



Gene E. Likens

Biogeochemistry of a Forested Ecosystem

Third Edition

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With assistance from

Donald C. Buso
Cary Institute of Ecosystem Studies



Gene E. Likens
Cary Institute of Ecosystem Studies
Millbrook, NY, USA

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I am pleased to dedicate this THIRD EDITION to my colleagues and friends, F. Herbert Bormann, John S. Eaton, Noye M. Johnson, and Robert S. Pierce.

These original coauthors made major contributions to the First Edition, published in 1977. Herb Bormann was a coauthor of the Second Edition, published in 1995. There have been many changes in the biogeochemistry of the Hubbard Brook Valley, several quite unexpected, since 1977. Unfortunately, Herb, John, Noye, and Bob are now deceased, but they are fondly remembered and acknowledged for their numerous scholarly and stimulating contributions and especially for their collegial interactions and friendship.

Special Dedication

A special dedication to my wife, Phyllis who, despite struggling with a serious illness, did all of the word processing and reference checking and much of the reference searching for this edition. Her dedication, enthusiastic support and love throughout this project are acknowledged with utmost appreciation and respect. Her insightful inputs and constant encouragement were vital to the completion of this book. I am most pleased to recognize her unique and profound contributions to this 3rd Edition and to the Hubbard Brook Ecosystem Study.

Preface to the Third Edition

As we approach 50 years of research in the Hubbard Brook Experimental Forest in the White Mountains of New Hampshire, it is a time again for analysis and synthesis, as well as for reflection. This is a momentous event for the Hubbard Brook Ecosystem Study (HBES), which officially began on 1 June 1963. These continuous, long-term data on precipitation and streamwater chemistry are, to my knowledge, the longest in existence. Remarkably, funding from the National Science Foundation for the HBES has been continuous and generous since 1963. And other sources of funding including The Andrew W. Mellon Foundation, the Environmental Protection Agency, and support from the home institutions of the numerous principal investigators working in the HBES, particularly Dartmouth College, Cornell University, Yale University, and the Institute of Ecosystem Studies during the early years of the project, are gratefully acknowledged for support of the research underpinning this Third Edition. This long-term work would not have been possible without the cooperation and support of Forest Service colleagues at the Durham, NH office of the Northern Research Station; U.S. Forest Service in Newtown Square, PA; and especially those Forest Service personnel stationed at the Hubbard Brook Experimental Forest.

This is the Third Edition of *Biogeochemistry of a Forested Ecosystem*, first published in 1977. At that time, there were five authors. Coauthors F. Herbert Bormann, Robert S. Pierce, John S. Eaton, and Noye M. Johnson are now deceased. The wise counsel of all four of these colleagues is greatly missed as I prepare this Third Edition, but more, I miss their close friendship, lively encouragement, and constructive generation and questioning of ideas and concepts.

The goal of this Third Edition is to update long-term data presented in earlier editions and to generate new syntheses and conclusions about the biogeochemistry of the Hubbard Brook Valley based on these longer-term data. There have been many changes, revelations, and exciting new insights generated from the longer-term data records. For example, the impact of acid rain peaked during the period of the HBES and is now declining. The longer-term data also posed challenges in that very marked changes in fluxes occurred in some components, such as hydrogen ion and sulfate deposition, calcium and nitrate export in stream water, and biomass

accumulation, during the almost 50 years of record. Thus, presenting “mean” or “average” conditions for many components for such a long period, when change was so prominent, does not make sense. In some cases, pentads or decades of time are compared to show these changes in a more smoothed and rational way for this long period. In some cases, a single period, often during periods of rapid change, such as acidification, is used to illustrate the main point(s). And, for some elements, a unique mass-balance approach, allowing the calculation of the net ecosystem flux (NEF), is shown on an annual basis throughout the study.

Because of new data and longer trends since the previous editions, the text of this Third Edition has been largely rewritten, figures added and redrawn, and tables reformulated, but the relatively open format of the First Edition has been retained in response to positive feedback received over the years. I believe the concepts and approaches originally laid out in the First Edition in 1977 and updated and enlarged here are still *compelling* for use in courses such as biogeochemistry, limnology, ecology, forestry, hydrology, and environmental science.

Throughout this third edition, “Hubbard Brook,” as used in earlier editions, has been replaced with HBEF (Hubbard Brook Experimental Forest) to avoid confusion between the river and the place that it drains.

