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The biogeochemistry of potassium at Hubbard Brook

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Abstract. A synthesis of the biogeochemistry of K was conducted during 1963–1992 in the reference and human-manipulated watershed-ecosystems of the Hubbard Brook Experimental Forest (HBEF), NH. Results showed that during the first two years of the study (1963–65), which coincided with a drought period, the reference watershed was a net sink for atmospheric inputs of K. During the remaining years, this watershed has been a net source of K for downstream ecosystems. There have been long-term declines in volume-weighted concentration and flux of K at the HBEF; however, this pattern appears to be controlled by the relatively large inputs during the initial drought years. Net ecosystem loss (atmospheric deposition minus stream outflow) showed an increasing trend of net loss, peaking during the mid-1970s and declining thereafter. This pattern of net K loss coincides with trends in the drainage efflux of SO_4^{2-} and NO_3^-, indicating that concentrations of strong acid anions may be important controls of dissolved K loss from the site. There were no long-term trends in streamwater concentration or flux of K. A distinct pattern in pools and fluxes of K was evident based on biotic controls in the upper ecosystem strata (canopy, boles, forest floor) and abiotic controls in lower strata of the ecosystem (mineral soil, glacial till). This biological control was manifested through higher concentrations and fluxes of K in vegetation, aboveground litter, throughfall and forest floor pools and soil water in the northern hardwood vegetation within the lower reaches of the watershed-ecosystem, when compared with patterns in the high-elevation spruce-fir zone. Abiotic control mechanisms were evident through longitudinal variations in soil cation exchange capacity (related to soil organic matter) and soil/till depth, and temporal and disturbance-related variations in inputs of strong-acid anions. Marked differences in the K cycle were evident at the HBEF for the periods 1964–69 and 1987–92. These changes included decreases in biomass storage, net mineralization and throughfall fluxes and increased resorption in the latter period. These patterns seem to reflect an ecosystem response to decreasing rates of biomass accretion during the study. Clearcutting disturbance resulted in large losses of K in stream water and from the removal of harvest products. Stream losses occur from release from slash, decomposition of soil organic matter and displacement from cation exchange sites. Elevated concentrations of K persist in stream water for many years after clearcutting. Of the major elements, K shows the slowest recovery from clearcutting disturbance.

Abbreviations: dbh – diameter at breast height, HBEF – Hubbard Brook Experimental Forest, HBES – Hubbard Brook Ecosystem Study, HIV – hydroxy-interlayered vermiculate, K – potassium, LOI – loss on ignition, mol_c – moles of charge (equivalents), NTF – net throughfall flux, SD – standard deviation, SKT – nonparametric seasonal Kendall Tau trend analysis, $s_{\bar{x}}$– standard error of the mean, W – watershed

Introduction

Potassium (AW = 39.08983) is a member of the alkali metals, a group characterized by its extreme metallic properties. Because of the very high second stage ionization energy, only one oxidation state (+1) occurs in this group and bonding is entirely ionic (Greenwood & Earnshaw 1984). Potassium (K) is the most common of these metals in Earth's crust and is the seventh most abundant element (2.3% of crustal mass; Bowen 1966; Clarke 1924; Press & Siever 1978). It is particularly concentrated in the silicic rocks (3.7% of granites) of the continents (Bowen 1979). Because of its charge and ionic radius, K occurs in primary minerals in the cavities between tetrahedra in the framework of orthoclase ($KAlSi_3O_8$) and in cavities formed by adjacent tetrahedral layers of biotite ($K[Si_3Al]Mg_2FeO_{10}(OH)_2$) or muscovite ($K[Si_3Al]Al_2O_{10}(OH)_2$). Potassium is weathered as a soluble cation from both primary and secondary minerals, moving readily into the soil solution. From there, it may become adsorbed onto the soil cation exchange complex, assimilated by plant or microbial biomass, or leached down through the profile.

Given the high solubility of K, it is easily lost from soils in humid regions. Nevertheless, because of its relative abundance in minerals, K is a common cation in soil solutions and fresh waters (e.g. Bowen 1979), and along with calcium, is the fourth most abundant element in seawater on a molar basis (Murray 1992). In marine sediments, K becomes concentrated as a hydrolysate in shales, or more rarely as an evaporite – sylvite (Rankama & Sahama 1950).

Potassium is an essential element for prokaryotes, fungi, plants and animals, occurring in cytoplasm primarily as a major electrolyte and secondarily in enzyme activation (Mengel & Kirkby 1979). At times and in certain locations it either may be inhibiting (Lehman 1976) or limiting to plant growth (Heiberg et al. 1964). Potassium is not important in the hard tissues of most organisms (Bowen 1979). Concentrations of K are relatively high (among the metals) in bacteria, fungi and higher plants (ca. 1.5% in woody angiosperms; Bowen 1966, 1979). As a soluble electrolyte, K is easily lost from living tissues such as foliage, as well as from dead materials such as leaf litter. Thus, K typically cycles rapidly when organisms are collectively disturbed; K can be lost readily from ecosystems at high rates until those organic pools are exhausted, or the capacity for biotic uptake recovers.

The biogeochemistry of K in a forested landscape like the Hubbard Brook Valley in New Hampshire, USA, is extremely complex. Soils at Hubbard Brook are relatively young, contain small amounts of clays and are acidic.

These factors suggest that K resources in the soil are relatively low and supply rates are dependent on primary mineral weathering and conservative cycling through organic matter.

Concentration of K in precipitation at Hubbard Brook is among the lowest for any region, whereas deposition of K is typical for much of the United States (Fig. 1). Values for K in precipitation at Hubbard Brook are characteristic of those for the northern hardwood forest.

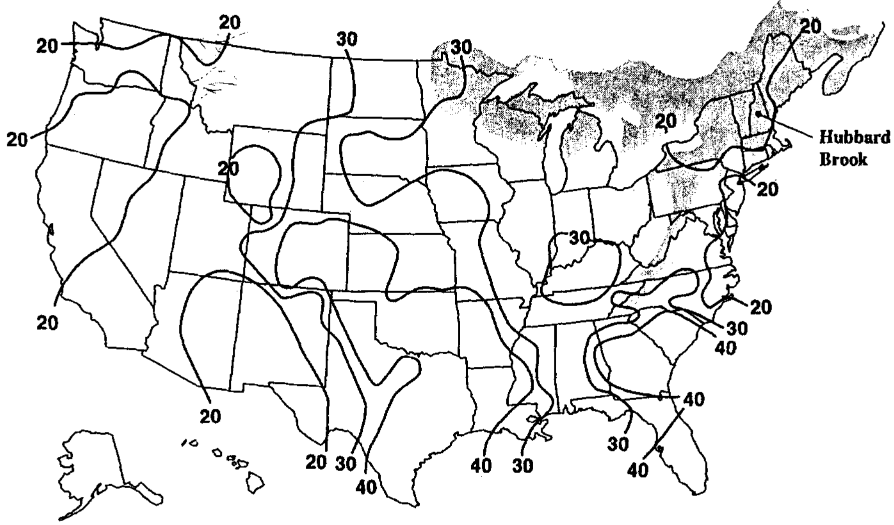
Because K is a macronutrient for higher plants, variation in K supply in space or time may be important to the growth and health of vegetation within a forest ecosystem. Disturbances, which may be natural or the result of forest management, may result in K losses from the ecosystem, possibly hindering recovery and long-term productivity (e.g. Likens et al. 1970; Mroz et al. 1985; Johnson et al. 1985; Johnson & Todd 1987; Mann et al. 1988). The situation is exacerbated at Hubbard Brook, and the northern hardwood region in general, by the atmospheric deposition of strong acids, enhancing the loss of metallic cations like K from the soil complex (Reuss & Johnson 1986). Long-term biogeochemical records and numerous biogeochemical studies at the Hubbard Brook Experimental Forest (HBEF) provide a unique opportunity to analyze the biogeochemistry of K in this kind of ecosystem. This paper provides such an evaluation based on 29 years of intensive study. In this analysis, ecosystem budgets for K are compared for two 5-yr periods: 1964–69, early in the Hubbard Brook Ecosystem Study, and a more recent period, 1987–92.

The Hubbard Brook Experimental Forest

The HBEF within the Hubbard Brook Valley of the White Mountains of north-central New Hampshire, USA, is a 3160-ha forested area, with a series of experimental watershed ecosystems (Fig. 2). Soils are acidic, well-drained Spodosols (Haplorthods). Soil pH ranges from 3.91 in the Oa horizon to 4.72 in the C horizon (Johnson et al. 1991b). The soils are shallow at high elevations and increase in depth with decreasing elevation (Lawrence et al. 1986; Likens et al. 1977). The average soil depth to the C horizon within the experimental watersheds is about 57 cm (Johnson et al. 1991a). There also is a well-developed and well-drained surface organic layer (O horizon, or forest floor), which is 3 to 15 cm in thickness. Soils in the Hubbard Brook Valley were formed in glacial till of variable depth, underlain by metamorphic rock of igneous and sedimentary origin (schists and quartz monzonite; Johnson et al. 1981; Likens et al. 1977). Ice remnants of the last glaciation melted some 14,000 B.P. in this area (Likens & Davis 1975).

Climate at the HBEF is cool-temperate, humid-continental with mean July and January temperatures of 19 °C and –9 °C, respectively (at 450 m elevation). Mean annual precipitation for the biogeochemical reference watershed (W6) is approximately 1395 mm (SD = 189), with 25–33% of the total occurring as snow (Federer et al. 1990). Monthly precipitation averages 140 mm, and has varied from a maximum of 182 mm in 1973 to a minimum of 111

1991 Annual Precipitation Weighted Mean Potassium Ion Concentrations (μg/L)



1991 Estimated Potassium Ion Deposition (kg/ha)

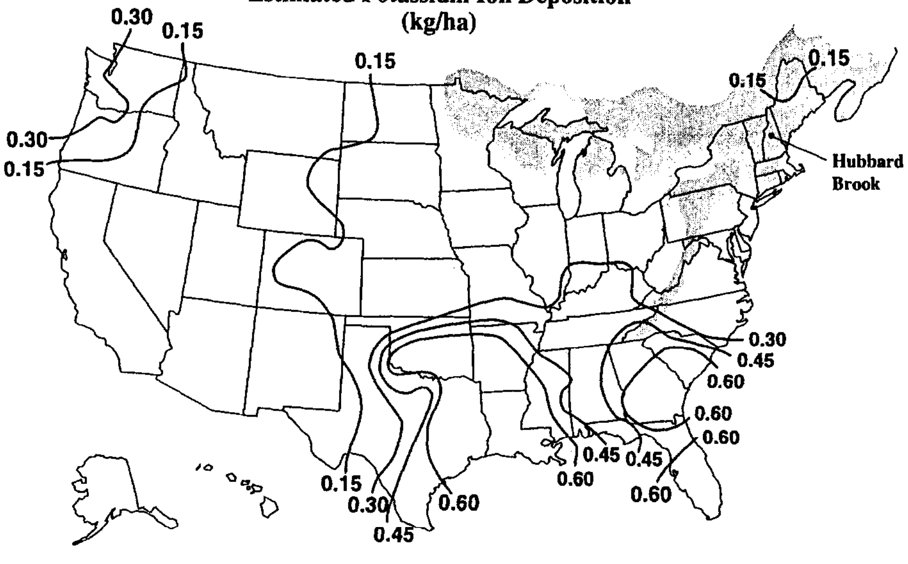


Fig. 1. Annual volume-weighted concentration and deposition of K throughout the US during 1991. The shaded area indicates the approximate range of the northern hardwood forest (precipitation chemistry data from the National Atmospheric Deposition Program).

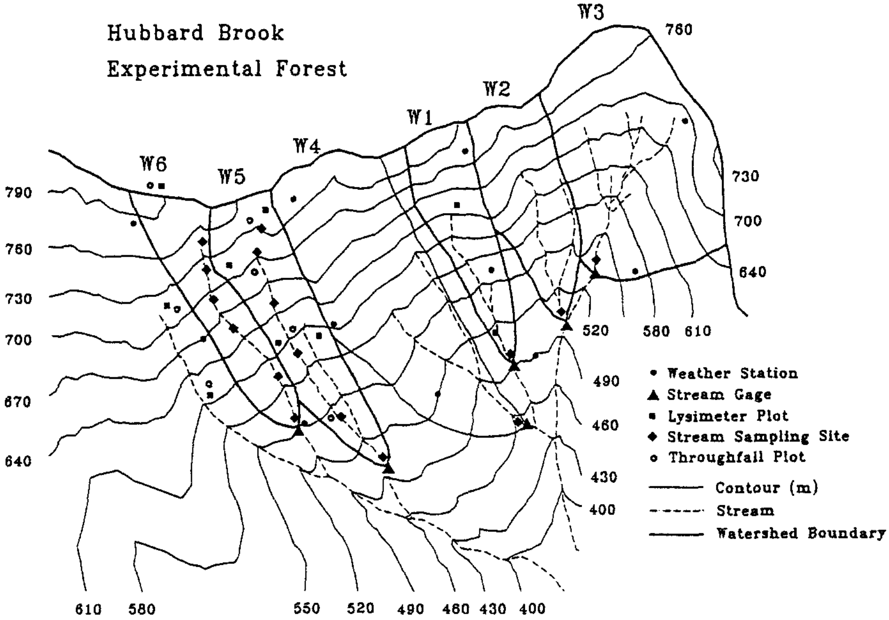


Fig. 2. Map of the southfacing, experimental watersheds within the HBEF. Instrumentation of watershed-ecosystems is shown.

mm in 1988. Based on long-term averages, maximum monthly precipitation occurs during December (133 mm, SD = 56) and the minimum occurs during February (97 mm, SD = 55) each year, although differences between months are not statistically significant. Mean annual streamflow from W6 is 869 mm (SD = 175), and has varied from 574 mm in 1988 to 1470 mm in 1973. On average, maximum monthly streamflow occurs during April (222 mm, SD = 82) and the minimum occurs during August (19 mm, SD = 24) each year. Some 52% of annual streamflow occurs during March, April and May of each year (Federer et al. 1990).

Northern hardwood forest covers the HBEF, with American beech (*Fagus grandifolia* Ehrh.), yellow birch (*Betula alleghaniensis* Britt.) and sugar maple (*Acer saccharum* Marsh.) dominating elevations from 500–730 m. White birch (*Betula papyrifera* var. *cordifolia* Regel Fern.), red spruce (*Picea rubens* Sarg.) and balsam fir (*Abies balsamea* (L.) Mill) largely dominate at elevations above 730 m. The HBEF was logged between 1909–1917, damaged in 1938 by a hurricane, but there is no evidence of recent fire (Bormann & Likens 1979; Bormann et al. 1970; Davis et al. 1985; Whittaker et al. 1974). Forest biomass has been monitored on W6 at the HBEF at about 5-yr intervals since 1965 (Table 1). Initially, the forest showed significant rates of aboveground biomass accumulation and associated element uptake (4.85 Mg/ha-yr, 1965–1977; Likens et al. 1977; Bormann & Likens 1979; Whittaker et al. 1979). However,

Table 1. Biomass of several components of Watershed 6 within the Hubbard Brook Experimental Forest during 1965–1992.

Year	Size Class (cm)	Aboveground (Mg/ha)	Belowground (Mg/ha)	Standing Dead[a] (Mg/ha)	Forest Floor (kg/m^2)		Aboveground Litterfall[b] (Mg/ha)
					total	organic matter	
1965	≥ 9.6 cm	123.3	25.5	—	—	—	—
	1.6–9.5 cm	8.69	2.52	—			
1968		—	—	—	—	—	5.7
1969		—	—	—	[c]		
1976		—	—	—	18.9	6.72	—
1977	≥ 9.6 cm	181.5	36.7	15.9	13.5	6.06	—
	1.6–9.5 cm	—	—				
1978		—	—	—	12.6	6.42	—
1982	≥ 9.6 cm	196.1	39.3	17.3			
	1.6–9.5 cm	6.02	1.77	0.76	10.9	6.21	—
1987	≥ 9.6 cm	194.9	38.7	21.2			
	1.6–9.5 cm	7.41	2.30	0.91	13.6	6.47	—
1992	≥ 9.6 cm	197.8	39.3	23.6			
	1.6–9.5 cm	8.97	2.98	0.64	17.5	8.26	—

[a] above and belowground

[b] Total aboveground litterfall (Gosz et al. 1972)

[c] Data of Gosz et al. 1976 not included here because of different sampling procedures (see text)

in recent years aboveground forest biomass accumulation has declined to a small rate (0.89 Mg/ha-yr, 1987–1992).

Procedures

General

Methods used for collecting most of the data utilized here are given elsewhere (e.g. Federer et al. 1990; Lawrence et al. 1986, 1987; Likens et al. 1977, 1984), but where necessary, methods are summarized briefly. We use a water-year (1 June – 31 May) to determine annual balances for water and chemical elements in experimental watershed-ecosystems at the HBEF because it is believed that the change in water storage in the soil of the watershed-ecosystems is minimal from one June 1st to the next (Federer et al. 1990). Bulk deposition collections (made on a weekly basis from continuously open collectors) are used to characterize the wet plus dry atmospheric inputs of elements like K at Hubbard Brook (e.g. Eaton et al. 1980; Likens et al. 1977). Likewise, because the relationship between discharge and concentration for most solutes is either nonexistent or weak (Johnson et al. 1969), a systematic weekly, streamwater sampling program has been found to be appropriate for developing long-term patterns of chemical change at Hubbard Brook.

To make quantitative assessments of mass balance, bulk deposition collectors are maintained at high density in cleared areas throughout the HBEF (see Likens et al. 1977; Fig. 2). A gauging weir is attached to the bedrock at the base of each watershed-ecosystem for quantitative measurement of drainage water. Deep seepage is negligible in these watershed-ecosystems (Likens et al. 1977).

Watershed 6 has the longest continuous biogeochemical record of data at the HBEF and is considered the biogeochemical reference watershed-ecosystem for these studies.

Throughfall

Throughfall was collected during the growing seasons (June – September) of 1989–1991 from six collectors at each of four sites, spanning the elevational range of the experimental watersheds and immediately outside the boundary of W6 (Fig. 2; Lovett et al. 1992). Each collector consisted of a 20-cm diameter polyethylene funnel draining directly into a polyethylene bag. Collections were made after each rain event to the extent possible, but in no case were samples left in the field longer than one week.

Throughfall and stemflow were collected during the 1969 growing season and reported by Eaton et al. (1973). The methods in the 1969 study were somewhat different because samples were collected on a weekly basis and stratified by placing collectors under two individuals of each of the three major tree species (see Eaton et al. 1973 for details). An outbreak of the leaf-eating insect *Heterocampa* spp. occurred during the period 1968–1970, and this event may have influenced the results of the 1969 study.

Soil solutions

Tension-free lysimeters were installed in fall 1983, adjacent to W6 in a low-elevation hardwood stand (600 m; LH), in a high-elevation hardwood stand (730 m; HH) and in a coniferous stand (750 m; SF; Fig. 1). Lysimeters were constructed of either 10-cm diameter polyethylene funnels filled with acid-washed silica sand that drain into 1-l polyethylene containers, or rectangular (20- by 3.5- by 14.5-cm) polyethylene containers filled with acid-washed Teflon beads that empty into 2-l polyethylene containers (Driscoll et al. 1988). After excavating soil pits, replicate lysimeters were placed immediately beneath the Oa horizon (6, 4 and 3 cm below the surface of the forest floor for SF, HH and LH sites respectively), beneath the Bh horizon (14, 18 and 10 cm below the surface of the mineral soil for SF, HH and LH sites respectively), and within the lower Bs2 horizon (40, 43 and 49 cm below the surface of the mineral soil for SF, HH and LH sites respectively) from the face of the pit at each site. Lysimeters were installed carefully to minimize soil disturbance. Our results show no statistically significant differences in the solution chemistry collected with sand and teflon lysimeters. Soil pits were backfilled to prevent accumulation of water and to eliminate freezing during winter sampling. Soil solutions were collected continuously and sampled at approximately monthly intervals beginning in January 1984. We used zero-tension lysimeters, because we are interested in relating soil water to stream water. We anticipate that these collectors sample both gravity flow and some matric water.

Sites along a gradient of elevation

Stream samples were collected at approximately monthly intervals along a gradient of elevation at 751, 732, 701, 663, 602 and 544 m within W6 beginning in June 1982 (Fig. 2). Cumulative drainage areas for these sites are 1.09, 2.65, 5.07, 6.58, 9.96 and 13.23 ha, respectively. The upper site (751 m) is located within coniferous vegetation. The site located at 732 m drains a transition zone between areas of coniferous and deciduous vegetation. The remaining stream collection sites are located in reaches flowing through northern hardwood forest.

