil N pools and net inorganic N mineralization rates.

Monthly net NO_3^- mineralization rates and mean soil temperature at 5 cm depth are inverse ($p < 0.05$) for birch, spruce, and alder. The relationship between monthly net NH_4^+ mineralization, total inorganic N mineralization, and soil temperature is inverse beneath spruce and alder.

Annual net N mineralization, averaged for all species types in this multi-year study, is 1.4 g N m^{-2} . For the dominant boreal species, birch and spruce, the rate is 1.1 g N m^{-2} .

Laboratory incubations, where only temperature and moisture are varied, show a significant increase in birch, spruce, and maple net NH_4^+ (equivalent to $18 \text{ mg N m}^{-2} \text{ d}^{-2}$, $p < 0.01$, $r^2 = 0.51$) and total inorganic N mineralization with temperature (equivalent to $22 \text{ mg N m}^{-2} \text{ d}^{-2}$, $p < 0.01$, $r^2 = 0.32$), and some increase in net NO_3^- mineralization ($12 \text{ mg N m}^{-2} \text{ d}^{-2}$, $p < 0.05$, $r^2 = 0.17$) with increased moisture in spruce and maple (Stottlemeyer et al. 1995). Most of the increase in inorganic N mineralization occurs in the mid temperature range (from 10 to 15°) and mid moisture level. Soil net NH_4^+ mineralization increases in birch ($24 \text{ mg N m}^{-2} \text{ d}^{-2}$, $p < 0.01$, $r^2 = 0.64$) and spruce ($21 \text{ mg N m}^{-2} \text{ d}^{-2}$, $p < 0.05$, $r^2 = 0.45$) with temperature, and net soil inorganic N mineralization increases in birch ($23 \text{ mg N m}^{-2} \text{ d}^{-2}$, $p < 0.001$, $r^2 = 0.64$, $n = 27$) with temperature and spruce with moisture (equivalent of $13 \text{ mg N m}^{-2} \text{ d}^{-2}$, $p < 0.05$, $r^2 = 0.47$).

Gross nitrification rates differ by species type ($p < 0.001$, $r^2 = 0.62$). Nitrification rates beneath alder are higher than birch ($p < 0.001$) or spruce ($p < 0.001$). Among all species types, there is no significant seasonal trend (May - October, no winter measurements) in gross nitrification rates. Beneath birch, the seasonal change in gross nitrification rates are significant ($p < 0.05$, $r^2 = 0.60$) with rates higher ($p < 0.05$) in June than October. Beneath spruce and alder seasonal change in gross nitrification rates are not significant.

Gross N mineralization rates do not significantly differ by species type. Seasonally, gross mineralization rates vary ($p < 0.05$, $r^2 = 0.70$) beneath spruce with rates higher ($p < 0.05$) in July than June. NH_4^+ immobilization rates differ by species type ($p < 0.01$, $r^2 = 0.30$, $n = 37$) with rates higher ($p < 0.01$) beneath alder than spruce and birch. There are no significant seasonal trends in NH_4^+ immobilization rates for any species type.

Soil respiration, as indicated by daily CO_2 efflux, is correlated (Pearson, $p < 0.001$) to mean soil temperature at 5 cm depth. Gross NH_4^+ mineralization rates are correlated to soil temperature ($p < 0.08$) as are NH_4^+ immobilization rates ($p = 0.05$). Soil respiration is correlated to gross NH_4^+ mineralization ($p < 0.05$) and inversely to NO_3^- immobilization ($p < 0.10$). NH_4^+ immobilization rates are correlated with gross nitrification rates ($p < 0.01$) and NO_3^- immobilization ($p < 0.05$). Gross nitrification rates are correlated to NO_3^- immobilization ($p < 0.001$). By species type, the Bartlett Chi-square tests suggest the correlation matrices are not positive definite and any correlations suspect.