Most of the routine long-term data are now accessible on the website for the HBES (<http://www.hubbardbrook.org>) in an unsynthesized form. These data have been accessed and used by numerous scholars, teachers, and students interested in long-term biogeochemical data. We have welcomed and encouraged this use but have urged users to be guided by ethical considerations, especially regarding attribution and partnerships. The HBES was one of the first long-term ecological projects to make data freely available by initiating a “Source of the Brook” effort to share our data with colleagues, scholars, and the public as this option became possible through computer technology (Anonymous 1990).

From the beginning, field notes were routinely and meticulously prepared at the time samples were collected to document and clarify environmental conditions and data relative to each sample collected. These notes have been of enormous value in providing an historical perspective and a context for critical conditions that otherwise may have become clouded in our memories with time.

In addition, samples of all kinds, but focused on precipitation and stream water collected throughout the period of the HBES, are archived in a special building constructed for this purpose. Robert Pierce’s leadership and vision was instrumental in the construction of this “Archive Building” at the Hubbard Brook Experimental Forest.

As mentioned in the Prefaces to previous editions, biogeochemical data from experimentally manipulated watershed-ecosystems are not featured in this book. Those data are presented and considered elsewhere, including our book, *Pattern and Process in a Forested Ecosystem* (Bormann and Likens 1979).

I am greatly indebted to Phyllis C. Likens for word processing, literature searches, and data management for this manuscript and to Donald C. Buso for data management, including a massive effort with figure and table preparation, and numerous helpful and stimulating discussions. Technical support with field collections and data compilation were provided most recently by Tammy Wooster and

Brenda Minicucci. The majority of the solute analyses conducted since the previous edition were done under the supervision of Kathleen Weathers and Denise Schmidt at the Institute of Ecosystem Studies (now the Cary Institute of Ecosystem Studies). Thanks to James LaBaugh for stimulating and helpful discussions. A special thanks to Scott Bailey for reviewing Chap. 5, to Mark Green and Kevin McGuire for reviewing Chap. 2, to Thomas J. Butler for reviewing Chap. 3, and to Gary Lovett for reviewing Chap. 6. Their helpful comments and insights are greatly valued and have contributed to a much improved final product. Acknowledgments to previous technicians, students, and postdocs contributing to these long-term data are given in the Prefaces to earlier editions. Significant writing was done while in residence at the University of Connecticut, Storrs and Uppsala University, Uppsala, Sweden. Generous support from these universities is much appreciated. I obtained a special OPUS grant from the National Science Foundation to help support the data management and writing of this Third Edition. This support is gratefully acknowledged.

Millbrook, NY, USA

Gene E. Likens

Preface to the Second Edition

When we originally published *Biogeochemistry of a Forested Ecosystem* in 1977, the Hubbard Brook Ecosystem Study (HBES) had been in existence for 14 years, and we included data through 1974, or a biogeochemical record of 11 years. Now our continuous, long-term biogeochemical records cover more than 31 years, and there have been many changes. The most notable change, however, is that three of our coauthors on the original volume are now deceased. They are deeply missed in so many ways.

In spite of the longer records, different trends, and new insights, we believe that the basic concepts and approaches we presented in 1977 represent the most valuable contribution of the original edition. They are still valid and useful, particularly for an introductory study of, or course in, biogeochemistry. Our goal in this revision is to preserve these features, correct errors, and revise or eliminate misleading or ambiguous short-term data (11 years!), while maintaining approximately the original length and the modest cost.

We have left the data of the original text largely unchanged; a few figures and tables have been replaced, revised, or added. We provide selected references to guide the interested reader to some of the longer-term data and newer research of the HBES. To accomplish these objectives, each chapter has a brief addendum of especially interesting new approaches, important long-term trends, and new insights gained from the longer-term perspective (31 years). We specifically draw attention to a few of the HBES articles published since 1977 for a more detailed description and analysis. A complete listing of the publications from the HBES can be found in “Publications of the Hubbard Brook Ecosystem Study” (Likens, 1994). Data from the HBES are available on a publicly accessible system (computer modem telephone number 603-868-1006) maintained by the U.S.D.A. Forest Service and the HBES.

As in the original version of this book, we do not include or consider here data from the experimentally manipulated (e.g., by clearcutting) watershed-ecosystems at Hubbard Brook, which is covered in our book, *Patterns and Processes in a Forested Ecosystem* (Bormann and Likens, 1979).

