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EFFECTS OF FOREST CUTTING AND HERBICIDE TREATMENT ON NUTRIENT BUDGETS IN THE HUBBARD BROOK WATERSHED-ECOSYSTEM¹

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Abstract. All vegetation on Watershed 2 of the Hubbard Brook Experimental Forest was cut during November and December of 1965, and vegetation regrowth was inhibited for two years by periodic application of herbicides. Annual stream-flow was increased 33 cm or 39% the first year and 27 cm or 28% the second year above the values expected if the watershed were not deforested.

Large increases in streamwater concentration were observed for all major ions, except NH_4^+ , $\text{SO}_4^{=}$ and HCO_3^- , approximately five months after the deforestation. Nitrate concentrations were 41-fold higher than the undisturbed condition the first year and 56-fold higher the second. The nitrate concentration in stream water has exceeded, almost continuously, the health levels recommended for drinking water. Sulfate was the only major ion in stream water that decreased in concentration after deforestation. An inverse relationship between sulfate and nitrate concentrations in stream water was observed in both undisturbed and deforested situations. Average streamwater concentrations increased by 417% for Ca^{++} , 408% for Mg^{++} , 1558% for K^+ and 177% for Na^+ during the two years subsequent to deforestation. Budgetary net losses from Watershed 2 in kg/ha-yr were about 142 for $\text{NO}_3\text{-N}$, 90 for Ca^{++} , 36 for K^+ , 32 for $\text{SiO}_2\text{-Si}$, 24 for Al^{+++} , 18 for Mg^{++} , 17 for Na^+ , 4 for Cl^- , and 0 for $\text{SO}_4\text{-S}$ during 1967-68; whereas for an adjacent, undisturbed watershed (W6) net losses were 9.2 for Ca^{++} , 1.6 for K^+ , 17 for $\text{SiO}_2\text{-Si}$, 3.1 for Al^{+++} , 2.6 for Mg^{++} , 7.0 for Na^+ , 0.1 for Cl^- , and 3.3 for $\text{SO}_4\text{-S}$. Input of nitrate-nitrogen in precipitation normally exceeds the output in drainage water in the undisturbed ecosystems, and ammonium-nitrogen likewise accumulates in both the undisturbed and deforested ecosystems. Total gross export of dissolved solids, exclusive of organic matter, was about 75 metric tons/km² in 1966-67, and 97 metric tons/km² in 1967-68, or about 6 to 8 times greater than would be expected for an undisturbed watershed.

The greatly increased export of dissolved nutrients from the deforested ecosystem was due to an alteration of the nitrogen cycle within the ecosystem.

The drainage streams tributary to Hubbard Brook are normally acid, and as a result of deforestation the hydrogen ion content increased by 5-fold (from pH 5.1 to 4.3).

Streamwater temperatures after deforestation were higher than the undisturbed condition during both summer and winter. Also in contrast to the relatively constant temperature in the undisturbed streams, streamwater temperature after deforestation fluctuated 3-4°C during the day in summer.

Electrical conductivity increased about 6-fold in the stream water after deforestation and was much more variable.

Increased streamwater turbidity as a result of the deforestation was negligible, however the particulate matter output was increased about 4-fold. Whereas the particulate matter is normally 50% inorganic materials, after deforestation preliminary estimates indicate that the proportion of inorganic materials increased to 76% of the total particulates.

Supersaturation of dissolved oxygen in stream water from the experimental watersheds is common in all seasons except summer when stream discharge is low. The percent saturation is dependent upon flow rate in the streams.

Sulfate, hydrogen ion and nitrate are major constituents in the precipitation. It is suggested that the increase in average nitrate concentration in precipitation compared to data from 1955-56, as well as the consistent annual increase observed from 1964 to 1968, may be some measure of a general increase in air pollution.

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INTRODUCTION

Management of forest resources is a worldwide consideration. Approximately one-third of the surface of the earth is forested and much of this is managed or deforested by one means or another.

Forests may be temporarily or permanently reduced by wind, insects, fire, and disease or by human activities such as harvesting or management utilizing physical or chemical techniques. Management goals range from simple harvest of wood and wood products, to increased water yields, to military stratagems involving defoliation of extensive forested areas.

Despite the importance of the forest resource, there is very little quantitative information at the ecosystem level of understanding on the biogeochemical interactions and implications resulting from large-scale changes in habitat or vegeta-

tion. This gap in our understanding results because it is particularly difficult to get quantitative ecological information that allows predictions about the entire ecosystem. The goal of the Hubbard Brook Ecosystem study is to understand the energy and biogeochemical relationships of northern hardwood forest watershed-ecosystems as completely as possible in order to propose sound land management procedures.

The small watershed approach to the study of hydrologic-nutrient cycle interaction used in our investigations of the Hubbard Brook Experimental Forest (Bormann and Likens 1967) provides an opportunity to deal with complex problems of the ecosystem on an experimental basis. The Hubbard Brook Experimental Forest, maintained and operated by the U.S. Forest Service, is especially well-suited to this approach since ecosystems can be defined as discrete watersheds with similar northern hardwood forest vegetation and a homogeneous bedrock, which forms an impermeable base (Bormann and Likens, 1967; Likens, *et al.*, 1967). Thus, the six small watersheds we have used at Hubbard Brook provide a replicated experimental design for manipulations at the ecosystem level of organization.

All vegetation on Watershed 2 (W2) was cut during the late fall and winter of 1965, and subsequently treated with herbicides in an experiment designed to determine the effect on 1) the quantity of stream water flowing out of the

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watershed, and 2) fundamental chemical relationships within the forest ecosystem, including nutrient relationships and eutrophication of stream water. In effect this experiment was designed to test the homeostatic capacity of the ecosystem to adjust to cutting of the vegetation and herbicide treatment. This paper will discuss the results of this experimental manipulation in comparison to adjacent, undisturbed watershed-ecosystems.

THE HUBBARD BROOK ECOSYSTEM

The hydrology, climate, geology, and topography of the Hubbard Brook Experimental Forest have been reported in detail elsewhere (Likens, *et al.*, 1967).

The climate of this region is dominantly continental. Annual precipitation is about 123 cm (Table 1), of which about one-third to one-fourth is snow. Although precipitation is evenly dis-

TABLE 1. Average annual water budgets for Watersheds 1 through 6 of the Hubbard Brook Experimental Forest. Watershed 2 has been excluded from the averages for 1965-68; 1967-68 is based on Watersheds 1, 3, and 6 only

Water Year (1 June-31 May)	Precipitation (P) (cm)	Runoff (R) (cm)	P-R (Evaporation and Transpiration) (cm)
1963-64.....	117.1	67.7	49.4
1964-65.....	94.9	48.8	46.1
1965-66.....	124.5	72.7	51.8
1966-67.....	132.5	80.6	51.9
1967-68.....	141.8	89.4	52.4
1963-68.....	122.2	71.8	50.4
1955-68.....	122.8	71.9	50.9

tributed throughout the year, stream flow is not. Summer and early autumn stream flow is usually low; whereas the peak flows occur in April and November. Loss of water due to deep seepage appears to be minimal in the Hubbard Brook area (Likens, *et al.*, 1967). The bedrock of the area is a medium to coarse-grained sillimanite-zone gneiss of the Littleton Formation and consists of quartz, plagioclase and biotite with lesser amounts of sillimanite. The mantle of till is relatively shallow and has a similar mineral and chemical composition to the bedrock. The soils are podzolic with a pH less than 7. Despite extremely cold winter air temperatures, soil frost seldom forms since insulation is provided by several centimeters of humus and a continuous winter snow cover (Hart *et al.*, 1962).

METHODS AND PROCEDURES

Precipitation is measured in the experimental watershed with a network of precipitation gauges,

approximately 1 for every 12.9 hectares of watershed. Streamflow is measured continuously at stream-gauging stations, which include a V-notch weir or a combination of V-notch weir and San Dimas flume anchored to the bedrock at the base of each watershed.

Weekly samples of precipitation and stream water were obtained from the experimental areas for chemical analysis. Rain and snow were collected in two types of plastic containers, 1) those continuously uncovered or 2) those uncovered only during periods of rain or snow. One-liter samples of stream water were collected in clean polyethylene bottles approximately 10 m above the weir in both the deforested and undisturbed watersheds. Chemical concentrations characterizing a period of time are reported as weighted averages, computed from the total amount of precipitation or streamflow and the total calculated chemical content during the period. Details concerning the methods used in collecting samples of precipitation and stream water, analytical procedures, and measurement of various physical characteristics have been given by Bormann and Likens (1967), Likens, *et al.* (1967), and Fisher, *et al.* (1968).

During November and December of 1965 all trees, saplings and shrubs of W2 (15.6 ha) were cut, dropped in place, and limbed so that no slash was more than 1.5 m above the ground. No roads were made on the watershed and great care was taken to minimize erosion. No timber or other vegetation was removed from the watershed. Regrowth of vegetation was inhibited by aerial application of the herbicide, Bromacil ($C_9H_{13}BrN_2O_2$), at 28 kg/ha on 23 June 1966. Approximately 80% of the mixture applied was Bromacil and 20% was largely inert carrier (H. J. Thome, personal communication). Also, during the summer of 1967, approximately 87 liters of an ester of 2, 4, 5-trichlorophenoxyacetic acid (2, 4, 5-T) was individually applied to scattered regrowths of stump sprouts.

The results reported cover the period immediately following the cutting of the vegetation on W2, 1 January 1966 through 1 June 1968.

HYDROLOGIC PARAMETERS

The annual hydrologic regime at Hubbard Brook has varied greatly since we began our study in 1963 (Table 1). The 1964-65 water-year was exceptionally dry, and 1967-68 was very wet. These fortuitous extremes have provided a wide range of hydrologic conditions for our study of the hydrologic-nutrient cycle interactions.

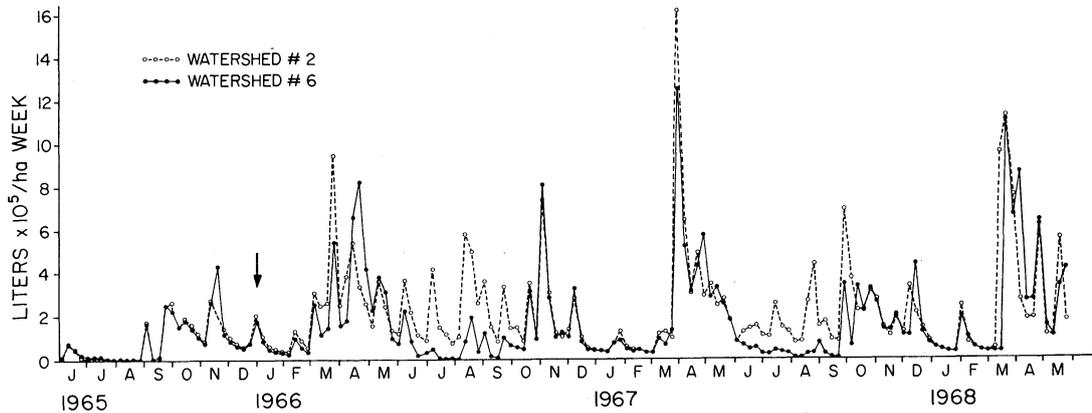


FIG. 1. Average weekly stream water discharge from Watersheds 2 and 6 during 1965-68. The vegetation on Watershed 2 was cut during November and December 1965. The arrow indicates the completion of the cutting.

Chemical input into a watershed from meteorological sources is based in part on the volume of precipitation, thus it is important to determine whether precipitation is distributed randomly throughout the watersheds. Our studies in 1963-64 and 1964-65 indicated no significant difference between rain gauges at different elevations (Likens *et al.*, 1967). Subsequent data indicate that there is generally very little difference in the precipitation pattern with elevation, but one or two storms of high intensity may significantly alter the spatial distribution for total annual precipitation within the area. Since the overall precipitation pattern for 1966-67 and 1967-68 was more variable than previous years, we have calculated the precipitation input for each watershed, for these two years, on the basis of Thiessen averages established for the area (see Thiessen, 1923). In spite of the variation in precipitation and runoff, the amount of water lost by evaporation and transpiration from undisturbed watersheds remained about the same each year during 1963 to 1968 (Table 1).

Cutting the vegetation of W2 produced a significant effect on the distribution of water loss from the watershed. These changes are reported in detail elsewhere (Hornbeck, *et al.*).

The annual runoff in 1967-68 and 1968-69 from the deforested ecosystem increased by 39% and 28%,³ respectively, over the values expected had the watershed not been cut (Table 2). The greatest difference occurred during June through September, when runoff values were 414% (1966-67) and 380% (1967-68) greater than expected.

³ The slight discrepancy from data presented by Hornbeck, *et al.*, is due to rounding errors incurred in the conversion of English to metric units.

The increased streamflow during summer is directly attributable to the removal of transpiring surface. In addition to the increased yield of

TABLE 2. Runoff and precipitation for Watershed 2 (cut-over) of the Hubbard Brook Experimental Forest, expressed in cm of water. The watershed was clear-cut in November and December of 1965. Predicted values for runoff were calculated from regression analyses established during a pretreatment calibration period. (After Hornbeck, *et al.*, 1970)

	1965-66	1966-67	1967-68
Precipitation	124.6	132.1	138.7
Predicted runoff	(77.7)	(86.5)	(96.7)
Measured runoff	79.9	119.9	123.4
Evaporation and Transpiration	44.7	12.2	15.4

drainage water from the watershed, the snowmelt was advanced a few days and was more rapid, particularly during 1967-68 (Fig. 1; Federer, 1969; Hornbeck and Pierce, 1969).