Watershed N Budget

For nitrogen (N), atmospheric inputs are $3.5 \text{ kg ha}^{-1} \text{ yr}^{-1}$. About 60% of the elemental N comes from NO_3^- input and 40% from NH_4^+ , but the proportion from NH_4^+ increases during the study period. On average, annual NH_4^+ flux slightly increases in canopy throughfall relative to precipitation due to increased NH_4^+ flux from spruce. However, birch retains precipitation NH_4^+ and alder alters NH_4^+ flux little. Conversely, spruce and birch canopies strongly retain NO_3^- ($5.4 \text{ kg ha}^{-1} \text{ yr}^{-1}$), as does alder ($3.6 \text{ kg ha}^{-1} \text{ yr}^{-1}$). On average, the canopy retains about 0.5 kg of precipitation N $\text{ha}^{-1} \text{ yr}^{-1}$. Above-ground N uptake is estimated at $33 \text{ kg ha}^{-1} \text{ yr}^{-1}$. Soil water inorganic N flux at the 30 cm depth is $0.9 \text{ kg ha}^{-1} \text{ yr}^{-1}$. The extractable inorganic N from the top 10 cm of Oe, Oa and mineral soil averages $26.7 \text{ kg N ha}^{-1}$ (Stottlemeyer et al. 1995). Watershed NH_4^+ output is $0.3 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ and NO_3^- 0.5 kg N ha^{-1} for a total of $0.8 \text{ kg N ha}^{-1} \text{ yr}^{-1}$. The watershed retains about 77% of bulk precipitation N input.

Discussion and Conclusions

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. Due to its ecotonal nature, the Upper Great Lakes region is characterized by large differences among forest ecosystems in potential N mineralization and nitrification rates (Zak et al. 1986). This information need led to our intensive studies of soil N mineralization rates and their response, both *in situ* and in the laboratory, to change in temperature and moisture.

In Wallace, the higher surface soil moisture content observed in mid-May and June reflects snowmelt inputs, an increase in seasonal rain input, and low evapotranspiration due to the absence of leaves. Site topography and low soil bulk density contribute to the high soil moisture beneath alder. Alder stands in Wallace usually occur on low elevation, relatively flat sites once flooded by beaver dams. The general soil moisture increase in fall reflects increased precipitation, reduced evapotranspiration, and lowering temperatures. Soil moisture is most variable beneath birch. Birch is characterized by a patchy canopy which leads to high variation in radiation input and greater spatial variation in distribution of understory biomass (Rutkowski and Stottlemeyer 1993).

Beneath hardwoods, the rapid soil temperature increases in May are in response to the loss of snowpack and the absence of canopy shading. The reduced temperature increase beneath alder sites likely reflects their high soil moisture and lowland topography which permits seasonal pooling of cool air.

At Wallace, the seasonal trend in soil inorganic N concentration is similar to other studies in unmanipulated forests (Nadelhoffer et al. 1984, Pastor et al. 1984). Soil NH_4^+ concentrations are larger

and more variable than NO_3^- with the highest total inorganic N content in spring and early summer, and the lowest in mid-summer.

Net soil N mineralization data provide a useful index of N supply as they primarily represent the cumulative difference between N immobilization and mineralization. The inverse correlation of monthly soil inorganic N concentrations and mineralization beneath alder and maple indicate the potential importance of microbial immobilization especially late in summer, fall, and early winter. High mineralization generally is followed in a month or so with increased soil inorganic N concentrations.

It appears low soil temperatures in winter inhibit microbial immobilization more than mineralization. This is most evident beneath alder. With warming soil temperatures beneath alder, net inorganic N mineralization declines during May, June, and early July. This suggests soil microbial immobilization exceeds mineralization with warming temperatures, and readily mineralized organic N becomes limiting. Net N mineralization rates decline beneath maple after mid May and beneath birch and spruce after mid June, concurrent with warming soils and declines in soil moisture. The spring release of snowpack inorganic N solutes (Stottlemeyer and Hanson, 1989), which can be up to 150 mg N m^{-2} , would add to available soil inorganic N. Much of this is NO_3^- , and soil NO_3^- concentrations do slightly increase by mid May in Wallace.

Beneath alder, nitrogen fixation may account for the high soil NO_3^- levels relative to other species types. If one estimates annual alder N fixation using the approach of Binkley et al. (1994 b), based upon alder foliage biomass in this watershed (Rutkowski and Stottlemeyer 1993), fixation would be approximately 1.5 g N m^{-2} . This is at the low end in fixation rates for this species.