We thank Phyllis C. Likens for help in preparing the manuscript for this revision. We also acknowledge the help of Donald C. Buso with data analysis. Major financial support for the HBES since 1977 has been provided by the National Science Foundation and the Andrew W. Mellon Foundation.

September 1994

Gene E. Likens
F. Herbert Bormann

Preface to the First Edition

About 15 years ago we began the Hubbard Brook Ecosystem Study with the development of an ecosystem model and the conception of a method whereby some major parameters of the model could be directly measured under field conditions. The method, called "the small watershed technique," allowed measurement of input and output of chemicals and the construction of ecosystem nutrient budgets. Although the Hubbard Brook study of nutrient cycling originated with ideas developed by F.H. Bormann and G.E. Likens, its early growth was aided by Robert Pierce, forest hydrologist; Noye Johnson, geochemist; and John Eaton, forest ecologist. Donald W. Fisher of the U.S. Geological Survey also cooperated in the early phases of the project and provided numerous data on the chemistry of precipitation and stream water. Particular credit is due the U.S. Forest Service, whose scientists chose the Hubbard Brook Valley as a hydrologic study site, selected particular watersheds for intensive measurement, carried out a variety of basic hydrologic studies, and in general cooperated with us in many ways to make the Hubbard Brook Ecosystem Study a reality.

The initial part of the ecosystem study was concerned primarily with nutrient flux and cycling, and it was done slowly and deliberately. The entire effort during the first few years of study was carried forward by three of us at Dartmouth College, with the cooperation of the U.S.D.A. Forest Service. We had no precedents to follow, because similar, comprehensive studies of natural ecosystems had not been done. We reasoned that it would be best to first construct a solid base of studies on nutrient-hydrologic interactions upon which subsequent studies could be built. In this regard, we were fortunate to rather quickly determine quantitative nutrient budgets for replicated ecosystems. These results gave us guiding insight into the function of natural ecosystems and into the development of future lines of research.

Nevertheless, we felt that slower growth would be more manageable and would allow for substantial interaction among all senior investigators to ensure proper coordination and development of the overall study. Generally, the method we used to guide the growth of the Hubbard Brook research proposals was as follows: First,

based on our own perceptions and feedback from ongoing studies, from cooperating scientists, and from outside advisors, we identified research problems that were timely and particularly pertinent to our overall goals. Some of the studies were launched under our direction; others were brought to the attention of an established investigator working in that area. We then sought a mutually satisfactory arrangement to allow the investigator to work at Hubbard Brook. From the beginning, we have called attention to the kinds of information a cooperative study might produce, but we have always encouraged individuality in the design and execution of research. *We deem this individual research freedom one of the greatest assets of the Hubbard Brook Study.* Individuality in selection of problems and conduct of research is also encouraged among graduate students at Hubbard Brook. Not only does this contribute to the intellectual ferment and sound growth of the Hubbard Brook Study, but as educators, we feel this approach absolutely necessary if the Hubbard Brook Study is to contribute to graduate education.

Over the last 15 years the study has grown to include not only hydrology and input-output chemistry, but also aspects of the structure, function, and dynamics of the forest ecosystem itself. In addition to studies of undisturbed ecosystems, entire ecosystems have been experimentally manipulated to allow comparative study of undisturbed and perturbed ecosystems. Stream and lake ecosystems within the Hubbard Brook Valley have been studied in detail, and the connection between the forest ecosystem and these interlinked aquatic ecosystems is now the focus of considerable attention.

Approximately 50 senior scientists and scores of graduate students have carried out studies at Hubbard Brook during the last 15 years. Over 200 publications have resulted from this work.

We now plan to organize some of this information in ways we consider useful both to the scientists concerned with the theory of biogeochemical cycles and the structure, function, and development of forested ecosystems, and to the land-use specialists who are concerned with the production of a variety of benefits, goods, and services from northern hardwood ecosystems.