In various experiments throughout the world, with 100% reduction in forest cover by clear-cutting or chemical treatment, stream flow increases averaged about 20 cm the first year after treatment (Hibbert, 1967). Detailed studies at the Coweeta Hydrologic Laboratory, Southeastern Forest Experiment Station in North Carolina showed maximum increases in water yield of about 41 cm during the first year following the complete removal of the hardwood forest vegetation on small watersheds (Hoover, 1944).

PRECIPITATION CHEMISTRY

Sulfate and hydrogen ions are the most abundant constituents (in terms of chemical equivalents) in precipitation falling on the watersheds

TABLE 3. Average weighted ion content of bulk precipitation collected within the Hubbard Brook Experimental Forest from 1 June to 31 May expressed in mg/liter.

	1965-66	1966-67	1967-68
calcium	0.22	0.21	0.20
magnesium	0.04	0.03	0.05
potassium	0.05	0.05	0.05
sodium	0.16	0.10	0.12
aluminum	***	0.1	***
ammonium	0.21	0.18	0.22
hydrogen ion	0.07	0.08	0.07
nitrate	1.41	1.49	1.56
sulfate	3.3	3.1	3.3
chloride	0.21 ⁺	0.50##	0.35
bicarbonate	#	#	#
dissolved silica	***	***	***

***Not determined; probably less than 0.1

#Virtually absent

##Based on samples for 9 months. Samples collected from 1 September through 30 November were discarded because plastic screens were used on the collection apparatus (Juang and Johnson 1967; Fisher, *et al.* 1968).

+Calculated for the period September through August (Juang and Johnson, 1967).

at Hubbard Brook. The pH of rain and snow samples is frequently less than 4.0. Nitrate is next in abundance, and significant amounts of ammonium, chloride, sodium and calcium are usually present. Lesser amounts of magnesium, potassium and aluminum are also found (Table 3).

Since precipitation samples are composited over weekly intervals, it is difficult to identify the origin of chemical impurities in individual air masses or storms.

Our chemical input data are based on bulk precipitation, i.e., a mixture of rain or snow and dry fallout (Whitehead and Feth, 1964). We have been concerned with the contributions from dry fallout since the beginning of the study. Juang and Johnson (1967) suggested that dry fallout was a source of chloride in the Hubbard Brook ecosystem. However, based upon comparisons between precipitation collectors that were continuous open (Likens, *et al.*, 1967) and those that opened only during periods of rain or snow (Wong Laboratories, Mark IV), it is clear that the bulk of chemical input to the ecosystem comes in rain and snow. Our attempts to quantify the much smaller contributions from dry fallout have been thus far inconclusive.

Average values for the ion content of precipitation, interpolated from isopleth maps for central New Hampshire (Junge, 1958; Junge and Werby, 1958), do not agree closely with the average weighted concentration of ions measured in precipitation at Hubbard Brook (Table 3). Considering the yearly variation in precipitation chemistry (Likens, *et al.*, 1967; Fisher, *et al.*, 1968; Table 3), and that our samples were taken in 1965-68, it is not surprising that there is not

better agreement between our values and those obtained in 1955-56 by Junge and Werby. Our cation values are nearly 50% lower than those reported by Junge (1958) and Junge and Werby (1958); whereas our anion values, with the exception of chloride, are somewhat higher.

Soil and road dust are among the principal sources of base metal ions in local precipitation (*e.g.*, Gambel and Fisher, 1966). In the Hubbard Brook area, the almost total forest cover strongly minimizes the generation of soil dust, thereby reducing the concentration of these ions in the local precipitation.

The weighted concentration of nitrate in precipitation at Hubbard Brook is considerably higher than the concentrations reported by Junge (1958) for New England, and in fact, for most regions of the U. S. Since air pollution can affect the concentration of nitrate in precipitation (*e.g.*, Junge, 1963), our data might reflect some measure of increased air pollution between 1955-56 and 1965-66, and its resultant effect on nutrient budgets in rural as well as urban areas. In this regard it is interesting that our average values for nitrate in precipitation (rain and snow plus dry fallout) has increased each year since 1964; whereas most of the other chemical constituents remained constant or fluctuated slightly (Table 3).

CHEMICAL INPUT THROUGH HERBICIDE APPLICATION

Our nutrient budgets are based on the difference between chemical input in precipitation and output in stream water from the watershed-ecosystems (Bormann and Likens, 1967). Thus, it is important to account for any extraneous chemical inputs to the ecosystem, such as an application of herbicide. Approximately 3650 liters of Bromacil solution were sprayed on the cutover watershed in June 1966. Based on a chemical analysis of the herbicide solution, and assuming complete decomposition, 0.04 Ca⁺⁺/ha, 0.09 kg Mg⁺⁺/ha, 0.01 kg K⁺/ha, 0.11 kg Na⁺/ha, and 10.6 kg NO₃⁻/ha were added to the watershed. These are relatively insignificant inputs to the budgets for the deforested watershed. Bromide is equivalent to chloride with the analytical method we use for chloride (Iwasuki *et al.*, 1952). Thus we have calculated a maximum possible input of 3.0 kg/ha to the chloride budget from Bromacil.

Approximately 87 liters of an ester (propylene glycol butyl ether) of 2, 4, 5-T were sprayed on the cutover watershed during the summer of 1967. This herbicide was mixed with water from

the drainage stream of the watershed to produce the spray solution. Chemical analyses of the solution showed that negligible amounts of cations were added to the watershed-ecosystem from this application of herbicide. However we calculated a maximum input of 0.7 kg Cl⁻/ha to the watershed from the herbicide solution. Inputs for other anions were negligible.

STREAMWATER PARAMETERS

Temperature

The drainage streams in the undisturbed watersheds during summer are in deep shade beneath the forest canopy; in winter they are under a deep snow pack. Thus, for most of the year, daily stream water temperatures are relatively constant and the annual temperature range is only about 16°C (Figs. 2 and 3).

The altitudinal temperature gradient in stream water varies somewhat in the undisturbed watersheds, and in Watershed 4 during midsummer it is about 5–7°C. At times it may be as much as 12°C, however the steepest portion of this thermal gradient is confined largely to the upper 50 m of the stream (McConnochie and Likens, 1969). Macan (1958) and others have shown that small streams usually warm and reach equilibrium temperatures rapidly, and that the average

water temperature approximates the average air temperature. In winter, the altitudinal temperature gradient in streams within the watersheds is not more than 1 or 2°C.

Streamwater temperatures in the deforested watershed (W2) were higher than in the undisturbed watersheds during both summer and winter. In the absence of shade, temperature varied by 3–4°C during the day in summer; the maximum temperature occurred about 1500 hours and the minimum at 0700–0800 hours (Fig. 3). The annual variation was about 18 to 20°C (Fig. 2).

Even though the mean January air temperature is –9°C (U. S. Forest Service, 1964), the streams do not freeze solid. In fact, they are relatively warm below the thick snow pack in winter (Figs. 2 and 3). A thicker snow depth in the stream channel of the deforested watershed could provide more insulation and may account for the somewhat higher streamwater temperature. As mentioned earlier, frost is uncommon in the soils of the watersheds.

The streams seem to have discrete summer and winter temperature regimes with rapid seasonal transitions. Warm-up during the spring is very rapid, occurring mostly in May in the undisturbed situation (Fig. 2).

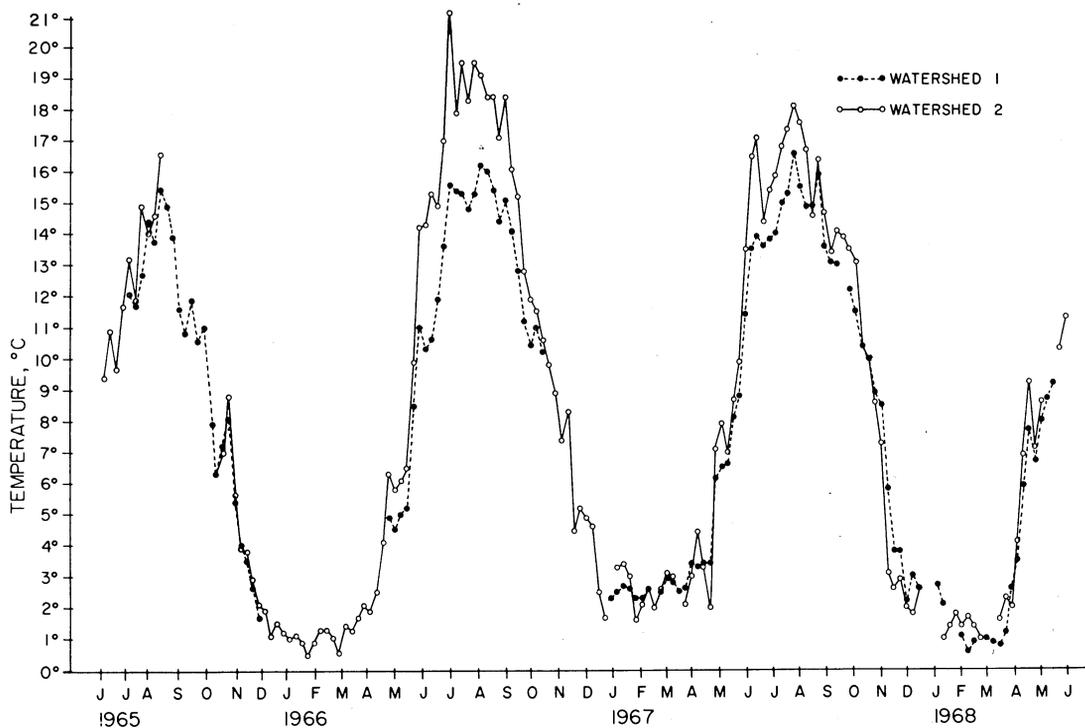


FIG. 2. Mean weekly stream water temperatures in Watersheds 1 and 2 (deforested) during 1965–68. The recording thermometers were located above the weirs in each stream. The points were not connected during periods when the stream discharge was negligible or when the thermograph functioned improperly.

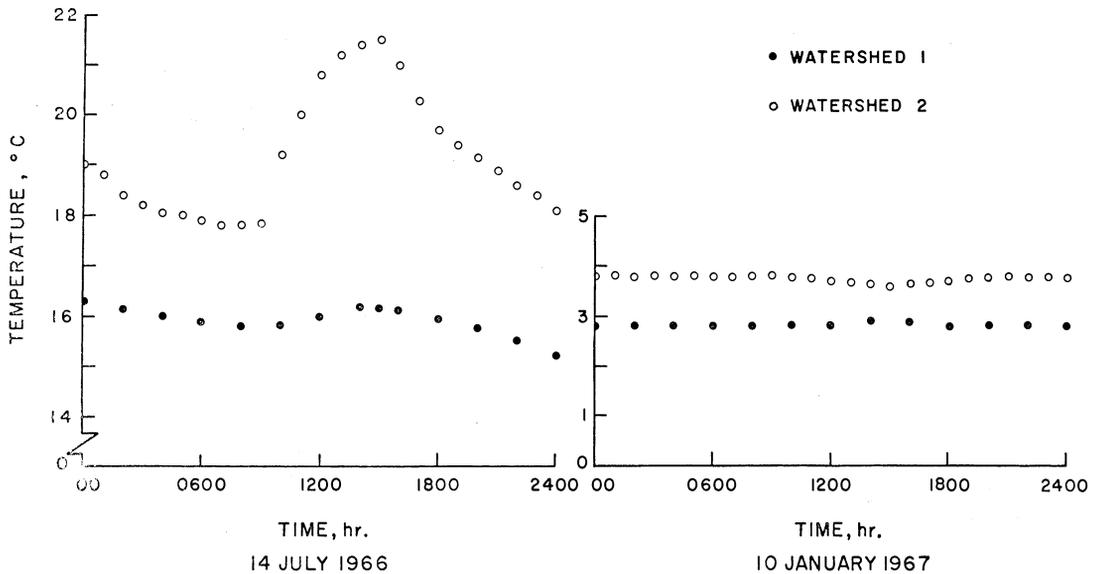


FIG. 3. Mean hourly stream water temperatures during one day in the summer and one day in the winter in Watersheds 1 and 2 (deforested).