Forest floor

The forest floor was sampled in 60 to 80 of the 208, 25 × 25-m units of W6 in 1976–78, 1982, 1987 and 1992. A 15 × 15-cm wooden template was placed randomly on the ground and stabilized in place with a nail in each corner. The soil was cut around the template with a saw and the surrounding forest floor pulled back to isolate the block of the forest floor material beneath the template. The block of forest floor then was undercut and removed to lie upside down on the template. The mineral soil was scraped off 'upwards' to the bottom of the Oa. The forest floor block was bagged as a unit in some years and in others separated into the Oie and the Oa which were taken separately. The material was oven-dried (80 °C) and ground in a Wiley Mill. Samples were ashed for loss on ignition (LOI) and the ash was eluted with 6 N HNO_3 and diluted to 50 ml. Standard errors ranged from 7.7 to 9.7% of the mean value for mass of organic matter determined for each sampling date on W6.

Soil chemistry

Quantitative estimates of soil mass by depth were determined in 60 soil pits located throughout W5 (Johnson et al. 1991a). Soils were sieved using 2-mm (mineral soil) or 5-mm (O horizons) pore size, stainless steel sieves. Exchangeable K was measured by displacement using 1 M NH_4Cl. Potassium concentrations in the extracts were determined by flame atomic absorption spectophotometry. Pool sizes were estimated by multipying exchangeable K concentrations by soil mass.

Mineralogy

Qualitative estimates of mineral abundance and quantitative estimates of mineral chemistry for the sand/silt size fractions of three Bs2 horizon soil samples from W5 were obtained using Scanning Electron Microscopy with Energy Dispersive Spectroscopy. The mineralogy of the clay-size fraction of soils collected from three soil pits within the Bear Brook watershed (including W6) was determined by X-ray diffractometry.

Computation methods

Differences in concentrations of K in soil solutions and stream waters were determined by a one-way analysis of variance. The nonparametric seasonal Kendall Tau (SKT) test (Hirsch et al. 1982) was used to detect monotonic trends (generally increasing or decreasing with time) in water chemistry at the HBEF. The SKT test is applicable to data that exhibit seasonal and non-normal distribution. The HBEF data also exhibited significant autocorrelation and, therefore a modification of the original SKT test was used in our analysis (Hirsch & Slack 1984). Slopes for long-term trends were estimated using the nonparametric seasonal-Kendall slope estimator (Hirsch et al. 1982). Slopes were calculated from all possible pairs of data that included the same months in different years. Results from all 12 months then were pooled together and the median value was taken as the long-term slope.

Flux and cycling of potassium in a forested ecosystem

Sources of potassium for the watershed-ecosystem

Atmospheric inputs in bulk deposition – concentrations, fluxes and trends

Inputs of K in rain and snow are significant to forested and associated aquatic ecosystems within the HBEF during an annual cycle (e.g. Likens et al. 1977, 1985). The long-term, volume-weighted mean concentration of K in precipitation is 1.37 μmol/l (53.6 μg/l) and comprised 10.2 and 18.7% of the sum of the base cations ($C_B = Ca^{2+} + Mg^{2+} + Na^+ + K^+$) or 5.8 and 11.3% of the sum of total cations ($C_B + NH_4^+ + H^+$) in bulk deposition at Hubbard Brook during 1963–1992 (percentages on a mass and equivalent basis, respectively). Annual volume-weighted mean concentrations have ranged from a low of 0.61 μmol K/l (24 μg/l) in 1986–87 to a high of 5.11 μmol K/l (200 μg/l) in 1963–64 (Fig. 3A). Average monthly concentrations in bulk deposition peaked in May and again in October (Fig. 4A). These high concentrations of K in bulk deposition in May could be related to the leafing out of the forest canopy and/or the abundance of plant pollen at that time. The peak in concentration in October also is unexplained, but it corresponds roughly with autumnal leaf abscission and fall (see below).

Although K concentrations in precipitation tend to be lower during the winter (Fig. 4A), concentrations in the snowpack are appreciably higher than in the incident precipitation (e.g. Hornbeck & Likens 1974). This pattern is in contrast to other nutrient ions such as $SO_4^=$, NO_3^- or Ca^{2+}. Also, concentrations of K tend to fluctuate less in the accumulated snowpack than other cations (e.g. Ca^{2+}). Mean concentrations in the snowpack varied between 70 and 100 μmol/l during most of the winter of 1972–73. The K in the snowpack originated not only from direct precipitation, but also from leaching of plant materials (e.g. birch cone scales and seeds, leaf and bark fragments) that were incorporated within the snowpack (Hornbeck & Likens 1974).

There has been a significant decline in the annual, volume-weighted concentration of K in bulk deposition during 29 years (Fig. 3A). Time-series analysis by SKT also showed a long-term decline in annual K concentration in bulk deposition (median slope of –0.0125 μmol K/l-yr with a 95% CI of –0.02 to –0.005, $p < 0.05$). All of this decline occurred during the first two years of the record (1963–65), however, which were drought years at Hubbard Brook (Likens et al. 1977). No significant long-term trend in concentration was observed during 1965–1992.

Both monthly and annual, volume-weighted K concentrations decreased with increasing amounts of precipitation (e.g. Fig. 5A), although the relationship is weak. Because of this relation, annual deposition of K did not increase with amount of precipitation, even though annual precipitation has varied by a factor of about 2 during the study. Rather, annual inputs tended to decrease with increasing amounts of precipitation (Fig. 5B). A similar inverse relationship between annual inputs and amount of precipitation was

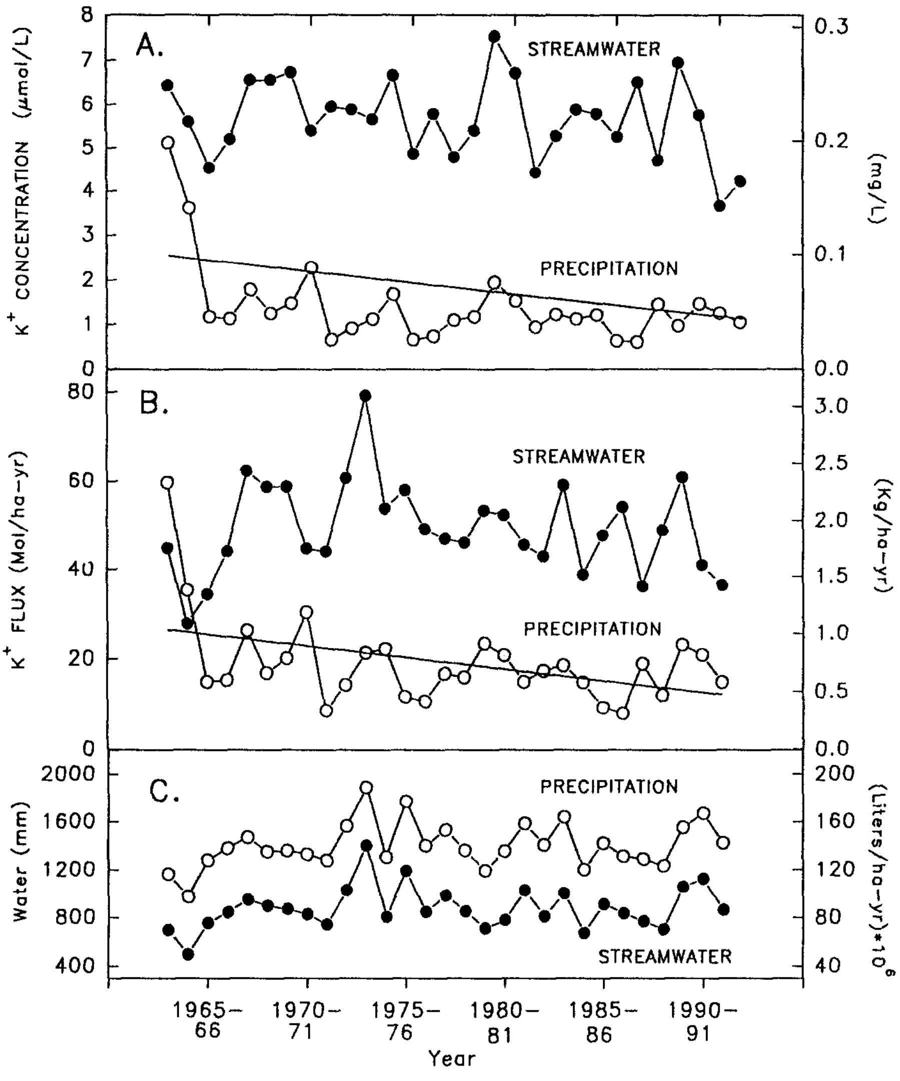


Fig. 3. (A) Annual volume-weighted concentrations of K in bulk precipitation (–o–) and stream water (–●–) for W6 of the HBEF during 1963–1992. The probability for a larger F-ratio for the regression line is < 0.02, but the r^2 value is only 0.22. (B) Annual inputs of K in bulk precipitation (–o–) and outputs in stream water (–●–) for W6 during 1963–1992. The probability of a larger F-value for the regression line is < 0.02, and the r^2 value is 0.19. (C) Annual amount of precipitation (–o–) and streamflow (–●–) for W6 of the HBEF during 1963–1992.

observed at a site remote from human activity in northern Australia (Likens et al. 1987).

The long-term (1963–1992) pattern of annual and monthly inputs followed closely that of annual and monthly K concentration (Figs. 3B and 4B). The input of K to W6 ranged from 60 mol/ha-yr (2.33 kg K/ha-yr) in 1963–64 to

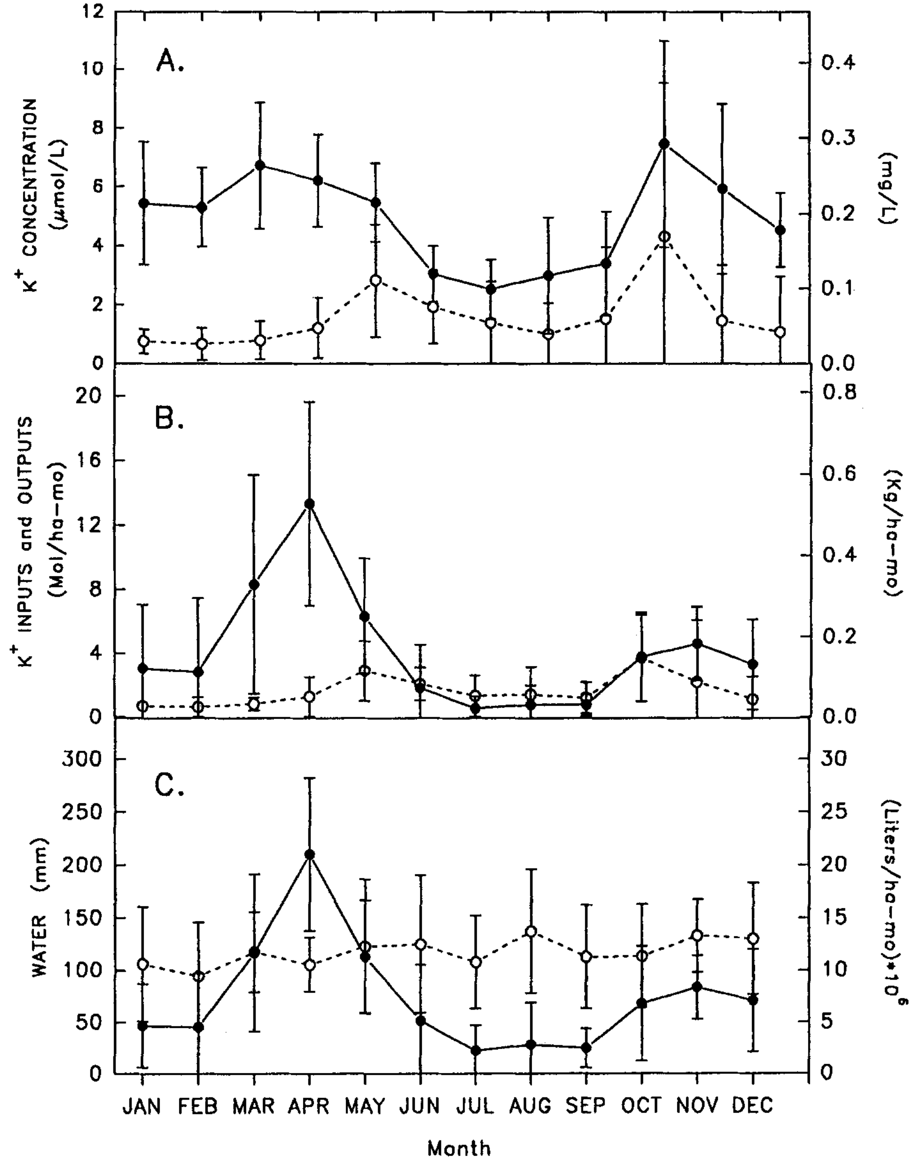


Fig. 4. (A) Monthly volume-weighted concentrations of K in bulk precipitation (-○-) and stream water (-●-) for W6 of the HBEF during 1963–1992. The vertical error bars represent ± one standard deviation for the mean value. (B) Monthly inputs of K in bulk precipitation (-○-) and outputs of K in stream water (-●-) for W6 during 1963–1992. The vertical bars represent ± one standard deviation for the mean value. (C) Monthly amounts of precipitation (-○-) and stream water (-●-) for W6 during 1963–1992. The vertical bars represent ± one standard deviation for the mean value.

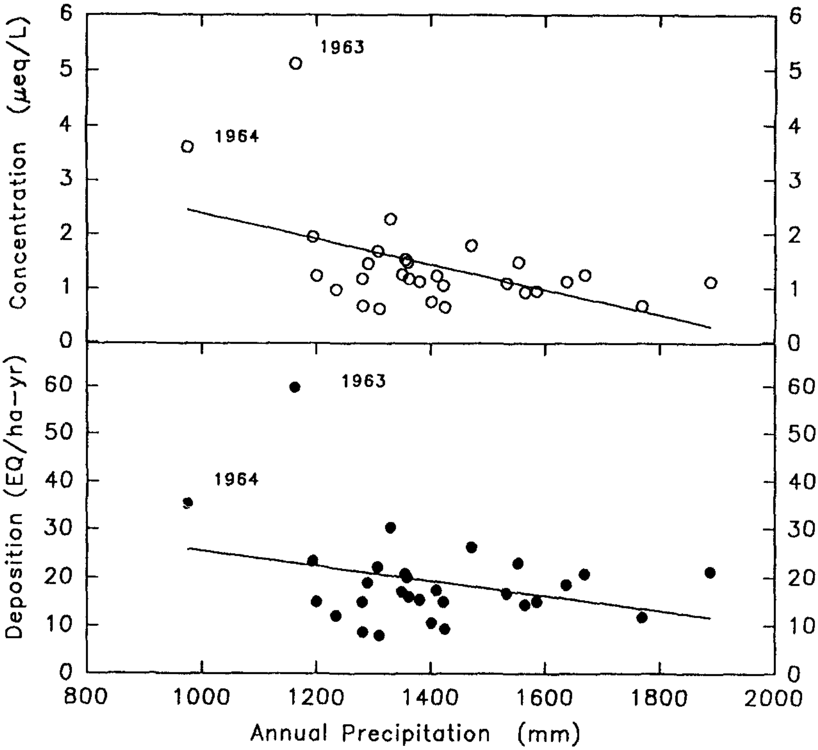


Fig. 5. Relationship between the annual concentration of K in bulk deposition (top) and annual input of K in bulk deposition (bottom) and the amount of precipitation for W6 of the HBEF during 1963–1992. Water-years 1963–64 and 1964–65 were drought periods. The probability for a larger F-ratio for the regression line is < 0.01 and < 0.1 and the r^2 value is 0.24 and 0.09 for concentration and input respectively.

8 mol/ha-yr (0.31 kg K/ha-yr) in 1986–87, and averaged 0.75 kg K/ha-yr ($s_{\bar{x}}$ = 0.07) during the period (Table 2). In contrast to the linear regression analysis (Fig. 3B), the SKT analysis showed no significant ($p < 0.05$) temporal trend in precipitation input of K.

Bulk deposition vs. wet deposition and dry deposition

Because bulk deposition collectors are continuously open, during dry periods they collect atmospheric particles that are large enough to fall. Particulate K in the atmosphere can be associated with dust, sea salt, and especially plant-derived material (Crozat 1978; Gosz 1980; Lovett & Lindberg 1984). Particles can be formed on plant surfaces by degradation of leaf tissue or by migration of salts from the interior to the exterior of leaves (Lovett et al. 1989; Reiners et al. 1986; Schaefer & Reiners 1989), and removed from the leaf surface by wind or by electrostatic forces (Beauford et al. 1977; Fish 1972). These aerosol particles can be transported by wind and deposited to the bulk deposition

Table 2. Annual input-output budgets for potassium in Watershed 6 of the Hubbard Brook Experimental Forest, New Hampshire.[a]

Water-Year	Bulk deposition input	Streamwater output	Net gain or loss
1963-64	2.33	1.75	0.58
1964-65	1.38	1.08	0.30
1965-66	0.58	1.34	-0.76
1966-67	0.60	1.72	-1.12
1967-68	1.03	2.43	-1.40
1968-69	0.66	2.30	-1.64
1969-70	0.78	2.29	-1.51
1970-71	1.19	1.75	-0.56
1971-72	0.34	1.72	-1.38
1972-73	0.56	2.37	-1.81
1973-74	0.83	3.09	-2.26
1974-75	0.87	2.10	-1.23
1975-76	0.46	2.26	-1.80
1976-77	0.41	1.92	-1.51
1977-78	0.65	1.83	-1.18
1978-79	0.62	1.80	-1.18
1979-80	0.91	2.09	-1.18
1980-81	0.81	2.04	-1.23
1981-82	0.59	1.78	-1.19
1982-83	0.68	1.68	-1.00
1983-84	0.72	2.31	-1.59
1984-85	0.58	1.52	-0.94
1985-86	0.36	1.87	-1.51
1986-87	0.31	2.12	-1.81
1987-88	0.74	1.41	-0.67
1988-89	0.47	1.91	-1.44
1989-90	0.90	2.38	-1.48
1990-91	0.81	1.60	-0.79
1991-92	0.58	1.42	-0.84
$\bar{x}$	0.75	1.93	-1.18
$s_{\bar{x}}$	0.07	0.08	0.11
max	2.33	3.09	0.58
min	0.31	1.08	-2.26

[a] Values in kg/ha-yr (1 kg K/ha-yr = 25.58 mol K/ha-yr).

collectors in clearings within the forest. In this study, samples were rejected where there was visible contamination by particles (e.g. pollen). However, deposition of particles that are not visible may have influenced sample chemistry.

To examine the differences between bulk deposition and wet deposition, a bulk collector and two wetfall-only collectors were maintained side-by-side for 11 years in a clearing near the Forest Service Headquarters at Hubbard Brook (about 250 m elevation). The wetfall-only collectors have an automatic lid which covers the sampling container during dry periods. One of these collectors was maintained as part of the National Atmospheric Deposition Program (NADP). All collectors were sampled weekly. The 11-yr volume-weighted mean bulk concentration of K was 2.7 times higher than the mean value for the two wetfall collectors (the long-term mean values for the two wetfall collectors were not statistically different; Table 3). This finding is consistent with other studies of bulk and wet deposition (Galloway & Likens 1978; Richter & Lindberg 1988) and indicates substantial particulate deposition to the bulk collector. Bulk deposition at the Headquarters site was very similar to bulk deposition on W6, which ranges from 550 to 800 m in elevation and is located approximately 3.3 km to the east (Table 3).

Table 3. Volume-weighted mean concentrations of K in bulk and wetfall-only deposition at the Forest Service Headquarters site (FS), and in bulk deposition at Watershed 6 from 1979 to 1989. Data are in μmol/l and were provided by D. Buso and C. W. Martin.

Year	Bulk W6	Bulk FS	Wet FS (NADP)	Wet FS
1979	1.51	0.72	0.43	0.59
1980	1.10	0.87	0.46	0.36
1981	1.30	1.00	0.41	0.46
1982	1.33	1.33	0.38	0.46
1983	0.90	0.84	0.51	0.54
1984	1.38	1.23	0.61	0.46
1985	0.79	1.07	0.38	0.41
1986	0.61	1.25	0.23	0.41
1987	1.18	1.13	0.36	0.54
1988	1.23	2.48	0.31	0.59
1989	1.41	1.46	0.36	0.69
Mean	1.16	1.22	0.40	0.50
standard error	0.08	0.14	0.03	0.03

The difference between bulk deposition and wet deposition can be considered an estimate of dry deposition if we assume (1) that particles large enough to deposit by gravitational sedimentation from the airstream account for all of the dry deposition, and (2) that deposition to the collector funnel is equivalent to deposition to a forest per unit surface area. Neither of these assumptions is strictly true, and both will lead to an underestimate of dry deposition. Sedimentation of particles constitute a substantial fraction, but not all, of K dry deposition (Davidson et al. 1982; Johnson & Lindberg 1992) and coarse particle deposition to a forest canopy is usually higher than deposition to artificial surfaces in a clearing (Lindberg et al. 1988). The difference in mean concentration between the wetfall-only and bulk collectors at the Headquarters site is 0.76 μmol/l. This difference implies that at least 63% of the bulk deposition is from dry particles. Applying this percentage to the bulk deposition in Table 2, of the 19 mol/ha-yr mean bulk deposition, 12 mol/ha-yr was as dry deposition and 7 mol/ha-yr was in wet deposition. Again, this is a lower-limit estimate for dry deposition.