We have developed two volumes so far, and a third is planned for the future. This, the first volume, presents a detailed examination of the biogeochemistry of an undisturbed, aggrading, second-growth northern hardwood forest at Hubbard Brook. Ecosystems similar to this cover a large area of northern New England and New York. Major emphasis in this book is on the physical aspects of nutrient and hydrologic flow through the ecosystem and nutrient budgetary. Not only are we concerned in this book with the presentation of data and conclusions that may be drawn from them, but we also discuss methodology as it influences results, and we try to share some of our experience at Hubbard Brook in the hope that other workers can avoid pitfalls where we have not been so fortunate. Moreover, we hope that the data presented in this volume can serve as a basis for decision-making and management schemes, including modeling within the northern hardwood forest landscape.

The second volume has as its primary concern the structure, function, and development through time of the northern hardwood ecosystem and is designed for the advanced student in ecology as well as for the ecosystem specialist. It concentrates

on the interrelationships among biogeochemical processes, structure, and species behavior within the ecosystem and how these change with time following perturbation. We plan for the information in these two volumes to interrelate and thus draw support for each other. Biogeochemistry is presented more fully in this first volume, whereas biological considerations are dealt with more fully in the second volume.

By no means do these two volumes summarize the Hubbard Brook Study. In the future we hope to put together a more comprehensive volume that involves contributions from the many cooperating scientists who have brought their particular specialties to bear on the Hubbard Brook Ecosystem.

There are many persons to acknowledge and thank for contributions to such a multidisciplinary study conducted over so many years. Many data were collected during rainstorms, blizzards, intense cold, darkness, and numerous other types of northern New Hampshire weather. Long, often tedious hours in the laboratory and at the computer center were also required. The ideas, devotion, loyalty, and encouragement and genuine enthusiasm of field technicians, laboratory technicians, students, and various other colleagues made the overall Hubbard Brook Ecosystem Study a reality and is beyond a simple "thank you."

For this little book, we owe debts great and small to many people—to those whose ideas and encouragement provided an intellectual thrust to move ahead; to those without whose devotion, skills, and endurance there would have been no progress at all; and to those mostly good-natured colleagues whose shafts of humor and criticisms have helped us all to keep a realistic perspective. For all of these things and more, we thank:

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We all acknowledge continued indulgence from our and our coauthors' wives (Kay, Chris, Carol, Diane, and Delores) and families for time spent away from them.

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January 1977

Gene E. Likens
F. Herbert Bormann

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Chapter 1

Ecosystem Analysis

An ecological system has a richly detailed series of inputs and outputs of energy and matter. Because of the lack of precise information about these relationships and the internal functions that maintain the ecosystem, it is often difficult to assess the impact of human activities on the biosphere. As a result, land-use managers and planners often cannot take into account or even foresee the full range of consequences a project may have. Without full information, the traditional practice in the management of land resources has been to emphasize strategies that maximize the output of some desirable product or service and give little or no thought to the long-term secondary effects. As a result often there is much conflict between conservation and management goals. For example, in an all-out effort to increase food production, drainage waters carry large burdens of pollutants from fertilizers, pesticides, and farm wastes. Forests may be cut with inadequate perception of the effects on regional water supplies, wildlife, recreation, and aesthetic values. And despite recent regulations to protect wetlands, they have been converted worldwide to commercial use with little concern over important hydrologic, biodiversity, esthetic, and commercial values lost in the conversion.

For some time, it has been evident that a new conceptual approach to the management of natural resources is desirable. One approach that has received considerable attention recently is to consider entire ecological systems as integrated interacting units, instead of limiting studies to only a few components of the system. In an experimental forest in New Hampshire, we have conducted a large-scale and long-term investigation aimed at supplying the kind of information that is usually lacking about ecosystems.

A vast number of variables, including biologic structure and diversity, geologic heterogeneity, climate, and season, control the flux and cycling of both water and chemicals through and within ecosystems. Clearly, both living and nonliving components of ecosystems are important in defining and regulating the flow of matter within and between ecosystems. Because chemicals tend to circulate from nonliving components to living organisms and back to the nonliving environment, the pathways have been termed biogeochemical cycles. Ecosystems continually exchange