DISSOLVED OXYGEN

The stream water from the Hubbard Brook watersheds is normally saturated or slightly supersaturated with dissolved oxygen, except during periods of very low flow, *e.g.*, late summer and early autumn (Fig. 4). There is no apparent

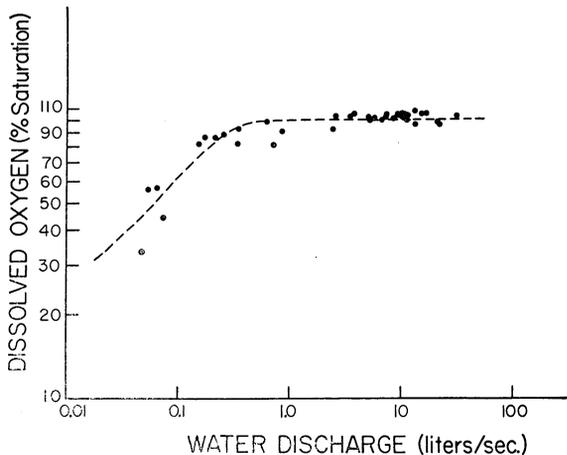


FIG. 4. Relationship between dissolved oxygen and stream water discharge in undisturbed Watershed 3 during 1965-66. The equation for the dashed line is $C = (1 - e^{-(D)^{0.06993}}) 79.26 + 22.59$, where C = dissolved oxygen in % saturation and D = stream discharge in liters/sec. The constants in this equation were determined by linear regression analysis and the F-ratio for the regression line is very highly significant (>0.001).

seasonal pattern separate from this dependence on discharge. The dissolved oxygen values are adjusted for altitude and streamwater temperature to calculate the percent saturation. Ruttner

(1953) indicates that the dissolved oxygen in streams, even in cascading water, should not exceed the saturation equilibrium with air. However, supersaturation of dissolved oxygen has been found by several other workers in natural streams and rivers (*e.g.*, Järnefelt, 1949; Harvey and Cooper, 1962; Minckley, 1963; Woods, 1960). The explanation of the supersaturated condition in streams tributary to Hubbard Brook is not readily apparent, although it may be "forced" to supersaturation by turbulence (Lindroth, 1957; Harvey and Cooper, 1962) or may be a function of the altitudinal temperature gradient in the streams. Photosynthetic organisms are not abundant in these tributary streams, and diel variations in dissolved oxygen are not apparent.

At low flows the water mostly seeps from one small pool to the next through gravel and organic debris dams. The biological oxygen demand from decaying leaves and other organic debris in the stream is apparently high enough to reduce significantly the dissolved oxygen concentration when flow and turbulence are low. Rapid depletion of dissolved oxygen resulting from decomposition of leaves in small streams has been demonstrated by several workers (see Minckley, 1963).

Increased water yield from the deforested watershed, particularly in the summer months (Fig. 1), results in greater discharge, more turbulence and a constant high level of dissolved oxygen in this stream. Thus, during the summer and autumn large differences in dissolved oxygen concentration may be anticipated between the streams

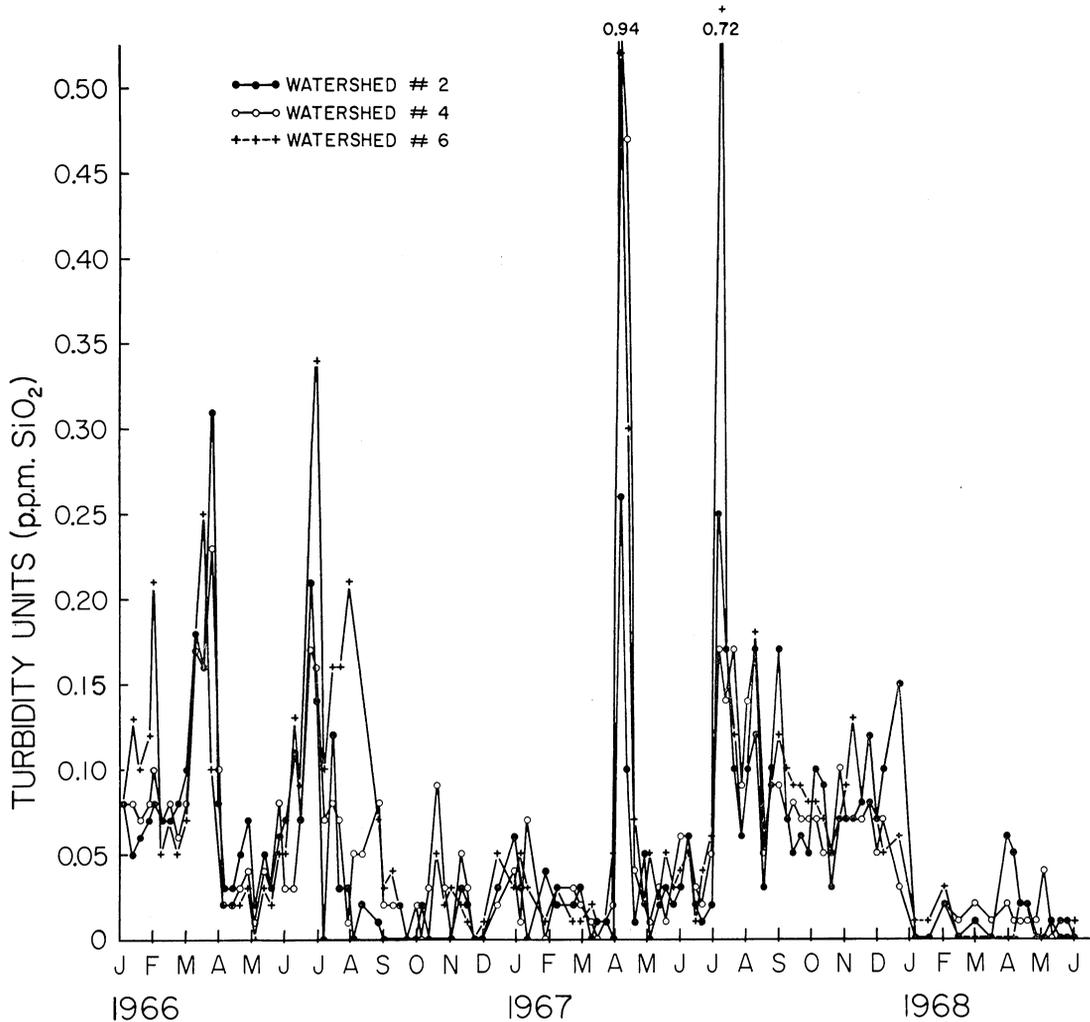


FIG. 5. Turbidity values for stream water from Watersheds 2 (deforested), 4 and 6 during 1966-1968.

in the deforested and undisturbed watersheds. With increased water temperature, sunlight and high concentrations of dissolved oxygen, more rapid decomposition of the organic debris would be expected in the stream of W2.

TURBIDITY

Following disturbance of the vegetation and litter in forested watersheds, drainage waters may become quite turbid as the result of erosion and transport of inorganic and organic matter from the watershed (*e.g.*, Lieberman and Hoover, 1948a; Tebo, 1955). For example, this frequently occurs as a consequence of unregulated commercial logging operations. However, with care and planning, turbidity and sedimentation in drainage streams may be minimized following commercial logging (Hewlett and Hibbert, 1961; Lieberman and Hoover, 1948b; Trimble and Sartz, 1957).

Stream water draining the Hubbard Brook Experimental Forest is very clear, and no obvious differences were noted in the turbidity of the stream water from W2 following the cutting and herbicide treatment of the vegetation (Fig. 5). In fact, the peak turbidity values seemed to be depressed in comparison with values for streams in the undisturbed watersheds. Of the three watersheds compared, W6 showed the greatest extremes in turbidity, and these extreme values were also slightly out-of-phase with changes in the other watersheds (Fig. 5). High values were not always correlated with high runoff values, *e.g.*, during June 1966 and July 1967. All in all, the measurements of turbidity were of little value in assessing the changes in water quality of the stream water of these forested and deforested ecosystems.

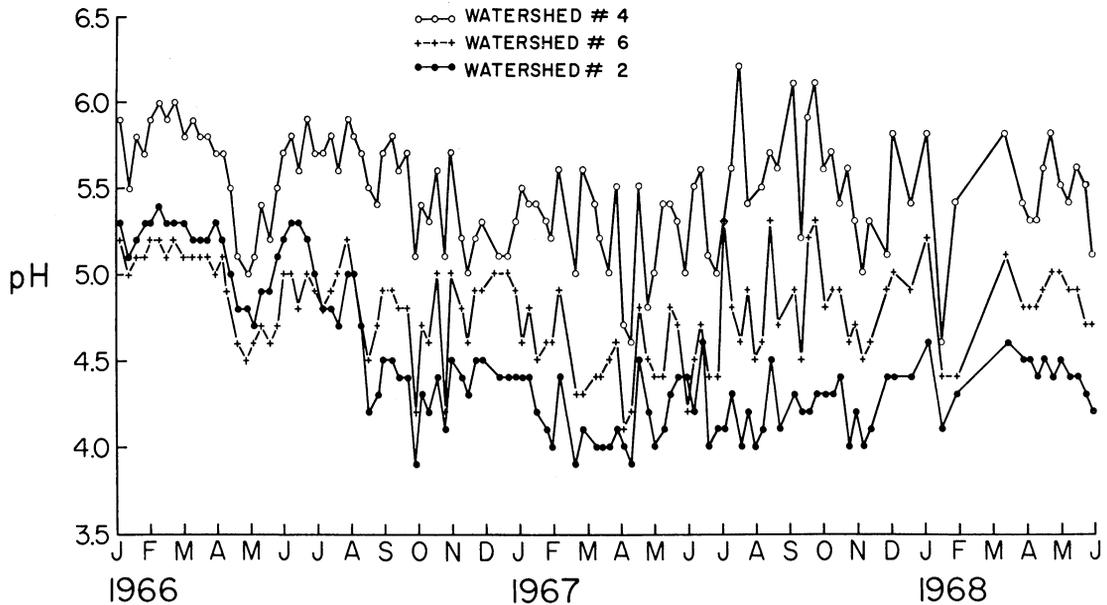


Fig. 6. pH values for stream water from Watersheds 2 (deforested), 4 and 6 during 1966-1968.

PARTICULATE MATTER

Undisturbed forest ecosystems lose relatively little organic and inorganic particulate matter. Average annual losses are about 25 kg/ha-yr., and are about equally divided between organic and inorganic particulate matter (Bormann, *et al.*, 1969). These minor particulate matter losses, about one-sixth of the dissolved substance losses, are attributed to the operation of biotic factors, which 1) decrease the erodability of the ecosystem, 2) decrease the amount of runoff and 3) tend to damp the frequency of high discharge rates.

The influence of these biotic factors has been severely limited by removal of the living vegetation in Watershed 2. Compared to undisturbed Watershed 6, the new conditions in Watershed 2 are reflected by a 4-fold increase in particulate matter in the settling basin above the V-notch weir for the period May 1966 to May 1968. Also, particulate matter output from Watershed 2 is becoming increasingly inorganic in content (76% inorganic, May 1966 to May 1968).

The increased output in particulate matter, and particularly the increased proportion of inorganic materials, from W2 occurred primarily from the unraveling of the stream channel. In many places the banks have been eroded and many of the small debris dams, composed of leaves, twigs, etc., that were common in the undisturbed stream, have worn away, with a subsequent release of trapped inorganic and organic materials. Because these dams no longer exist, and without the annual

replenishment of leaves and other organic debris to build new dams, stream water is able to transport much more particulate material downslope. Also, stream channel erosion is increased since the binding action of roots has been reduced, and leaves, which provide a protective cover on the banks, have been removed and not replenished.

pH

Acidic water characterizes the drainage streams from the undisturbed watersheds. This is typical for many streams in New England with podzolic soils (*e.g.*, Anderson and Hawkes, 1958). The pH values are variable throughout the year, but consistently show the same relationship between watersheds (Fig. 6). There was particularly good agreement in pattern between the undisturbed watersheds, W4 and W6, although stream water from W4 was relatively less acidic.

As a result of deforestation, and concurrently with other chemical changes in the drainage waters during June 1966, the hydrogen ion content (calculated from pH measurements) in stream water from W2 increased by 5-fold (Fig. 6). That is, the weighted average pH, decreased from 5.1 during 1965-66 to 4.3 during 1966-67 and 1967-68 (Likens, *et al.*, 1969). During the same period the weighted pH value remained relatively unchanged for W4 and W6.

ELECTRICAL CONDUCTIVITY

Electrical conductivity averages about 20 $\mu\text{mhos}/\text{cm}^2$ at 25°C in stream water of the undis-

TABLE 4. Weighted average concentration in stream water from watersheds 2, 4, and 6 of the Hubbard Brook Experimental Forest, expressed in mg/liter

Ion	W2			W4#		W6		
	1965-66	1966-67	1967-68	1965-66	1966-67	1965-66	1966-67	1967-68
Ca ⁺⁺	1.81*	6.45	7.55	1.82*	1.80	1.36*	1.27	1.28
Mg ⁺⁺	0.37	1.35	1.51	0.41	0.40	0.36	0.35	0.36
K ⁺	0.19	1.92	2.96	0.22	0.24	0.18	0.20	0.26
Na ⁺	0.87	1.51	1.54	1.13	1.10	0.83	0.80	0.93
Al ⁺⁺⁺	0.22	1.5	2.0	0.12	0.12	0.32	0.33	0.32
NH ₄ ⁺	0.14	0.07	0.05	0.12	0.06	0.12	0.05	0.02
NO ₃ ⁻	0.94	38.4	52.9	0.86	0.88	0.85	0.69	1.30
SO ₄ ⁼	6.8	3.8	3.7	6.4	6.2	6.2	6.0	6.1
Cl ⁻	0.54	0.89	0.75	0.56**	0.53	0.57***	0.55	0.56
HCO ₃ ⁻	0.8	0.1	0	1.6	2.0	0.1	0.2	0.3
SiO ₂ -aq	4.1	5.6	5.7	5.4	5.5	4.1	4.4	3.8
Total	16.8	61.6	78.7	18.6	18.9	15.0	14.8	15.2

*Values for the initial 7 months of the water-year have been increased by a factor of 1.6 to compensate for analytical interferences (Likens, *et al.*, 1967; Johnson, *et al.*, 1968).

