



HAL
open science

Effect of clear cutting on nutrient fluxes in a subalpine forest at Fraser, Colorado

J. O. Reuss, R. Stottlemyer, C. A. Troendle

► **To cite this version:**

J. O. Reuss, R. Stottlemyer, C. A. Troendle. Effect of clear cutting on nutrient fluxes in a subalpine forest at Fraser, Colorado. *Hydrology and Earth System Sciences Discussions*, 1997, 1 (2), pp.333-344. hal-00304402

HAL Id: hal-00304402

<https://hal.science/hal-00304402>

Submitted on 18 Jun 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Effect of clear cutting on nutrient fluxes in a subalpine forest at Fraser, Colorado

J.O. Reuss, R. Stottlemyer, and C.A. Troendle

USDA Forest Service, Rocky Mountain Forest and Range Experiment Station, 240 West Prospect Road, Fort Collins, Colorado, USA

Abstract

Nutrient fluxes were investigated on a forested and a clearcut plot in a mixed conifer high elevation (2900 m) forest at the Fraser Experimental Forest in Fraser, Colorado, USA. Plots were located on a coarse loamy mixed Dystric Cryochrept with relatively high base saturation (30–90%) and underlain by an impermeable clay subsoil. Following harvest in late 1984, annual mean NO_3 concentrations of 195 to 198 $\mu\text{mol l}^{-1}$ were observed from 1988 through 1990 and concentrations were still above reference levels in 1993. Total nitrogen loss attributable to leaching following harvest was estimated at 48 kg ha^{-1} over 8 years. Over this same period, atmospheric nitrogen inputs exceeded annual outflow of NH_4 plus NO_3 from the control plots by approximately 11 kg N ha^{-1} . A slight enrichment of SO_4 and Cl was observed from the harvested plot in 1986 but concentrations later fell below control plot levels, apparently due to dilution by the increased discharge from the harvested plot which was three to four times that from the control plot.

Elevated Ca, Mg, and Na concentrations followed a similar pattern to NO_3 due to exchange reactions, while a depression in alkalinity of about one-third the amount of NO_3 found was also observed. Enrichment of K occurred primarily in water collected at less than 1 m depth. Increases in base cation loss due to leaching after harvest were about twice the amount that can be accounted for by the increased flux of NO_3 , SO_4 , and Cl anions. The excess reflects the increased water flux and consequent leaching of base cations in association with HCO_3 and organic anions.

Introduction

Increased outflow of nutrients in streamflow following clear felling of forests has been known for well over quarter of a century (Likens *et al.*, 1970). Numerous reports from both Europe and North America (e.g., Hornbeck and Kropelin, 1982, Martin *et al.*, 1986, Johnson and Todd, 1987, Adamson *et al.*, 1987, Mann *et al.*, 1988, Hornbeck *et al.*, 1990, Stevens and Hornung, 1990, Hornbeck and Swank, 1992, Reynolds *et al.* 1995) have confirmed that, while increased nutrient flux following clear felling is almost universal, the pattern of flux of the various nutrients varies widely. With the exception of the special case of the nitrogen-fixing red alder, (*Alnus rubra*) (Mann *et al.*, 1988), increased nitrogen outflow seems to occur at virtually all sites. Peak nitrogen leaching occurs typically in the first or second year after harvest, and returns to control levels within three to four years as reported by Martin *et al.*, (1986). Increased calcium outflow is also nearly universal, and elevated potassium levels are common, although the amounts and pattern of loss of these nutrients are highly variable. Almost all of the reports from North America are from either eastern sites or from the Pacific Northwest. Except for a leaching loss of about

10 kg N ha^{-1} in the second year following harvest of a lodgepole pine (*Pinus contorta*) forest in southern Wyoming (Knight *et al.*, 1991), there seems to be little information on this phenomenon from forests in the central Rocky Mountains.

This report describes the changes in biogeochemical fluxes that occurred as a result of clear cutting in a high altitude mixed conifer forest. Hydrological data are reported separately (Troendle and Reuss, 1997). The objectives are (1) to monitor the effect of timber harvest on nutrient fluxes, and (2) to interpret the responses observed from an ecological perspective. Data reported here are necessarily at a fairly high level of aggregation. There are some inconsistencies in collection periods and a few gaps in some of the records. In spite of these limitations, a coherent picture emerges of the fluxes in the undisturbed forest and of the changes brought about by harvesting.

Methods

Two plots at the Fraser Experimental Forest (FEF) near Fraser, Colorado, one of which was clearcut in late 1984, were monitored from 1980 to 1990, and again in 1993. Data collected include volume of discharge as measured

from two interception trenches serving as large zero tension lysimeters, amount and chemical composition of precipitation, snow depths and water content, chemical composition of the discharge waters, and a brief characterization of soil chemical properties.

SITE DESCRIPTION

The FEF is located 137 km west of Denver, Colorado. The study area is located on a 10 ha segment of a lateral moraine at 2900 m elevation. The 30% west facing slope is fully forested with 210 m³ ha⁻¹ Engelmann spruce (*Picea engelmannii*), subalpine fir (*Abies lasiocarpa*), lodgepole pine (*Pinus contorta*), and an occasional aspen (*Populus tremuloides*). The soil, a coarse-loamy mixed Dystric Cryochrept (formerly Leal sandy loam) is distributed uniformly on the slope and is underlain with a relatively impermeable clay subsoil. The bedrock is dominated by gneiss and schist. The long-term mean annual precipitation at the forest headquarters (2725 m) is 580 mm, most of which falls as snow.

LAYOUT

The physical layout and the collection system have been described by Troendle (1985, 1987) and Troendle and Nilles (1987). While the plots were unbounded, (Troendle and Reuss, 1997), drainage areas are 0.109 ha for plot 1 (harvested in late 1984), and 1.64 ha for plot 2 (control) respectively. Lateral flow was collected from the surface (on or above the mineral soil), from the shallow subsurface which included the developed horizons, i.e., from the mineral soil surface to the interface of the sandy clay loam/clay loam at about 1 m deep, and from the deeper subsurface, i.e., below the shallow subsurface to a depth of about 4 m. Hydraulic conductivity measurements indicate that the flux below 4 m is negligible.

SAMPLING

Water samples were collected for chemical analyses starting in 1982 but, as laboratories and procedures were changed in 1983, the 1982 data are not reported. Sampling continued through the 1990 season. No samples or flow measurements were taken in 1991 and 1992 but flow was again measured in 1993 and samples taken. Flow was delivered from the collection system to the measuring flumes through PVC pipe and samples were taken from the outflow of the PVC pipe, prior to entering the metal flumes. Samples were collected in 500 ml amber Nalgene bottles. The intent was to collect three to four samples per week during the snowmelt period and one to two samples per week during the recession period. Sampling schedules varied substantially from year to year, primarily due to large differences in flow among years. Numbers of samples actually collected each year are shown in Table 1.

Table 1. Number of subsurface flow samples by plot and year.