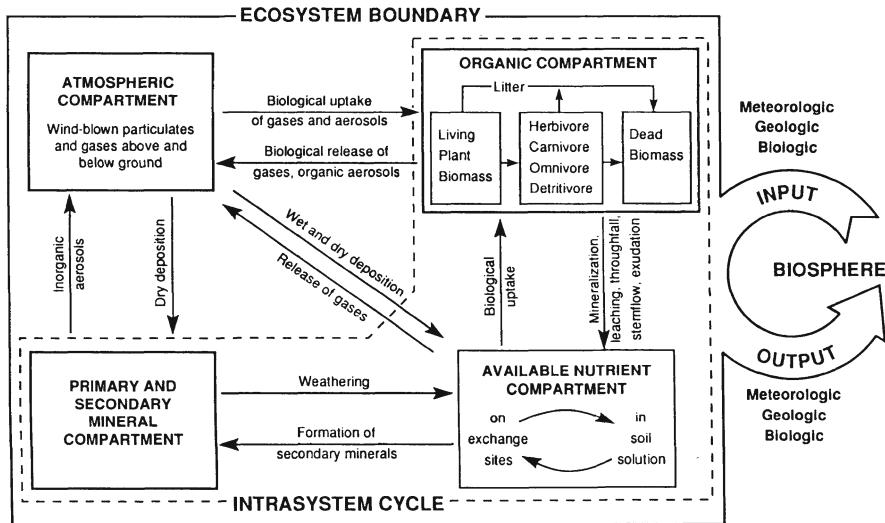


Fig. 1 Conceptual model depicting nutrient relationships in a terrestrial ecosystem. Inputs and outputs to the ecosystem are moved by meteorologic, geologic, and biologic vectors (Bormann and Likens 1967; Likens and Bormann 1972). Major sites of accumulation and major exchange pathways within the ecosystem are shown. Nutrients that, because they have no prominent gaseous phase, continually cycle within the boundaries of the ecosystem between the available nutrient, organic matter, and primary and secondary mineral components tend to form an intrasystem cycle. Fluxes across the boundaries of an ecosystem link individual ecosystems with the remainder of the biosphere. Modified from Likens (1992)

(gain or lose) matter and energy with other ecosystems and the biosphere as a whole. These biogeochemical fluxes and the internal cycles are vital to the functioning and continuance of the system. Comparisons of biogeochemical data from natural ecosystems with those that have been manipulated by humans or otherwise disturbed then provide important information about the functional efficiency or “health” of an ecosystem.

For almost five decades, the biogeochemistry of the Hubbard Brook Experimental Forest, hereafter referred to as HBEF (Fig. 1), has been the subject of continuous and detailed study, referred to as the Hubbard Brook Ecosystem Study (HBES). More than 35,000 water samples, including rain, snow, stream water, ground water, throughfall, and stemflow, have been collected and chemically analyzed. In addition, thousands of samples of air, soil, rocks, and biota have been collected and chemically analyzed. These extensive data now provide the means and the perspective to identify, isolate, and quantify some of the complex and interlocking biogeochemical processes of a forest ecosystem. As this study shows, seasonal and year-to-year variations in flux rates and associated biologic responses often require long-term analysis before reliable generalizations can be drawn about such complex natural systems. This book summarizes the understanding, as derived from almost

50 years of data, of the biogeochemical flux and cycling of water and nutrients for a northern hardwood forest ecosystem in New England, refers to the timescale at which the various biogeochemical processes operate, and relates these data to other ecosystems with long-term data.

Studies began in 1963 to determine the magnitude of the biogeochemical flux and cycling of water and nutrients in northern hardwood forest ecosystems in the White Mountains of New Hampshire. The ecosystem unit we used is a watershed or drainage area, with vertical and horizontal boundaries defined functionally by biologic activity and the drainage of water (Bormann and Likens 1967). Six adjacent, small south-facing and three north-facing watersheds within the HBEF, with roughly similar vegetation, geology, and climate, have been used for these studies (Bormann and Likens 1967; Likens and Bormann 1972). Differences across the valley and on south-facing and north-facing slopes gave opportunities for other comparisons and analyses (e.g., Likens and Buso 2006). This series of watershed-ecosystems provided the possibility for replication, as well as a design for experimental manipulation of entire natural ecosystems (e.g., Likens et al. 1970). Nevertheless, this book will focus largely on the long-term biogeochemical results of Watershed 6 (W6), the biogeochemical reference watershed for the HBEF.