**Juang and Johnson (1967) calculated a value of 0.51 for the period September through August.

***Juang and Johnson calculated a value of 0.50 for the period September through August.

#Data not available for 1967-68.

turbed watersheds and changes very little either on a daily or seasonal basis. This would be expected from the relative constancy of cation and anion concentrations in stream water at Hubbard Brook (Likens, *et al.*, 1967; Fisher, *et al.*, 1968; Johnson, *et al.*, 1969).

In contrast, the conductivity of stream water from the deforested watershed is quite variable, ranging from 65 and 160 μ mhos/cm² at 25°C. Usually the conductivity decreased during rain storms. However occasionally the conductivity increased or was unaffected. The hydrogen ion concentration of rain water added to the stream water is important in this regard, as well as other variables such as amount of rainfall, its duration, streamwater discharge, and water content of the soil.

IONS

Ammonium and Nitrate

The ammonium ion occurs in very low concentration in stream water from undisturbed watersheds of the Hubbard Brook Experimental Forest (Fisher, *et al.*, 1968). Essentially no change was observed in the concentration of this ion in drainage water from the deforested watershed. In contrast the nitrate concentration increased from an average weighted value of 0.9 mg/liter prior to cutting of the vegetation, to 53 mg/liter, two years later (Table 4). Measured concentrations soared to 82 mg/liter in October 1967 (Fig. 7). It should be noted that the initial increase (June 1966) in streamwater nitrate concentration in W2 occurred 16 days before the application of the Bromacil and at the same time the nitrate

concentration in the stream water from the undisturbed watershed showed the normal late-spring decline (Fig. 7; Bormann, *et al.*, 1968).

Nitrate concentrations in stream water from the undisturbed watersheds, show a pronounced, recurring seasonal pattern (Bormann, *et al.*, 1968; Fisher, *et al.*, 1968). Average monthly concentrations are low (<0.1 mg/l) throughout the summer growing season, increase in November, and reach values as high as 2 mg/liter during the spring (April) thaw (Fig. 8). This variation may be explained by a combination of mechanical and biological effects (Johnson, *et al.*, 1969).

The decline of nitrate concentrations during May and the low concentrations throughout the summer correlate with heavy nutrient demands by the vegetation and increased heterotrophic activity associated with warming of the soil. The winter pattern of NO₃⁻ concentration may be explained in strictly physical terms, since the input of nitrate in precipitation from November through May largely accounts for nitrate lost in stream water during this period (Bormann, *et al.*, 1968). Also, sublimation and evaporation of water from the snow pack could account for some 15-20% increase in concentration of NO₃⁻ in the stream water in the spring. Concentration of nitrate in stream water after deforestation show a pattern that is nearly the reciprocal of the undisturbed situation (Fig. 8).

Since yearly input of nitrate-nitrogen in precipitation exceeds losses in stream water in the undisturbed ecosystems (Table 5), the concentration of nitrate in stream water provides no conclusive evidence for nitrification in these un-

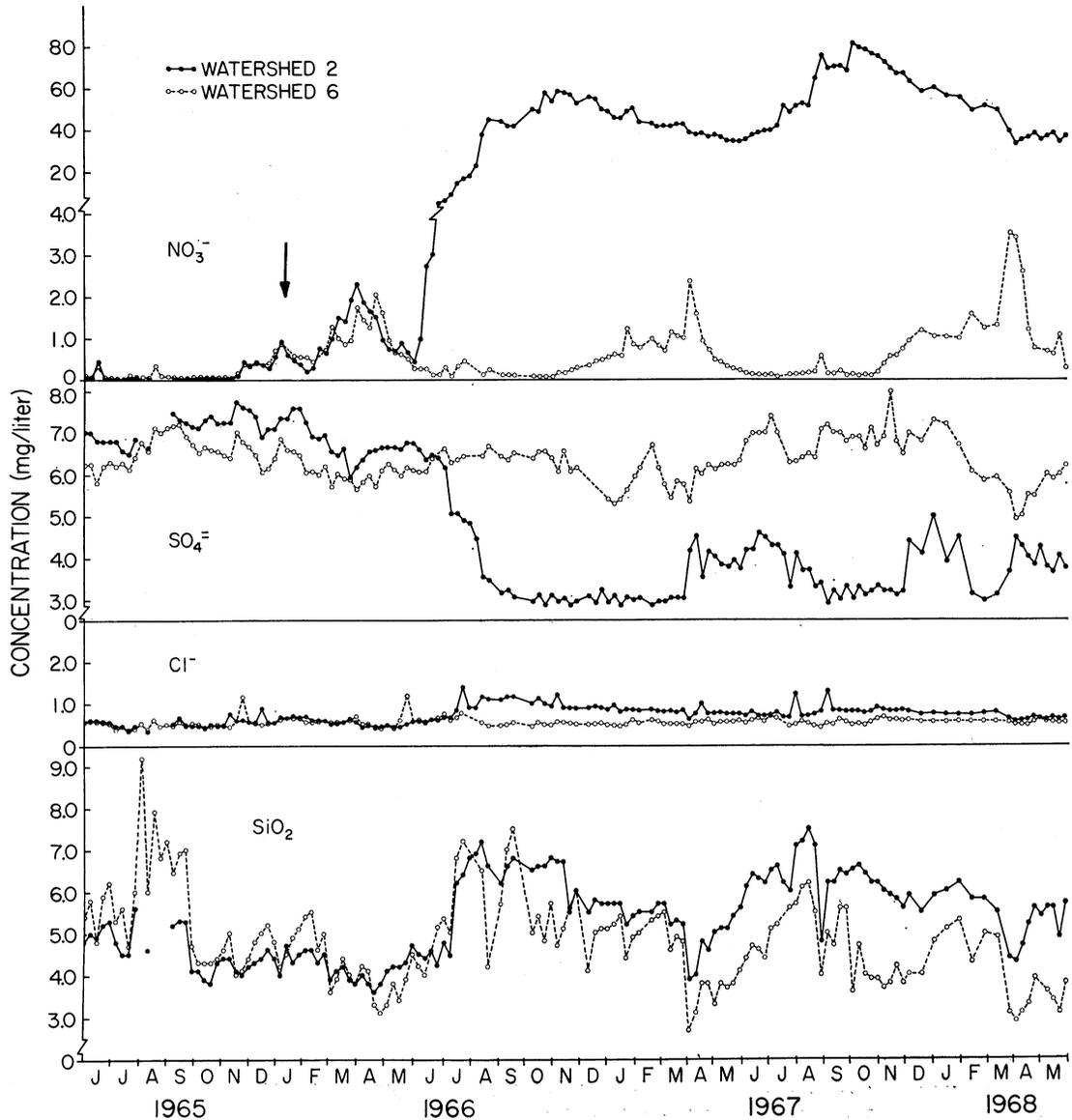


FIG. 7. Measured streamwater concentrations for nitrate, sulfate, chloride and dissolved silica in Watersheds 2 (deforested) and 6. Note the change in scale for the nitrate concentration. The arrow indicates the completion of cutting in W2.

disturbed acid soils. The low levels of ammonia and nitrate in the drainage water of the undisturbed ecosystem (W6) may attest to the efficiency of the oxidation of ammonia to nitrate, and to the efficiency of the vegetation in utilizing nitrate. However, Nye and Greenland (1960) state that growing, acidifying vegetation represses nitrification; thus the vegetation may draw directly on the ammonium pool, and little nitrate may be produced within the undisturbed ecosystem. However, in the absence of forest vegetation, the microflora of the deforested watershed apparently oxidize ammonia to nitrate, and the

nitrate is rapidly flushed from the watershed-ecosystem (Bormann, *et al.*, 1968; Likens, *et al.*, 1969).

Many microorganisms convert organic nitrogen into ammonia. The ammonia then may be oxidized to nitrite by bacteria of the genus *Nitrosomonas*. The nitrite may be further oxidized to nitrate by bacteria of the genus *Nitrobacter*. The important end products of these reactions in terms of nutrient losses from the watershed-ecosystem are the increased production of nitrate and hydrogen ions. Increased biological nitrification apparently is the principal factor responsible for

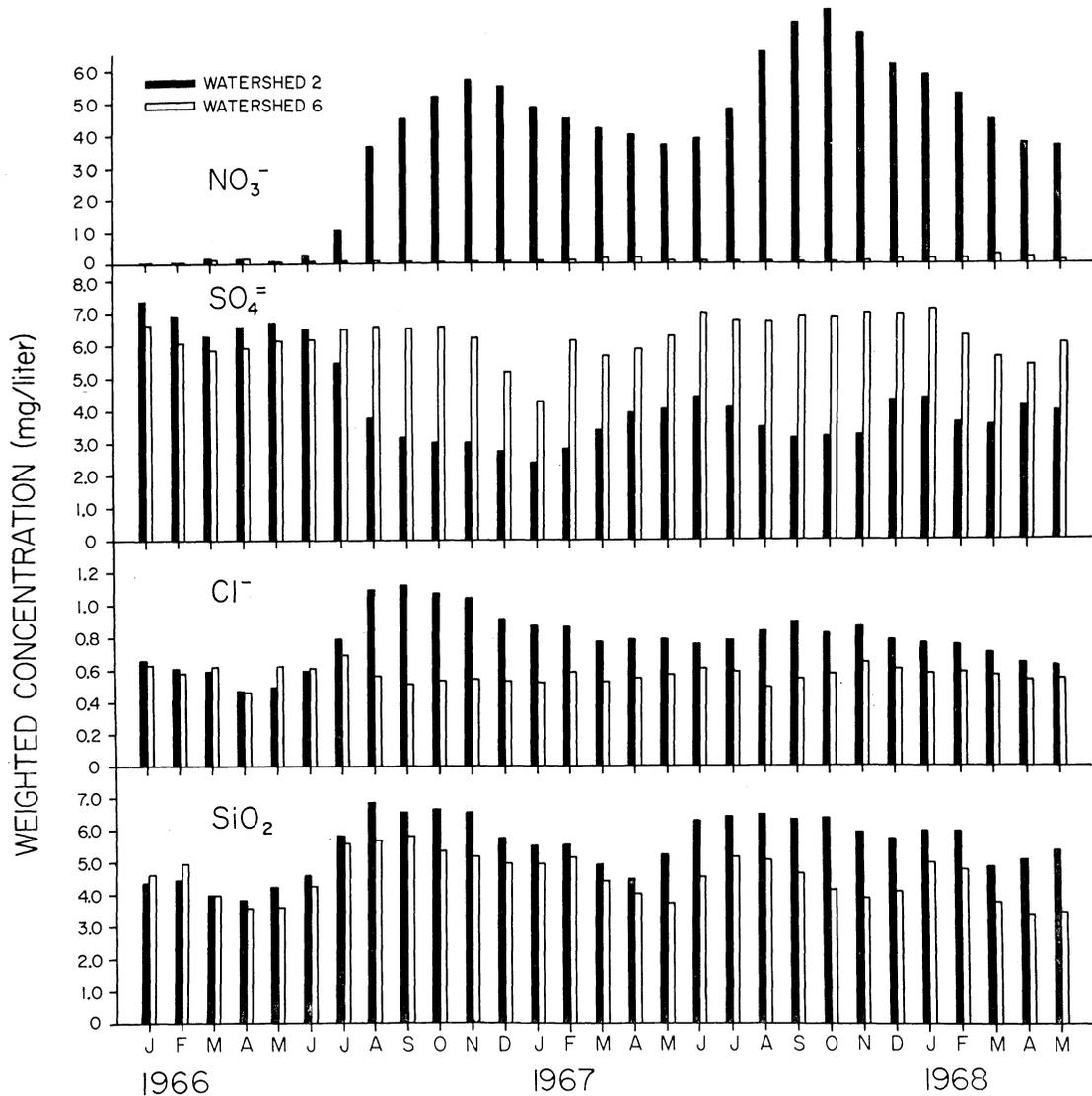


FIG. 8. Weighted average monthly concentrations of nitrate, sulfate, chloride and dissolved silica in stream water from Watersheds 2 (deforested) and 6.

the total flush of ions from the deforested watershed. The increase in the milliequivalent value for nitrate in the water years subsequent to cutting, balances (within 10–15% error limits for the watershed systems) the increased net losses of cations and the decreased net losses of anions (Likens, *et al.*, 1969). This will be discussed in more detail in a later section.

Alexander (1967) indicates that nitrification usually decreases greatly below a pH of 6.0 and becomes negligible at a pH of 5.0. Our data would indicate that this is not the case for our deforested watershed as shown by the increased concentration of nitrate in the drainage water during 1966–68 (Fig. 7), and the low pH of stream wa-

ters (Fig. 6) and soils. Also, in comparison with soils under undisturbed forest, bacteria of the genera *Nitrosomonas* and *Nitrobacter* have increased 18-fold and 34-fold, respectively, in the soil of Watershed 2 (Smith, *et al.*, 1968). Other workers have shown nitrification at similarly low pH's (Boswell, 1955; Weber and Gainey, 1962). It may be that we are dealing with relatively little known species of nitrifying bacteria adapted to more acid conditions (*e.g.*, Alexander, 1967).