Year	Harvested		Surf	Control		Total
	Shall	Deep		Shall	Deep	
1983	1	3	1	3	3	11
1984	10	22	4	9	20	65
1985	7	15	6	14	18	60
1986	6	26	1	16	20	69
1987	10	34		14	21	79
1988	4	29		10	19	62
1989	9	27		12	27	75
1990	10	28		10	20	68
1993	20	39		20	33	112
Total	77	223	12	108	181	601

Precipitation samples were collected weekly from May 1984 through 1993 at the forest headquarters using Aerochem Metrics (Miami, FL) 'event' precipitation collectors. In 1990 the collection did not start until 13 March, so much of the winter period is missing from the 1990 water year.

Soil samples were collected in the late summer of 1987 from the 0–4, 4–15, and 15–38 cm depths. Three locations were sampled in each plot and, each location sample was a composite of three borings. The samples from each location were analyzed separately.

LABORATORY

Water samples were brought to room temperature for pH and alkalinity determinations at the forest field laboratory. A Fischer (Pittsburgh, PA) AC meter was used to measure pH and alkalinity. Alkalinity was determined by titration to a pH 4.5 endpoint (American Public Health Association, 17th ed., page 2.36), and a correction was applied for the H⁺ ion concentration at the endpoint as recommended by Neal (1988). All alkalinity and pH determinations were completed within 8 hours of sample collection. Up to and including 1990, a field method using calibrated pipettes was employed for alkalinity titrations, but the more accurate buret titrations were used in 1993. Filtered (0.45 µm) sub-samples were saved for the remaining analyses. Macro ions (Ca²⁺, Mg²⁺, Na⁺, K⁺, NH₄⁺, PO₄³⁻, Cl⁻, NO₃⁻, and SO₄²⁻) were determined on an automated Dionex (Sunnyvale, CA) Model 2020 ion chromatograph (IC).

Soil samples were air dried and passed through a 2 mm sieve prior to analysis. Organic matter content was determined on oven-dried samples (65 °C for 24 hrs.) by ashing in a muffle furnace at 550 °C for 8 hours (Nelson and

Sommers, 1982). Soil pH was determined using both water and 0.01 M CaCl₂, with a weight to volume ratio of 1:2 for mineral horizons and 1:5 for organic horizons (McLean, 1982). Exchangeable base cations were determined by extraction with 1 N NH₄Cl and analyzing the filtered extracts using an atomic absorption spectrometer (NCASI 1983).

Laboratory quality assurance procedures included splitting weekly National Atmospheric Deposition Program (NADP) samples, participation in the Environmental Protection Agency's National Acid Precipitation Assessment Program (NAPAP) quality assurance program, routine use of National Bureau of Standards inorganic standards and the long term comparison of paired cation results from atomic adsorption (AA) and IC (Stottlemeyer *et al.*, 1989).

Results and Discussion

SOILS

For the most part, the soils are high in bases. Base saturation is consistently higher in the control plot where the mean above 15 cm is over 50%, whereas in the clearcut plot the mean is 30% (Table 2). While these differences appear to be consistent over depth, the number of samples taken from each plot is very low, so that sampling error cannot be ruled out. It is highly unlikely that these differences are due to harvest, as changes in soil pools between harvest in late 1984 and sampling in 1987 would be very

small. Soil pH values (water suspension) range from 5.5 to 6.5, with the lower values near the surface increasing with depth. CEC is closely related to both total nitrogen and organic carbon. The regression of CEC on organic carbon (Fig. 1) suggests a mineral component of about 8.1 cmol(-) kg⁻¹, and an increase of about 6.07 cmol(-) kg⁻¹ for each 1% of organic carbon. Apparently, the CEC below about 15 cm arises primarily from the mineral fraction, while at shallower depths organic charges are more prevalent.

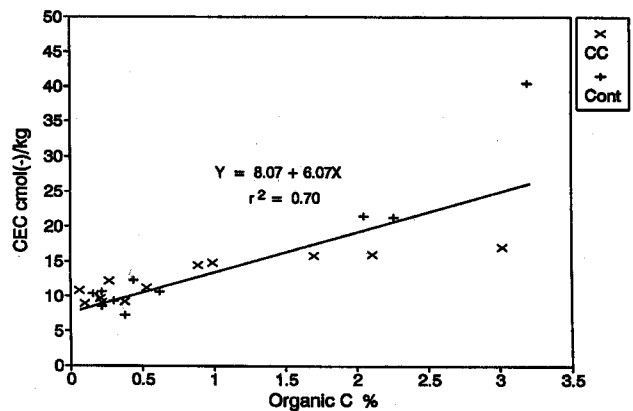


Fig. 1. Regression of cation exchange capacity on soil organic carbon over all depths and samples.

Table 2. Means and standard deviations of selected soil parameters.

Depth cm	n		pH (water)	Organic C %	CEC cmol(-) kg ⁻¹	Bases* cmol(-) kg ⁻¹	Base Sat %
Harvested							
0-4	3	mean	5.42	2.28	16.3	4.9	30
		s.d.	0.28	0.68	0.7	1.7	9.4
4-15	3	mean	5.76	0.80	13.5	4.1	30
		s.d.	0.25	0.24	2.0	0.9	3.9
15-38	3	mean	6.23	0.23	10.3	6.9	68
		s.d.	0.27	0.03	1.6	0.4	13
38-56	3	mean	6.10	0.18	9.6	6.9	71
		s.d.	0.09	0.17	1.0	1.4	7
Control							
0-4	3	mean	5.79	2.50	27.8	17.1	58
		s.d.	0.58	0.61	11.1	11.5	15
4-15	2	mean	6.00	0.53	11.4	7.9	70
		s.d.	0.42	0.13	1.2	0.2	5
15-38	3	mean	6.24	0.28	9.0	7.5	84
		s.d.	0.48	0.11	1.6	1.7	10

* Bases include Ca+Mg+K. Exchangeable Na was not determined.

PRECIPITATION CHEMISTRY

Collection and analyses of samples for precipitation chemistry started in May 1984, and the record is fairly complete until January 1990. In 1990, the first data recorded are from March 13, so much of the winter period is missing from the 1990 water year. Also, a few gaps and inconsistencies occurred for individual constituents. A few very high Ca values ($> 70 \mu\text{mol}(+) \text{ liter}^{-1}$), mostly from the early years, were dropped on the basis of likely contamination, and the Mg, Na, and K values from these samples were also excluded. All precipitation pH values for 1987, 1988, and 1989 were unrealistically low. As the H^+ ion concentrations calculated from these values generally exceeded the sum of NO_3 , SO_4 , and Cl, they were discarded.

Calculation of individual year means is complicated by an inverse relationship between volume and concentration, so that use of simple means would overestimate inputs by an average of about 17%. There is also a clear tendency for the individual values to follow a lognormal distribution, so that use of a log transformation is appropriate for statistical analysis. Therefore, individual year means were calculated by volume weighting the log transformed values, followed by a back transformation that includes a 'smearing' correction (Duan, 1983). These individual year means were used as inputs in the mass balance calculations below, except for 1984 and 1990 where there are significant gaps in the rainfall record. Overall means as shown in Table 3 were used for these years. In most cases, year effects can be shown to be significant by analysis of variance, but no temporal trends were detected. Thus, while concentrations do tend to vary by years, there is no evidence of any systematic increases or decreases over time. Because there are strong seasonal effects for a number of parameters, the fundamental replication is assumed to be years, so the overall means in Table 3 were calculated as the simple

Table 3. Rainfall chemistry. Means of year means. 1984 and 1990 excluded due to incomplete record. Mg and K for 1991 also excluded due to missing data. Values are $\mu\text{moles charge per liter}$ except for conductance ($\mu\text{S/cm}$) and pH.