A conceptual model of these deciduous forest ecosystems was formulated at the outset to facilitate the development of key questions and to guide the quantitative evaluation of the input–output flux and cycling of water and chemicals (Bormann and Likens 1967; Likens and Bormann 1972). The continuous flow of energy, water, nutrients, and other materials across the ecosystem’s boundaries is considered to be inputs and outputs, which are transported by meteorologic, geologic, and biologic vectors (Fig. 1). Meteorologic inputs and outputs consist of wind-borne particulate matter, dissolved substances in rain and snow, aerosols, and gases (e.g., CO₂). Geologic flux includes dissolved and particulate matter transported by surface and subsurface drainage and the mass movement of colluvial materials by gravity. Biologic flux results when chemicals or energy gathered by animals in one ecosystem are deposited in another (e.g., local exchange of nitrogen or phosphorus in fecal matter, seed dispersal by seasonal bird movements, or transport of calcium or phosphorus in moose antlers). These input–output categories are therefore defined as vectors or “vehicles” for transport of nutrients, matter, or energy rather than sources; i.e., a leaf blown into an ecosystem represents meteorologic input rather than biologic input.

Within the ecosystem, the nutrients may be thought of as occurring in any one of the four major compartments: (1) atmosphere, (2) living and dead organic matter, (3) available nutrients, and (4) primary and secondary minerals (soil and rock). The atmospheric compartment includes all elements in the form of gases or aerosols both above- and belowground. Available nutrients are ions that are absorbed on or in the soil complex or dissolved in soil water. The organic compartment includes all nutrients incorporated in living and dead biomass. The woody tissues of living vegetation are considered a part of the living biomass. The primary and secondary minerals contain nutrients that comprise the inorganic soil and rock portions of the ecosystem.

The biogeochemical cycling of elements involves an exchange between these various compartments within the boundaries of the ecosystem. Available nutrients and gaseous nutrients may be taken up and assimilated by the vegetation and micro-organisms; some may be passed on to heterotrophic consumers and then made available again through respiration, biologic decomposition, and/or leaching from living and dead organic matter. Insoluble primary and secondary minerals may be converted to soluble available nutrients through the general process of weathering; soluble nutrients may be redeposited as secondary minerals.

Small Watershed Approach

In humid regions, chemical flux and cycling are intimately linked to the hydrologic cycle. Hence, it is impossible to measure the input and output of nutrients without simultaneously measuring the input and output of water. The problem usually is that subsurface flows of water, which can be a significant fraction of the hydrologic cycle, are very difficult to measure quantitatively.

About 50 years ago, it occurred to us that under certain circumstances, the interaction of the nutrient cycle and the hydrologic cycle could be turned to good advantage in the quantitative study of an ecosystem. The requirements were that the ecosystem be a watershed underlain by watertight bedrock or some other relatively impermeable base. In that case, the only inputs to the ecosystem would be meteorologic and biologic; geologic input need not be considered because there is no transfer by gravity between adjacent watersheds on an ecological timescale. In humid areas where surface wind abrasion is a minor factor, losses from the system are only geologic and biologic. Given an impermeable base, all the geologic output would inevitably turn up in the streams draining the watershed where it could be measured quantitatively. When the watershed is part of a larger and fairly homogenous biotic unit, the biologic output tends to balance the biologic input because most animals move indiscriminately into and out of the watershed, randomly acquiring or releasing nutrients. Therefore, it is necessary to measure only the meteorologic input and the geologic output (net hydrologic flux, NHF) of nutrients to arrive at the net gain or loss of a given nutrient in the ecosystem. Watershed-ecosystems in the HBEF are small enough to allow quantitative evaluation of ecosystem complexity and permit whole-watershed manipulations, but large enough to be relevant to management considerations.

Using this approach, it has been possible to obtain quantitative annual NHF budgets for most of the major chemical nutrients. The flux of some nutrients with a gaseous phase (e.g., N and S) is more difficult to evaluate, but the ecosystem approach allowed realistic assumptions and estimates to be made about some of these unmeasured gaseous components. More recently, the use of isotopes, "flux towers," and other techniques has provided more quantitative estimates of these fluxes. Incorporating other components, such as weathering, net soil release, dry deposition, and long-term biomass storage, allowed calculations of net ecosystem

flux (NEF) for watershed-ecosystems. Despite its apparent simplicity, the NEF is a powerful tool for understanding the biogeochemistry of watershed-ecosystems, particularly when done for long periods.

We have used these approaches in an intensive study of the biogeochemistry of six contiguous south-facing watersheds and three contiguous north-facing watersheds within the HBEF (Fig. 2). These watershed-ecosystems are all tributary to Hubbard Brook. As mentioned above, this book will focus on W6 of the HBEF.