Sulfate

Sulfate concentration in stream water from the undisturbed watersheds is relatively constant in relation to the highly variable stream discharge

TABLE 5. Nutrient budgets for undisturbed (W6) and cut-over (W2) watersheds of the Hubbard Brook Experimental Forest. Values are expressed in kg/ha for the period 1 June to 31 May

Element	W6			W2		
	Input	Output	Net los. or gain	Input	Output	Net loss or gain
Ca	2.4	10.7	-8.3	2.3	77.3	-75.0
Mg	0.4	2.9	-2.5	0.5	16.2	-15.7
K	0.6	1.7	-1.1	0.5	23.0	-22.5
Na	1.3	6.8	-5.5	1.3	18.1	-16.8
Al	1.4	2.8	-1.4	1.3	18.2	-16.9
NH ₄ -N	1.9	0.3	+1.6	1.8	0.7	+1.1
NO ₃ -N	4.6	1.3	+3.3	6.8	104	-97.2
SO ₄ -S	14.4	17.1	-2.7	13.6	15.3	-1.7
Cl	6.9**	4.6	+2.3	9.5**	10.6	-1.1
HCO ₃ -C	*	0.4	-0.4	*	0.2	-0.2
SiO ₂ -Si	*	17.2	-17	*	31.3	-31
1967-68						
Ca	3.0	12.2	-9.2	2.7	93.1	-90.4
Mg	0.8	3.4	-2.6	0.7	18.6	-17.9
K	0.8	2.4	-1.6	0.7	36.5	-35.8
Na	1.8	8.8	-7.0	1.7	19.0	-17.3
Al	*	3.1	-3.1	*	24.5	-24
NH ₄ -N	2.6	0.2	+2.4	2.4	0.5	+1.9
NO ₃ -N	5.2	2.8	+2.4	4.9	147	-142
SO ₄ -S	16.0	19.3	-3.3	15.16	15.15	0
Cl	5.2	5.3	-0.1	5.5	9.2	-3.7
HCO ₃ -C	*	0.5	-0.5	*	0	0
SiO ₂ -Si	*	17.0	-17	*	32.6	-32

*Not determined, but very low.

**Based on data for 9 months.

(Figs. 7 and 8; Fisher, *et al.*, 1968); and on close examination the sulfate concentration shows a very small and irregular volume concentration effect (Johnson, *et al.*, 1969). In addition stream-water concentrations of sulfate seem to show some general, recurring seasonal patterns. There is a gradual rise to maximum values in the autumn with lower values during the late winter and early spring. This pattern is nearly the reciprocal of the nitrate pattern (Figs. 7 and 8).

The weighted concentration of SO₄⁼ in drainage water from the deforested watershed decreased by about 45% in the first year subsequent to cutting and herbicide treatment (Table 4). The decrease in sulfate concentration was somewhat delayed in relation to the increase in nitrate concentration (Fig. 7). The explanation for this decrease in sulfate concentration is complicated and will be elaborated in the section on Nutrient Budgets.

Chloride

Since the quantity of chloride bearing rocks in the Hubbard Brook watershed-ecosystems is small (Juang and Johnson, 1967), and since biological immobilization is small, we expected the weighted concentration of Cl⁻ in precipitation after correction for evapotranspiration, to balance the concentration in drainage water from undis-

turbed ecosystems. However, during 1965-66 a higher concentration was found in the stream water of the undisturbed watersheds than could be accounted for by precipitation input (Juang and Johnson, 1967). The excess Cl⁻ was attributed to the accumulation of Cl⁻ in the ecosystem by dry removal of aerosols through impaction on the forest canopy. More recent comparisons of the chemical results from precipitation collectors that are continuously open and those that open only during periods of rain or snow are inconclusive, but do not support the dry fall-out hypothesis. Data for years subsequent to 1965-66 show that the long-term, mean chloride concentration in stream water is about the same as the average concentration in precipitation, after adjustment for water loss by evapotranspiration (Johnson, *et al.*, 1969). We feel that the problems encountered previously in the chemical analysis and collection of chloride samples (*e.g.*, Fisher *et al.*, 1968) were greatly minimized during 1967-68, and significantly, the chloride input in precipitation balanced the output in stream water in undisturbed W6 (Table 5).

After deforestation of W2, the streamwater concentration of chloride increased, but the increase was somewhat delayed relative to most of the other ions (Fig. 7). The weighted concentration of chloride in drainage waters from W2

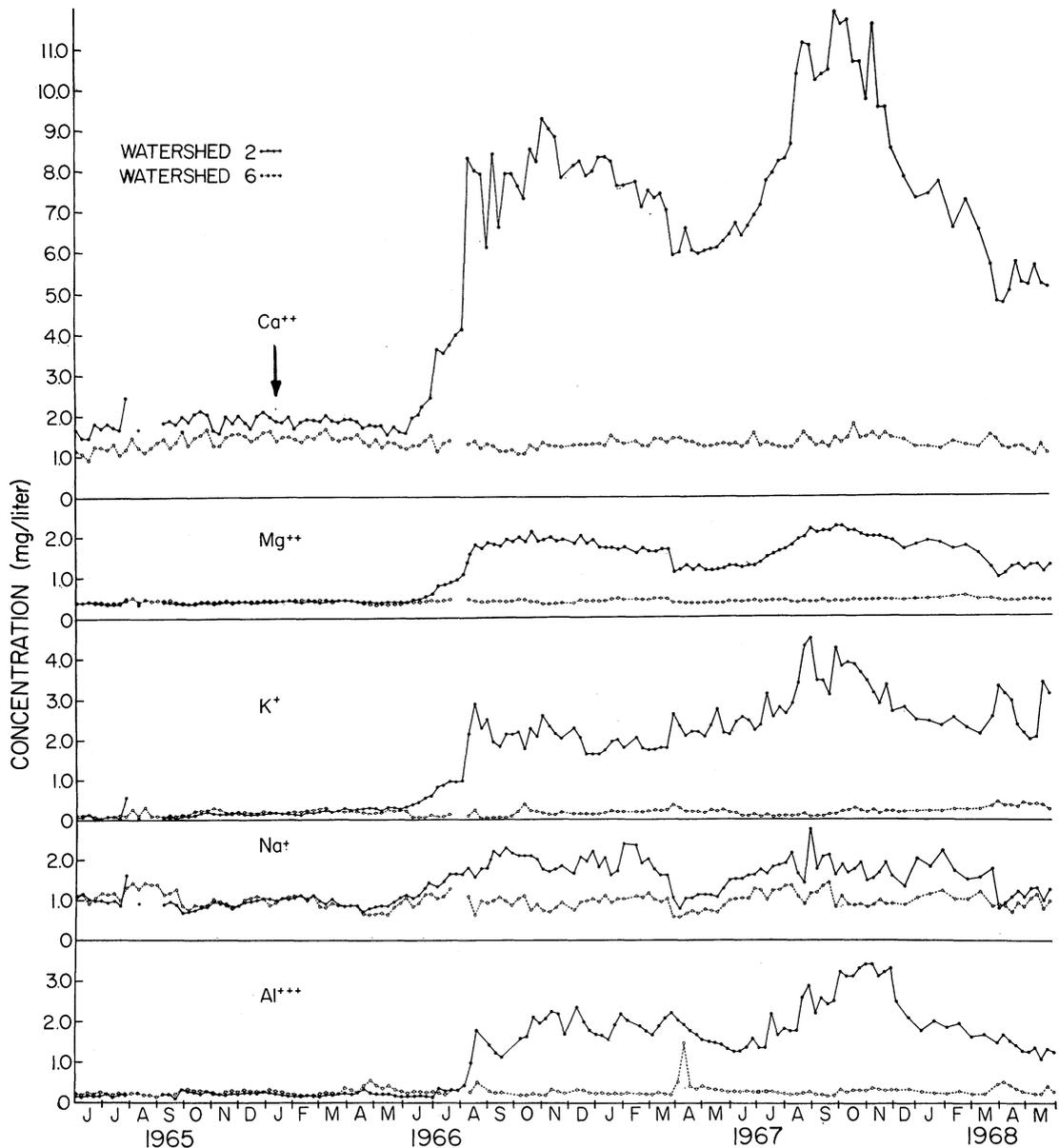


FIG. 9. Measured streamwater concentrations for Ca^{++} , Mg^{++} , K^+ , Na^+ , and Al^{+++} in Watersheds 2 (deforested) and 6. The points were not connected during periods when the stream discharge was negligible. The arrow indicates the completion of cutting in W2.

increased about 65% in the first year (Table 4), indicating the existence of a small chloride reservoir within the ecosystem. A maximum of about 70% of this increased chloride concentration could be explained by the addition of the Bromacil solution to the watershed, however not all of the Bromacil was lost from the watershed during the first year (Pierce, 1969). A continuing but relatively smaller increased chloride concentration also was observed in stream water from W2 during the second year, 1967–68 (Table 4; Fig. 7). Some 30% of the increase in streamwater con-

centration during 1967–68 may be attributed to the addition of the 2, 4, 5-T solution to the watershed.

Calcium, Magnesium, Potassium and Sodium

The concentration of these cations characteristically has been relatively constant in stream water of the undisturbed watersheds despite the highly variable discharge of water (Likens, *et al.*, 1967). The constancy of magnesium is phenomenal in this regard. The relatively small variations that do occur may be explained by appropriate equations for dilution and concentration, based on

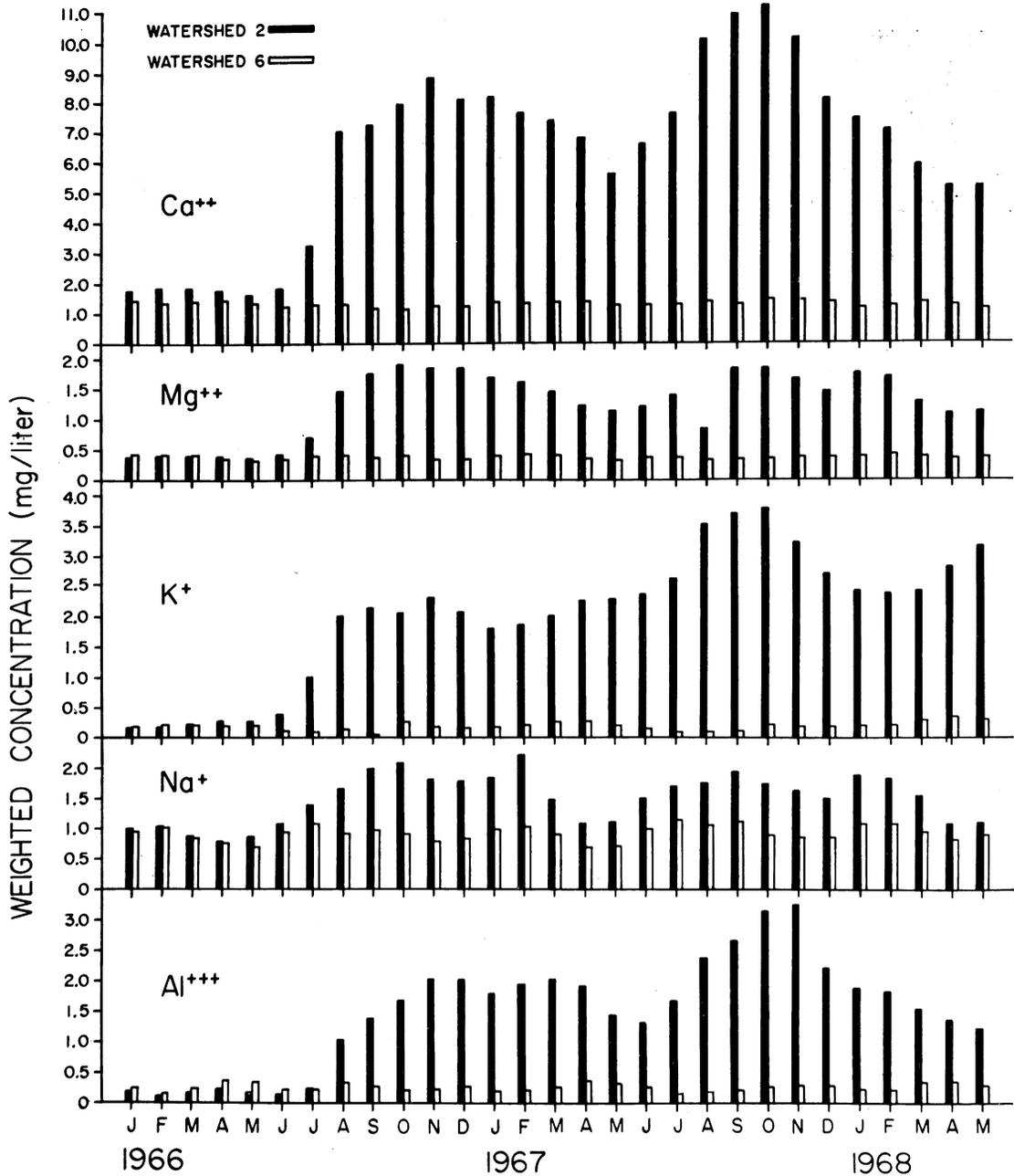


FIG. 10. Weighted average monthly concentrations of Ca^{++} , Mg^{++} , K^+ , Na^+ , and Al^{+++} in stream water from Watersheds 2 (deforested) and 6.

water discharge (Johnson, *et al.*, 1969). In the deforested watershed the volume-concentration model still applies but is less important as a controlling factor than the effect of nitrification.