Parameter	n	Mean	s.e.	Confidence Interval of the Mean	
				lower	upper
pH	5	5.09	0.07	4.92	5.26
Cond	8	6.76	0.23	6.23	7.30
Ca	8	16.35	1.42	13.08	19.62
Mg	7	3.18	0.25	2.58	3.78
Na	8	4.62	0.81	2.76	6.48
K	7	2.09	0.40	1.14	3.05
NH ₄	8	7.35	1.19	4.60	10.11
NO ₃	8	10.69	0.39	9.78	11.60
SO ₄	8	11.15	0.75	9.41	12.88
Cl	8	3.99	1.04	1.58	6.40

averages of the year means. The relatively wide confidence intervals are the result of year-to-year fluctuations and a fairly short record.

With the exception of Ca, values are very similar to others reported from selected sites in the central Rocky Mountains (Reuss *et al.*, 1993; Baron *et al.*, 1991; Caine and Thurman, 1990). However, the Ca mean $16.4 \mu\text{mol}(+) \text{ l}^{-1}$, is substantially higher than the other reports which range from $8.5 \mu\text{mol}(+) \text{ to } 9.4 \mu\text{mol}(+) \text{ l}^{-1}$. Possible explanations include contamination with calcareous dust from local sources, analytical inconsistencies, or simply site variation.

SUBSURFACE FLOW

The sample numbers for subsurface flow (Table 1) varied greatly by years. This was due primarily to variations in flow resulting from annual variations in precipitation and from the effect of harvest on discharge (Fig. 2). Depth differences were generally small, so annual volume-weighted means as reported in Table 4 are combined over depths. Intraseasonal patterns are not reported here due to space limitations.

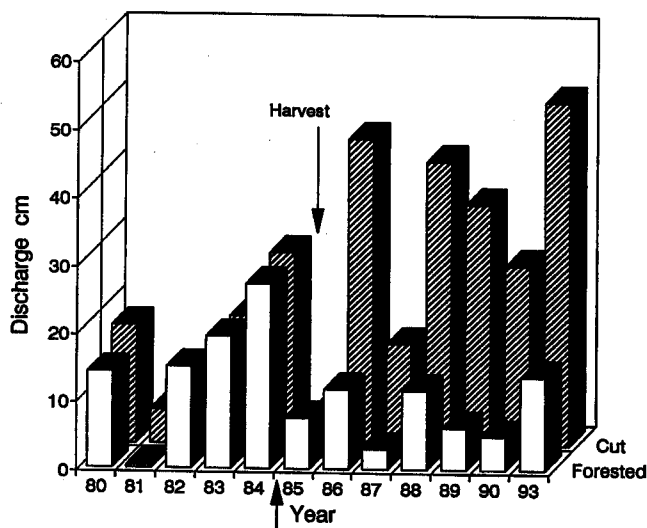


Fig. 2. Effect of harvest on discharge.

The largest and most obvious effect of the harvest in late 1984 is in the NO_3 concentration (Table 4). From 1983 through 1985, NO_3 values were very low and there was little or no difference between the two plots. A slight increase in the concentration was apparent in 1986, but the major effect did not occur until 1987 when flow weighted mean concentrations increased to $161 \mu\text{mol}(-) \text{ l}^{-1}$. The highest individual values occurred in 1988 when two measurements in the deep samples exceeded $750 \mu\text{mol}(-) \text{ l}^{-1}$, but on an annual flow-weighted basis, the concentrations were nearly identical during the 1988–1990 period with flow-weighted means for all three years falling in the range of 195 to $198 \mu\text{mol}(-) \text{ l}^{-1}$. By 1993, the flow-weighted

mean concentration ($39 \mu\text{mol}(-) \text{ l}^{-1}$) was still far above the almost negligible amounts in the control plot. This decrease most likely represents both decreased NO_3 production and an increase in dilution due to higher precipitation in 1993. While on the basis of previous reports (e.g., Likens *et al.*, 1970, Hornbeck and Kropelin, 1982, Johnson and Todd, 1987, Mann *et al.*, 1988, Knight *et al.*, 1991, Reynolds *et al.*, 1995) elevated NO_3 concentrations were expected, the fact that concentrations were still above control levels some nine years after harvest was surprising; from the literature two to four year durations seem to be more typical. This prolonged NO_3 outflow is most likely due to a lack of nitrogen uptake as, during the course of the experiment, there was practically no regeneration of trees nor was there significant growth of brush or forbs at the site.

In contrast to the NO_3 ion which did not rise significantly until 1988, the highest SO_4 concentrations occurred in 1986 when the annual flow-weighted mean was $70.2 \mu\text{mol}(-) \text{ l}^{-1}$ (Table 4), dropping to near or below control levels by 1988. Apparently, this was caused by continued mineralization of SO_4 after uptake by the trees had stopped. By 1993, SO_4 levels in the clearcut were about $38 \mu\text{mol}(-) \text{ l}^{-1}$ below those from the control, probably due to dilution as a result of increased discharge. One would expect that the concentration peak would be small, as it would be buffered by chemical adsorption of SO_4 in the soil. However, the rapid drop off after discharge increased

suggests a very limited SO_4 adsorption capacity. Sulphate peaks and/or depressed concentrations after clear cutting have been observed (Adamson *et al.*, 1987, Hornbeck *et al.*, 1990), but the depression observed here seems to be particularly well expressed.

Elevated Cl concentrations were also evident in 1986 and 1987 when the concentration from the clearcut plot exceeded that from the control by $53.4 \mu\text{mol}(-) \text{ l}^{-1}$ and $27.5 \mu\text{mol}(-) \text{ l}^{-1}$, respectively (Table 4). Elevated Cl concentrations persisted for some three years, dropping off to near the control level by 1989 and falling slightly below the control thereafter. As with SO_4 , this Cl pulse seems to be associated with mineralization from the litter or perhaps even a simple flushing stimulated by the disturbance during clear cutting. However, the Cl seems to interact either chemically or physically with the ecosystem and no adequate explanation is offered for the high variation in Cl concentrations in the control and in the pre-harvest values in the harvest plot.

The annual weighted mean alkalinity values in the range of 132 to $234 \mu\text{mol}(-) \text{ l}^{-1}$ for the control plot indicates that HCO_3 is a major anion in this system. The 1993 control value of $138 \mu\text{mol}(-) \text{ l}^{-1}$ is probably the most reliable as a more sensitive titration method was adopted for that year. Unfortunately, no reliable data are available prior to 1985. While early values using the calibrated pipette are relatively imprecise and may be subject to operator differences, the differences between the two plots should be

Table 4. Mean chemical composition of outflow by plot and year. Depth weighted by annual discharge.