The Hubbard Brook Ecosystem

The HBEF was established in 1955 by the U.S. Forest Service as the principal research area for forest hydrology and the management of watersheds in New England (Hornbeck 2001; McGuire and Likens 2011; Likens and Bailey 2013). It is operated and managed by the Northeastern Research Station of the U.S. Forest Service in cooperation with the White Mountain National Forest. The name of the area is derived from the major drainage stream in the valley, Hubbard Brook. Hubbard Brook flows generally from west to east for about 13 km (Fig. 2) until it joins with the Pemigewasset River, which ultimately forms the Merrimack River and discharges into the Atlantic Ocean in Massachusetts. Water from more than 20 tributaries enters Hubbard Brook along its course. Mirror Lake, a small oligotrophic lake, also discharges into Hubbard Brook at the lower end of the valley. Hubbard Brook is a fifth-order river at its outlet from the HBEF.

Location

The HBEF is located within the townships of North Woodstock (~60 %), Ellsworth (~40 %), and Warren (<1 %), NH, within the White Mountain National Forest of north central New Hampshire. Coordinates of 43°56'N, 71°45'W bisect the area. The Atlantic Ocean is about 116 km to the southeast. The nearest town is West Thornton, NH.

Climate

Although the climate varies with elevation, it is classified as humid continental with short, cool summers and long, cold winters (Trewartha 1954). The climate may be characterized by (1) changeability of the weather, (2) a large range in both daily and annual temperatures, and (3) equable distribution of precipitation on a monthly basis. The HBEF lies in the heart of the middle latitudes, and the majority of the air masses therefore flow from west to east. During the winter months, these are