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

For dominant forest species types at Wallace, net mineralization rates are a small fraction of gross mineralization rates indicating a much higher internal cycling of N than net mineralization and nitrification rates suggest. The small NO_3^- pool size and low net nitrification rates in soils beneath spruce might indicate NO_3^- cycling is not important for this species. However, gross nitrification rates were more similar among species. Our results indicate large seasonal responses in gross mineralization and nitrification rates likely due to temperature. It appears small increases in soil temperatures from warming air temperatures shortening the snowpack season and/or directly increasing the soil temperature, especially in late spring and early summer, will markedly increase internal N cycling rates at Wallace.

To conclude, atmospheric N inputs as NO_3^- or NH_4^+ do not appear to have a direct or indirect effect on seasonal or annual trends in surface water chemistry. The probability of atmospheric N inputs affecting aquatic production or diversity also appears minimal despite the chronic and relatively high precipitation inputs. However, the strong terrestrial ecosystem retention of atmospheric N inputs suggests this limiting nutrient is affecting terrestrial biomass and biodiversity. Based upon the soil N immobilization results, the main impact of atmospheric N inputs at present would appear to be on soil microbial communities and function. But, since the soil microbial community regulates the quantity and quality of N and carbon available to the above-ground community, effects on the soil microbial community will be felt above-ground in time if not already present. The strong increase in ecosystem cycling of available N with small increases in soil temperature indicates climate change has much more potential to affect the biodiversity, biomass, and basic ecosystem functioning of Isle Royale National Park than predicted increases in precipitation N inputs from human activity.

Literature Cited

- Aber, J. D., A. McGill, R. Boone, J. M. Melillo, P. Steudler, and R. Bowden. 1993. Plant and soil responses to chronic nitrogen additions at the Harvard Forest, Massachusetts. *Ecol. Appl.* 3(1):156-166.
- Binkley, D., R. Stottlemeyer, F. Suarez, and J. Cortina. 1994 a. Soil nitrogen availability in some arctic ecosystems in northwest Alaska: Responses to temperature and moisture. *Ecoscience* 1(1):64-70.
- Binkley, D., K. Cromack, Jr., and D. D. Baker. 1994 b. Nitrogen fixation by red alder: Biology, rates, and controls. In: *Biology and management of red alder*, D. Hibbs, D. DeBell, and R. Tarrant (eds), Oregon State Univ. Press, Corvallis, OR, p. 57-72.
- Botkin, D. B., and L. G. Simpson. 1990. Biomass of the North American boreal forest. *Biogeochemistry* 9:161-174.
- Brooks, P. D., J. M. Stark, B. B. McInteer, and T. Preston. 1989. Diffusion method to prepare soil extracts for automated nitrogen-15 analysis. *Soil Sci. Soc. Am. J.* 53:1707-1711.
- Cropper, Jr., W. P., K. C. Ewel, and J. W. Raisch. 1985. The measurement of soil CO₂ evolution in situ. *Pedobiologia* 28:35-40.
- Davidson, E. A., S. C. Hart, C. A. Shanks, and M. K. Firestone. 1991. Measuring gross nitrogen mineralization, immobilization, and nitrification by ¹⁵N isotope dilution in intact soil cores. *J. Soil Sci.* 42:335-349.
- Davidson, E. A., S. C. Hart, and M. K. Firestone. 1992. Internal cycling of nitrate in soils of a mature coniferous forest. *Ecology* 73(4):1148-1156.
- Eno, F. 1960. Nitrate production in the field by incubating the soil in polyethylene bags. *Soil Sci. Soc. Amer. Proc.* 24:277-279.
- Ewel, K. C., W. P. Cropper, Jr., and H. L. Gholz. 1987. Soil CO₂ evolution in Florida slash pine plantations. II. Importance of root respiration. *Can. J. For. Res.* 17:330-333.
- Fenn, M. E., M. A. Poth, J. D. Aber, J. S. Baron, B. T. Bormann, D. W. Johnson, A. D. Lemly, S. G. McNulty, D. F. Ryan, and R. Stottlemeyer. 1998. Nitrogen excess in North American ecosystems: predisposing factors, ecosystem responses, and management strategies. *Ecol. Appl.* 8(3):706-733.
- Graumlich, L. J. 1993. Response of tree growth to climatic variation in the mixed conifer and deciduous forests of the upper Great Lakes region. *Can. J. For. Res.* 23:133-143.
- Gundersen, P. 1991. Nitrogen deposition and the forest nitrogen cycle: role of denitrification. *For. Ecol. Manage.* 44:15-28.
- Hart, S. C., and A. J. Gunther. 1989. In situ estimates of annual net nitrogen mineralization and nitrification in a subarctic watershed. *Oecologia* 80:284-288.
- Hart, S. C., J. M. Stark, E. A. Davidson, and M. K. Firestone. 1994. Nitrogen mineralization, immobilization, and nitrification. In: *Methods of soil analysis, Part 2, Microbiological and biochemical properties*, Book Series No. 5, Soil Science Soc. Amer., Madison, WI, p. 985-1018.
- Hauck, R. D., J. J. Meisinger, and R. L. Mulvaney. 1994. Practical considerations in the use of nitrogen tracers in agricultural and environmental research. In: *Methods of soils analyses, Part 2*, R. W. Weaver,