An alternative means of estimating dry deposition makes use of atmospheric particulate sampling done during 1974 and 1976 at Hubbard Brook (Eaton et al. 1978). The mean annual concentration of K in air was 3.4 nmol/m^3 during this period with 26% of the particles in the diameter range 3.6–20 µm, 14% in the range 0.65–3.6 µm, and 35% in the size range 0.1–0.65 µm. Deposition can be estimated from these concentration data when deposition velocities are specified. Assuming that the particles in the largest size class are depositing by sedimentation, a reasonable deposition velocity is the mean fall speed for the size class, 0.5 cm/s. We assume annual average deposition velocities for the smaller particles of 0.1 cm/s (Lindberg et al. 1986) and estimate dry deposition to be 2.6 mol K/ha-yr (Table 4).

Table 4. Calculation of K dry deposition from atmospheric concentrations (Eaton et al. 1978) and deposition velocities.

Particle Diameter Class (µm)	Concentration (nmol/m^3)	Deposition Velocity (cm/sec)	Deposition Flux (mol/ha-yr)
3.6–20	1.2	0.5	1.8
0.65–3.6	0.64	0.1	0.26
0.1–0.65	1.6	0.1	0.51
Total	3.4		2.6

We do not know why the two estimates of dry deposition disagree, but it may be that the Lundgren impactor used to measure particle concentrations did not adequately sample the particles deposited in the bulk deposition funnel. This difference could occur if the particles were large, because air filtration techniques often undersample large particles (Noll et al. 1985), or if the particles were localized in small clearings and not present in the larger clearing where the particle sampler was operated. The uncertainty in the dry deposition value, however, has a relatively small effect on input-output balances (see General Discussion).

A related issue is whether the K deposition represents a true input to the ecosystem (e.g. dust emanating from distant sources), or is part of an intrasystem cycle (e.g. pollen or plant debris from local vegetation). Gosz (1980) found decreasing K deposition in bulk collectors with increasing distance from forest stands in mountainous ecosystems in New Mexico, suggesting that these forests were largely an internal source of some of the K found in the collectors. Likewise, Lovett & Lindberg (1992) found decreasing particulate K deposition with increasing height within and above an oak forest in Tennessee, again suggesting the forest itself to be a strong source. We also cannot separate local from distant sources of K with our bulk deposition collections, however, it seems likely that they contain some internally generated material that is cycling internally and thus may overestimate the true input flux by an unknown amount. Richter & Lindberg (1988) found bulk precipitation collectors to overestimate total (wet and dry) K deposition by a factor of two in Tennessee.

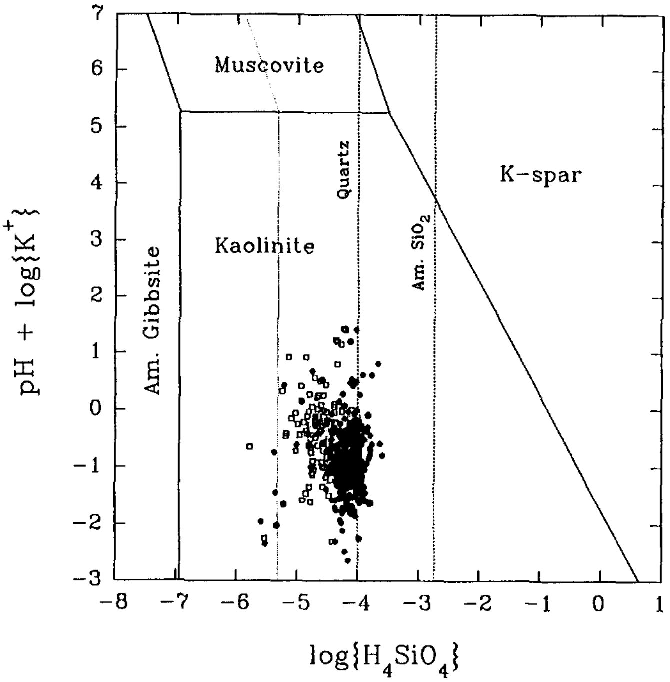
Thus, our bulk deposition collectors probably collect only a portion of the total particulate deposition to the ecosystem, but some of that particulate deposition likely represents internal recycling rather than a true ecosystem input. With these uncertainties in mind, we will use bulk deposition as an estimate of total (wet plus dry) atmospheric deposition in this paper.

Supply of K from weathering and cation exchange

Weathering release from soil and parent material is an important source of soluble K at Hubbard Brook (Likens et al. 1967) and elsewhere (e.g. Mast & Drever 1990; Paces 1986; Williams et al. 1986). The bedrock, glacial till, and soils of the HBEF contain 2–5% K (as K_2O), similar to average crustal values (Johnson et al. 1968). Relatively few K-bearing primary minerals have been identified at Hubbard Brook. Biotite and muscovite are the dominant K minerals in bedrock, till, and soil, and K feldspar has been found in small amounts. Secondary minerals found in Hubbard Brook soils include kaolinite, illite, hydroxy-interlayered vermiculite (HIV), and mixed-layer biotite/vermiculite (similar to hydro-biotite). Of these, the mixed-layer biotite/vermiculite and the illite contain appreciable amounts of K.

Potassium-bearing primary minerals at Hubbard Brook are not stable at Earth-surface conditions. Soil solutions and streamwater samples from W6 and the larger Bear Brook watershed, which includes both W5 and W6, are highly undersaturated with respect to the solubility of muscovite and K feldspar (Fig. 6). However, the dissolution rates of the three K-bearing primary minerals vary widely, with biotite widely regarded as the most weatherable (Sverdrup & Warfvinge 1988), followed by K feldspar and muscovite. Thermodynamic calculations suggest that under the solution conditions found at Hubbard Brook, the congruent dissolution of K feldspar should result in the re-precipitation of kaolinite (Fig. 6). Muscovite commonly undergoes incongruent dissolution, in which K is removed from interlayer spaces, producing an intermediate phase indistinguishable from illite, and ultimately kaolinite (Nahon 1991, p. 58). Incongruent dissolution of biotite produces mixed-layer biotite/vermiculite as an intermediate product to HIV (Fanning et al. 1989; Fordham 1990). In acidic forest soils, weathering of K feldspar, muscovite and biotite to the end-products kaolinite and HIV is a source of dissolved K over the long term. However, over shorter time scales vermiculite can fix K in interlayer spaces, thus serving as a potential sink for K in the soil (Douglas 1989).

Estimates of chemical weathering rates in small catchments typically are



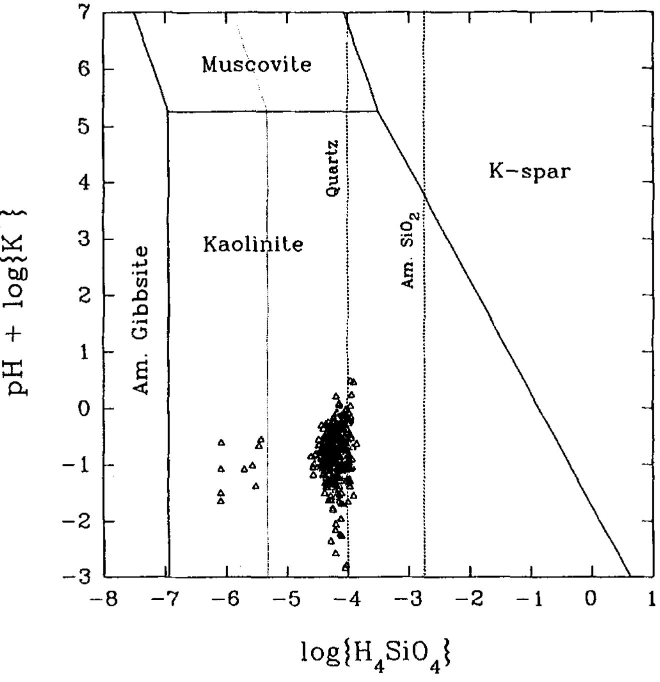


Fig. 6. Stability diagram for the SiO_2-K_2O-H_2O system, showing (top) soil solutions; (bottom) stream waters. Open squares indicate soil solutions from the spruce-fir zone. Stream samples include data from six longitudinal sampling sites within W6.

based on the differences observed in input-output budgets. For example, the mass balance for soluble K can be written as:

$$P_K + W_K = S_K + \Delta B_K \pm \Delta O_K \pm \Delta X_K \pm \Delta M_K \tag{1}$$

where P is the atmospheric input, W is the weathering release (primary minerals), S is the streamwater loss, ΔB is the net uptake into biomass, ΔO is the change in the soil organic matter pool, ΔX is the change in exchangeable pool, and ΔM is the change in the secondary mineral pool. Equation (1) can be rearranged to express the rate of net soil release of K. We consider net soil release to represent the sum of primary mineral weathering (W_K), net changes in secondary mineral pools (ΔM_K), net release by cation exchange (ΔX_K) and change in the soil organic matter pool (ΔO_K):

$$\text{Net soil release} = W_K \pm \Delta M_K \pm \Delta X_K \pm \Delta O_K = S_K + \Delta B_K - P_K \tag{2}$$

Since the K fluxes S_K, ΔB_K and P_K have been measured since 1965, estimates of the net soil release rate of K can be made for W6 (Table 5). Based on Equation (2), the net soil release rate of K represents the net loss or gain of K in soil-mediated processes. The value of the soil release rate is largely determined by the rate of plant assimilation of K. Thus, the rate has changed markedly between 1965 and 1992 (Table 5). During the period of highest biomass aggradation (1964–1977), an average of 230 mol/ha-yr of K was mobilized from the soil and till. In 1982–1992, little K was assimilated in forest biomass, and the net soil release rate of K fell to an average of about 30 mol/ha-yr.

Direct estimates of W_K, ΔX_K, ΔM_K andΔO_K are not possible from available data. Likens et al. (1977) estimated that some 7.1 kg K/ha (180 mol K/ha) were released annually in the Hubbard Brook watershed-ecosystems by weathering. Using this value, computed as the right-hand side of Equation (2), the implicit assumption was that rock at Hubbard Brook undergoes congruent dissolution, i.e. no net change occurred in the pools of K in secondary minerals or the soil exchange complex; $\Delta X_K = 0$ and $\Delta M_K = 0$. Under this assumption, we would conclude from data in Table 5 that net soil release (weathering) of

Table 5. Rate of storage of K in living and dead biomass (B_K), net soil release rate of K (estimated from $S_K + B_K - P_K$), and sodium supply release (W_{Na}) in W6 at the Hubbard Brook Experimental Forest, 1965–1992. Units are mol/ha-yr.

Period	Storage	Net soil release	Sodium supply
1965–77	200	230	300
1977–82	130	160	370
1982–87	–30	2	300
1987–92	33	60	300

K has varied by two orders of magnitude between 1965 and 1992. However, observations at the HBEF tend to contradict this hypothesis. First, the total H^+ load in the soil (the sum of external and internal sources), which drives the weathering process, has declined by about 50% since 1965, not two orders of magnitude. The data for sodium (Na) also argue against the hypothesis. In the case of Na, the ΔX_{Na} and ΔM_{Na} terms are negligible, because Na is not a quantitatively important component of the soil exchange complex and secondary minerals. Thus, the weathering release of Na can be estimated reasonably by the supply rate (Table 5). The relatively constant rate of Na weathering is a strong argument that the fluctuations in net soil release of K cannot be explained fully by changes in K weathering. Thus, it would appear that the secondary mineral (vermiculite in particular) and exchangeable pools probably play an important role in regulating losses of K from the forest ecosystem. The relative importance of these two pools cannot be determined without detailed laboratory investigations, which have not been done.

Likens et al. (1977) also hypothesized differential weathering in the following relation: Ca > Na > Mg > K > Al > Si, with a correction for net biomass accretion. It follows that the terrestrial ecosystem would become enriched with time in the reverse order of the differential weathering. In fact, there appear to have been marked reductions in the calcium content of the ecosystem at Hubbard Brook (Federer et al. 1989; Likens 1992), as well as decreases in the rate of biomass accretion with time (Tables 1 and 7). Thus, weathering release apparently has been decreasing since the earlier estimates were made at Hubbard Brook.

Net rates of soil release of K for other forested watersheds in the eastern US are generally consistent with the values for Hubbard Brook (Table 6). In two cases (Mundberry, MA and Caldwell Creek, MA), negative net K soil release rates were observed, indicating net accumulation of K in the watershed. However, these negative rates may have been caused by unusually high inputs of ΔX_K (93 mol/ha-yr and 110 mol/ha-yr at Mundberry Brook and Caldwell Creek, respectively; Batchelder & Yuretich 1991; Yuretich & McManamon 1992) or from underestimates of P_K. Also, no corrections were made for biomass accumulation in the studies included in Table 6.

Intrasystem cycling

The living biomass pool and accretion

Above and belowground biomass and potassium accrual for the forest on W6 have been calculated for 1965, 1977, 1982, 1987 and 1992 using parabolic, volume-based allometric equations described by Whittaker et al. (1974), together with forest inventories (all stems $\geq$ 9.6 cm dbh, subsample of stems > 1.6 cm and $\leq$ 9.6 cm dbh) and plant chemistry from 1966 (Table 7). Allometric equations and plant chemistry have been revised periodically (TG Siccama, unpublished data) and all of the calculated information reported here is based on this updated information. Chemical composition of plant parts

Table 6. Rates of net soil release of K in forested catchments in the eastern U.S. (mol/ha-yr).

Site	Bedrock	Study Period	Rate of Net K Mineralizaton	Reference
Fort River, MA	Gneiss	July 1981–Dec. 1982	51	Yuretich & Batchelder 1988
Mundberry Br., MA	Schist	Dec. 1987–Dec. 1988	–14	Yuretich & McManamon 1992
Caldwell Cr., MA	Gneiss/Granite	1983	–63	Batchelder & Yuretich 1991
Biscuit Br., NY	Sandstone/Shale	Oct. 1983–Oct. 1985	21	Murdoch 1991
Panther Lake, NY	Granitic Gneiss	1978–80	33	April et al. 1986
Woods Lake, NY	Granitic Gneiss	1978–80	21	April et al. 1986

are used as given in Likens & Bormann (1970) and Whittaker et al. (1979) except for light wood of sugar maple, which was sampled and analyzed from cores and cross sections in 1984–1992 and found to be different than values reported for 1966 (Fig. 7). It is not clear whether this difference for sugar maple is due to a real change in wood chemistry or procedural differences during the study, but we have assumed the differences were the result of sampling vagaries in 1966 and have used the more recent determinations here. Dark-wood concentrations were not different and the 1966 values were used. The light-wood K concentration for the other major tree species was unchanged from the values reported in 1966 (Fig. 7). Patterns of K concentration in the wood with respect to age of the wood are weak at best and there is no sign of sequestering of K in older light wood. However, K is more concentrated in the dark wood.

In the 1977 inventory and thereafter, standing dead trees were included in the forest inventory in two classes – standing dead trees, which were dead but retaining most of their smaller branches, and stubs, which were trees broken off above dbh or with most of their major limbs broken off back to the main trunk. The K content of the standing dead boles of trees was assumed to be the same as for the live trees; although no studies of the chemistry of standing dead boles have been reported for eastern deciduous forest, Fahey (1983) observed that K concentration in the boles of standing dead lodgepole pine (*Pinus contorta* spp. *latifolia* [Engelm ex Wats] Critchfield) was similar to that of live boles. Once boles reach the ground, however, K is probably lost very rapidly (see section on Forest Floor Pools and Dynamics).

Total biomass and K content of live trees on a per hectare basis ceased to increase after about 1980 (Fig. 8). Thus, the mass of trees dying increased, keeping pace with the net growth increment of the live trees plus the ingrowth of stems into the smallest sampled size class (1.6 cm). We do not have a direct

Table 7. Above and belowground biomass and potassium content of live and dead standing trees on W6 of the Hubbard Brook Experimental Forest.

Biomass	Year (metric tons/ha)				
Size Class	*1965*	*1977*	*1982*	*1987*	*1992*
Live					
≥ 9.6 cm dbh	149	218	235	234	237
1.6–9.5	11	—	8	10	12
Dead					
≥ 9.6 cm dbh	—	16	17	21	24
1.6–9.5	—	—	0.8	0.9	0.6
Potassium	Year (moles/ha)				
Size Class	*1965*	*1977*	*1982*	*1987*	*1992*
Live					
≥ 9.6 cm dbh	4021	7104	7647	7577	7636
1.6–9.5	447	—	309	396	585
Dead					
≥ 9.6 cm dbh	—	411	446	520	504
1.6–9.5	—	—	16	21	15
Potassium	Year (kg/ha)				
Size Class	*1965*	*1977*	*1982*	*1987*	*1992*
Live					
≥ 9.6 cm dbh	188	278	299	296	299
1.6–9.5	17	—	12	15	23
Dead					
≥ 9.6 cm dbh	—	16	17	20	20
1.6–9.5	—	—	0.6	0.8	0.6

measure of ingrowth since our inventories are not based on individually marked stems. It would, however, be a very small fraction of the values reported in the 1.6- to 9.5-cm diameter classes (Table 7).

We have estimated the amount of K sequestered in the living trees of W6 during 1991 to 1992 by taking tree cores and measuring annual, radial growth increments on the 3 major species at 3 elevations adjacent to W6. These trees had an annual diameter growth rate of about 0.3 cm per year. Using this average, we calculated the total biomass and K content of the forest after reducing the diameter of all the live trees in 1992 by 0.3 cm. This calcula-

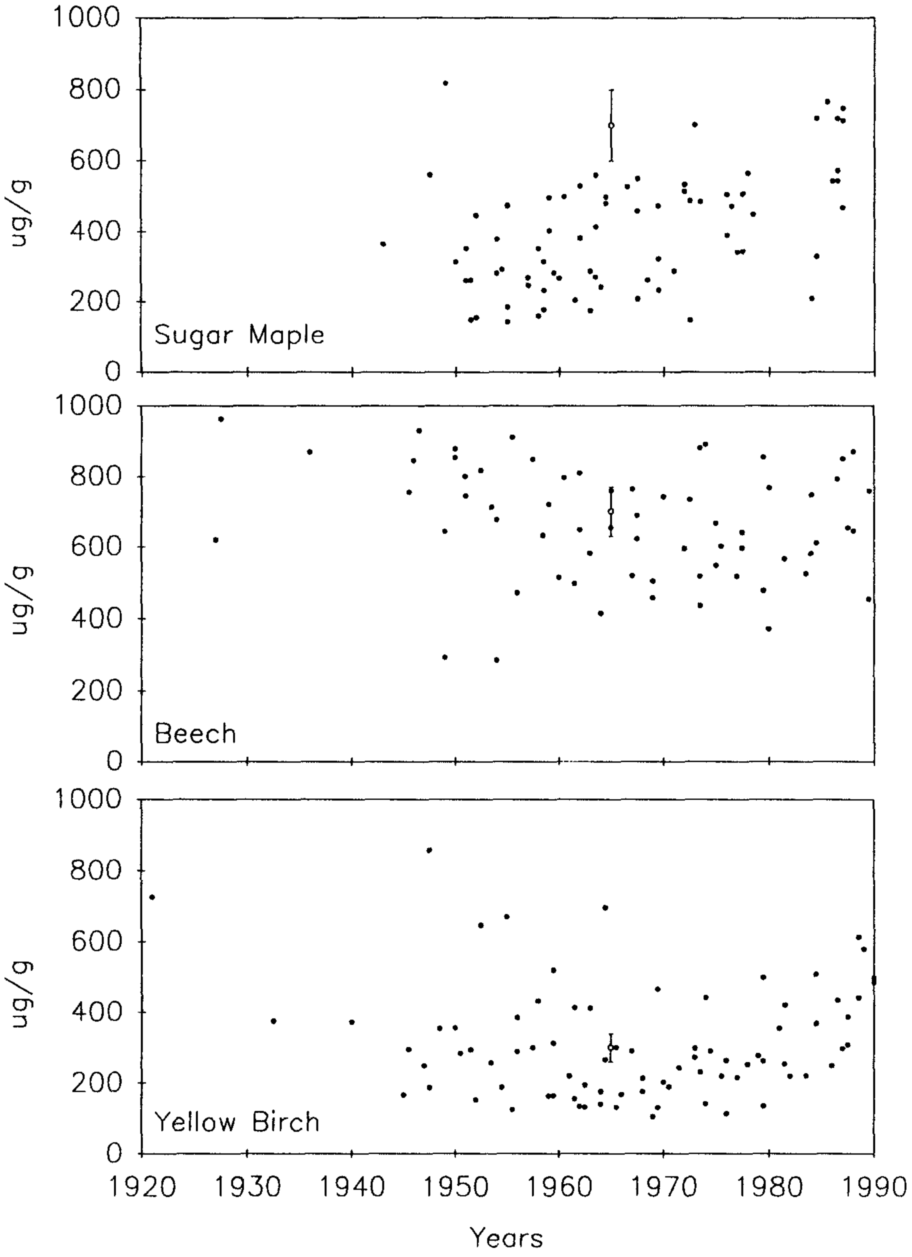


Fig. 7. Potassium concentration in light wood obtained from analysis of 1-cm lengths of tree cores from four trees of each species at low, mid and high hardwood forest west of W6. Cores taken in 1992. The open circle and error bars are the K concentrations reported by Likens & Bormann (1970) (1 μg K/g wood = 0.026 μmol K/g wood).