Remarkable increases in average stream water concentration (417% for Ca^{++} , 408% for Mg^{++} , 1558% for K^+ and 177% for Na^+) were observed during the two years subsequent to deforestation (Figs. 9 and 10; Table 4). The increased concentration and resultant net losses

of these cations in drainage waters is dependent upon the increased concentration of nitrate and hydrogen ions brought about by nitrification (Likens, *et al.*, 1969). With decreasing pH and available nitrate these cations are more readily mobilized and leached from the watershed. This may occur 1) as the hydrogen ions replace the cations on the humic-clay ion exchange complexes of the soil, 2) as organic compounds are decomposed and 3) as chemical decom-

position of bedrock and till is accelerated. However, since nitrification is occurring in the humic layers of the soil, the excess ions are most likely released from the decay of humic substances (Likens, *et al.*, 1969). This is best shown by the changes in the ratio of Ca:Na in the drainage water of Watershed 2 before and after deforestation. Prior to cutting, the Ca:Na ratio in the stream water of Watershed 2 was 1.6/1.0. This ratio is consistent with that observed in adjacent undisturbed watersheds, and has been attributed to the steady-state chemical weathering of bedrock and till (Johnson, *et al.*, 1968). However, after deforestation, the ratio climbed to an average of 4.8/1.0 for the period 1966–68. More significantly, the Ca:Na ratio for the “excess” ions of the stream (that is, the amount added above the undisturbed condition) is 7.4/1.0. Thus, the net chemical effect of the deforestation was to differentially produce soluble calcium within the ecosystem. Hardwood forest litter is rich in calcium relative to sodium (Ca:Na is $>20/1.0$; Scott 1955) in contrast to average bedrock for the Hubbard Brook watershed-ecosystems (Ca:Na is 0.9/1.0; Johnson, *et al.*, 1968), suggesting that most of the “excess” ions produced are derived from the bulk decomposition of humic materials (Likens, *et al.*, 1969).

Only a small portion of the 6- to 22-fold increase in net losses of calcium, magnesium and potassium were apparently derived from an accelerated rate of chemical weathering (Table 5). Based on the change in the sodium budget of Watershed 2, and attributing net sodium losses solely to chemical weathering (Johnson, *et al.*, 1968), the chemical decomposition of bedrock and till within Watershed 2 has apparently accelerated no more than 3-fold.

Aluminum

Aluminum concentrations in stream water from the undisturbed watersheds show seasonal pattern and differences between watersheds (Fisher, *et al.*, 1968). Concentrations of aluminum are highest in April during peak runoff (Figs. 9 and 10). In fact, there is a direct relationship between aluminum concentration and stream discharge (Johnson, *et al.*, 1969). Concentration of aluminum in stream water varies with watershed, with W4 lower than the other streams (Table 4). The average stream water concentration for W4 is about 1/3 of the value for W6.

Deforestation resulted in an increased concentration of aluminum in stream water from W2, but the increase was delayed relative to other ions

(Figs. 9 and 10). Aluminum concentration increased by 10-fold in two years following deforestation. The primary source for aluminum in the system is the bedrock and till. Hence, the increase in aluminum concentration indicates the importance of decreasing pH on the solubility of common minerals containing aluminum in the soils, especially the clay minerals such as kaolin and vermiculite. The decrease in pH from 5.2 to 4.3, we observed as a result of the deforestation, is critical to the solubility of alumina (*e.g.*, Mason, 1966, p. 167).

Dissolved Silica

Seasonal variations in the concentration of dissolved silica in stream water are inversely correlated with runoff (Johnson, *et al.*, 1969). Maximum streamwater concentrations occur in late summer, whereas minimum concentrations occur during peak flow periods associated with spring thaw. There is apparently a yearly recurring slump in the dissolved silica concentration in August preceding the seasonal decline in September (Fig. 7) for which the explanation is not clear.

After forest cutting the average weighted concentration of dissolved silica increased by about 37%. This increase probably reflects the increased solution or weathering of the geologic substrate, or both.

The relatively new finding that the solubility of amorphous silica is inversely related to pH between about pH 3 and 7 (see Marshall, 1964, p. 81) partially explains the increase in dissolved silica in stream water from the deforested watershed.

Bicarbonate

Although the bicarbonate ion is normally the most abundant in freshwaters, it is a relatively minor constituent of the acidic runoff water from the undisturbed Hubbard Brook watersheds (Fisher, *et al.*, 1968; Johnson, *et al.*, 1968; Likens, *et al.*, 1969; and Table 4). In fact, it is barely detectable with routine methods in the stream water from W6.

In W2 the measured concentration dropped to nearly zero by the middle of the first year after cutting (1966–67), and concurrently with the decrease in streamwater pH. Thus the weighted value for 1966–67 (Table 4) reflects the conditions during the first part of the water-year and is somewhat misleading as a temporal average for the year. The streamwater concentration is zero for 1967–68 as expected since the average pH was 4.3.

TABLE 6. Dependence of chemical concentration on the volume of water discharged from Watersheds 2 (cut-over) and 6 during 1967-68. Regression lines were fitted to the relationship $y = ax + b$, where y = chemical concentration in mg/liter, a = slope, x = a function of discharge $\left(\frac{1}{1 + \beta D}\right)$, β is a proportionality constant, and D is stream discharge in liters/ha-day, and $b = y$ intercept (Johnson, *et al.*, 1969). The F-ratio for the values given for slope are significant at the 0.01 level

		W2	W6
calcium	slope	ns*	ns
	Y-intercept	—	—
magnesium	slope	ns	ns
	Y-intercept	—	—
sodium	slope	1.08	0.66
	Y-intercept	1.23	0.69
potassium	slope	-1.79	-0.36
	Y-intercept	4.40	0.50
aluminum	slope	ns	-0.34
	Y-intercept	—	0.57
hydrogen	slope	ns	ns
	Y-intercept	—	—
nitrate	slope	ns	-1.63
	Y-intercept	—	1.49
sulfate	slope	ns	ns
	Y-intercept	—	—
chloride	slope	ns	ns
	Y-intercept	—	—
dissolved silica	slope	1.85	3.24
	Y-intercept	5.31	2.78

*Not significant

EFFECT OF NITRIFICATION ON CATION LOSSES

In the undisturbed watersheds, the relatively small variations in cation and anion chemistry may be explained almost entirely by the effects of dilution and concentration as brought about by changes in stream discharge and biological activity (Johnson, *et al.*, 1969). Initially we thought that the large oscillations in streamwater chemistry after deforestation (Figs. 7, 8, 9 and 10) should be explained by this same model. However a regression analysis showed that only sodium, potassium, and dissolved silica were significantly (<0.01) related to discharge of water after deforestation (Table 6).⁴ Moreover, the slope of the regression lines and the Y-intercepts for these three elements were changed greatly,

⁴ The same pattern of results was obtained for 1966-67, however, the following discussion is based entirely on 1967-68 because of the complexities associated with the sharp chemical transition period that occurred during the water-year of 1966-67 (Figs. 7 and 9).

relative to the undisturbed situation (Table 6; Johnson, *et al.*, 1969). The correlation coefficients for these regression lines were all less than 0.57, which indicates a great deal of scatter in the points and suggests either experimental error or other important controlling factors. In addition to large changes in the slope and Y-intercept for the solutes that show volume or concentration effects with changes in stream discharge after deforestation (Johnson, *et al.*, 1969), aluminum and nitrate, which usually were related to discharge, no longer show any significant relationship (Table 6). Thus, the increased nitrification after deforestation has swamped the rather small volume and concentration effects of discharge, characteristic of these ions in the undisturbed watersheds.

Regression analyses for each ion on nitrate concentration in stream water showed very high significance (<0.001) for all ions except hydrogen, ammonium and dissolved silica (Table 7). The more important cations (Ca^{++} , Mg^{++} , and Al^{+++}), in terms of milliequivalent values, had extremely high correlation coefficients in the regression analysis; whereas the correlation coefficients were lower for Na^+ and K^+ (Table 7;

TABLE 7. Relationship between the nitrate concentration and other ions in stream water from the cut-over watershed (W2) during 1967-68. Regression lines fitted to the relationship $y = ax + b$, where y = chemical concentration in mg/liter, a = slope, x = concentration of nitrate in mg/liter, and $b = y$ intercept. An F-ratio > 12.6 for the slope is significant at the 0.001 level for these regression analyses

	Slope	Correlation coefficient	F-ratio for slope
magnesium	0.024	0.97	673
calcium	0.137	0.95	424
aluminum	0.044	0.93	279
potassium	0.023	0.60	23.9
sodium	0.014	0.57	20.4
sulfate	-0.023	-0.01	30.4
chloride	0.005	-0.28	21.5
dissolved silica	0.017	0.37	6.8
ammonia	0.0006	-0.28	1.0
hydrogen	0.0003	0.08	0.3

Figs. 11 and 12). Thus, these data show the quantitative importance of nitrification as a major controlling factor in determining the quantity and quality of dissolved materials flushed from the cutover watershed in drainage waters. Thus, in the undisturbed watershed, dilution and concentration effects on water discharge were the principal mechanisms controlling ionic concentrations, while in the deforested watershed nitrification was the more important controlling factor.

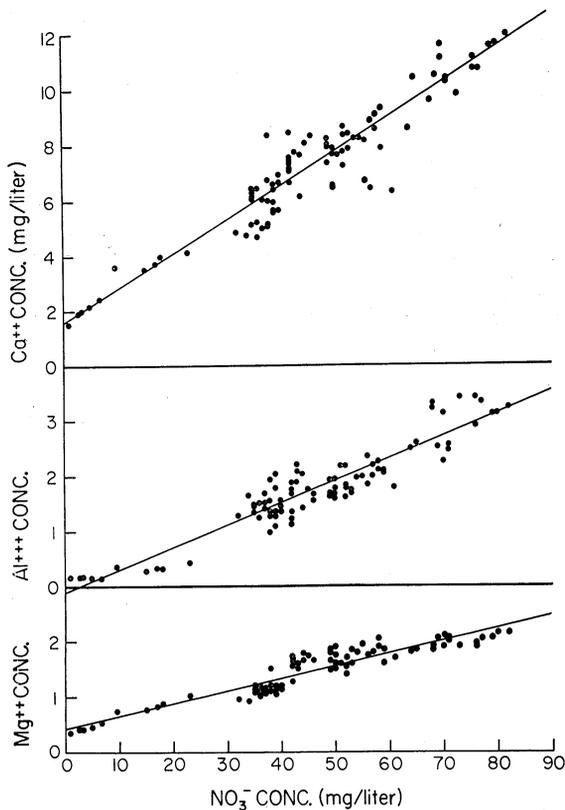


FIG. 11. Relationship between nitrate concentration and calcium, magnesium and aluminum concentrations in stream water from Watershed 2 during 1 June 1966 to 31 May 1968.

Plots of the actual points in the regression of Na^+ and K^+ on NO_3^- show an interesting relationship and indicate the relative importance of 1) nitrate concentration and 2) discharge in regulating ionic concentration of stream water (Fig. 12). That is, if the regression line is taken as the reference, points above the line represent concentration of Na^+ or K^+ and points below the line represent dilution of Na^+ or K^+ over that expected for the relationship between each of these cations and nitrate. An analysis of the temporal distribution for these points reveals that this is just the case. The points above the line for K^+ vs. NO_3^- (Area A) are all associated with periods of high spring runoff; Area B is associated with higher runoff periods in November; and Area C is a mixture of summer and winter points with lower runoff values. According to the volume-concentration model for undisturbed watersheds, K^+ concentrations are directly related to volume of water discharge (Table 6; Johnson, *et al.*, 1969).