Plot	Year	pH	Cond	Alk	Ca	Mg	Na	K	μmoles charge ⁻¹			
									NH ₄	NO ₃	SO ₄	Cl
Harvest	83	6.13	32.9	*	225	68	50	11.3	1.5	4.9	50.2	9.3
	84	6.37	36.5	*	190	56	61	38.6	0.8	4.6	55.1	27.8
	85	5.88	37.8	261	180	71	63	13.6	0.6	0.5	49.9	9.6
	86	6.20	45.8	217	226	104	76	14.1	1.3	15.1	70.2	59.4
	87	6.16	49.1	193	262	64	76	16.1	4.1	161.5	47.0	38.0
	88	5.88	*	120	335	132	75	33.9	4.8	195.0	47.2	19.0
	89	5.69	31.6	147	321	111	66	26.6	2.8	198.0	43.3	13.5
	90	6.10	38.4	146	248	84	60	18.3	0.0	196.9	42.4	14.4
	93	6.25	25.4	146	163	78	47	18.6	0.2	38.6	32.7	3.8
Control	83	5.80	33.8	*	240	89	45	17.8	0.0	1.3	51.6	7.4
	84	6.25	38.0	*	221	72	66	63.4	0.7	1.6	60.3	28.7
	85	5.81	33.1	203	200	88	64	16.8	2.5	4.7	66.0	9.3
	86	6.05	33.3	162	196	108	72	16.0	3.4	0.9	55.2	6.0
	87	5.97	24.6	160	116	37	55	13.6	4.6	0.6	43.8	10.5
	88	5.66	*	143	236	96	74	18.9	4.8	0.4	57.6	9.1
	89	5.69	21.2	156	299	100	73	15.8	2.6	2.8	67.5	12.6
90	6.06	29.5	134	207	79	70	7.6	0.0	1.3	74.8	20.5	
93	6.03	31.0	138	198	112	73	15.9	0.0	0.1	69.1	9.2	

unbiased. Prior to and immediately after cutting, the alkalinity in the cut plot was 50–60 $\mu\text{mol}(-) \text{ l}^{-1}$ higher than that in the control. However, by 1988 the control alkalinity was above that of the clearcut plot, resulting in a highly significant ($P < 0.004$) plot \times year interaction. A rough estimate of the effect of cutting on alkalinity can be had by comparing the mean difference between the two plots in 1985/86 (57 $\mu\text{mol}(-) \text{ l}^{-1}$) to the difference in 1988–90 ($-7 \mu\text{mol}(-) \text{ l}^{-1}$) for a total depression of 64 $\mu\text{mol}(-) \text{ l}^{-1}$. This decrease in alkalinity is undoubtedly due largely to the NO_3 pulse. Firstly, the end product of the mineralization process is HNO_3 . Secondly, the accompanying increase in solution concentration results in decreased alkalinity and pH as a result of ion exchange reactions (Reuss and Johnson, 1985, 1986). These effects were very apparent in the very high NO_3 samples collected in early 1988, where alkalinity values actually dropped to zero. Simple empirical models of acidification due to acidic deposition (Henriksen, 1980, Brakke *et al.*, 1990) rely on an empirical factor (F) to describe the fraction of the acidic input that is neutralized by soil processes. The acidification due to nitrogen processes is analogous, and the fraction of the acid formed that actually decreases alkalinity in the groundwater is of considerable interest. During 1988–90, the difference in NO_3 concentration averaged 195 $\mu\text{mol}(-) \text{ l}^{-1}$. Thus, a depression of 64 $\mu\text{mol}(-) \text{ l}^{-1}$ alkalinity suggests that about one-third of the HNO_3 formed decreased the alkalinity in the soil solution, the remaining two-thirds being consumed by soil buffering processes, primarily the release of base cations from the exchange complex.

Base cation concentrations are subject to considerable year to year variation, even in the control plots. The flow-weighted annual mean concentrations of Ca, Mg and Na generally indicate increased concentrations following clear cutting, primarily in response to the high concentrations of NO_3 . As pre-harvest values tended to be higher in the control plot than in the harvest plot, the most valid interpretation is probably that based on the plot \times year interaction as shown in Fig. 3. Prior to cutting, the Ca and Mg concentrations were generally below those in the control, i.e., the plot \times year interaction values as shown in Fig. 3 were negative but, after harvest, a reversal occurred. Some increase was apparent by 1986, but the major peak occurred in 1987 and 1988. That the reversal was apparent in 1986 is somewhat surprising as NO_3 increased very little in 1986. Apparently, the initial pulse was in response to increased Cl and SO_4 rather than NO_3 . The highest base cation values were observed in 1987. Alkalinity remained quite high in 1987, falling off considerably in 1988. When the alkalinity became depressed in 1988, the Ca and Mg declined. A pulse of Na was observed, primarily in 1988.

The patterns of K enrichment in the shallow and deep samples, are shown in Fig. 4. In the shallow samples, K enrichment was evident almost immediately after cutting and persisted through 1993 but there was little or no evi-

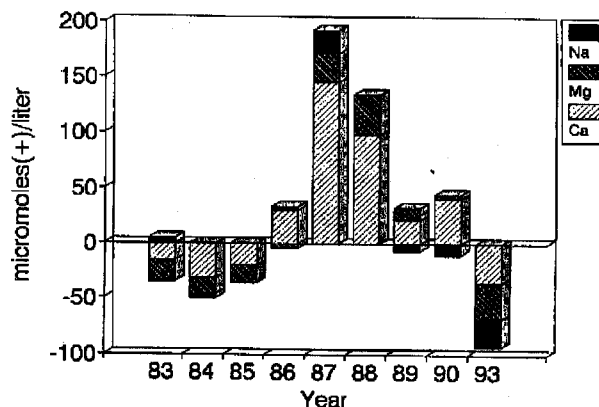


Fig. 3. Plot by year interactions for Ca, Mg, and Na concentrations in the subsurface outflow. Values are differences in mean concentrations of harvest and control plots. Volume weighted over depths.

dence of a change in K concentration in the deep samples. During the 1987–1990 period, yearly K means for the shallow samples averaged 29.4 $\mu\text{mol}(+) \text{ l}^{-1}$ higher in the clearcut than in the control, while in the deep samples the difference was only 1.1 $\mu\text{mol}(+) \text{ l}^{-1}$. Potassium in plant material is highly mobile but, apparently, any K released from the branches and needles of the harvested trees was immobilized by the soil biota before reaching the deep layers. Previous investigators have noted increased K concentrations following harvest (e.g., Martin *et al.*, 1986, Adamson *et al.*, 1987), but the authors are not aware of previous reports of depth effects.