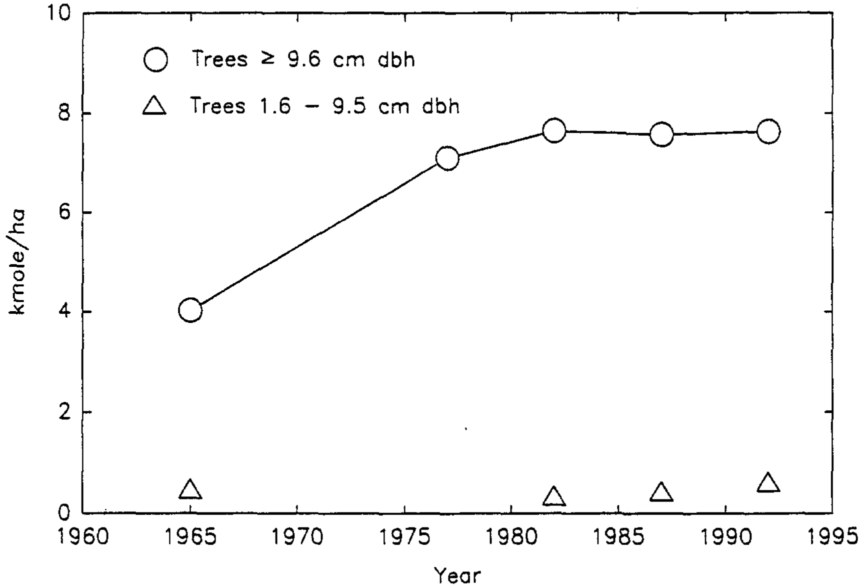


Fig. 8. Potassium pool in live tree biomass of W6 at the Hubbard Brook Experimental Forest (above- and belowground).

tion indicated a sequestering of K in these currently living trees (1992) of 105 mol K/ha-yr in 3.3 tons/ha of biomass accrual. Since there has been no net increase in the total biomass and K content during 1980 to the present, there must have been an equal amount of tree mortality (mass) during this period. Thus, about 105 mol K/ha-yr is transferred to the standing and downed dead wood compartment. There were no trees uprooted on the watershed in the 1992 inventory and few live trees were broken off during this recent (1–2-yr) period. Most trees die while standing at Hubbard Brook. We have not measured the rate at which the mass of dead boles (standing or down) are decomposing or the rate at which K is recycled via this pathway. However, the biomass of standing dead trees has been increasing from our first inventories of this component in 1977 through 1992 (Tables 1 and 7).

Throughfall and stemflow

The concentration and flux of K increase markedly during the passage of precipitation through the canopy. During the 1969 growing season (June – September), the sum of throughfall plus stemflow was estimated to be 600 mol K/ha (Eaton et al. 1973). Stemflow contributed about 77 mol K/ha (13%) of the total throughfall plus stemflow flux during the growing season (Eaton et al. 1973). In 1989–91, Lovett et al. (1992) estimated throughfall to be 257 mol K/ha during the growing season using somewhat different methods (see above). We do not know for certain why the throughfall flux of K appears to have decreased between 1969 and 1989–1991. Several possibilities exist to explain this change: (1) different sampling methods used in the two throughfall studies; (2) an outbreak of defoliating insects may have temporarily increased foliar leaching of K in 1969; or (3) a general decrease in the foliar pool of K or the 'leachability' of that pool.

On a charge equivalent basis, K contributes about 11% of the total cationic charge in bulk deposition, but it is the single most abundant cation in throughfall, contributing some 33% of the total cations during the growing season. The mean flux in throughfall for W6 during 1989–91 is about 40 times higher than the mean flux in bulk deposition during the growing season (Fig. 9).

The difference between throughfall flux and bulk deposition flux is called the net throughfall flux (NTF) and can be attributed to washoff of dry deposited material and to leaching from the canopy (Eaton et al. 1973; Lovett & Lindberg 1984). If bulk deposition collectors accurately estimate wet + dry deposition (see discussion above), then the NTF would represent entirely canopy leaching. The mean NTF for W6 during June – September of 1989–1991 (247 mol/ha) is much higher than dry deposition values estimated above or reported in the literature (e.g. Lindberg et al. 1986 measured 13 mol/ha-yr dry deposition), supporting the view that the NTF results mainly

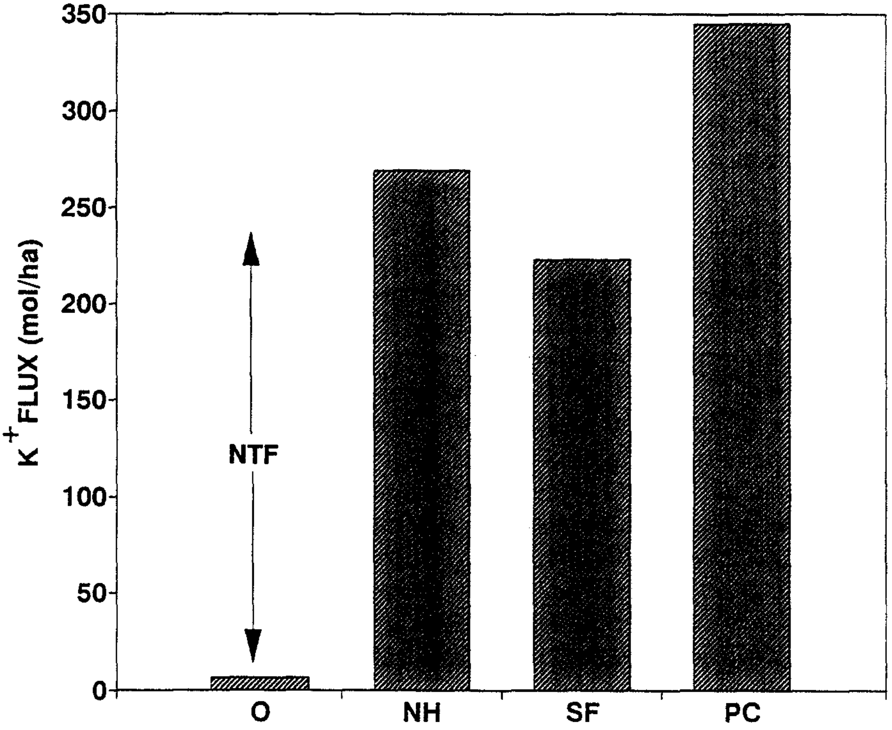


Fig. 9. Mean flux of K^+ in open bulk precipitation (O) and in throughfall under three vegetation types: northern hardwoods (NH), spruce-fir (SF), and pin cherry (PC). Net throughfall flux (NTF) is the difference between the fluxes in throughfall and precipitation. Data are means of June – September periods, 1989–1991.

from canopy leaching. The NTF for balsam fir stands at nearby Mt. Moosilauke, NH was 135 mol K/ha-yr (Olson et al. 1985), substantially lower than the NTF value reported here for a northern hardwood forest.

Spatial and temporal patterns in the NTF can provide some insight into the factors that regulate K leaching from the canopy at Hubbard Brook. Stepwise multiple regression of NTF for individual rain events against (1) the amount of precipitation, (2) the length of the dry period prior to the rain event, and (3) the acidity [H^+] of the rain event, showed that precipitation amount is the only significant predictive variable among the three, and that it explained 54% of the variance in the NTF for K. The NTF increases significantly with increasing precipitation amount ($p = 0.0007$), and the regression coefficient indicates that, on average, 1.5 mol/ha of K are leached per centimeter of precipitation during a rain event. The lack of significance of the length of the dry period in this regression again supports the conclusion that dry deposition is an unimportant contributor to the NTF (Lovett & Lindberg 1984). The lack of significance of precipitation acidity indicates that foliar leaching of K is not enhanced by acidic deposition, which occurs at Hubbard Brook (e.g. Likens et al. 1972). This conclusion is supported by branch chamber studies and highlights the contrast between K and the divalent cations, Ca^{2+} and Mg^{2+}, for which foliar leaching is increased markedly by acidic deposition (Lovett & Hubbell 1991).

While temporal patterns of canopy leaching of K are controlled mainly by precipitation amount, spatial patterns appear to reflect different rates of canopy leaching from different tree species. There is no significant difference in mean NTF between northern hardwood stands at different elevations on W6, but the NTF is significantly lower in the spruce/fir/birch stand near the top of the watershed, and higher in nearby W5, which is dominated by a successional pin cherry stand (Fig. 9). Within the northern hardwood community, Eaton et al. (1973) found no significant differences in K concentrations in throughfall under beech, maple and yellow birch trees.

In general, the behavior of K in the canopy is that of a highly mobile ion that is lost in significant quantities whenever the canopy is wet, irrespective of the variations in acidity of precipitation commonly observed at Hubbard Brook. The mobility of K results from its role as an electrolyte in the plant, rather than being bound in biomass structure (Kramer & Kozlowski 1979). As a result, the foliar content of K is low and is subject to substantial turnover. Total NTF during the growing season (June – September) represents 28% of the foliar pool of K for the watershed as a whole. Adding the leaching that occurs during leaf senescence in the fall would increase this value for turnover substantially (Eaton et al. 1973).

Resorption

During the autumn, there is a decrease of the K content of foliage of northern hardwood trees as leaves undergo senescence prior to abscission (Kramer & Kozlowski 1960; Mitchell 1936; Ryan & Bormann 1982). Potassium is mobile in the phloem of plants and has been observed to be resorbed (translocated) from the senescing leaves into the parts of the plant which survive the winter; K subsequently can be remobilized to support growth in the following growing season (Kramer & Kozlowski 1960). This movement is potentially a large flux of K within the plant biomass. We estimated the resorption of K from foliage of W6 during the autumn, as the change in the K content of canopy leaves during senescence minus leaching of K from the canopy by precipitation.

For the period 1964–69 the content of foliage before senescence was estimated as the product of the biomass of foliage (unpublished estimate for 1965 by T. Siccama) and the concentration of K in leaves collected in July and August on or near W6 (Likens & Bormann 1970).

The K contents in fresh leaf litter measured by Gosz et al. (1972), adjusted to have the same foliar biomass as before senescence, were used to estimate foliar K contents after senescence. To estimate the leaching of K from leaves during senescence, the net leaching of K from the canopy in throughfall plus stemflow, measured in September and October 1969 by Eaton et al. (1973), was used.

For the period 1987–1992, the K content of foliage before senescence was calculated as the biomass of leaves (unpublished average of 1987 and 1992 values from T. Siccama), multiplied by the mid-summer concentrations of K in foliage (Likens & Bormann 1970).

The K contents of leaf litter (Gosz et al. 1972) were adjusted to have the same leaf biomass as before senescence in 1987–1992. Foliar leaching during senescence was estimated as NTF measured in September and October 1990 (G.M. Lovett, unpublished data), plus 13% to account for stemflow (Eaton et al. 1973).

The quantities used to estimate resorption of K are summarized in Table 8. The change from the mid-summer contents of canopy leaves to that of fresh leaf litter was 349 mol K/ha (1964–69), and 447 mol K/ha (1987–92), for a change in leaf K contents of 50% during senescence for both periods. Canopy leaching could account for 77% (1964–69) or 36% (1987–92) of the change in foliar K contents during senescence. Resorption was markedly different in

Table 8. Estimate of resorption of potassium for W6 at the Hubbard Brook Experimental Forest, New Hampshire.

Process	K (mol/ha)	
	1964–69[a]	1987–92
Leaf Content Before Senescence = F_1	699	896
Leaf Content After Senescence = F_2	350	449
Leaching = L	276	160
Resorption = $(F_1 - F_2) - L$	73	287

[a] Modified from Ryan 1979

the two periods because of smaller canopy leaching and larger foliar biomass estimated for the latter period.

By comparison, for two other elements that also undergo autumn decreases in foliar contents, nitrogen (N) and phosphorus (P), foliar leaching could account for only 5% and 3%, respectively, of the autumn decline in leaf contents of these elements on W6 (Ryan & Bormann 1982). Resorption of K is probably affected more by year-to-year variation in foliar leaching than is resorption of elements such as N or P, which leach only slightly.

Litterfall

Gosz et al. (1973) studied litterfall and associated element flux at the HBEF. They found that total litterfall dry mass on W6 was 5.7 Mg/ha-yr during 1968–69. Leaf fall during 1968 was 2.65 Mg/ha and 2.57 Mg/ha in 1969. Relatively large inputs of K to the forest floor occur due to total litter inputs (469 mol/ha-yr, 18.3 kg/ha-yr). These inputs are largely associated with deciduous tissue (400 mol/ha-yr, 15.6 kg/ha-yr), and mostly as leaves (323 mol/ha-yr, 12.6 kg/ha-yr). Perennial tissue litter from the overstory (54 mol/ha-yr, 2.1 kg/ha-yr), shrub layer (7.7 mol/ha-yr, 0.3 kg/ha-yr) and herbaceous layer (7.7 mol/ha-yr, 0.3 kg/ha-yr) represented relatively minor inputs.

Potassium inputs in aboveground litter in the higher elevation spruce-fir zone of W6 (300 mol/ha-yr, 11.7 kg/ha-yr) were considerably lower than the lower elevation hardwood forest (541 mol/ha-yr, 21.1 kg/ha-yr). This pattern is consistent with the observations of elevational differences in K stocks associated with tree species (see Whittaker et al. 1979). In the high elevation spruce-fir zone, K stocks were 4590 mol/ha (179 kg/ha), while in the lower elevation hardwood forest K pools were 6330 mol/ha (247 kg/ha). Lower fluxes of K in litter in the high elevation spruce-fir zone than the hardwood zone are also similar to the patterns of throughfall inputs (see above).

Root processes

The intrasystem fluxes of K associated with root dynamics are very difficult to quantify, but probably very large. For example, Cox et al. (1977) estimated that 86% of all fluxes of K into the soil was derived from root losses – root death, consumption, leaching and exudation – in a 43-yr-old *Liriodendrum tulipifera* stand in Tennessee. Given the anatomy and chemical composition of root tissue and its associated mycorrhizae, the high turnover rates known for fine roots, and the exudation rates from roots, it seems likely that rates of K uptake and loss by root-mycorrhizal systems are high (Cox et al. 1977; Dighton & Mason 1984; Harris et al. 1980; Marshall & Waring 1985; McClaugherty et al. 1982; Smith 1972, 1976). Recent studies of fine roots at Hubbard Brook allow us to estimate K flux from roots for the northern hardwood ecosystem.

The pool of K in woody roots (> 1 mm diameter) was estimated for W5 at Hubbard Brook (Fahey et al. 1988), based upon quantitative sampling from soil pits in 1983 (1013 mol/ha, 39.5 kg/ha). The pool of K in the dynamic, fine root compartment can be calculated from data of Fahey (1994), Fahey & Arthur (1994) and Fahey et al. (1988). Midsummer fine root biomass (< 1 mm diameter) in the forest adjacent to W5 averaged 4.08 Mg/ha in 1987, with about 46% in forest floor and 54% in mineral soil. Concentration of K was much higher in forest floor than mineral soil fine roots (0.24 vs. 0.13% dry weight; Fahey & Arthur 1994). Thus, the midsummer pool of K in fine roots is about 186 mol/ha (7.25 kg/ha), with 62% in forest floor and 38% in mineral soil. Losses of K from the fine root pool include root turnover, exudation and leaching. Root exudation of K was estimated by Smith (1976) at 206 mol/ha-yr (8.05 kg/ha-yr), or slightly larger than the fine root K pool; however, this exudation flux must be considered highly uncertain because of difficulties of measurement.

Fahey (1994) estimated fine root production and longevity for the northern hardwood zone at Hubbard Brook using ingrowth cores and *in situ* screens, respectively. The picture of fine root turnover provided by these two approaches was generally consistent and agreed reasonably well with a carbon budget for the soil for the site and with direct observations of fine root longevity using minirhizotrons in a sugar maple forest in Michigan (Hendrick & Pregitzer 1992). The best current estimate of fine root turnover at Hubbard Brook is 5.08 Mg/ha-yr. Assuming no K retranslocation from fine roots (Nambiar 1987) and no differences in root longevity between forest floor and mineral soil horizons, total annual K return to soil from root turnover would be about 230 mol/ha-yr (9 kg/ha-yr). Although there is limited evidence that longevity of fine roots is lower for forest floor than mineral soil horizons (Schoettle & Fahey 1994), no quantitative basis to correct for this error is available for Hubbard Brook.

The current estimate of total inputs of K to soil from fine root processes (turnover plus exudation; 436 mol/ha-yr, 17 kg/ha-yr) appears to be smaller than that for aboveground litter plus canopy leaching (770 mol/ha-yr; Fig. 19). However, the root flux does not include turnover of woody roots (> 1 mm diameter) for which longevity is unknown. This flux could be substantial. For example, if the average longevity of roots 1 to 10 mm in diameter were about 5 yr (Schoettle & Fahey 1994), then K from this compartment would be about 113 mol/ha-yr (4.4 kg/ha-yr). In sum, although considerable uncertainty remains in estimates of K flux from roots to soil, it seems likely that the proportion of K return to soil from roots is comparable to aboveground returns.

Forest floor pools and dynamics

The O horizon, or forest floor in the Spodosols at Hubbard Brook, is a thick (avg. = 6.9 cm) layer of organic-rich soil containing some 46% of the total lateral root biomass (Fahey et al. 1988). Organic matter enters the forest floor as litter, which is gradually decomposed, resulting in the solubilization of organic compounds, and the release of soluble K and other solutes through mineralization. The turnover of K in the forest floor is believed to be rapid, due to high rates of K leaching from leaf litter. Gosz et al. (1973) reported 70–80% reductions in K content in decomposing leaf litter over a 6-month period. Potassium loss from woody litter was also high, approximately 60% in a 12-month period.

Arthur et al. (1993) observed very rapid decay of dead boles on W2 at Hubbard Brook and the release of K also appeared to be very rapid. Twenty-four years after the trees were felled on W2 only 7% of K remained in decaying boles, and it appears likely that much of that K release occurred during the first decade of decay.

As discussed above, root litter also provides a large source of K to the forest floor. Leaching and mineralization of K from dead fine roots is very rapid. Following clearcutting of W5, fine roots incubated in mesh bags in the forest floor lost 80% of their original K within about 2 months (Fahey et al. 1988), and a similar pattern was observed for roots decaying *in situ* after clearcutting (Fahey & Arthur 1994). The rate of K release from fine roots following chronic mortality has never been measured, but given the high mobility of K in plant tissues it seems likely that rapid release occurs.