The reverse is shown for the relationship for Na^+ vs. NO_3^- . Area A, represents the spring

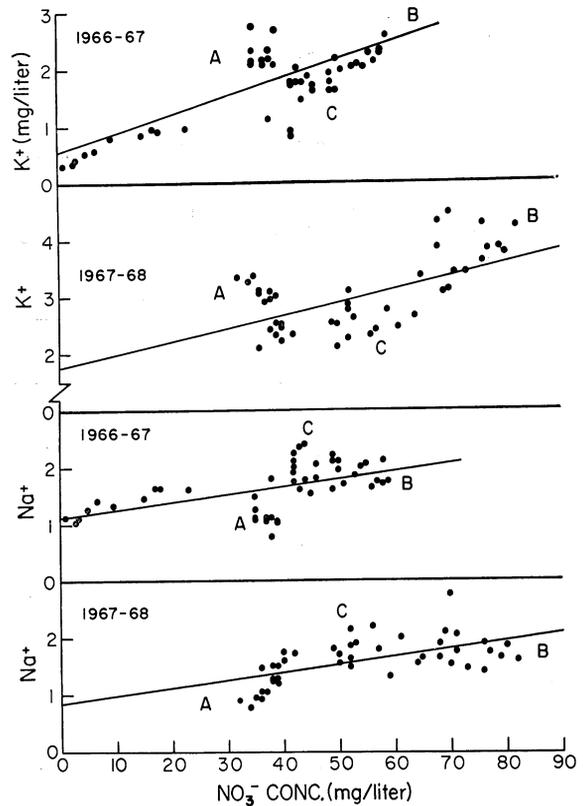


FIG. 12. Relationship between nitrate concentration and sodium and potassium concentrations in stream water from W2 during 1 June 1966 to 31 May 1968. All points in Area A were observed during the period of high spring runoff; points in Area B were observed in relatively high runoff periods in November; and Area C is a mixture of summer and winter points with lesser runoff. The points for nitrate concentrations < 25 mg/liter represent the chemical transitional period between undisturbed and deforested conditions (1 June 1966 through 31 July 1966). See text for full explanation.

runoff period; B is the November period; and C is the summer and winter periods. Sodium is inversely related to the volume of discharge in the undisturbed watersheds (Johnson, *et al.*, 1969; Table 6), and in the cutover watershed (Table 6).

The sodium and potassium were normalized for volume and concentration effects during 1967-68 according to the equations presented by Johnson, *et al.* (1969). As a result, the F-ratio and correlation coefficients for a regression analysis of nitrate and normalized sodium and potassium concentrations were improved. The residual scatter of points about this latter regression line indicates the presence of other minor controlling factors.

The significant slope but poor correlation coefficient for NO_3^- vs. $\text{SO}_4^{=}$ (Table 7) is the result of the marked curvilinear relationship after deforestation shown in Fig. 14.

NUTRIENT BUDGETS

Nutrient budgets for dissolved ions and dissolved silica for the Hubbard Brook watershed-ecosystems were determined from the difference between the meteorologic input per hectare and the geologic output per hectare (Bormann and Likens, 1967). Input was calculated from the product of the ionic concentration (mg/liter) and the volume (liters) of water as precipitation (Likens, *et al.*, 1967 and Fisher, *et al.*, 1968). Additional input from applications of herbicides was added to the precipitation input. Output was calculated as the product of the volume (liters) of water draining from the watershed-ecosystems and its ionic concentration (mg/liter). Budgets for all of the ions and substances measured are given in Table 5.

Net losses were greatly increased after deforestation and herbicide treatment for all ions except ammonium, sulfate, and bicarbonate. Two factors are involved in the removal of nutrients from the deforested watershed: 1) increased runoff and 2) increased ionic concentrations in stream water. If the concentrations had not increased from the undisturbed condition, increased runoff would have accounted for a 39% increase in gross export the first year and a 28% increase the second year after deforestation. However, the gross outputs for 1967–68 were greater than the undisturbed watershed, W6 (Table 5), by 7.6-fold for Ca^{++} , 5.5-fold for Mg^{++} , 15.2-fold for K^+ , 2.2-fold for Na^+ , 46-fold for $\text{NO}_3\text{-N}$, 1.8-fold for Cl^- , 7.9-fold for Al^{+++} and 1.9-fold for $\text{SiO}_2\text{-Si}$, clearly indicating that increased stream water concentrations are primarily responsible for the increased nutrient loss from the ecosystem.

Nitrogen losses from W2 after deforestation, although very large already, do not take into account volatilization. Allison (1955) reported volatilization losses averaging 12 percent of the total nitrogen losses from 106 fallow soils. However, denitrification is an anaerobic process and requires a nitrate substrate generated aerobically (Jansson, 1958); consequently, for substantial denitrification to occur in fields, aerobic and anaerobic conditions must exist in close proximity. The large increases in subsurface flow of water from the deforested watershed suggests that such conditions may have been more common than in the undisturbed ecosystem. Moreover, Alexander (1967) points out, "When ammonium oxidation takes place at a pH lower than 5.0 to 5.5, or where the acidity produced in nitrification increases the hydrogen ions to an equivalent ex-

tent, the formation of nitrite can lead to a significant chemical volatilization of nitrogen."

Net losses of $\text{SO}_4\text{-S}$ from the deforested ecosystem were about 40% lower in 1966–67, and 100% lower in 1967–68 than from undisturbed watersheds. In fact, the 1967–68 budget for $\text{SO}_4\text{-S}$ in W2 was balanced in contrast to the undisturbed situation (Table 5). Precipitation is by far the major source of sulfate for the undisturbed watersheds (Fisher, *et al.*, 1968). Although the amount of sulfate added by precipitation in 1967–68 was increased slightly relative to previous years, the net export of sulfate was zero, with sulfate input in precipitation exactly balancing streamwater export (Table 5). The decreases in streamwater sulfate concentration and gross export from the ecosystem occurred concurrently with the increases in streamwater nitrate concentration and gross export after forest cutting (Figs. 7 and 8).

Average sulfate concentrations in stream water were 3.8 and 3.7 mg/liter during 1966–67 and 1967–68 (Table 4), far below the 6.4 and 6.8 mg/liter values recorded in 1964–65 and 1965–66 before cutting (Fisher, *et al.*, 1968). Much of this change can be explained by two facts, 1) the 39 to 28% increase in streamwater discharge from 1966 to 1968, which resulted from the elimination of transpiration by deforestation, and 2) the elimination of sulfate generation by sources internal to the ecosystem. If the decreases in sulfate concentrations were wholly due to increased runoff after deforestation, concentrations calculated on the basis of expected runoff (*i.e.*, normal for the undisturbed system, Table 2) and measured gross sulfate lost from W2 during 1966–67 and 1967–68 (Table 5), should approximate the weighted streamwater concentrations for the undisturbed period, 1964–66. However, these calculated concentrations (5.3 and 4.7 mg/liter) equal only 79 and 70% respectively of the average weighted concentrations for 1964–66. These differences in concentration may be due to some year-to-year variation, but are largely explained by a sharp reduction in the internal release of sulfate from the ecosystem, which we earlier attributed to chemical weathering and biological activity (Fisher, *et al.*, 1968, Likens, *et al.*, 1969). The average annual internal release of sulfate (*i.e.*, an amount equivalent to net loss) supplies about 10 kg/ha in the undisturbed watersheds (Table 5). Removal of this source of sulfate would account for the lower than expected adjusted sulfate concentrations mentioned above.

Thus, apparently, the normal, relatively small release of $\text{SO}_4^{=}$ from the ecosystem by chemical weathering and microbial activity (Table 5) probably became negligible following forest cutting. There are at least two possible mechanisms, operating simultaneously or separately, which may account for this:

i) There may be decreased oxidation of various sulfur compounds to $\text{SO}_4^{=}$. Waksman (1932) has suggested that a high concentration of nitrate is very toxic to sulfur oxidizing bacteria, such as *Thiobacillus thiooxidans*. This species may be important in sulfate oxidation in the deforested watershed since *T. thiooxidans* is capable of active growth at low pH (Alexander 1967). In the undisturbed watersheds we have observed a highly significant inverse linear relationship between the concentration of nitrate and sulfate in drainage water. This relationship is particularly clear in plots of sulfate concentrations against nitrate concentration using data from November through April, when the vegetation is dormant (Fig. 13). The inverse relationship between NO_3^- and

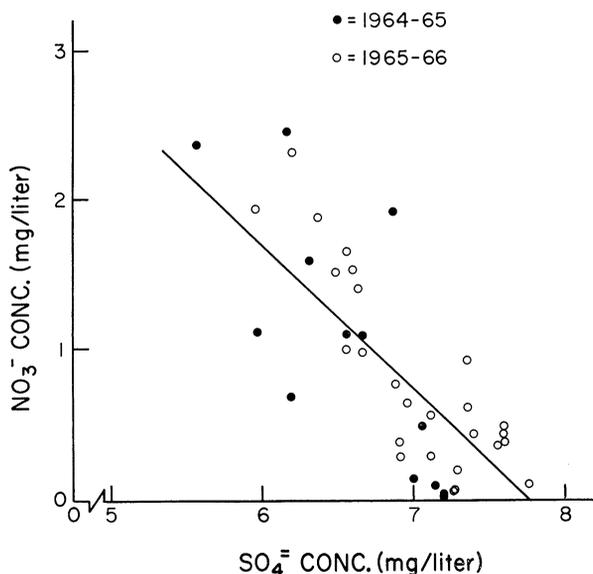


FIG. 13. Relationship between nitrate and sulfate concentrations in stream water from Watershed 2. Data were obtained during November through April of 1964-65 and 1965-66, which was prior to the increase in nitrate concentration resulting from clearing of the forest vegetation (Fig. 7). The F-ratio for this regression line is very highly significant ($p < 0.001$) and the correlation coefficient is 0.79.

$\text{SO}_4^{=}$ concentrations is very obvious in the first water-year after deforestation, 1966-67, when nitrate concentrations in stream water increased from normal (undisturbed) values to very high concentrations (Fig. 14). During the second wa-

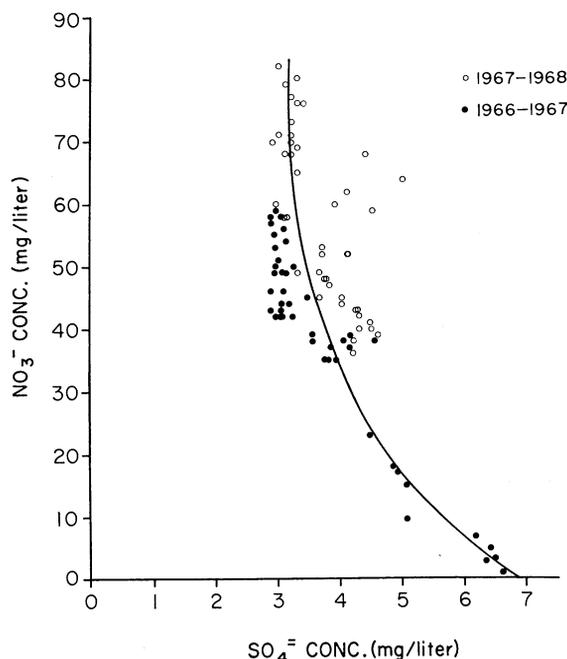


FIG. 14. Relationship between nitrate and sulfate concentrations in stream water from Watershed 2 during 1966-67 and 1967-68. Nitrate values less than 25 mg/liter indicate the chemical transition period (1 June 1966 through 31 July 1966, Fig. 7) between undisturbed and deforested conditions.

ter-year after cutting, 1967-68, the nitrate concentration in stream water from W2 increased even more, whereas the sulfate concentration decreased very little and coincided with the concentration of sulfate in precipitation after adjustment for water loss by evaporation. Perhaps there is an intricate feedback mechanism between the toxicity of the nitrate concentrations and microbial oxidation of sulfur compounds within the soil. Another possibility is that the number of sulfur oxidizing bacteria have been selectively reduced by the herbicides in the deforested watershed.

ii) Although somewhat unlikely, there may be increased sulfate reduction brought about by more anaerobic conditions, particularly in the lower more inorganic horizons of the soil (e.g., Waksman, 1932). That is, an increased zone of water saturation in the deeper layers and in topographic lows on the cutover watershed probably has less free oxygen than in the undisturbed situation, promoting sulfur reduction. One difficulty, however, is that the growth of the most important sulfur reducing bacteria (*Desulfovibrio* spp.) is greatly retarded by acid conditions (Alexander, 1967). Also, molecular hydrogen released by anaerobic bacterial decomposition of organic matter may be used for the reduction of sulfate (Postgate, 1949; Rankama and Sahama, 1950).

The chloride budget for the undisturbed watershed during 1966–67 showed that input in precipitation exceeded the gross output, whereas the budget was essentially balanced during the 1967–68 water-year (Table 5). However after deforestation, significant net losses of chloride were observed (Table 5). The application of Bromacil in 1966–67 potentially added the equivalent of 3.0 kg Cl/ha or about 50% of the chloride input as precipitation. From the pattern of chloride changes in stream water following the addition of this herbicide (Fig. 7), it would appear that the herbicide and/or its degradation products were lost from the watershed quite gradually throughout the year. Measurements of Bromacil in stream water seemed to confirm this (Pierce, 1969). Since the Bromacil (1966–67) and possibly 2, 4, 5-T (1967–68) were not all flushed from the ecosystem within a year, then the internal release of chloride from the ecosystem probably represented an even greater percentage of the gross annual output (Table 5). Based upon streamwater concentrations in W2 and W6 (Fig. 7), it would appear that the internal reservoir (plus external inputs from herbicides) of chloride within the ecosystem has been essentially exhausted in two years following deforestation.

GENERAL DISCUSSION AND SIGNIFICANCE

The intrasystem cycle of a terrestrial ecosystem links the organic, available nutrient, and soil and rock mineral compartments through rate processes including decomposition of organic matter, leaching and exudate from the biota, nutrient uptake by the biota, weathering of primary minerals, and formation of new secondary minerals (Fig. 15). The deforestation experiment was designed to test the effects of blockage on a major ecosystem pathway, *i.e.*, nutrient and water uptake by vegetation, on other components of the intrasystem cycle and on the export behavior of the system as a whole. The block was imposed by cutting all of the forest vegetation and subsequently preventing regrowth with herbicides. We hoped that this experimental procedure would provide information about the nature of the homeostatic capacity of the ecosystem. The deforested condition has been maintained since 1 January 1966.