ION BALANCE AND ALKALINITY IN 1993

When interpreting the chemistry of oligotrophic fresh waters, ion balance is commonly used as a quality check,

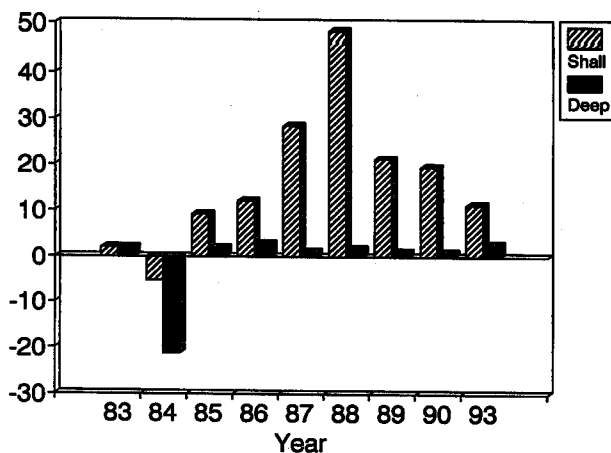


Fig. 4. Plot \times year interactions for K concentrations from the shallow and deep samples.

i.e., cation excesses or deficits are likely to indicate either that an important component is missing, or that analytical errors are significant. In subsurface flow samples from forest soils, anion deficits may be due to the presence of organic anions. Attempts to interpret ion balance, calculated from subsurface flow samples collected earlier in this project, were complicated by the fact that alkalinity measurements were carried out by a simplified titration that lacked precision. Even though special care was taken to improve precision for the 1993 alkalinity analyses, substantial anion deficits persisted, suggesting that organic anions are an important constituent.

Alkalinity is commonly determined by titration with an acid and, in this case, a fixed end point was used and a correction for H^+ present at the endpoint (pH 4.5) applied (Reynolds and Neal, 1987, Neal, 1988). The alkalinity measurement will thus include both the HCO_3^- ion and that portion of the organic charge that is protonated during the titration. This portion of the organic charge has been designated as (o_t), while the portion of the organic charge having sufficiently low $pK(H^+)$ values so that it is not protonated during titration, is residual charge (o_r). Thus, alkalinity as measured here may be defined as,

$$\text{alk} = (HCO_3^- + o_t - H). \quad (1)$$

The amount of residual charge is estimated by the apparent anion deficit (or cation excess) as determined by ion balance calculations.

$$o_r = (Ca + Mg + Na + K + NH_4 + H) - (Cl + SO_4 + NO_3 + HCO_3 + o_t) \quad (2)$$

Eqns. (1) and (2) may be combined to obtain Eqn. (3).

$$o_r = (Ca + Mg + Na + K + NH_4) - (Cl + SO_4 + NO_3 + \text{alk}) \quad (3)$$

A time course plot for the residual charge for the 1993 deep samples is shown in Fig. 5. The small negative values are well within the error of the method and should be taken as near zero. Any organic charge neutralized during the titration (o_t) would not be included in this calculation and, while it is likely that this is small, the amounts shown in Fig. 5 should be taken as a minimum. Shallow samples exhibited a very similar pattern but the period of outflow was much shorter. Residual charge is very high in the samples from the control plot, and, accepting the value of 10 ueq charge per mg of dissolved organic carbon (DOC) (Oliver *et al.*, 1983), the deep samples would be expected to range from near zero to about 17 mg^{-1} DOC. Unfortunately, no DOC analyses are available for any of the samples. A sharp rise occurred early in the period of high flow, probably due to the flushing of organic anions from the litter layer. This rise was accompanied by a drop of about 0.6 pH units in control plot outflow. The correspondence between the patterns of residual charge and pH indicates that an important process is taking place. Residual charge levels were much lower in the clearcut

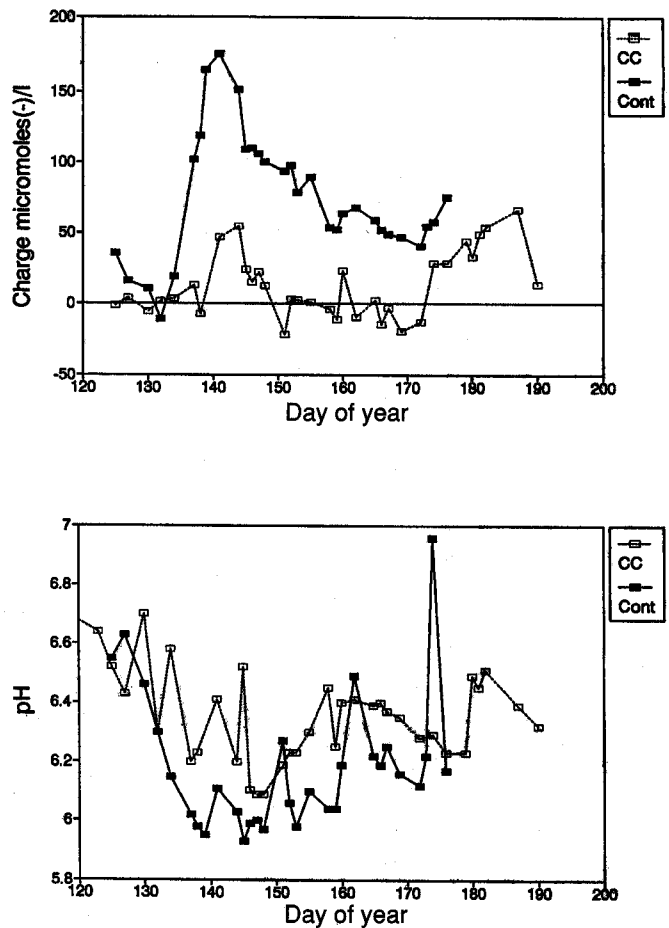


Fig. 5. Time course plots of pH and residual organic charge in the 1993 deep samples.

outflow, and at 10 $\mu\text{mol}(-) l^{-1}$ per mg DOC, the DOC levels would be below about 5 $mg l^{-1}$ during most of the season. During the latter part of the season when flow was very low, residual charge rose in the harvested plot and tends to converge with that in the control plot.

It is tempting to explain the difference in residual charge between the forested and clearcut plots as being due to a change in the character of the litter following the harvest; a decrease in organic acids is reasonably to be expected if fresh litter is no longer available each year. Another related explanation would be the greater dilution of the organic anions in the clearcut due to increased discharge. In either case, the anion deficits (residual charge) in the two plots should have been similar prior to harvest and the differences observed in 1993 would have developed after the clear cutting. While the question of whether or not the difference in residual charge in the two plots is due to treatment is of considerable interest, it cannot be answered here due to lack of alkalinity data prior to 1985, and to analytical uncertainties in the early alkalinity data.

MASS BALANCES

Mass balance estimates require the aggregation of large amounts of data collected over a span of nearly a decade. Each measurement used in these calculations is subject to a variety of errors. Also, there are gaps in the record, as no discharge or subsurface flow data were collected in 1991 and 1992, and gaps of several months' duration in the precipitation chemistry record. In spite of these limitations, a clear and robust pattern emerges of the effect of the harvest on the mass balance of most of the components.

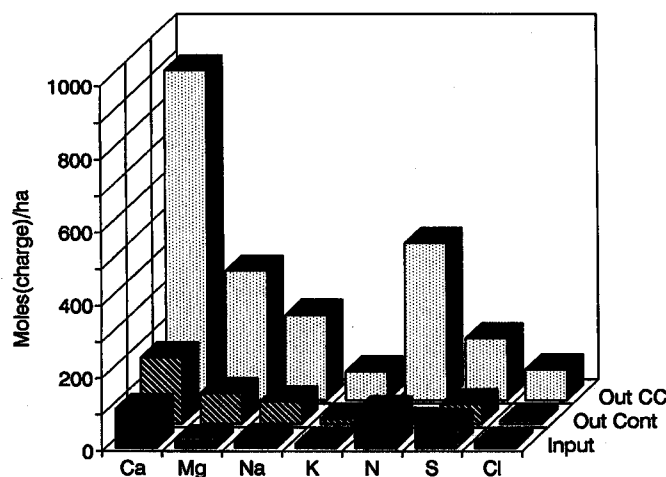


Fig. 6. Mean annual inputs and outputs for clearcut and control plots including 1986–1990 and 1993 values.