Determining the pool of K associated with forest floor organic matter is surprisingly difficult, due to the large difference in K concentrations in mineral and organic soil fractions. There is a strong, negative correlation (r, –0.96) between the concentration of K and loss-on-ignition (LOI: i.e. organic matter concentration) in O horizon soils (Fig. 10). Johnson et al. (1968) reported an average K concentration in E horizon soil of 2.4% (2.9% as K_2O), while Gosz et al. (1972) reported K concentrations in fresh leaf litter of 0.36 to 0.54%. Because of rapid leaching during decomposition, the concentration of K associated with organic matter in the forest floor is expected to be even lower than leaf litter. Using the regression equation for Fig. 10 ($\%K = 1.95 - 0.0193 \times \%LOI$), the concentration of K in mineral material in the forest floor ($LOI = 0\%$) is approximately 1.95%, while the concentration of K in 'pure' organic matter ($LOI = 100\%$) is about 0.02%. These estimates lead to two conclusions. First, it is apparent that most of the K in the forest floor is associated with mineral matter, even at sites where LOI is large. For example, a soil with 90% LOI would have approximately 0.018% 'organic' K and 0.2% 'mineral' K. Second, the difference between mineral and organic K concentrations makes the estimation of the total K pool in the forest floor extremely sensitive to differences in sampling and analysis. The forest floor – mineral soil boundary is typically distinct, but in many cases, the cut-off requires a subjective decision (Federer 1982). Since the mineral content near the forest floor – mineral soil boundary increases with depth, a small difference in forest floor sampling depth can produce a large difference in the estimate of the pool size. Also, since most of the K is associated with mineral material, a more aggressive extractant yields more K. These factors explain the wide range of reported forest floor K pools for Hubbard Brook. For example, Gosz et al. (1976) reported a forest floor K pool of 916 mol K/ha, while Johnson (1989) reported a value of 15,300 mol K/ha. Gosz et al. (1976) sampled to an average depth

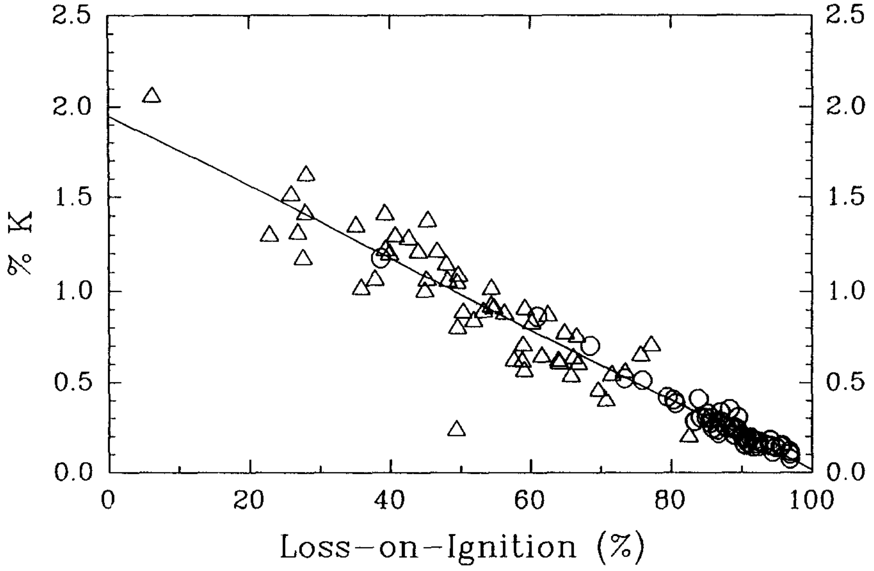


Fig. 10. Relation between % K and loss on ignition in O horizon soils of W5 at the HBEF.

of 5.3 cm and used 6 M HCl, while Johnson (1989) sampled to an average depth of 6.9 cm and used a combination of concentrated HCl and HF.

The Johnson (1989) estimate (15,300 mol K/ha) for the forest floor is probably a reasonable approximation of total K in the forest floor. Because of the less severe chemical treatment, the Gosz et al. (1976) estimate (916 mol K/ha) is likely a better representation of the pool of K associated with organic matter. Alternatively, the pool of 'organic' K can be estimated by multiplying the forest floor organic matter pool (54 Mg/ha; Johnson 1991a) by the approximate concentration of K in organic matter (0.02%, from Fig. 10). This calculation yields an estimate of approximately 280 mol K/ha in forest floor organic matter. The forest floor of the high-elevation spruce-fir zone contains significantly less total K than hardwood-zone soils (7060 mol/ha vs. 17,400 mol/ha).

A better measure of the labile K in the forest floor is the amount of exchangeable K in the Oa horizon. This pool is also significantly smaller in the spruce-fir zone than in the hardwood zone (290 mol/ha vs. 440 mol/ha). This difference is a reflection of the greater mineral content (lower LOI) of the forest floor of the hardwood zone. Moreover, the lower values of K in the forest floor of the high elevation coniferous zone is consistent with lower inputs of K from throughfall and litterfall in this zone as compared to the hardwood zone at lower elevations.

Soil pools and potassium dynamics

Soils contain K at exchange sites, in interlayers of clay minerals ('non-exchangeable' or 'difficultly exchangeable' K), and in the mineral matrix

(Barber 1984, Chapter 10). Release of K to the soil solution is relatively slow from clay interlayers and minerals (see section on Supply from Weathering and Cation Exchange). However, equilibrium between the exchangeable pool and soil solution generally is thought to be attained readily (e.g. Sparks 1989, Chapter 5). Thus exchangeable K can buffer changes in concentration of K in soil solutions.

The pool of exchangeable K in HBEF soils is small, due to low cation exchange capacity (CEC) and base saturation. In the mineral soil, exchangeable K concentrations range between 0.03 $\mathrm{cmol_c/kg}$ (C horizon) and 0.14 $\mathrm{cmol_c/kg}$ (Bh horizon). The pool of exchangeable K in the mineral soil is 2400 mol/ha, representing 1.2% of the total CEC (Johnson et al. 1991b).

The Oa horizon is richer in exchangeable K, and exchangeable base cations in general. The mean concentration of exchangeable K is 0.79 $\mathrm{cmol_c/kg}$, or 4.3% of the CEC (Johnson et al. 1991b). The pool of exchangeable K in the Oa horizon (410 mol/ha) is 15% of the total exchangeable K in the solum. The ratios of the total exchangeable K pool (2840 mol/ha) to the total living biomass pool (1:2.8) and to the annual average dissolved and particulate streamwater flux (49:1) for the period 1987–92 are the lowest among the base cations, indicating a short residence time for soluble K in the soil. The size of the exchangeable K pool varies with forest type at the HBEF. Soils in the spruce-fir zone have significantly smaller pools of exchangeable K than hardwood soils (1900 mol K/ha vs. 2970 mol K/ha, significant at the $P \leq 0.05$ level). This difference is largely attributable to the smaller soil mass within the spruce-fir zone (Johnson 1989).

There are marked elevational variations in exchangeable K within the watershed ecosystems. Soil concentrations of exchangeable K are higher at high elevation (~ 0.1 $\mathrm{cmol_c/kg}$) and decline at lower elevations (Fig. 11). This pattern of exchangeable K concentrations is likely due to elevational variations in soil organic matter concentrations (and associated cation exchange sites), and is qualitatively consistent with patterns of K concentrations in deeper mineral soil solutions and stream water (discussed below). For both the forest floor and mineral soil, concentrations of exchangeable K are significantly correlated with soil organic matter (forest floor: exchangeable K = $0.442 + 0.000676 \times$ organic matter (OM), $r^2 = 0.18$; mineral soil: exchangeable K = $0.0382 + 0.0000556 \times$ OM, $r^2 = 0.21$, where exchangeable K is in $\mathrm{cmol_c/kg}$ and OM is in g OM/kg soil. Other than a few higher values at one location of the high elevation, spruce-fir zone, saturation of exchange sites with K tended mostly to be between 0.5 and 2.0%, and there was no statistically significant change in K saturation of the soil with elevation.

Patterns in soil solution chemistry

Potassium concentrations in soil solutions were high in Oa horizon leachate and decreased as solutions migrated through the mineral soil (Fig. 12). This pattern likely is due to high inputs of K to the forest floor, occurring from throughfall and mineralization of litter. Potassium draining through the forest

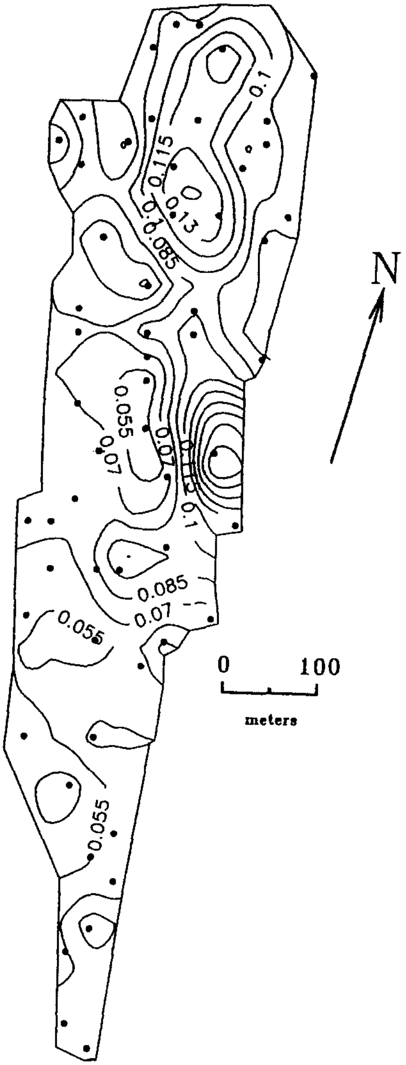


Fig. 11. Map showing spatial patterns in the concentration of exchangeable K (cmol$_c$/kg) in the mineral soil of W5 at the HBEF.

floor was immobilized readily in the mineral soil. A number of processes undoubtedly contribute to the decline in K concentrations in water through the soil profile. Most prominent of these are root uptake and retention on the soil exchange complex.

Differences in soil water K were evident between the soilwater collection sites. Mean concentrations of K in Oa horizon leachate were lowest in the high elevation coniferous zone (SF: 26 μmol/l) and exhibited modest decreases in the mineral soil (to 6.3 μmol/l in Bs2 horizon leachate). In contrast, the

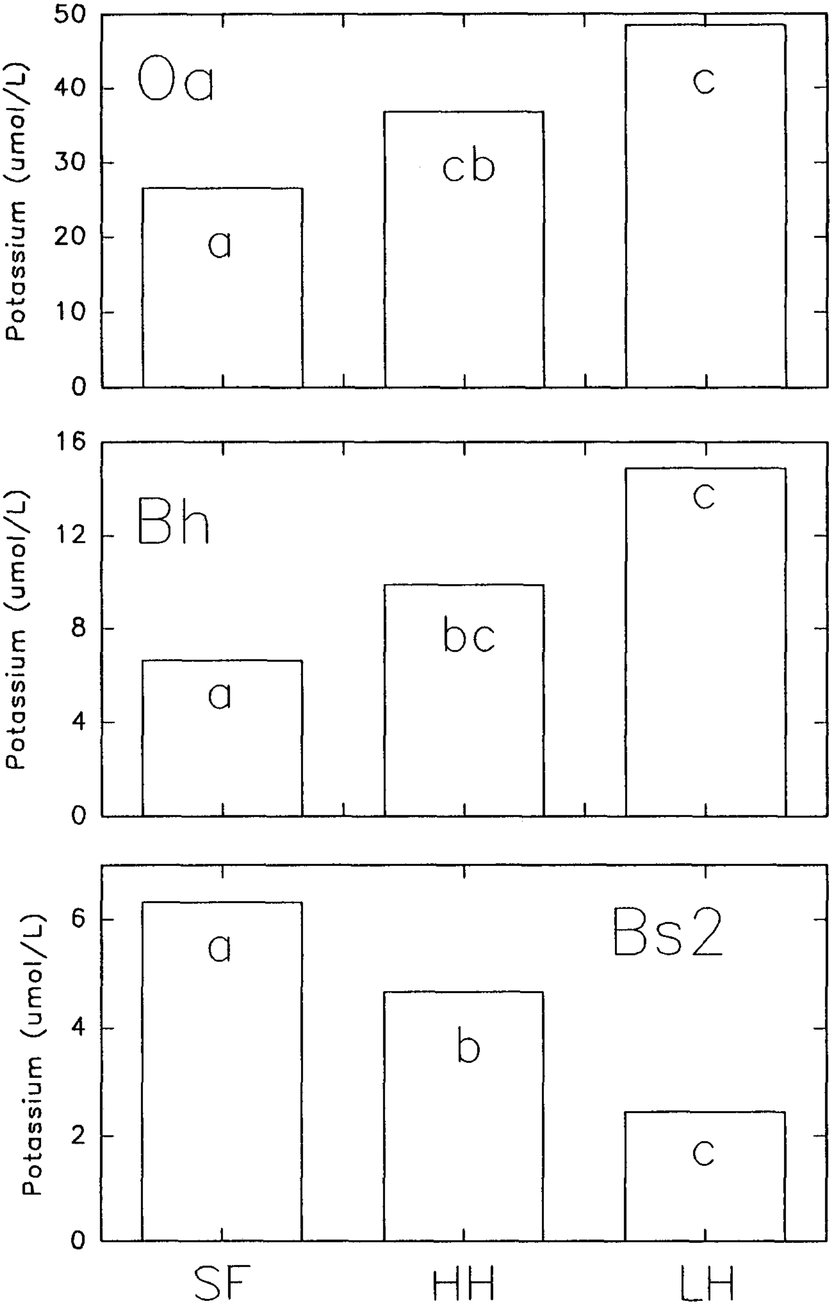


Fig. 12. Mean values of soil water concentrations of K by horizon and elevational zone (see Fig. 2) for W6 of the HBEF. SF indicates spruce-fir zone, HH indicates high elevation hardwood zone and LH indicates low elevation hardwood zone. Differences in letters indicate that solution concentrations are different at $p = < 0.05$.

low elevation hardwood site (LH) had very high K concentrations in Oa horizon solutions (mean concentration 48 µmol/l), which decreased markedly with depth in the mineral soil (15 µmol/l in Bh horizon and 2.4 µmol/l in the Bs2 horizon). The elevational patterns of K in forest floor leachate are quantitatively consistent with higher inputs of K to the forest floor via throughfall and litter (see above). An explanation for lower concentrations of K in solutions within the lower mineral soil horizons of the hardwood zone as compared to the coniferous zone is more problematic. Elevational variations seem to be consistent with differences in exchangeable K concentrations, which appear to be due to variations in concentrations of soil organic matter. Mineral soil in the coniferous zone is characterized by higher concentrations (but lower pools) of K associated with the soil exchange complex (Fig. 11). In contrast, within the lower-elevation hardwood zone, concentrations of exchangeable K are lower. Elevational patterns in soilwater K in the mineral soil also may be influenced by variations in HIV, which may limit the fixation by clays.

Seasonal variations in concentrations of soil water K might be anticipated at the HBEF, with lower concentrations during the summer season resulting from vegetation accumulation. However, no discernable seasonal pattern in soil water K was evident at any of the elevational sites or horizons monitored. Moreover, by SKT time series analysis, no long-term trends were evident in soil water K concentrations at any of the sites or horizons monitored.

Losses of potassium from the watershed-ecosystem

Dissolved losses in stream water – concentrations, trends and patterns

Losses of K in stream water are significant from forested watershed-ecosystems at Hubbard Brook during an annual cycle (e.g. Likens et al. 1977, 1985). The long-term, volume-weighted mean concentration in stream water is 5.61 µmol K/l (219 µg/l), and represents 4.7 and 9.1% of the sum of C_B or 3.8 and 8.9% of the sum of total cations at Hubbard Brook during 1963–1992 (percentages on a mass and equivalent basis, respectively). Annual, volume-weighted mean concentrations in stream water have ranged from a low of 3.66 µmol K/l (143 µg/l) in 1990–91 to a high of 7.52 µmol K/l (294 µg/l) in 1979–80 (Fig. 3A). Average monthly concentrations are correlated with the growing season, with lowest concentrations of K occurring after bud break (about 15 May) and before leaf fall (about 15 September). Thus, streamwater concentrations peak in October and are highest from October through May (Fig. 4A). There is no statistically significant correlation between average monthly concentrations in bulk deposition and stream water in these long-term data.

Elevational patterns of K concentration are evident in stream water draining W6 (Fig. 13). Stream K concentration was highest at a stream sampling site within a coniferous stand at the highest elevation within W6 (mean concentration 11.5 µmol/l), then decreased markedly as water drains from the conif-

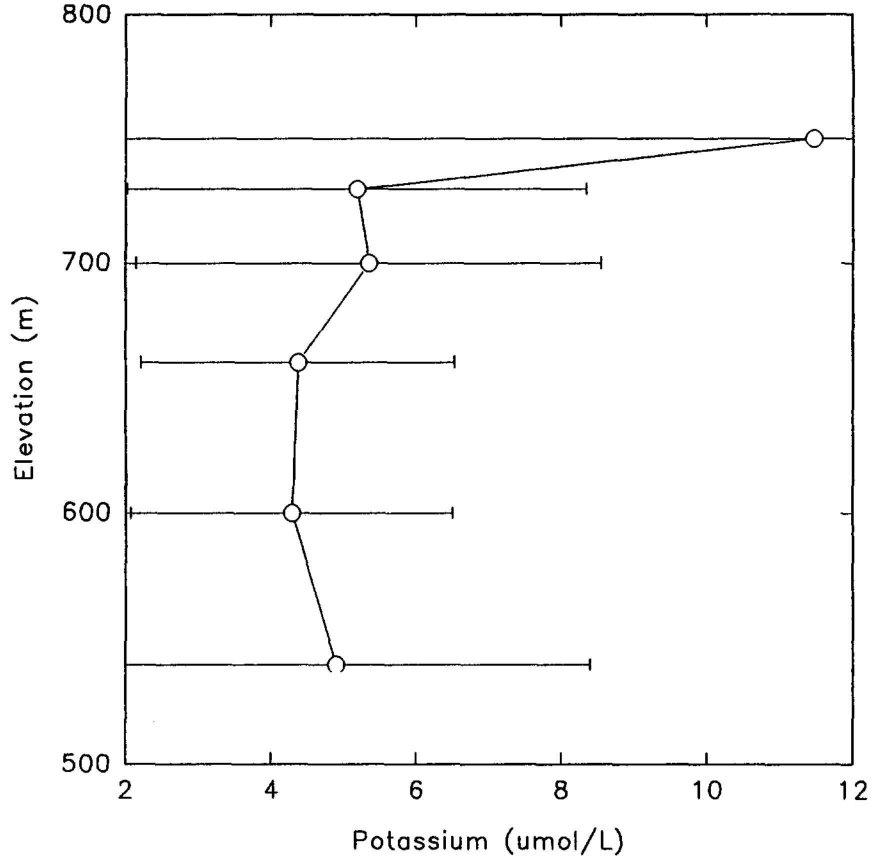


Fig. 13. Average elevational patterns in the concentration of K in streamwater in W6 at the HBEF, obtained from monthly samples collected since 1982. Error bars represent ± one standard deviation.

erous zone to the hardwood zone below (Fig. 13). Mean concentrations of K were remarkably uniform between the sampling sites within the hardwood zone, from 4.3 to 5.4 μmol/l. Elevational patterns in stream K concentration are qualitatively consistent with other observations: (1) higher concentrations of K in mineral soil water at high elevations, and (2) high concentrations of K on the soil exchange complex at high elevations. This pattern appears to be the result of elevational differences in concentrations of soil organic matter associated with cation exchange sites and exchangeable K.

Seasonal patterns of K concentration in stream water also were evident along the elevational gradient (Fig. 14). At the highest elevation sites, concentrations of K were generally high throughout the year, with the exception of September, which was characterized by low concentrations. It is difficult to assess seasonal patterns in stream chemistry at high-elevation sites, however, because flow often is ephemeral during the summer months. At

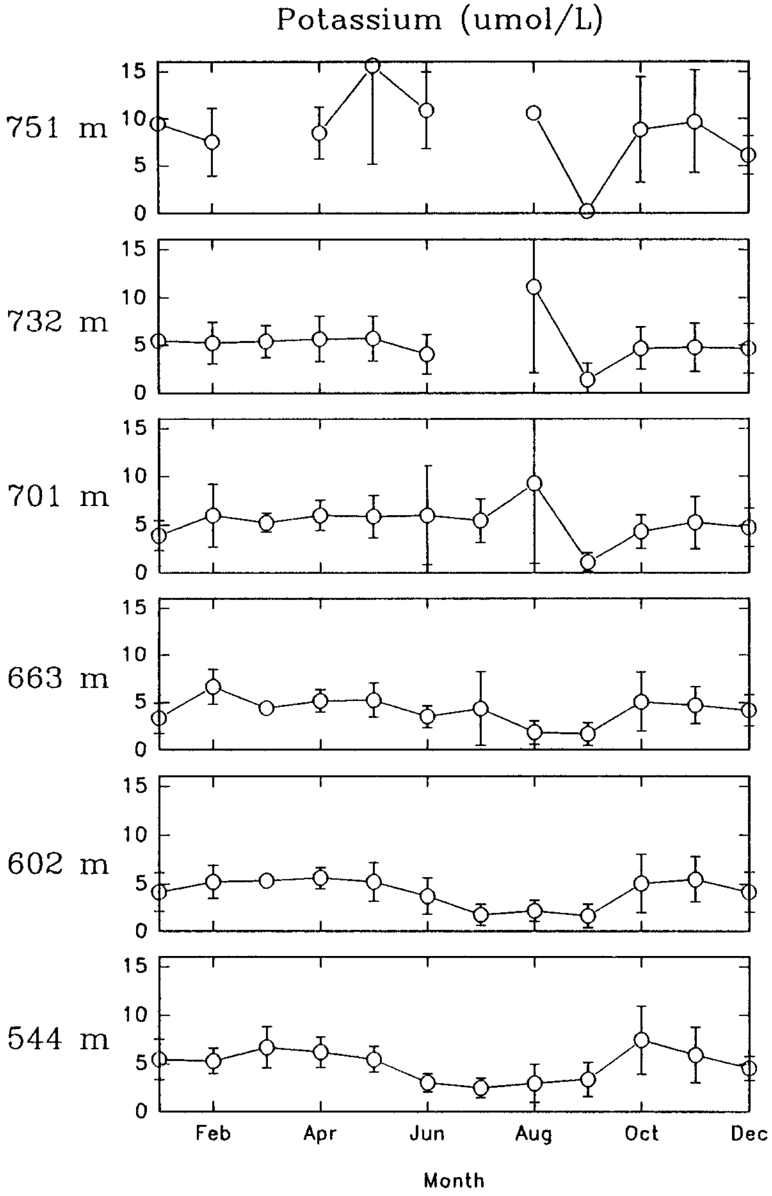


Fig. 14. Mean monthly concentrations of K (μmol/l) in streamwater at sites along an elevational gradient within W6 of the HBEF. Error bars represent ± one standard deviation. Because of small sample number, no standard deviations are given for August and September at 751 m elevation.

lower elevations, the seasonal pattern is clearer, with decreases in stream K occurring during the summer months. The extent of the summer decline in K was more pronounced at lower elevation sites (Fig. 14). This summer decrease in K concentration was first evident at 663 m in elevation and occurred only briefly during August and September. At the gauging station (544 m), stream K concentrations were lowest during June through September (Fig. 4A).