Forest clearing and herbicide treatment had a profound effect on the hydrologic and nutrient relationships of our northern hardwood ecosystem. Annual runoff (water export) increased by some 33 cm or 39% in the first year and 27 cm or 28% in the second year over that expected. Moreover, the discharge pattern was altered so

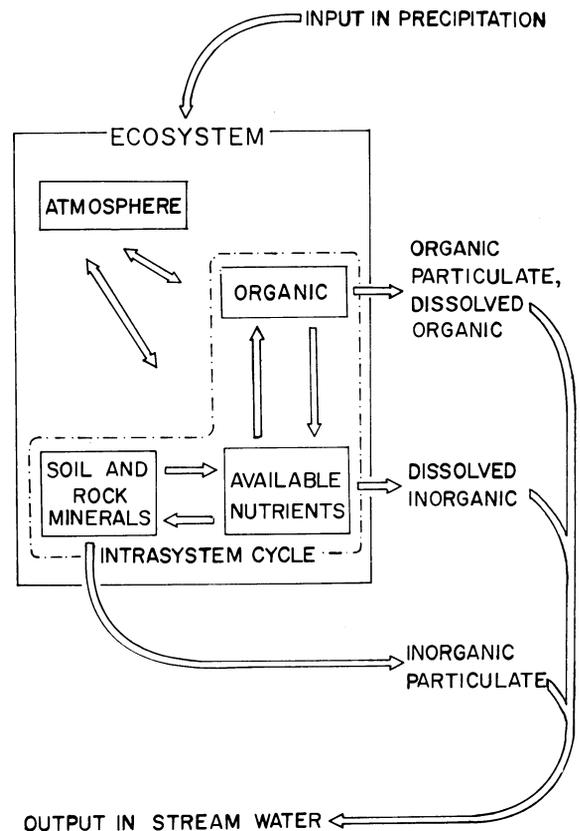


FIG. 15. Diagrammatic model for sites of accumulation and pathways of nutrients in the Hubbard Brook ecosystem (after Bormann, *et al.*, 1969).

that sustained, higher flows occurred in the summer months and the snow pack melted earlier in the spring. This overall increase in stream runoff is large compared to the average increase (about 20 cm) found for other such experiments throughout the world (Hibbert, 1967), but is less than the maximum increase of 41 cm found for clear-cut watersheds in North Carolina (Hoover, 1944).

No previous comprehensive measurements have been made of the homeostatic ability of a watershed-ecosystem to retain nutrients despite major shifts in the hydrologic cycle, including increased discharge, following deforestation (Odum, 1969).

Our results showed that cation and anion export did not change for the first 5 months (winter and spring) after deforestation, but then the ionic concentrations increased spectacularly, and remained at high levels for the 2 years of observation (Tables 4 and 5, Figs. 7, 8, 9 and 10). Annual net losses in kg/ha amounted to about 142 for nitrate-nitrogen, 90 for calcium, 36 for potassium, 32 for dissolved silica, 24 for aluminum, 18 for magnesium, 17 for sodium, and 4 for chlorine during 1967–68. These losses are much

TABLE 8. Comparative net gains or losses of dissolved solids in runoff following clear-cutting of Watershed 2 in the Hubbard Brook Experimental Forest for the period 1 June to 31 May. In metric tons/km²-yr

	1966-67		1967-68	
	W2	W6	W2	W6
Ca.....	-7.5	-0.8	-9.0	-0.9
K.....	-2.3	-0.1	-3.6	-0.2
Al.....	-1.7	-0.1	-2.4	-0.3
Mg.....	-1.6	-0.3	-1.8	-0.3
Na.....	-1.7	-0.6	-1.7	-0.7
NH ₄	+0.1	+0.2	+0.2	+0.3
NO ₃	-43.0	+1.5	-62.8	+1.1
SO ₄	-0.5	-0.8	0	-1.0
HCO ₃	-0.1	-0.2	0	-0.3
Cl.....	-0.1	+0.2	-0.4	0
SiO ₂ -aq.....	-6.6	-3.6	-6.9	-3.6
Total.....	-65.0	-4.6	-88.4	-5.9

greater than for adjacent undisturbed ecosystems (Table 5). Ammonium-nitrogen was essentially unchanged relative to the undisturbed condition during this period and showed an annual net gain of about 1 to 2 kg/ha. In comparison with the undisturbed watershed-ecosystems the greatest changes occurred in nitrate-nitrogen and potassium export. Nitrate-nitrogen is normally accumulated in the undisturbed ecosystem in contrast to this very large export, and the net potassium output increased about 18-fold. The total net export of dissolved inorganic substances from the deforested ecosystem is 14-15 times greater than from the undisturbed ecosystem (Table 8).

The terrestrial ecosystem is one of the ultimate sources of dissolved substances in surface water. The contribution of dissolved solids (gross export) by our undisturbed forest ecosystems, 13.9 metric tons/km² (Bormann, *et al.*, 1969) is only about 25% of the dissolved load predicted by Langbein and Dawdy (1964) for regions with 75 cm of annual runoff. Their estimates were based on data from watersheds of the north Atlantic slope, which probably include areas disturbed by agriculture or logging. The difference between our undisturbed forest ecosystems and the regional prediction is credited in part to the operation of various regulating biotic factors associated with mature undisturbed forest (Bormann, *et al.*, 1969).

Deforestation markedly altered the ecosystem's contribution of dissolved solids to the drainage waters. Total gross export, exclusive of dissolved organic matter, was about 75 metric tons/km² in 1966-67 and 97 metric tons/km² in 1967-68. These figures exceed the regional prediction of Langbein and Dawdy (1964). However, it should be noted that the accelerated export of

dissolved substances results primarily from mining the nutrient capital of the ecosystem and cannot be sustained indefinitely.

Surprisingly, the net export of dissolved inorganic substances from the cutover watershed is about double the annual value estimated for particulate matter removed by debris avalanches in the White Mountains (Bormann, *et al.*, 1969). Thus, the effects of deforestation may have almost twice the importance of avalanches in short-term catastrophic transport of inorganic materials downslope in the White Mountains.

Coupled with this increase in gross and net export of dissolved substances, there has been at least a 4-fold increase in the export of inorganic and organic particulate matter from the deforested ecosystem. This increase indicates that the biotic mechanisms that normally minimize erosion and transport (Bormann, *et al.*, 1969) are also becoming less effective.

The greatly increased export of nutrients from the deforested ecosystem resulted primarily from an alteration of the nitrogen cycle within the ecosystem. Whereas in the undisturbed system, nitrogen is cycled conservatively between the living and decaying organic components, in the deforested watershed, nitrate produced by microbial nitrification from decaying organic matter, is rapidly flushed from the system in drainage waters. In fact, the increased nitrate output accounts for the net increase in total cation and anion export from the ecosystem (Likens, *et al.*, 1969). With the increased availability of nitrate ions and hydrogen ions from nitrification, cations are readily leached from the system. Cations are mobilized as hydrogen ions replace them on the various exchange complexes of the soil and as organic and inorganic materials decompose. Based upon the increased output for sodium, chemical decomposition of inorganic materials in the deforested ecosystem is also accelerated by about 3-fold.

If the streamwater concentrations had remained constant after deforestation, increased water output alone would have accounted for 39% of the increased nutrient export the first year and 28% of the increased nutrient export the second year. However, the very large increase in annual export of dissolved solids from the deforested ecosystem occurred primarily because the streamwater concentrations were vastly increased, mostly as a direct result of the increased nitrification. The increased output of nutrients originated predominantly from the organic compartment of the watershed-ecosystem (Fig. 15).

Our study shows that the retention of nutrients within the ecosystem is dependent on constant and efficient cycling between the various components of the intrasystem cycle, *i.e.*, organic, available nutrients, and soil and rock mineral compartments (Fig. 15). Blocking of the pathway of nutrient uptake by destruction of one sub-component of the organic compartment, *i.e.*, vegetation, leads to greatly accelerated export of the nutrient capital of the ecosystem. From this we may conclude that one aspect of homeostasis of the ecosystem, *i.e.*, maintenance of nutrient capital, is dependent upon the undisturbed functioning of the intrasystem nutrient cycle, and that in this ecosystem no mechanism acts to greatly delay loss of nutrients following sustained destruction of the vegetation.

The increased output of water from the deforested watershed was readily visible during the summer months, however the increased ion and particulate matter concentrations were not. The stream water from the deforested watershed appeared to be just as clear and potable as that from adjacent, undisturbed watersheds. However this was not the case. By August, 1966, the nitrate concentration in stream water exceeded (at times almost doubled) the concentration recommended for drinking water (Public Health Service, 1962).

The high nutrient concentrations, plus the increased amount of solar radiation (absence of forest canopy) and higher temperature in the stream, resulted in significant eutrophication. A dense bloom of *Ulothrix zonata* (Weber and Mohr) Kütz, has been observed during the summers of 1966 and 1967 in the stream of W2. In contrast the undisturbed watershed streams are essentially devoid of algae of any kind. This represents a good example of how an overt change in one component of an ecosystem, alters the structure and function, often unexpectedly, in another part of the same ecosystem or in another inter-related ecosystem. Unless these ecological inter-relationships are understood, naive management practices can produce unexpected and possibly widespread deleterious results.

CONCLUSIONS

1. The quantity and quality of drainage waters were significantly altered subsequent to deforestation of a northern hardwoods watershed-ecosystem. All vegetation on Watershed 2 of the Hubbard Brook Experimental Forest was cut, but not removed, during November and December of 1965; and vegetation regrowth was inhibited by periodic application of herbicides.

2. Annual runoff of water exceeded the expected value, if the watershed were undisturbed, by 33 cm or 39% during the first water-year after deforestation and 27 cm or 28% during the second water-year. The greatest increase in water discharge, relative to an undisturbed situation, occurred during June through September, when runoff was 414% (1966-67) and 380% (1967-68) greater than the estimate for the untreated condition.

3. Deforestation resulted in large increases in streamwater concentrations of all major ions except NH_4^+ , $\text{SO}_4^{=}$ and HCO_3^- . The increases did not occur until 5 months after the deforestation. The greatest increase in streamwater ionic concentration after deforestation was observed for nitrate, which increased by 41-fold the first year and 56-fold the second year above the undisturbed condition.

4. Sulfate was the only major ion in stream water from Watershed 2 that decreased in concentration after deforestation. The 45% decrease the first year (1966-67) resulted mostly from increased runoff of water and by eliminating the generation of sulfate within the ecosystem. The concentration of sulfate in stream water during 1967-68 equalled the concentration in precipitation after adjustment for water loss by evaporation. Sulfate concentrations were inversely related to nitrate concentrations in stream water in both undisturbed and deforested watersheds.

5. In the undisturbed watersheds the stream water can be characterized as a very dilute solution of sulfuric acid (pH about 5.1 for W2); whereas after deforestation the stream water from Watershed 2 became a relatively stronger nitric acid solution (pH 4.3), considerably enriched in metallic ions and dissolved silica.

6. The increase in average nitrate concentration in precipitation for the Hubbard Brook area compared to data from 1955-56, as well as the consistent annual increase observed from 1964-1968, may be some measure of a general increase in air pollution.

7. The greatly increased export of dissolved nutrients from the deforested ecosystem was due to an alteration of the nitrogen cycle within the ecosystem. Whereas nitrogen is normally conserved in the undisturbed ecosystem, in the deforested ecosystem nitrate is rapidly flushed from the system in drainage water. The mobilization of nitrate from decaying organic matter, presumably by increased microbial nitrification, quantitatively accounted for the net increase in

total cation and anion export from the deforested ecosystem.

8. Increased availability of nitrate and hydrogen ions resulted from nitrification. Cations were mobilized as hydrogen ions replaced them on various exchange complexes of the soil and as organic and inorganic materials were decomposed. Chemical decomposition of inorganic materials in the deforested ecosystem was accelerated about 3-fold. However, the bulk of the nutrient export from the deforested watershed originated from the organic compartment of the ecosystem.

9. The total net export of dissolved inorganic substances from the deforested ecosystem was 14-15 times greater than from undisturbed ecosystems. The increased export occurred because the streamwater concentrations were vastly increased, primarily as a direct result of the increased nitrification, and to a much lesser extent because the amount of stream water was increased.

10. The deforestation experiment resulted in significant pollution of the drainage stream from the ecosystem. Since August, 1966, the nitrate concentration in stream water has exceeded, almost continuously, the maximum concentration recommended for drinking water. As a result of the increased temperature, light and nutrient concentrations, and in sharp contrast to the undisturbed watersheds, a dense bloom of algae has appeared each year during the summer in the stream from Watershed 2.

11. Nutrient cycling is closely geared to all components of the ecosystem; decomposition is adjusted to nutrient uptake, uptake is adjusted to decomposition, and both influence chemical weathering. Conservation of nutrients within the ecosystem depends upon a functional balance within the intrasystem cycle of the ecosystem. The uptake of water and nutrients by vegetation is critical to this balance.

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