Mean annual inputs and outputs for both the clearcut and control plots during the post-harvest period, i.e., 1986–90 plus 1993, are shown in Fig. 6. This period was selected to give a valid comparison between the harvested and control treatments. The annual net loss of base cations in the control plot over the 1984 to 1993 period averaged 265 mol(+) ha⁻¹ but during the post-harvest period averaged only 182 mol(+) ha⁻¹, reflecting the generally lower discharge during this period. These compare to about 350 mol(+) ha⁻¹ at East Glacier Lake and 720 mol(+) ha⁻¹ at West Glacier Lake catchments, located in the Snowy Range of southern Wyoming (Reuss *et al.*, 1993). Even though the alkalinity of the discharge waters from the forested plot at Fraser is 3 to 4 times higher than at the Glacier Lakes, the actual base cation export is lower, due to the much lower discharge per unit area. At Fraser, the total output of base cations is about two to two and one-half times the precipitation input. The net annual Ca loss from the control plots averaged 126 mol(+) ha⁻¹ or about 2.5 kg ha⁻¹.

Base cation losses from the clearcut plot were about the same as the control in 1984 and 1985, but the effect of the clear cutting became evident in 1986 and continued through 1993 (Fig. 6). Mean annual net loss of Ca following cutting was 795 mol(+) ha⁻¹ (15.9 kg ha⁻¹) as compared

to 76 mol(+) ha⁻¹ (1.5 kg ha⁻¹) from the control. Assuming similar losses occurred in 1991 and 1992 when the plots were not monitored, we estimate the total difference in Ca losses as a result of clear cutting is estimated to be 115 kg ha⁻¹ through 1993. For Mg the annual net losses averaged 64 mol(+) ha⁻¹ (0.78 kg ha⁻¹) from the control and 335 mol(+) ha⁻¹ (4.1 kg ha⁻¹) from the clearcut, while for K the average net loss from the control was 3.3 mol(+) ha⁻¹ (0.13 kg/ha) and 67 mol(+) ha⁻¹ (2.6 kg ha⁻¹) from the clearcut. Even though these losses seem high, they are only a small fraction of the exchangeable pool in these relatively base-rich soils. Rough calculations indicate that the exchangeable pools, based on 56 cm of soil, are of the order of 6000–8000 kg/ha for Ca, 900–1300 kg ha⁻¹ for Mg, and 1600–2200 kg ha⁻¹ for K.

While there is considerable year to year variation due primarily to the wide annual fluctuations in discharge, the mass balance calculations suggest that, in the control plot (Fig. 6) the SO₄ inputs and outputs are very nearly in balance. For the eight years the plots were monitored there was an average annual net gain of 5 mol(-) ha⁻¹ (0.06 kg S ha⁻¹), while for the six monitored post-harvest years the net gain averaged 11.9 mol(-) ha⁻¹. Again the different estimates for the two periods reflected the lower average discharge from the control plots during the post-harvest years. These values may be compared to an annual input of 71 mol(-) ha⁻¹ indicating that SO₄ is very nearly in balance. Post-harvest SO₄ outflows from the clearcut plot averaged 169 mol(-) ha⁻¹, which is 104 mol(-) ha⁻¹ (1.7 kg S ha⁻¹) greater than the control. Increased SO₄ outflows have persisted through 1993, primarily due to increased flows, as the SO₄ concentrations actually decreased after an initial pulse in the first years after cutting, primarily in 1986. However, this concentration decrease is much less than would be expected from simple dilution. The pattern is what would classically be expected from a concentration-dependent desorption process, but its persistence is perhaps a little surprising. Most likely microbial mineralization of organic S was also involved. Total net export on the clearcut plots for the six post-harvest years was 10 kg S ha⁻¹, while the control plots exhibited small net gains over the same period.

Mass balances for Cl (Fig. 6) are similar in some ways to those observed for SO₄. For the post-harvest period the mean outflow from the control was 8.5 mol(-) ha⁻¹, while the rainfall input was 14.8 mol(-) ha⁻¹, suggesting a net accumulation of 6.3 mol(-) ha⁻¹. While the percentage difference in input and outflow is substantial, the actual numbers were small and subject to considerable uncertainty. Furthermore, the period is generally one of low discharge which would tend to decrease outflow, so this is hardly evidence of a net accumulation.

Nitrogen mass balances are of considerable interest. Normally, the nitrogen outflow is less than the precipitation input. During the eight years monitored, the control plot retained an average of 40 mol(+) ha⁻¹ of NH₄ and 64

mol(-) ha⁻¹ of NO₃, or an average net N retention of 1.4 kg ha⁻¹ per year. If only the post-harvest period is considered, the net N retention is the same, as there is very little outflow of N from the control plot and the value is not much affected by the variation in water discharge. Over time, this seemingly small amount of N can be ecologically significant. The retention pattern for NH₄ in the clearcut plot was affected only marginally by the harvest, averaging 32 mol(+) ha⁻¹.

Increased NO₃ concentrations in the outflow became evident in 1987, but total outflow in that year was limited by the very low discharge. The average post-harvest outflow of NO₃ from the clearcut was 422 mol(-) ha⁻¹ (5.9 kg N ha⁻¹), while the input averaged 62 mol(-) ha⁻¹ (0.87 kg N ha⁻¹), so the annual net loss of NO₃-N was 360 mol(-) ha⁻¹ (5.0 kg N ha⁻¹). This may be compared to a net retention of 61 mol(-) ha⁻¹ (0.85 kg N ha⁻¹) in the control. Combining NO₃ and NH₄, the annual average depletion from the clearcut was 4.6 kg N ha⁻¹ while the net retention in the control was 1.4 kg ha⁻¹. Thus, when compared to the control, the annual N depletion averaged 6.0 kg ha⁻¹, or a total of about 48 kg N ha⁻¹ over the 1986 to 1993 period. This may be compared to a net mineralization in the forest floor and the top 15 cm of soil of 2-5 kgN ha⁻¹ at the Fraser site (Stump and Binkley, 1993), while an annual N uptake of 6-12 kgN ha⁻¹ may be calculated from data of Ryan and Waring (1992), and Schoettle (1989). It is difficult to assess the significance of this loss in terms of potential for regrowth; again, it is small in relation to the total soil nitrogen which is estimated from soil analyses to be in the range of 1600 to 2200 kg/ha. However, it undoubtedly represents a higher fraction of the more readily mineralizable N in the system.