The net fluxes in drainage waters can be viewed as resulting from the balance of processes of supply occurring in the soil, and processes of storage occurring in the plant compartment. Therefore, on a monthly scale, streamwater fluxes vary based on the timing of plant activities, hydrological flowpaths and weather. Plant uptake and transpiration are low in the winter and early spring. In spring, temperatures and leaching rates increase during the melting of the snowpack and while plants are largely dormant. By late April, spring ephemeral plants begin to sequester K (Muller 1978). In May, when all of the vegetation becomes active, two important biotic effects occur: (1) plant uptake of K becomes significant, and (2) possibly more importantly, the initiation of transpiration by vegetation reduces the amount of soil water. In the fall, plant uptake and transpiration decrease and leaves are shed by deciduous vegetation. At that time, K and other constituents are leached from leaves at a high rate (Eaton et al. 1973; Gosz et al. 1973, 1975; Ryan 1979). Finally, with soil cooling in late fall and early winter, and with much of the water input accumulating in the snow pack instead of leaching through the forest floor and soil, biotic effects (uptake and transpiration) become minimal. Because so many processes interact to control K loss rates, it is not surprising that there is no correlation between bulk deposition concentrations and dissolved K in streamflow during the year (Fig. 3).

Thus, we attribute the longitudinal and seasonal variations in stream K concentrations to biotic effects and to changes in hydrologic flowpaths. At the highest elevation stream sites the high concentrations of K throughout the year (Fig. 13) are consistent with higher soilwater concentrations in the deeper mineral soil of this area (Fig. 12). At the lower elevation sites, deposits of glacial till are thicker and promote deeper hydrologic flowpaths. During the low-flow summer period, water entering the soil generally percolates to the C horizon prior to emergence in the stream channel (e.g. Chen et al. 1984). Potassium concentrations during summer at lower elevations in W6 (Fig. 14) are similar to those observed in waters draining the lower mineral soil at the lower elevation sites (Fig. 12), reflecting the deeper flowpaths of drainage water. During the fall through spring, more water enters the soil because transpiration losses are low. During high inputs of water, the ability of deeper deposits of glacial till to transmit water may be exceeded, resulting in the upward migration of the water table (R. Long, unpublished data). When the water table intersects upper horizons with high hydraulic conductivity, water readily migrates along shallower flowpaths to the stream channel. Potassium concentrations in soil waters are high at shallow depths and decrease with increasing depth in the mineral soil (Fig. 12). As a result, stream K concentrations increase as incoming ground water increasingly migrates along shallow flowpaths and decreases when water predominately moves along deep flowpaths.

Of course, temporal dynamics in K flux to streamwater source areas probably also occur on shorter time scales relating to storm events, and especially with long inter-storm periods. At longer time scales, corresponding to vegetation succession, temporal dynamics may take a different form than shown for W6 in Fig. 4. Where net ecosystem production (NEP) is sufficiently high atmospheric inputs exceed streamwater outputs of K during the growing season (Fig. 4B). In cases where NEP is virtually zero, and especially when forest floor decomposition processes are accelerated by microclimatic influences of direct sunlight, summer streamwater K outflows can exceed atmospheric inputs (e.g. Likens et al. 1970).

Based on linear regression analysis, no significant long-term trends in annual concentration of K in stream water have been observed (Fig. 3A), although numerous short-term patterns are apparent. However, time series analysis by SKT showed a long-term decline in annual stream concentration of K (median slope of –0.038 µmol K/l-yr with a 95% CI of –0.05 to –0.02, $p < 0.05$). Because concentration of K is not inversely related to streamflow, gross annual outputs in stream water were significantly related to amount of annual streamflow during 1963–1992 (Fig. 15). Neither linear regression (Fig. 3B) nor SKT showed a significant long-term trend in streamwater output of K at Hubbard Brook.

Particulate losses in stream water

The amount of particulate matter transported from hillslopes at Hubbard Brook is highly dependent upon stormflow events (e.g. Bormann & Likens 1979; Bormann et al. 1969, 1974; Likens et al. 1977). For example, at HBEF 86% of the particulate matter was exported from a forested watershed-ecosystem in 1.6% of the total time during a 4-yr period, and with only 23% of the total streamwater export. Large storms are particularly effective at eroding and transporting disproportionately large amounts of particulate matter. During 1965–66 through 1969–70 particulate losses of K in stream water from W6 amounted to 13.3 mol K/ha-yr (Bormann et al. 1974). Some 98% of this loss was as inorganic particulate matter. In comparison, net loss of dissolved K (streamwater loss – bulk deposition input) during this period was 38.4 mol K/ha-yr.

Particulate matter transported from watershed-ecosystems at Hubbard Brook were partitioned into three categories: suspended and bed load materials collected in the ponding basin at the mouth of the gauged watershed-ecosystem, suspended material collected in a 1-mm mesh net from water passing through the gauging weir, and suspended material collected on a 0.45-µm pore filter from samples collected behind the net at the weir (Bormann et al. 1969). During an 8-yr period, material collected in the ponding-basin fraction represented more than 77% of the total particulate matter trans-

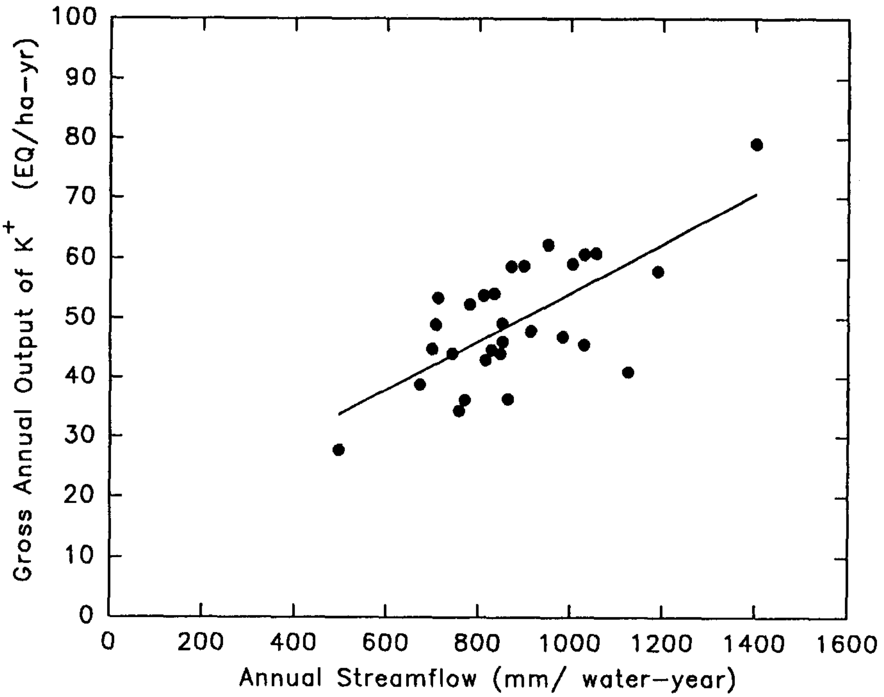


Fig. 15. Relationship between the gross, annual output of K in stream water and the amount of stream water for W6 of the HBEF during 1963–1992. The probability for a larger F-ratio for the regression line is < 0.001, and the r^2 is 0.47.

ported (Likens et al. 1977). We expect that the K transported out of the watershed-ecosystem in particulate matter during 1963–1992 to be in a similar proportion.

Biotic flux

Burton & Likens (1975) reported that the standing crop of K in mammals was 0.23 mol/ha (8.9 g/ha), salamanders 0.8 mol/ha (3.1 g/ha) and birds 0.5 mol/ha (1.8 g/ha) at Hubbard Brook during the early 1970s. Sturges et al. (1974) estimated that the maximum net loss from watershed-ecosystems via birds during 1969 and 1970 was 0.2 mol/ha-yr (0.8 g K/ha-yr) as compared to 15.4 mol/ha-yr (600 g/ha-yr) and 12.8 mol/ha-yr (500 g/ha-yr) net export of dissolved and particulate K in streamwater during this rather average hydrologic period (Fig. 3C). The bird population during this period was relatively large (e.g. Likens 1992).

Thus, the transport of K across watershed-ecosystem boundaries at Hubbard Brook by animals (e.g. birds and mammals) is negligible (e.g. Sturges et al. 1974), primarily because large mammal populations are very small (e.g. Siegler 1968; Pletscher 1982, 1987). This flux could be altered in the future as moose populations currently are increasing at the HBEF.

General discussion/budgetary considerations

Element flux and cycling within forested watershed-ecosystems have been a central theme of the HBES since its inception in 1963. Long-term biogeochemical records have been invaluable to our research because they provide: (1) important insight into ecosystem function (e.g. Bormann & Likens 1970; Likens 1992; Likens et al. 1977); (2) an empirical data base for the testing of models and the generation of hypotheses about the function and temporal development of northern hardwood forest ecosystems (e.g. Bormann & Likens 1979; Fuller et al. 1986; Johnson et al. 1969); (3) an opportunity to assess the effects of disturbance (e.g. Bormann & Likens 1985; Reiners 1992; Smith & Siccama 1981); (4) a baseline to evaluate experimental manipulations of whole ecosystems (e.g. Lawrence et al. 1987; Likens et al. 1970); (5) a record of extreme or unusual events (e.g. Likens et al. 1990); and (6) important ecological information relevant to environmental issues of regional, national and global significance (e.g. Likens 1992; Likens & Bormann 1974; Likens et al. 1972).

The utility of the watershed-ecosystem approach for constructing quantitative, mass-balance analyses for chemical elements has been described elsewhere (e.g. Bormann & Likens 1967, 1979; Likens 1992; Likens et al. 1977, 1985; Schindler 1980). The relatively water-tight nature of the watershed-ecosystems (Likens et al. 1977) make these attempts particularly meaningful at Hubbard Brook.

Streamwater outputs of K exceed atmospheric inputs during each of the nongrowing months of the year (Fig. 4B). During the months of June, July, August and September, biotic and abiotic storage apparently exceeds the inputs in atmospheric deposition plus internal release from weathering and cation exchange. During the course of an annual cycle, however, streamwater outputs normally exceed atmospheric inputs by a large margin (Fig. 4B; Table 2). An exception occurred during the drought years of 1963–65 when atmospheric inputs were relatively large; also, streamwater losses during 1964–65 were the smallest for the entire period (Fig. 4B). Annual atmospheric inputs and streamwater outputs for several of the watersheds-ecosystems are given in Tables 2, 9 and 10.

A plot of the annual net watershed flux (bulk deposition input-streamwater output) revealed that although annual net losses varied from a net gain of about +15 to a net loss of about –60 mol/ha-yr during 1963–64 through 1991–92, there was no single overall trend during this period (Fig. 16). Following the drought years of 1963–65 when inputs exceeded outputs, a striking change occurred where net outputs increased markedly until 1968–69 (r^2, 0.94, line A) and generally until 1973–74 (r^2, 0.66, line B). Net outputs of K tended to decline after 1974 (r^2, 0.10, line C) (Fig. 16). It is counterintuitive, therefore interesting, to note that some of the largest net streamwater losses of K (Fig. 16) occurred during the period (1967–76) of maximum biomass storage of K (Tables 1 and 7). This also, however, was the period of

Table 9. Annual bulk deposition input to forested and disturbed (W2, W4, W5) watersheds of the Hubbard Brook Experimental Forest. Values in grams of K per hectare (1 g K/ha = 0.026 mol K/ha).

Water-Year	W1	W2	W3	W4	W5	W6	Mean	$\pm s_{\bar{x}}$
1963–64	2281	2278	2232	2308	2316	2331	2291	14
1964–65	1334	1332	1310	1352	1364	1379	1345	10
1965–66	547	545	548	554	565	583	557	6.0
1966–67	565	565	543	581	584	601	573	8.2
1967–68	924	925	937	937	980	1025	955	16
1968–69	616	612	626	636	644	660	632	7.4
1969–70	742	740	752	754	767	783	756	6.6
1970–71	1119	1115	1109	1146	1163	1186	1140	13
1971–72	327	326	327	327	329	336	329	1.5
1972–73	529	529	530	526	538	558	535	4.9
1973–74	813	809	802	820	822	831	816	4.2
1974–75	802	804	815	812	833	867	822	10
1975–76	435	433	434	435	436	458	439	3.9
1976–77	397	397	395	395	396	413	399	2.9
1977–78	634	632	635	635	635	653	637	3.2
1978–79	586	585	588	605	609	623	599	6.3
1979–80	855	851	853	874	877	913	870	9.6
1980–81	748	746	750	777	784	812	769	11
1981–82	555	553	561	579	580	585	569	5.8
1982–83	640	635	643	667	669	679	655	7.5
1983–84	688	686	684	710	712	723	701	6.8
1984–85	529	526	530	562	567	582	549	9.8
1985–86	338	337	333	355	356	360	346	4.8
1986–87	290	290	290	305	306	309	298	3.8
1987–88	679	677	686	722	728	739	705	11
1988–89	430	431	432	452	458	469	445	6.8
1989–90	850	845	847	875	879	900	866	9.1
1990–91	793	792	787	813	813	812	802	5.0
1991–92	553	552	557	579	580	581	567	5.9
Total (g/ha)	20,599	20,548	20,536	21,093	21,290	21,751	20,967[a]	
Annual mean (g/ha-yr)	710	709	708	727	734	750	723	
$s_{\bar{x}}$	70.6	70.5	69.0	71.3	71.8	72.3	70.9	

[a] Mean for all watersheds

highest rates of net soil release (Table 5). Of course, these values are highly autocorrelated in this budgetary analysis. The smallest net loss of K also occurred during this period (1970–71, Fig. 16). Overall, annual net loss of K is significantly, but weakly ($r^2 = 0.40$), related to annual amount of streamflow (Fig. 17). Net outputs were largest during the wettest (1972–73, 1973–74 and 1975–76) years (Fig. 3C and Fig. 16).

Table 10. Annual stream output from forested and disturbed (W2, W4, W5) watersheds of the Hubbard Brook Experimental Forest. Values in grams of K per hectare (1 g K/ha = 0.026 mol K/ha).

Water-Year	W1	W2	W3	W4	W5	W6	Mean[b]	$\pm s_{\bar{x}}$
1963–64	1986	1895	1401	1949	1633	1751	1713	170
1964–65	786	904	888	1281	1276	1085	920	88
1965–66	1496	*1551*	1110	1619	1434	1342	1316	112
1966–67	1775	*23,330*	1315	2018	1618	1721	1604	145
1967–68	2310	*36,661*	1676	2566	2289	2433	2140	235
1968–69	2691	*33,348*	1787	2438	1986	2295	2258	262
1969–70	2292	30,793	1715	2400	1954	2292	2100	192
1970–71	1778	15,543	1609	*2316*	1557	1746	1711	52
1971–72	1678	5873	1627	2928	1541	1721	1675	27
1972–73	2351	5130	1758	*4537*	2184	2370	2160	201
1973–74	3229	7061	2380	7933	2965	3091	2900	263
1974–75	2345	3675	1282	*4042*	1694	2104	1910	322
1975–76	2532	5596	1823	7175	2179	2263	2206	207
1976–77	2196	4256	1463	5872	1742	1922	1860	214
1977–78	2290	4714	1494	5847	1763	1834	1873	231
1978–79	2137	3253	1547	4461	1771	1799	1828	171
1979–80	2264	4182	1616	5287	1940	2088	1989	193
1980–81	2176	3676	1535	5094	1858	2045	1919	196
1981–82	1968	4496	1448	5901	1690	1782	1733	152
1982–83	1571	3044	1125	4038	1407	1679	1458	170
1983–84	1890	3596	1443	4920	*4167*	2307	1880	249
1984–85	1325	1970	1052	2842	9603	1516	1298	135
1985–86	1736	2432	1236	4181	9491	1867	1613	192
1986–87	1045	2221	1178	3288	5117	2115	1446	337
1987–88	1277	2356	1074	3504	3386	1412	1254	98
1988–89	1381	2118	1097	3158	3483	1910	1463	238
1989–90	1874	3752	1550	5649	4549	2376	1933	240
1990–91	1388	3269	1468	4834	4026	1602	1486	62
1991–92	1134	1822	1019	3146	3060	1421	1191	120
Total (g/ha)	54,901	222,517	41,715	115,224	83,363	55,889	50,837[b]	
Annual mean (g/ha-yr)	1893	7673	1438	3973	2875	1927	1753[b]	—
$s_{\bar{x}}$	101	1864	58.3	313	393	76.5	74.0[b]	—

[a] Values during periods when experimental treatments were occurring are underlined and shown in italics.

[b] Mean for W1, W3 and W6 only.

The uncertainty in the annual dry deposition estimate has a relatively small effect on these budget calculations. For example, during 1974–76 we calculated total deposition of K in two ways: (1) measured bulk deposition, and (2) estimated wet deposition (37% of bulk deposition, Table 3), plus an estimate of particle dry deposition (Table 4). The budgetary calculations in Fig. 16 are based on the bulk deposition estimates. Using the other estimate

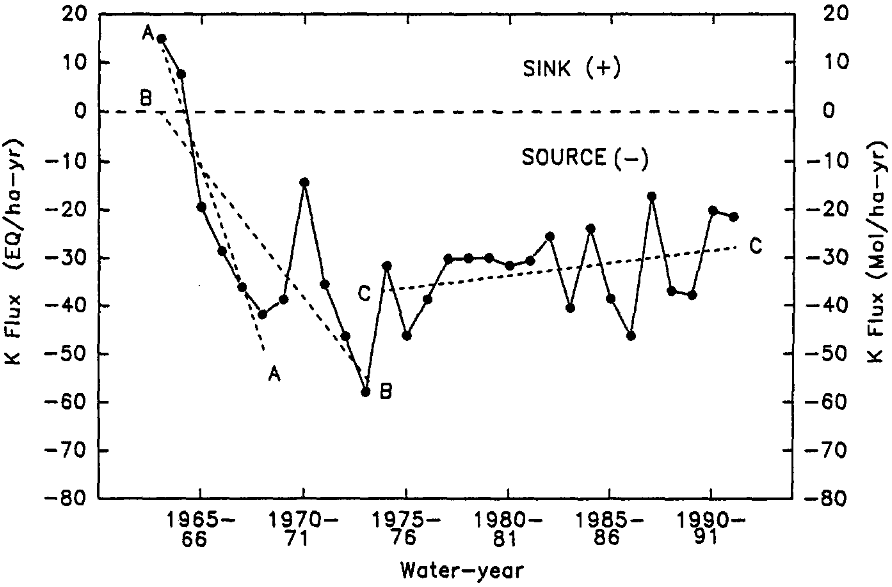


Fig. 16. Annual net flux (bulk precipitation input – streamwater output) for W6 of the HBEF during 1963–1992. A positive K flux indicates that the watershed-ecosystem was a net sink for K, whereas a negative flux indicates a net source relative to biospheric relations.

would reduce the average annual net budget by 6.7 mol/ha or 17% during the period 1974–76.