S. Angle, P. Bottomley, D. Bezdicek, S. Smith, A. Tabatabai, and A. Mollum (eds.), Soil Science Soc. Amer. Book Series No. 5, Chap. 40, American Society of Agronomy, Madison, WI, p. 936-941.

Johnson, E. L., and K. K. Haak. 1983. Anion analysis by ion chromatography. In: Liquid chromatography in environmental analyses, J. F. Lawrence (ed.), Humana Press, Clifton, NJ., pp. 263-299.

Jones, E. A., D. D. Reed, G. D. Mroz, H. O. Liechty, and P. J. Cattellino. 1993. Climate stress as a precursor to forest decline: paper birch in northern Michigan, 1985-1990. *Can. J. For. Res.* 23:229-233.

Molot, L., and P. J. Dillon. 1996. Storage of terrestrial carbon in boreal lake sediments and evasion to the atmosphere. *Global Biogeochem. Cycles* 10:483-492.

Mooney, H. A., B. G. Drake, R. J. Luxmoore, W. C. Oechel, and L. F. Pitelka. 1991. Predicting ecosystem responses to elevated CO₂ concentrations. *Bioscience* 41(2):96-104.

Morrison, D. F. 1967. Multivariate statistical methods, McGraw-Hill Book Co., New York, N.Y., p. 186-197.

Nadelhoffer, K. J., J. D. Aber, and J. M. Melillo. 1983. Leaf-litter production and soil organic matter dynamics along a nitrogen-availability gradient in southern Wisconsin (U.S.A.). *Can. J. For. Res.* 13:12-21.

Nadelhoffer, K. J., J. D. Aber, and J. M. Melillo. 1984. Seasonal patterns of ammonium and nitrate uptake in nine temperate forest ecosystems. *Plant Soil* 80:321-335.

Nay, S. M., K. G. Mattson, and B. T. Bormann. 1994. Biases of chamber methods for measuring soil CO₂ efflux demonstrated with a laboratory apparatus. *Ecology* 75(8):2460-2463.

Olson, J. S., J. A. Watts, and L. J. Allison. 1983. Carbon in live vegetation of major world ecosystems. Oak Ridge National Laboratory, Tech. Rept. No. ORNL-5862.

Pastor, J., J. D. Aber, C. A. McLaugherty, and J. M. Melillo. 1984. Aboveground production and N and P cycling along a nitrogen mineralization gradient on Blackhawk Island, Wisconsin. *Ecology* 65:256-268.

Pastor, J., B. Dewey, R. J. Naiman, P. F. McInnes, and Y. Cohen. 1993. Moose browsing and soil fertility in the boreal forests of Isle Royale National Park. *Ecology* 74(2):467-480.

Pastor, J., and W. M. Post. 1988. Response of northern forests to CO₂ -induced climate change. *Nature (London)* 344:55-58.

Raisch, J. W. and K. J. Nadelhoffer. 1989. Belowground carbon allocation in forest ecosystems: Global trends. *Ecology* 70(5):1346-1354.

Reuss, J. O., and D. W. Johnson. 1986. Acid deposition and the acidification of soils and waters. *Ecol. Studies* #59, Springer-Verlag, New York, NY, 119 p.