The annual net base cation loss in the clearcut plot exceeds that in the control by 1223 mol(+) ha⁻¹ while the difference in the strong acid anions is only 613 mol(-) ha⁻¹. This means that the acceleration of base loss is well in excess of that which can be attributed to increased flux of the strong acid anions i.e., NO₃, SO₄ and Cl. In fact nearly half the increased base cations fluxes are attributable to increased leaching from the increased water flux in association with HCO₃ and organic anions. This effect is evident from the regression parameters shown in Table 5. The r² values for the linear regression of Ca, Mg, and Na on cm discharge range from 0.88 to 0.9, reflecting a close dependency of base loss on water flux.

It is also useful to consider the accelerated leaching brought about by clear cutting in relation to the nutrients contained in the standing biomass prior to cutting. Estimates of the foliage biomass (11,790 kg/ha) and stem volume (210 m³) were obtained from the basal area (Kaufmann *et al.*, 1982). Harvest wood biomass was 72.9 m³, and stem densities were assumed to be 375 kg/m³. Bark biomass was taken as 10% of that of wood. Nitrogen contents of the foliage were taken from Yin (1993) while the remaining nutrient contents are from Pearson *et al.*

Table 5. Regressions (no intercept) of base cation output in moles(+) ha⁻¹ on cm discharge from the control plots.

Cation	n	Coefficient	r ²	S.E. (y est)
Ca	98	22.3	0.973	29.6
Mg	9	8.61	0.878	22.3
Na	9	6.32	0.900	15.2
K	9	3.71	0.600	33.4

Table 6. Approximate mass balance showing effect of clear cutting on nutrient removal over a period of 8 years.

Nutrient	Above Ground	Bole Removal*	Accelerated Leaching**	Removal due to harvest***
	kg ha ⁻¹	kg ha ⁻¹	kg ha ⁻¹	kg ha ⁻¹
Ca	101.5	47.2	115.2	162.4
Mg	22.5	9.1	26.2	35.3
K	66.0	14.8	20.1	34.9
N	122.7	16.5	47.8	64.3

* Includes bark

** Amount leaching in harvested plot exceeded that in control.

*** Accelerated leaching plus bole removal.

(1987). Results are summarized in Table 6. The 'accelerated leaching' column in Table 6 is the difference in leaching loss between the clearcut plot and the control, i.e., the increase in nutrient leaching attributable to the harvest. The 'removal due to harvest' is the sum of the 'accelerated leaching' and the removal due to bole harvest. Mean values were used for the two years that were not monitored. The values for total above-ground nutrients are generally similar to those shown by Mann *et al.* (1988) for pine forests in the southern U.S., but values for bole removal are substantially lower than they report for harvesting of 'saw logs'. This difference is almost entirely due to lower amounts of harvested timber. Total removal of Ca, Mg, K, and N represented about 162%, 157%, 53%, and 52% respectively, of the amount in the standing biomass. As noted above, the loss of bases is still small in relation to the total exchangeable pools in the soil, and the loss of N is small in relation to the total soil supply. Therefore, it seems reasonable to conclude, at least for the foreseeable future, that nutrient loss is probably not a significant limitation for harvest and regrowth cycles in these forests, at least if only the boles are removed.

However, accelerated leaching losses have not stopped after eight years. While NO₃ levels in the drainage water have decreased, they still have not returned to pre-harvest levels. Even without elevated NO₃, increased leaching of bases continues due to the increased water discharge, a situation that may well persist for decades. Given the fairly high level of bases in these soils, this probably does not

pose a serious problem, but a complete evaluation would require very long term studies.

As regards the effect of removal of the total above ground portion on the leaching losses, it seems likely that some of the losses observed resulted from mineralization of nutrients in the foliage and stems left on the plot. Thus, if the foliage and stems were removed, the total losses would not exceed the sum of the 'accelerated leaching' losses plus the 'above ground' nutrients in Table 6. This would result in approximately 1.7 times the observed losses for Ca and Mg, and perhaps three times the observed loss of N and K. While this is a considerable increase, such losses would still be small in relation to soil supplies.

Conclusions

While the effect of clear cutting on the nutrient fluxes in a high elevation mixed conifer forest at Fraser, Colorado, U.S.A. was similar in many respects to what has been reported from other areas, there are also important differences. As in other cases, the uncut forest accumulates N from atmospheric sources, and NO₃ levels are elevated in the drainage water after harvest when significant amounts of N are lost. This accelerated NO₃ loss is accompanied by a loss of Ca, Mg, K, and Na ions. Curiously, at Fraser the increased K levels occurred only in the shallow drainage samples while other ions increased in both shallow and deep samples. Also, elevated NO₃ concentrations persisted substantially longer than would be expected from reports from other areas, and were still above control plot levels after eight years. While nutrient losses were significant relative to the amount in the standing biomass, they are small in relation to total soil pools.

During the period of peak NO₃ concentrations, drainage water alkalinity was depressed. Slightly elevated SO₄ and Cl levels were observed in the second year after cutting but these later fell to below control levels, apparently due to dilution by increased water flux. Outputs of SO₄ and Cl from the control plots were nearly in balance with atmospheric inputs. After harvest, increases in base cation leaching were larger than could be accounted for simply by balancing of charges from the loss of NO₃, apparently due to increased HCO₃ leaching brought about by the increased water flux. Charge balance calculations indicate that organic anions are an important source of negative charge in the drainage waters, particularly in the control plot, and that these reach a maximum early in the period of high water discharge.