Potassium is a dominant and ecologically important cation in the forest ecosystem of the HBEF. The 1964–69 pentad was characterized by moderate to high rates of biomass accretion and net soil release of K. In contrast, the 1987–92 pentad with decreasing rates of living biomass accretion had low rates of biomass storage and net soil release of K. The rate of annual K storage in biomass declined from 148 mol/ha-yr during 1964–69 to 33 mol/ha-yr during 1987–92 (Figs. 18 and 19). During the latter pentad, vegetation resorption of K was 3.9 times greater and throughfall and stemflow were 2.6 times less than during the 1964–69 pentad (Figs. 18 and 19). These differences may reflect nutrient conservation responses of the biota during the latter pentad when overall nutrient availability may have been less. Different methodologies for throughfall and root litter make comparisons between the two pentads more difficult.

The K budget shows that the biomass and soil pools are large relative to atmospheric inputs and streamwater losses (Figs. 18 and 19). Atmospheric deposition of K in bulk precipitation to W6 averaged 22 mol/ha-yr during 1964–69 and has decreased slightly to 18 mol/ha-yr recently (1987–92). These inputs represent about 15% and 54% respectively, of the annual net uptake (storage) by above- and belowground vegetation in W6 during these periods.

Recent observations (Fig. 19) show that K fluxes increase as soil water

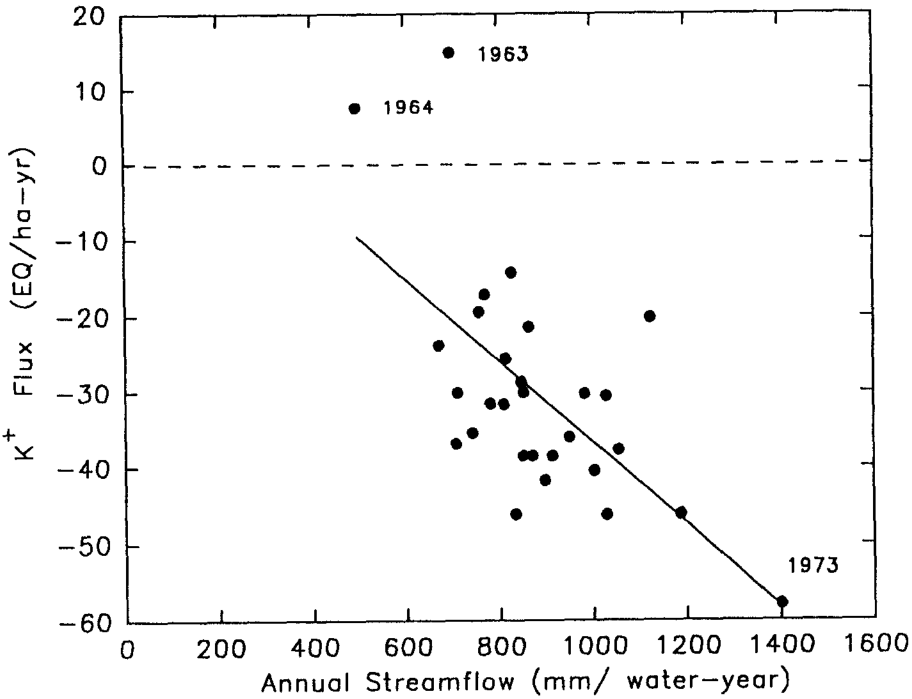


Fig. 17. Relationship between the net annual loss of potassium and amount of streamflow for W6 of the HBEF during 1963–1992. 1963–64 and 1964–65 were drought years and 1973–74 was a very wet year. The probability for a larger F-ratio for the regression line is < 0.001 and the r^2 value is 0.40.

passes through the O horizon of the soil (429 mol/ha-yr), then diminishes during transport through the uppermost mineral soil (Bh horizon: 114 mol/ha-yr), lower mineral soil (Bs2 horizon: 37 mol/ha-yr) and to the stream. The flux of K from the Bs2 horizon (37 mol/ha-yr) is similar to the flux in stream water (45 mol/ha-yr) suggesting that little K is supplied to drainage water from weathering and cation exchange from within the glacial till. By SKT analysis, there was no significant temporal change in soil water (Oa, Bh and Bs2 horizons) concentrations of K during 1984 to 1992.

The average annual dissolved loss of K in stream water was the same (45 mol/ha-yr) in 1964–69 and in 1987–92 (Figs. 18 and 19). Because of the decrease in annual net uptake by the biota in recent years, annual streamwater output represented some 30% of net uptake in 1964–69, but increased to 136% in 1987–92.

While rock and biomass pools of K are large, pools of K associated with the exchange complex in the mineral soil are relatively small. The rate of supply of K and other base cations to stream water is low at the HBEF because of the small pools of exchangeable base cations and the low abundance of K-bearing minerals and/or their low weathering rates. Although K is highly

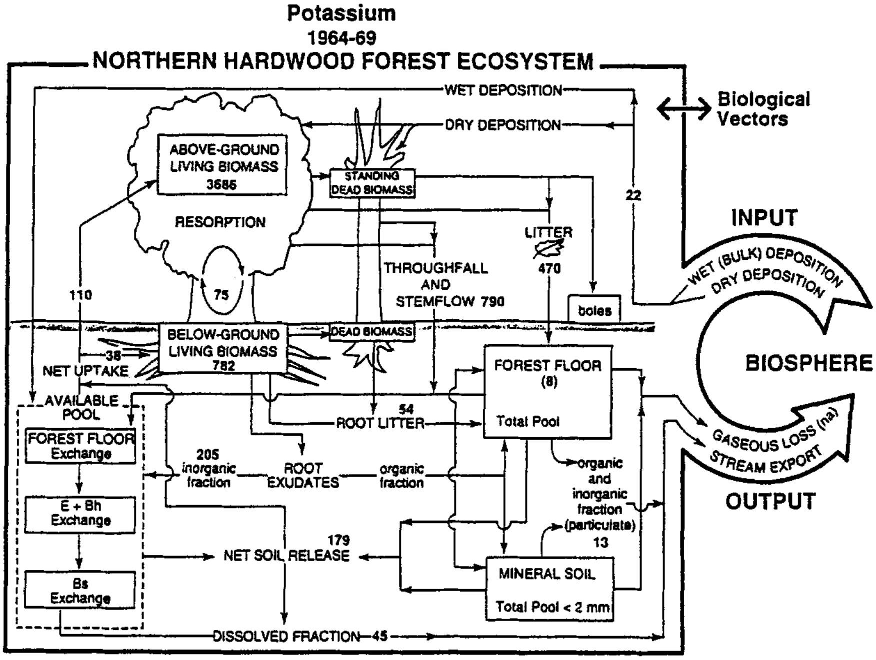


Fig. 18. Ecosystem pools (boxes) and fluxes (arrows) of K during 1964–69 for W6 of the HBEF. Values in mol/ha or mol/ha-yr (values are modified from Likens et al. 1977).

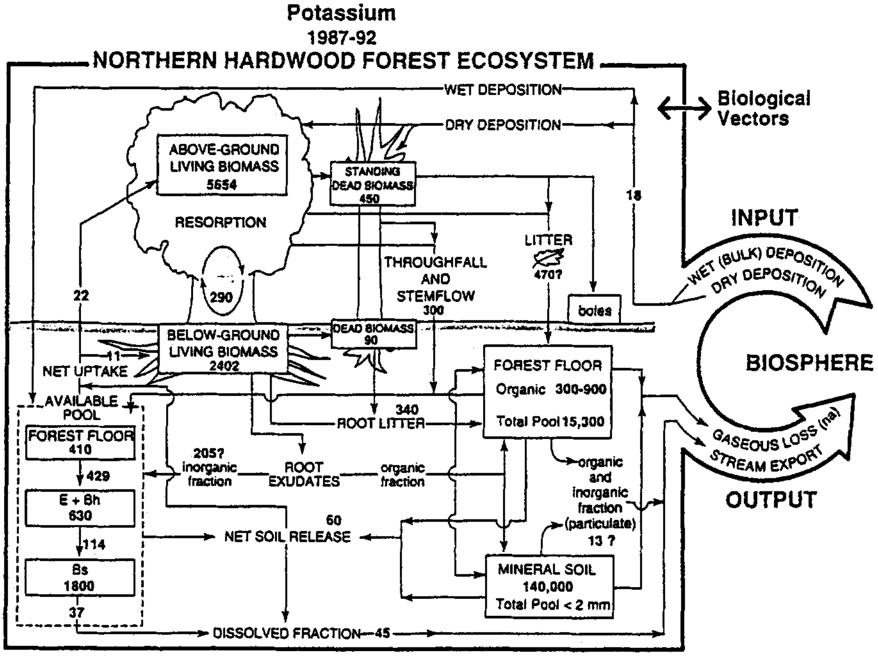


Fig. 19. Ecosystem pools (boxes) and fluxes (arrows) of K during 1987–92 for W6 of the HBEF. Values in mol/ha or mol/ha-yr.

mobile, the average annual amount of dissolved K lost in stream water in 1964–69 was only about 6% of the stemflow plus throughfall flux, or 10% of the annual flux in litter (Fig. 18). These values increase to 15% of stemflow and throughfall and 10% of litter in 1987–92 (Fig. 19). Thus, overall K is held tightly within the ecosystem against losses in stream water.

The residence time for K in the forest floor and mineral soil can be estimated as:

$$T_n = \text{Pool}/\Delta K \tag{3}$$

where T_n is the residence time for K, and ΔK is either the input or the output of K. Currently, inputs are thought to approximate outputs for the forest floor and mineral soil, but measured or estimated inputs (Fig. 19) to the mineral soil pool are not strictly inputs to the pool of K found in minerals. Gosz et al. (1976) estimated the residence time for K in the forest floor to be 0.7 years, using:

$$\Delta K = \text{litter} + \text{stemflow} + \text{throughfall} \tag{4}$$

This value was the lowest residence time among the elements reported by Gosz et al. (1976). Because of different sampling methods this value is not comparable to current values.

In any event exchangeable (or labile) K is rapidly cycled within the forest floor, and the mineral soil residence times are 0.4 and 3.4 yr, respectively (Table 11). Based on an estimate of the total amount of K in forest floor and mineral soil (Johnson 1989), the estimated residence times for K are about 15 and 190 yr, respectively. These calculations assume that the pool of interest is at steady state, which probably is not the case. Nevertheless, the residence-time calculations provide some insight about the relative dynamics of the system.

Response of the K cycle to disturbance

The northern hardwood forest may experience many different types of disturbance, including natural disturbances such as climatic changes, weather events, insect outbreaks, and anthropogenic disturbances like inputs of strong acids from the atmosphere, changes in land-use and forest cutting (e.g. Bormann & Likens 1979; Aber et al. 1978; Johnson & Todd 1987; Mann et al. 1988; Hendrickson et al. 1989). One of the most important of these disturbances is forest harvest, such as by clear cutting. Different forest cutting practices have been evaluated through whole-watershed experiments at Hubbard Brook (e.g. Bormann & Likens 1979; Likens et al. 1970; Martin & Hornbeck 1989).

Watershed 2 (W2) was experimentally deforested in the winter of 1965–66 without removal of forest products, and regrowth was inhibited with herbi-

Table 11. Estimates of residence times (T_n) of potassium in the forest floor and mineral soil of the Hubbard Brook Experimental Forest during 1987–92.

	Pool size (mol/ha)	Input (mol/ha-yr)					Total input (mol/ha-yr)	T_n (yr)
		aboveground litter	stemflow and throughfall	root litter	root exudates	Oa horizon leachate		
Forest floor								
Exchangeable	410	470	300	156[a]	94[a]	—	1020	0.40
Total	15,300	470	300	156[a]	94[a]	—	1020	15
Mineral soil								
Exchangeable	2,430	—	—	184[b]	111[b]	430	725	3.4
Total	140,000	—	—	184[b]	111[b]	430	725	190

[a] assumes root litter and root exudates are proportional to distribution of root biomass (Fahey et al. 1988; 46% of total)

[b] assumes root litter and root exudates are proportional to distribution of root biomass (Fahey et al. 1988; 54% of total)

cide until the summer of 1969 (Bormann & Likens 1979). This experiment was not designed to simulate a commercial clear cut, but rather to assess the role of vegetation in the biogeochemistry of forest ecosystems. Very large losses of NO_3^-, H^+ and Al^{n+} occurred in drainage water from W2 during the three years after cutting when regrowth was suppressed (1966–69), primarily as a result of increased decomposition and nitrification (e.g. Bormann & Likens 1979; Bormann et al. 1968; Likens et al. 1969, 1970, 1978). Clearly, the deforestation treatment and subsequent vegetation regrowth had enormous impacts on K behavior. Concentrations of K increased about 15-fold in stream water during the devegetated period (Fig. 20) and stream outputs of dissolved material alone increased nearly as much (Fig. 21). Particulate losses of K, both organic and inorganic, for the water-years 1966–1970 were 16 mol/ha-yr (0.62 kg/ha-yr) for W6, the reference watershed, versus 109 mol/ha-yr (4.24 kg/ha-yr) for W2, a 6.8-fold difference (Bormann et al. 1974). Dissolved losses over the same period were 38 mol/ha-yr (1.5 kg/ha-yr) for W6 versus 774

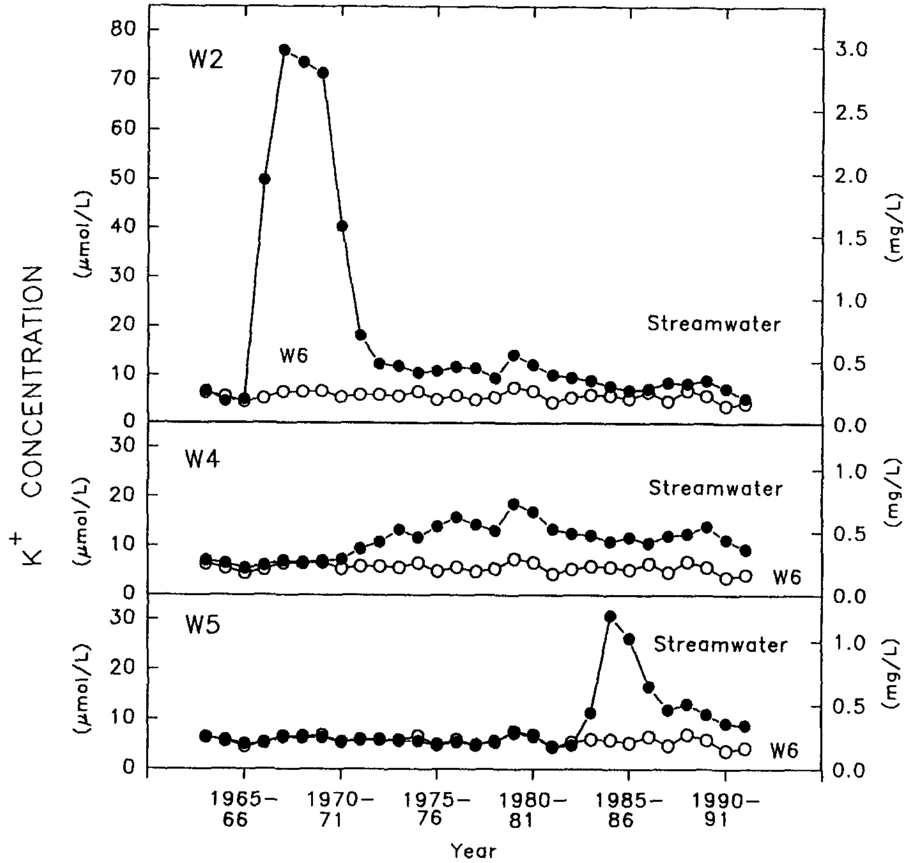


Fig. 20. Concentration of K with time for stream water in W2, W4 and W5 (–○–), and W6 (–●–) of the HBEF (see text for details of treatment).

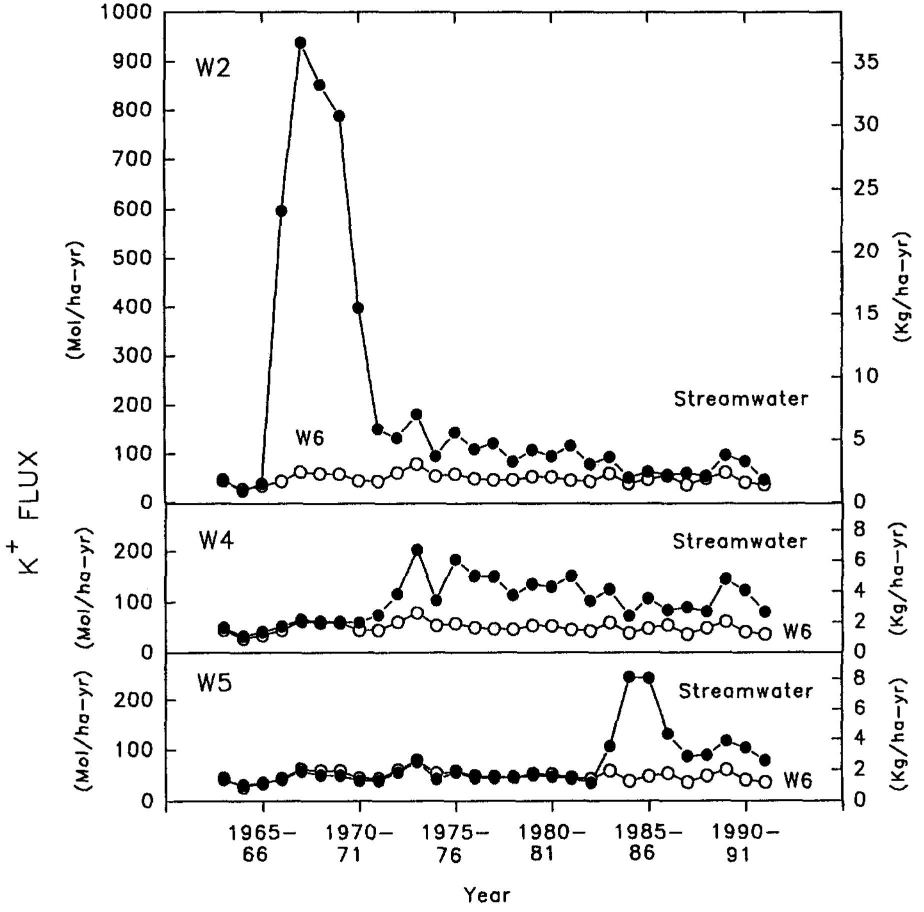


Fig. 21. Flux of K in stream water from W2, W4 and W5 (-○-), and W6 (-●-) of the HBEF with time (see text for details of treatments).

mol/ha-yr (30.2 kg/ha-yr) for W2, a 20-fold difference (Bormann et al. 1974). Clearly, the dissolved fraction was quantitatively larger than and more responsive than the particulate fraction to the loss of vegetation cover and the breakdown of retention properties of the soils and stream ecosystem (Bormann & Likens 1979; Bormann et al. 1974; Likens et al. 1978).

Even before vegetation regrowth began in summer 1969, there was a tendency for dissolved stream outputs of K to decrease. Normal inter-year variation clouds any clear conclusions as to the cause, although apparently nitrification, which provided the mobile anion, NO_3^-, for the streamwater loss of cations from W2 (Likens et al. 1970) was declining (Bormann & Likens 1979). After cessation of the herbicide treatment, uptake by regrowing vegetation caused further declines in stream K concentrations. By 1970–71 a downward trend in K loss was apparent (Fig. 21), and by 1972–73, stream K export was much lower, although still higher than for W6.

Other clearcutting experiments have been done at the HBEF. These include a strip-cut of W4, a block clear-cut of W101 (an ungauged watershed) and a whole-tree harvest of W5 (Johnson et al. 1990; Lawrence et al. 1987; Likens & Bormann 1974; Martin & Hornbeck 1989). The strip-cut experiment involved cutting W4 in 25-m wide strips, which paralleled the watershed contour. The first third was cut in 1970, the second in 1972 and the final third in 1974. A buffer area of trees was left uncut adjacent to the stream channel. Watershed 101 was clear-cut as a block in 1970 and timber products were removed. Watershed 5 was logged by a commercial, whole-tree clear-cut in 1983–84.

Stream concentrations of K increased in response to strip-cut and whole tree harvest treatments and declined during regrowth (Fig. 20). In the strip-cut of W4, concentrations of K increased from 1970, peaking in 1979 and declined thereafter. The increases in stream K concentrations were much lower than observed in W2; the maximum annual volume-weighted concentration of K was less than 20 μmol/l.

In the whole-tree harvest of W5, stream concentrations of K peaked two years after the manipulation (annual volume-weighted concentrations in 1984–85 were 30.7 μmol/l). Concentrations of K readily decreased from 3 to 5 years after the clear-cut. However, as observed with the W2 experiment, stream concentrations of K in both W4 and W5 have not declined to reference values by 1992.