Rutkowski, D., and R. Stottlemeyer. 1993. Composition, biomass and nutrient distribution in mature northern hardwood and boreal forest stands. *Amer. Midl. Nat.* 130(1):13-30.

Shaver, G. R., W. D. Billings, F. S. Chapin III, A. E. Giblin, K. J. Nadelhoffer, W. C. Oechel, and E. B. Rastetter. 1992. Global change and the carbon balance of Arctic ecosystems. *BioScience* 42(6):433-441.

- Shetron, S. G., and R. Stottlemeyer. 1991. Isle Royale National Park Soil Survey and map. School of Forestry, Michigan Technological Univ., Houghton, MI 49931, 365 p.
- Solomon, A. M. 1988. Transient response of forests to CO₂ - induced climate change: simulation modeling experiments in eastern North America. *Oecologia* 68:567-579.
- Solomon, A. M., and P. J. Bartlein. 1992. Past and future climate change: response by mixed deciduous-coniferous forest ecosystems in northern Michigan. *Can. J. For. Res.* 22:1727-1738.
- Stottlemeyer, R. 1992. Nitrogen mineralization and streamwater chemistry, Rock Creek Watershed, Denali National Park, Alaska, U.S.A. *Arct. Alp. Res.* 24(4):291-303.
- Stottlemeyer, R., and D. Hanson, Jr. 1989. Atmospheric deposition and ionic concentrations in Forest Soils of Isle Royale National Park, Michigan. *Soil Sci. Soc. Am. J.* 53(1):270-274.
- Stottlemeyer, R., and R. Herrmann. 1999. Boreal ecosystem response to atmospheric nitrogen inputs and climate change. In: *Disturbance in Boreal Forest Ecosystems: Human Impacts and Natural Processes*, U.S. Forest Gen. Tech. Rept. (in press)
- Stottlemeyer, R., D. Rutkowski, D. Hanson, Jr., C. Friesen, and M. Larson. 1984. Effects of atmospheric acid deposition on watershed/lake ecosystems of Isle Royale and Michigan's Upper Peninsula. GLARSU Tech. Rept. #9, Dept. Biol. Sci., Michigan Technological Univ., Houghton, MI 49931.
- Stottlemeyer, R., and D. Toczydlowski. 1991. Stream chemistry and hydrologic pathways during snowmelt in a small watershed adjacent Lake Superior. *Biogeochemistry* 13:177-197.
- Stottlemeyer, R., and D. Toczydlowski. 1999a. Seasonal relationships between precipitation, soil, and streamwater nitrogen, Isle Royale, Michigan. *J. Soil Sci. Soc. Amer.* (in press)
- Stottlemeyer, R., and D. Toczydlowski. 1999b. Nitrogen mineralization in a mature boreal forest, Isle Royale, Michigan. *J. Environ. Qual.* (in press)
- Stottlemeyer, R., D. Toczydlowski, and R. Herrmann. 1998. Biogeochemistry of a mature boreal ecosystem: Isle Royale National Park, Michigan. National Park Service Scient. Monogr. No. 98-1 (in press)
- Stottlemeyer, R., B. Travis, and D. Toczydlowski. 1995a. Nitrogen mineralization in boreal forest stands of Isle Royale, northern Michigan. *Water Air Soil Polln.* 82:191-202.
- Stottlemeyer, R., B. Travis, and D. Toczydlowski. 1995b. Nitrogen mineralization in boreal forest stands of Isle Royale, northern Michigan. In: *Boreal Forests and Global Change*, M. J. Apps, D. T. Price and J. Wisniewski (eds), Kluwer Academic, London, p. 191-202.
- Strain, B., and F. Bazzaz. 1983. Terrestrial plant communities. In: E. Lemon (ed) *CO₂ and Plants: The Response of Plants to Rising Levels of Carbon Dioxide*. AAAS Selected Symposium #84, Amer. Assoc. Advance Sci., Washington, D.C., pp. 172-222.
- Zak, D. R., K. S. Pregitzer, and G. E. Host. 1986. Landscape variation in nitrogen mineralization and nitrification. *Can. J. For. Res.* 16:1258-1263.