References

- Adamson, J.K., Hornung, M., Pyatt, D. G. and Anderson, A.R., 1987. Changes in solute chemistry of drainage waters following the clearfelling of a Sitka spruce plantation. *Forestry*. **60**: 165-177.
- American Public Health Association (1989). *Standard methods for the Examination of Water and Wastewater*. Washington D.C. pp. 2-36, 38.
- Baron, J., Denning, A.S. and McLaughlin, P., 1991. Deposition. In: Baron, J., (Editor) *Biogeochemistry of a subalpine ecosystem. Loch Vale watershed*. Ecol. Stud. **90**. Springer-Verlag, New York, pp. 48-75.
- Brakke, D.F., Henriksen, A. and Norton, S.A., 1990. A variable F-Factor to explain changes in base cation concentrations as a function of strong acid deposition. *Verh. Internat. Verein. Limmol.* **24**: 146-149.
- Caine, M. and Thurman, E.M., 1990. Temporal and spatial variations in an alpine stream, Colorado Front Range. *Geomorphology* **4**: 55-72.
- Duan, N., 1983. Smearing estimate: A nonparametric retransformation method. Theory and Methods Section, *J. Am. Stat. Assoc.* **78**: 605-610.
- Henriksen, A., 1980. Acidification of freshwaters—a large scale titration. In: D. Drablos and A. Tollan (Editors), *Ecological impact of Acidic Precipitation: Proceedings of an International Conference March 11-14, Sandefjord*. Norway SNSF Project, Oslo, Norway. pp. 68-74.
- Hornbeck, J.W. and Kropelin, W., 1982. Nutrient removal and leaching from a whole-tree harvest of northern hardwoods. *J. Environ. Qual.* **11**: 309-316.
- Hornbeck, J.W., Smith, C.T., Martin, Q.W., Tritton, L.M. and Pierce, R.S., 1990. Effects of intensive harvesting on nutrient capitals of three forest types in New England. *For. Ecol. Manag.* **30**: 55-64.
- Hornbeck, J.W. and Swank, W.T., 1992. Watershed ecosystem analysis as a basis for multiple use management of eastern forests. *Ecol. Appl.* **2**: 238-247.
- Johnson, D.W. and Todd, D.E., 1987. Nutrient export by leaching and whole tree harvesting in a loblolly pine and mixed oak forest. *Plant Soil.* **102**: 99-109.
- Kaufmann, M.R., Edminster, C.B. and Troendle, C.A., 1982. Leaf area determinations for subalpine tree species in the central Rocky Mountains. USDA For. Serv., Rocky Mount. For. Range Exp. Stn., Fort Collins, CO, Res. Pap. 238, 7 pp.
- Knight, D.H., Yavitt, J.B. and Joyce, G.D., 1991. Water and nitrogen outflow from lodgepole pine forest after two levels of tree mortality. *For. Ecol. Manag.* **46**: 215-225.
- Likens, G.E., Bormann, F.H., Johnson, N.M., Fisher, D.W. and Pierce, R.S., 1970. Effects of forest cutting and herbicide treatment on nutrient budgets in the Hubbard Brook watershed-ecosystem. *Ecol. Monogr.* **40**: 23-47
- Mann, L.K., Johnson, D.W., West, D.C., Cole, D.W., Hornbeck, J.W., Martin, C.W., Riekerk, H., Smith, C.T., Swank, W.T., Tritton, L.M. and van Lear, D.H., 1988. Effect of whole tree and stem only clear cutting on post harvest hydrologic losses, nutrient capital, and regrowth. *For. Sci.* **34**: 412-428.
- Martin, C.W., Pierce, R.S., Likens, G.E. and Bormann, F.H., 1986. Clear cutting affects stream chemistry in the White Mountains of New Hampshire. *USDA For. Serv., Northeast. For. Range Exp. Stn., Radnor, PA, Res. Pap.* **579**, 12 pp.
- McLean, E.O., 1982. Soil pH and lime requirement. In: *Methods of soil analysis, Part II*, A.L. Page, R.H. Miller, and D.R. Keeney (Editors), Soil Sci. Soc. Am. J., Madison, WI, pp. 199-224.
- Neal, C., 1988. Bicarbonate estimation from alkalinity determi-

- nations for neutral to acidic low alkalinity natural waters: theoretical considerations. *Hydrol. Sci. J.* 33: 619–623.
- NCASI., 1983. *Field study program to assess the sensitivity of soils to acidic deposition induced alterations in forest productivity*. Tech. Bull. 404. National Council of the Paper Industry for Air and Stream Improvement, Inc. 260 Madison Ave. NY. 85p.
- Nelson, D.W. and Sommers, L.E., 1982. Total carbon, organic carbon and organic matter. In: *Methods of soil analysis, Part II*, A.L. Page, R.H. Miller, and D.R. Keeney (Editors), Soil Sci. Soc. Am., Madison, WI, pp. 199–224.
- Oliver, B.G., Thurman, E.M. and Malcom, R.L., 1983. The contribution of humic substances to the acidity of colored natural waters. *Geochim. Cosmochim. Acta.* 47: 2031–2035.
- Pearson, J.A., Knight, D.H. and Fahey, T.J., 1987. Biomass and nutrient accumulation during stand development in Wyoming lodgepole pine forests. *Ecology* 68 (6): 1966–1973.
- Reuss, J.O. and Johnson, D.W., 1985. Effect of soil processes on the acidification of water by acid deposition. *J. Environ. Qual.* 14: 26–31.
- Reuss, J.O. and Johnson, D.W., 1986. *Acid deposition, soils and waters*. Ecological Studies Series No. 59. Springer-Verlag, New York. 109 pp.
- Reuss, J.O., Vertucchi, F.A., Musselman, R.C. and Sommerfeld, R.A., 1993. Biogeochemical fluxes in the Glacier Lakes catchments. *USDA, For. Serv., Rocky Mount. For. Range Exp. Stn.*, Fort Collins, CO, Res. Pap. R.M-314, 27 pp.
- Reynolds, B. and Neal, C., 1987. A comment on the use of acidimetric titrations for the estimation of the alkalinity and bicarbonate content of acid upland surface waters. *Sci. Tot. Environ.*, 65: 155–161.
- Reynolds, B., Stevens, P.A., Hughes, S., Parkinson, J. A., and Weatherley, N.S., 1995. Stream chemistry impacts of Conifer harvesting in Welsh catchments. *Wat., Air, Soil Pollut.* 79: 147–170.
- Ryan, M.G. and Waring, R.H., 1992. Maintenance respiration and stand development in a subalpine lodgepole pine forest. *Ecology* 73: 2100–2108.
- Schoettle, A.W., 1989. Potential effect of premature needle loss on the foliar biomass and nutrient retention in lodgepole pine. In: Olson, R. K., and A.S. Lefohn. (Editors), *Effects of air pollution on western forests*. Air and Waste Management Association. Pittsburgh, PA. pp. 443–454.
- Stevens, B.A., and M. Hornung., 1990. Effect of harvest intensity and ground flora establishment on inorganic-N leaching from a Sitka spruce plantation in North Wales U.K. *Biogeochemistry* 10: 53–65.
- Stottlemeyer, R., Kepner, R., Lewin, J., Rutkowski, D., Toczydlowski, D. and Toczydlowski, P., 1989. Effects of atmospheric acid deposition on watershed/lake ecosystems and Michigan's Upper Peninsula. *Great Lakes Area Resources Study Unit, Tech Rep.* 41. 1989 Progress report submitted to Dr. Ron Hiebert, Chief Scientist, Midwest Region, National Park Service, Omaha, NE. 37 pp.
- Stump, L.M. and Binkley, D.H., 1993. Relationships between litter quality and nitrogen availability in Rocky Mountain forests. *Can. J. For. Res.* 23: 492–502.
- Troendle, C.A., 1985. Streamflow generation from subalpine forests. In: Jones, B. and T. Ward. (Editors), *Watershed Management in the Eighties*. Am. Soc. Civil Eng. New York, NY. pp. 240–247.
- Troendle, C.A., 1987. Effect of clear cutting on streamflow generating processes from a subalpine forest. In: Swanson, R.H., Bernier, P.Y. and Woodard, P.D. (Eds), *Forest Hydrology and Watershed Management*. International Association of Hydrological Sciences. Pub. No. 167. pp. 545–552.
- Troendle, C.A. and Nilles, M.A., 1987. The effect of clear cutting on chemical exports in lateral flow from different depths on a subalpine forest slope. In: Swanson, R.H., Bernier P.Y. and Woodard P.D. (Eds), *Forest Hydrology and Watershed Management*. International Association of Hydrological Sciences. Washington, D.C., Pub. No. 167. pp. 423–432.
- Troendle, C.A., and Reuss, J.O., 1997. Effect of clear cutting on snow accumulation and water outflow at Fraser, Colorado. *Hydrol. Earth Sys. Sci.* 1(2) 313–324.
- Yin, X., 1993. Variation in foliar nitrogen concentration by forest type and climatic gradients in North America. *Can. J. For. Res.* 1587–1602.