There were distinct differences in patterns of K loss immediately after clearcutting in these experiments. The loss of K was very high in the W2 devegetation experiment. This loss was likely due to the release of K from mineralization of organic matter and displacement from the soil exchange complex by high concentrations of H^+ and Al^{n+}, coupled with suppression of vegetation regrowth by herbicide. Hydrogen ion and NO_3^- were generated by increased nitrification, and loss of dissolved K in stream water was correlated strongly with loss of NO_3^- (Likens et al. 1970). The strip-cut exhibited relatively small increases in stream concentrations of K, although this increase occurred over a longer period. The commercial, whole-tree harvest resulted in relatively high concentrations of K in stream water, although not as high as W2.

In an effort to compare and contrast patterns of K response for each of the clear-cutting treatments at Hubbard Brook, mass balances were constructed for the eight years following disturbance (Fig. 22). These mass balances include atmospheric inputs, biomass removal associated with the treatment and stream loss. In this analysis the devegetation and herbicide (W2), block-cut (W101), strip-cut (W4) and whole-tree clear-cut (W5) treatments were compared to the reference watershed (W6). During this eight-year analysis, the whole-tree harvest (W5) showed the greatest loss of K (6640 mol/ha), largely associated with the loss of K with biomass harvested (5540 mol/ha).

The devegetation and herbicide treatment (W2) showed the next greatest loss of K, 3890 mol/ha, occurring entirely as stream outflow (vegetation was left on the watershed after cutting). The two other commercial treatments resulted in loss of K lower than the devegetation and herbicide treatment and the whole-tree harvest. The strip-cut (W4) showed the lowest K loss of the four treatments (2100 mol/ha), largely because less K was removed with biomass (1020 mol/ha). Stream losses of K were similar in the strip-cut and the whole-tree harvest. It appears that the strip-cut procedure did not appreciably reduce stream losses of K as it had for NO_3^- (Likens & Bormann 1974). Greater stream losses of K were evident in the block clear-cut (W101), than the other forest harvest treatments (W4 and W5). This difference may be due to the fact that W101 is situated on a lower slope than W4 or W5 and is characterized by thicker deposits of glacial till, or that a different nitrification response occurred, or both.

To illustrate the probable causes of the contrasting behavior of K among the different clear-cutting treatments, mass balances were calculated for W2 and W5 during two intervals after treatment. The first interval (yr 1–3) corresponded to the herbicide treatment of W2 and the second (yr 4–8) to the period of maximum vegetation accumulation when stream outflow of K declined. The treatment of W2 and W5 differed in two major respects: (1) on

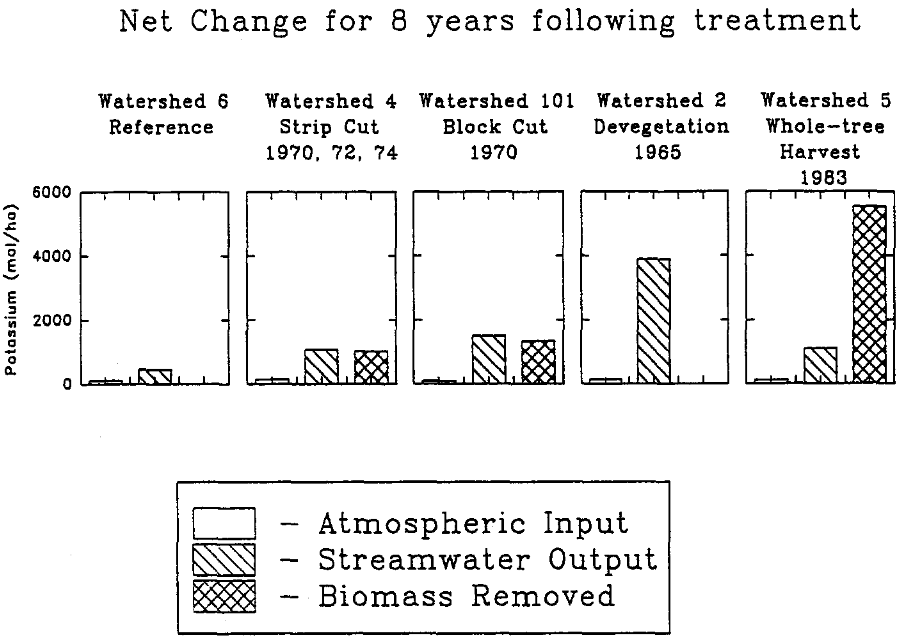


Fig. 22. Mass balance of K during a period of 8 years comparing atmospheric inputs, stream output and biomass removed from harvesting in a strip-cut (W4; 1970–78), a block clear-cut (W101; 1970–78), a whole-tree clear-cut (W5; 1983–91) and an experimental devegetation (W2; 1966–74) with the reference watershed (W6; 1983–91).

W2, aboveground vegetation was cut and left in place, whereas most of the aboveground woody material was removed from W5; and (2) vegetation regrowth was suppressed on W2 for 3 yr, whereas normal revegetation occurred on W5. Together, these differences probably account for most of the contrasting pattern of K loss between W2 and W5 (Fig. 23), and calculations of K fluxes associated with decay of logging slash and accumulation in vegetation were conducted to examine this assertion.

Aboveground plant biomass and nutrient content were estimated for W2 between 1969 and 1988 (Table 12) and for W5 between 1985 and 1990 (T.G. Siccama, unpublished data). Belowground K content for each of these years was estimated by calculating a ratio of belowground K content of plants for each stratum as measured at HBEF by Whittaker et al. (1979). Belowground K content of plants was estimated as fixed ratios of aboveground biomass,

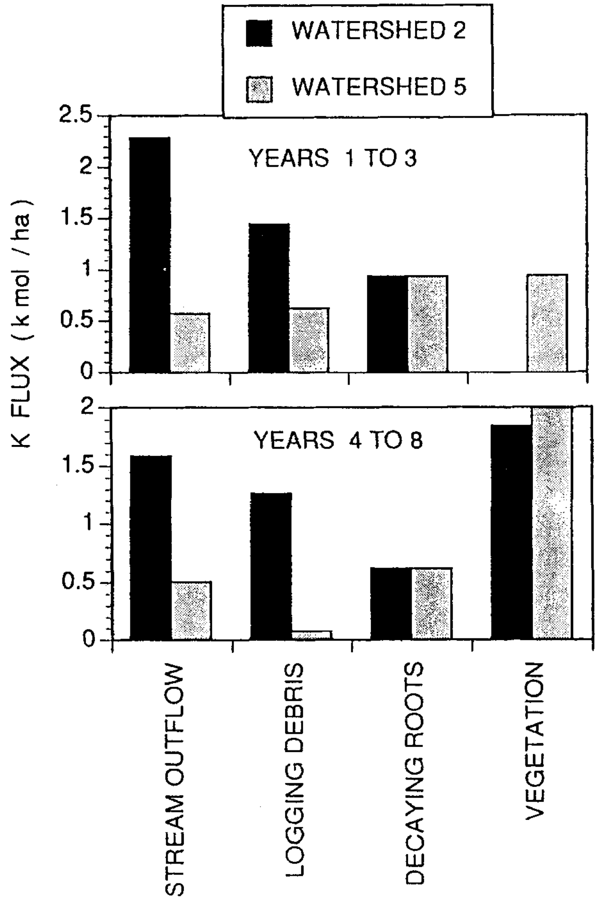


Fig. 23. Comparison of K fluxes, including stream outflow, estimated release from logging debris and decaying roots, and storage in regrowing vegetation in W2 and W5 for the periods 1–3 and 4–8 years after deforestation.

Table 12. Potassium content of vegetation of Watershed 2, Hubbard Brook Experimental Forest, through succession. Aboveground data are means of 70 plots distributed evenly across the watershed. Belowground data are estimated as fixed percentages of aboveground nutrient contents as follows: Trees and sampling belowground = 41%; Aboveground, shrubs = 53%, herbs = 14%. Data are in grams of K per hectare (1 g K/ha = 0.026 mol K/ha).

Stratus	Year 1 (1969)			Year 2 (1970)			Year 3 (1971)			Year 5 (1973)			Year 11 (1979)			Year 20 (1988)		
	above	below	total	above	below	total	above	below	total	above	below	total	above	below	total	above	below	total
Herbs	1,799	252	2,051	3,712	520	4,232	4,919	689	5,608	8,285	1,160	9,445	7,297	1,022	8,319	14,519	2,033	16,552
Shrubs	758	402	1,160	2,188	1,160	3,348	6,330	3,355	9,685	14,884	7,889	22,773	6,946	3,681	10,627	2,314	1,226	3,540
Saplings	0	0	0	1,150	472	1,622	9,286	3,807	13,093	30,531	12,518	43,049	41,305	16,935	58,240	16,783	6,881	23,664
Trees	0	0	0	0	0	0	0	0	0	0	0	0	29,297	12,012	41,309	47,214	19,358	66,572
TOTAL	2,557	654	3,211	7,049	2,151	9,201	20,535	7,851	28,386	53,700	21,566	75,266	84,845	33,650	118,495	80,830	29,498	110,328

independently for trees, shrubs and herbs. For W5, the K content for the eighth year after harvest (1991) was obtained by a linear extrapolation of values for 1988 and 1990.

Potassium release from logging debris on W2 and W5 was estimated by calculating the K content of this debris and applying a K release rate based upon literature observations of wood decay. For W2, the K content of stems and branches was available for the HBEF in 1965 from Whittaker et al. (1979). The biomass of logging slash on W5 was measured directly in random plots distributed across the watershed, and the K content of this material was calculated assuming a K concentration equal to that of branches for the HBEF (Likens & Bormann 1970).

A variety of studies of decay of woody tissues provided guidelines for estimating release of K from logging debris on W2 and W5 (Arthur et al. 1993; Fahey et al. 1988; Gosz et al. 1973; Lambert et al. 1980). Based on these studies, we assumed release of 15% of the K content of bole wood and bark in the first 3 years of decay and an additional 65% release in the next 5 years. For purposes of this calculation, we assumed release of 90% of the K content of branches in the first 3 years and the remaining 10% in the following 5 years.

Detailed studies of the decay of small and large roots following clearcutting at Hubbard Brook (Fahey & Arthur 1994; Fahey et al. 1988) provided information for estimating K release from tree roots for each time interval after treatment. Although some differences between W2 and W5 seem likely, we had no good basis for evaluating these differences, and values for W5, only, are used.

These calculations illustrate that most of the K loss from W2 during the first 3 years after harvest could have been supplied by release from decaying logging debris (Fig. 23). Similarly, on W5 there appears to be a balance between sources of K from slash and root decay and sinks in vegetation accumulation and stream outflow.

There was, however, increased decomposition of the existing forest floor (Bormann & Likens 1979; Dominski 1971; Likens et al. 1970) and possible release of K from the soil exchange complex following deforestation of W2. Because vegetation regrowth was inhibited with herbicides for 3 yr, transpiration and soil shading were minimal. As a result, decay was accelerated during this period in the relatively warm and moist forest floor of W2 (e.g. Bormann & Likens 1979). Thus, it is not clear how the release of K was apportioned between the decay of logging debris, the decay of forest floor materials and the release from the soil exchange complex. It does appear that the large difference in K outflow between W2 and W5 in the first 3 years after disturbance is mostly accounted for by the combined effects of: lack of vegetation uptake, and increased decay of the forest floor and logging debris on W2 (Fig. 23).

During the second interval (yr 4–8 after treatment), the behavior of K became more complex. First, the much larger K loss from W2 than W5 during this interval may be explained almost entirely by the estimated continued release of K from woody debris on W2 because vegetation accumulation of K was remarkably similar in the two watersheds during this interval (Fig. 23). It is clear, however, that during this interval, sources of K within the ecosystem in addition to decaying roots and logging debris would be required in both W2 and W5. Pools of K in the forest floor and mineral soil apparently could provide this source, and the release of K by weathering of primary minerals and cation exchange probably contributed to K leaching and to the maintenance of K availability to plants.

An alternate explanation is that the estimates for release from logging debris (Fig. 23), particularly from large woody debris, during the first three years following deforestation of W2 are too high and that decay of forest floor predominated. Decay of large woody debris, then, may have become larger during the second interval (4 to 8 yr after cutting).

One of the most intriguing features of the long-term assessment of the clearcutting disturbance is that concentrations of K failed to return to reference values for many years after disturbance at Hubbard Brook, and generally tended to return more slowly than other base cations (Nodvin et al. 1988; Fig. 20). For example, the volume-weighted, average annual stream concentration in W2 for 1987–92, some 25 yr after deforestation was 7.6 μmol K/l, resulting in an annual stream loss of 68 mol K/ha-yr. These values are considerably higher than the mean concentration (5.1 umol/l) and loss (45 mol/ha-yr) for W6, the reference watershed, during the same period. Both watersheds had similar values prior to disturbance (Fig. 20). We do not know the mechanism responsible for this extended delay in the recovery of stream outputs of K. Unfortunately, soil and soil solution data are not available for W2. However, Romanowicz (1994) investigated the dynamics of soil K following the whole-tree harvest of W5. Marked losses of K were evident in the Oa horizon leachate during the first 3 years after the treatment (1800 mol/ha-yr), due to mineralization of soil organic matter and leaching from slash. A portion of this input of K was immobilized subsequently on cation exchange sites in the mineral soil during the initial 3-yr period (1200 mol/ha-yr). During the 5 yr that followed, approximately 39% (470 mol/ha-yr) of the K bound to exchange sites was displaced. This mobilization of K from slash and forest floor, and immobilization of K in the mineral soil, increased pools of K on the mineral soil exchange complex. The subsequent displacement of this K from the mineral soil exchanger may be the mechanism responsible for the elevated concentrations of K that occur in stream water for many years following clear-cutting disturbance.

An alternate possibility is that cation exchange sites associated with secondary minerals may have been disrupted by the disturbance. Vermiculite, a prominent clay mineral at Hubbard Brook, is important in the fixation of K in forest soils. Low pH values (pH 4.3 in stream water) that occurred immediately following the clear-cut of W2 may have accelerated the weathering of vermiculite. More likely, high concentrations of Al^{n+} may have displaced interlayer K and hydrolyzed, forming HIV and restricting K fixation by this mineral. Such disturbance might greatly diminish the ability of the mineral soil to buffer the ecosystem against K loss.

Inputs of acidic deposition and leaching of strong acid anions (e.g. SO_4^{2-}, NO_3^-) may result in displacement of exchangeable base cations and declines in the nutrient status of forest ecosystems (Reuss & Johnson 1986). At Hubbard Brook the temporal pattern of stream loss of K from W6 generally coincides with stream efflux of SO_4^{2-} + NO_3^- (Fig. 24). The outflux of SO_4^{2-} + NO_3^- increased from 1965 to 1975 when the ecosystem mass balance of K (bulk deposition inputs minus stream outputs) shifts from net retention to large net losses (Fig. 16). From the mid 1970s to 1992, inputs and losses of SO_4^{2-} plus NO_3^- have declined and this decline has coincided with a small decline in the net loss of K from W6. The significant relationship with stream K flux and SO_4^{2-} + NO_3^- export suggests that acidic deposition has facilitated to some extent the loss of K from the forest ecosystem and recent declines in atmospheric inputs of strong acid anions (e.g. Likens 1992) coincide with somewhat reduced K leaching.

Damage to the biological integrity of the forest canopy also can affect the cycling of K from trees to soil. As noted in the section on throughfall and stemflow, partial defoliation of the canopy by *Heterocampa* spp. larvae during 1968–1970 may have been responsible for the high fluxes of K in throughfall during 1969 (Eaton et al. 1973). Concentrations of K in stream water were

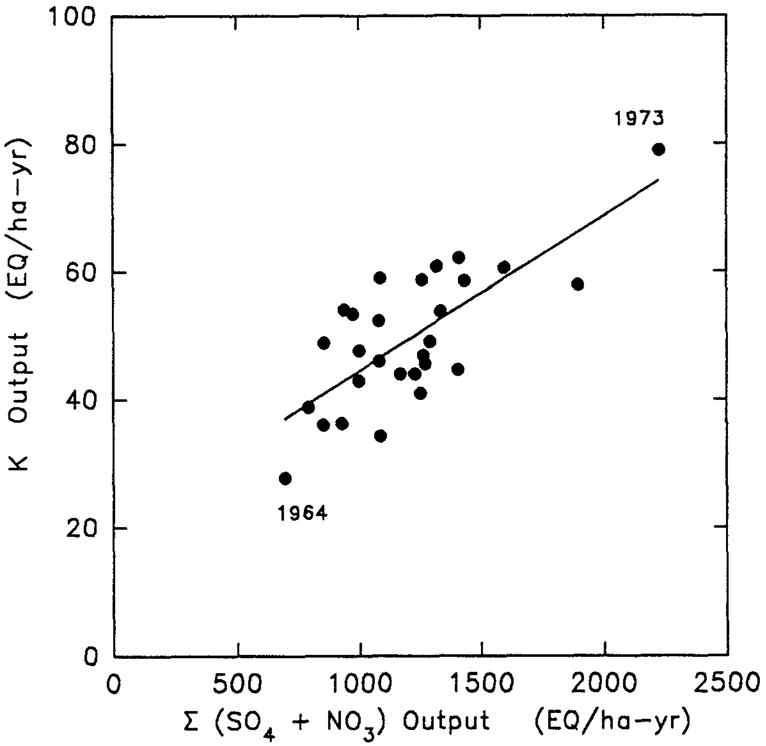


Fig. 24. Stream outflow of K as a function of the sum of stream SO_4^{2-} + NO_3^- loss in W6 of the HBEF (stream K flux = 20.23 + 0.024 × (stream SO_4^{2-} + NO_3^- flux); in eq/ha-yr; $r^2 = 0.55$).

also relatively high during this period, but higher concentrations have been measured during periods without defoliation (Fig. 4A). Insect defoliation has been shown to increase throughfall fluxes of N and P (e.g. Hollinger 1986; Stachurski & Zimka 1984), but to our knowledge this effect has never been measured for K. In contrast, K leaching from the canopy does not seem to respond to acid precipitation (at least at ambient levels), in contrast to Ca^{2+} and Mg^{2+} (Lovett & Hubbell 1991).

Summary and conclusions

- Long-term declines in annual volume-weighted concentrations and flux of K in precipitation were observed, but these trends were determined by the first two years of the study (1963–65), which were drought years.
- No statistically significant, long-term trends in streamwater concentration or flux were observed.
- Both annual concentration and flux of K in precipitation were inversely related to annual amount of precipitation.

- Dry deposition seems to be a substantial fraction of the total atmospheric K deposition, as measured by bulk deposition, but it is not possible to discern what fraction of the K in bulk deposition is generated internally from within the forest ecosystem.
- Concentration and flux of K increase markedly as precipitation passes through the canopy. The amount of increase varies temporally with the amount of precipitation in a rain event, and varies spatially among different forest canopy types.
- Average streamwater concentration of K peaks in March – April and in October and increases with increasing elevation. In contrast, precipitation concentration of K peaks in May and October and showed no trend with elevation.
- Seasonal patterns of average streamwater concentrations of K are controlled by biological uptake and hydrologic flowpath in the soil.
- Amounts (standing stocks) of K increased in tree biomass through 1982, but not thereafter.
- Concentrations of K in soil solutions and stream water are highest at high elevations within the coniferous zone of the HBEF.
- In the upper strata of the forest ecosystem (canopy – forest floor) concentration and fluxes of K are strongly regulated by biotic processes, as evidenced by lower concentrations and fluxes of K in the high elevation spruce-fir forest when compared to the lower elevation hardwood forest. In the lower strata controls of K are strongly linked to abiotic processes, such as cation exchange (which is strongly coupled to soil organic matter), depth of surficial deposits and inputs of strong acid anions, which facilitated leaching losses of K.
- Turnover rates for K in forest floor and mineral soil are relatively fast, 0.40 yr and 3.4 yr respectively, for exchangeable K at the HBEF.
- Although large quantities of K are found in abiotic and biotic pools, and residence times are short, relatively little K is lost in stream water at the HBEF.
- Comparing ecosystem processes from 1964–69 to the more recent period 1987–92, biomass storage of K decreased, net soil release decreased, throughfall decreased and resorption increased. These changes appear to be in response to decreasing rates of living biomass accretion during this period.
- Watershed-ecosystems at Hubbard Brook were a net sink for atmospheric inputs of K during 1963–65, drought years, and a net source thereafter relative to biospheric connections.
- The flux of K by biological vectors across watershed- ecosystem boundaries is negligible at the HBEF.
- Disturbance such as clearcutting, releases large amounts of K to stream water and large losses of K occur in forest products removed in harvest. The elevated concentration of K in stream water persist for many years fol-

lowing clearcutting disturbance. Compared with other major elements, K is the slowest to recover to pre-disturbance conditions.
- Acid rain seems to have little effect on the leaching of K from the forest canopy, but streamwater losses are correlated with flux of acid anions.

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