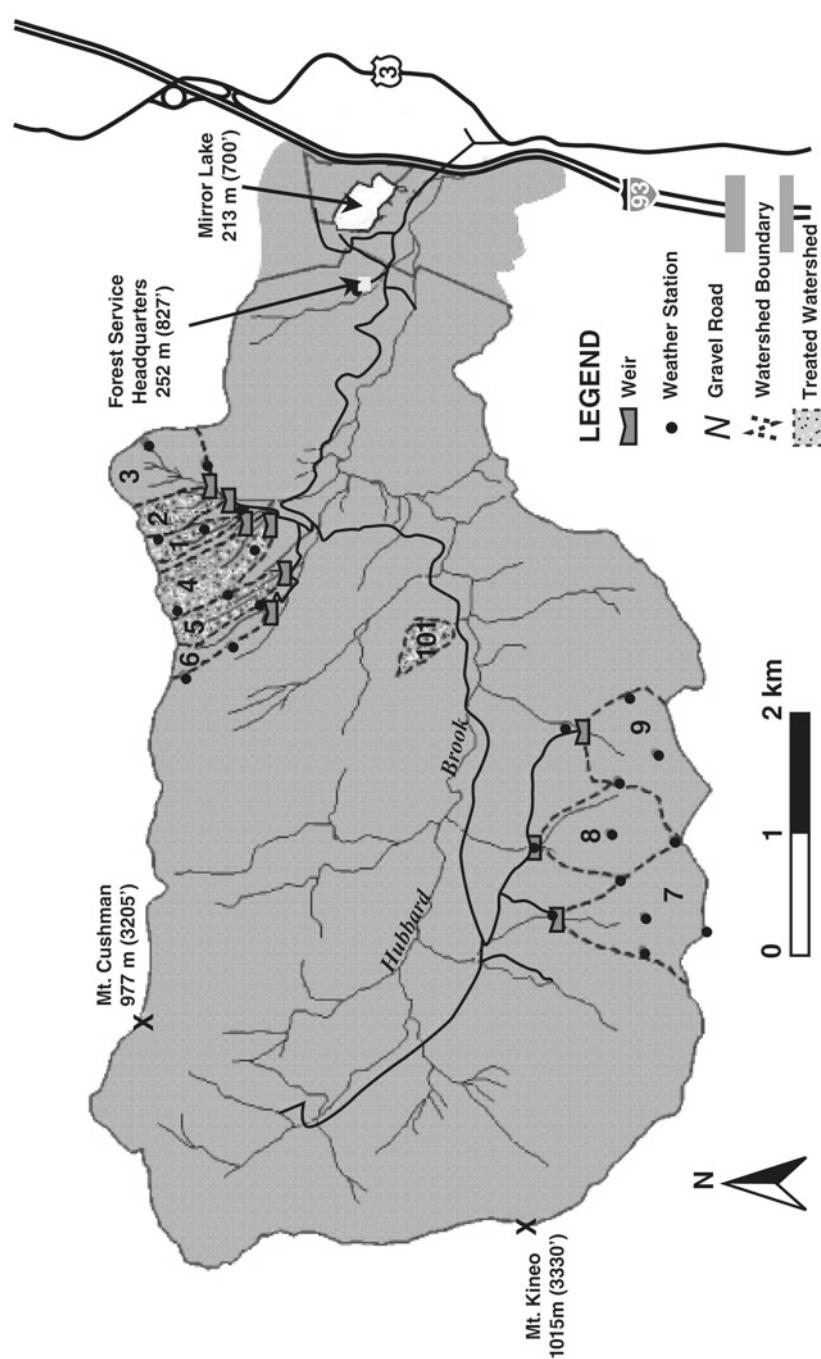


Fig. 2 Hubbard Brook Experimental Forest, located in the townships of North Woodstock, Ellsworth, and Warren, New Hampshire, USA. Modified from J. Campbell, USDA Forest Service, Northern Research Station - 7

northwesterlies, and during the summer, the air generally flows from the southwest. Therefore, the air affecting HBEF is predominantly continental. However, during the autumn and winter, cyclonic disturbances periodically move up the east coast of the USA providing an occasional source of maritime air. The mean air temperature in July is 18.7 °C and in January is –8.3 °C (Federer et al. 1990; A. Bailey et al. 2003). A continuous snowpack normally develops each winter to a depth currently of about 1 m. Occasionally, mild temperatures in midwinter partly or wholly melt the snowpack. A significant microclimatologic feature of this area is that even the uppermost layer of the forest soils usually remains unfrozen during the coldest months because of the thick humus layer and a deep snow cover (Hart et al. 1962). The depth of snow cover and its duration, the occurrence of soil frost, and the date of spring snowmelt have been decreasing/advancing during the past 50 years or so (e.g., Campbell et al. 2007; Huntington et al. 2009; Vadeboncoeur et al. 2009; Judd et al. 2011).

Area, Topography, and Aspect

The HBEF covers an area of about 32 km² and ranges in altitude from 222 to 1,015 m. The experimental watershed-ecosystems (Watersheds 1–6, 7–9; Fig. 2) range in size from 12 to 77 ha and in altitude from 500 to 910 m. These headwater watersheds are all steep (average slope of 20–30 %), with well-incised channels and relatively distinct topographic divides. The height of the land surrounding each watershed-ecosystems, the area, and the topography all have been determined from ground surveys and aerial photography and most recently augmented by Laser Imaging Detection and Ranging (LIDAR). Experimental Watersheds 1–6 face S to SE; Watersheds 7–9 face N to NE.

Geology

The geologic substrate, outcrops of bedrock and stony till, in the Hubbard Brook Valley was exposed some 14,000 years ago when the glacial ice sheet retreated northward (Likens and Davis 1975; Davis and Ford 1985). The eastern portion of the Hubbard Brook Valley is underlain by a complex assemblage of metasedimentary and igneous rocks (Barton et al. 1997). The major component is the Silurian Rangeley Formation, consisting of quartz–mica schists and quartzite, metamorphosed to sillimanite grade. These metaphoric rocks also were intruded by a variety of igneous rocks, including the Concord granite, quartz diorite, pegmatite, and diabase and lamprophyre dikes. The western portion of the valley is underlain by Devonian Kinsman Granodiorite, a foliated, granitic rock distinguished by large phenocrysts of potassium feldspar (Barton et al. 1997). Much of the area of the experimental watersheds is covered with glacial till derived from local bedrock,

primarily granites, schists, and quartzites; materials from other lithologies N-NW of HBEF are common in small quantities (Bailey and Hornbeck 1992). Movement of surface water by deep seepage through the compacted till and crystalline bedrock is considered minimal (Bormann and Likens 1967; Likens et al. 1967; see Chap. 2).

Soils

Soils are diverse, but well-drained spodosols (Haplorthods) of sandy loam texture, with a thick organic layer at the surface, are most common. Most liquid precipitation infiltrates into the soil at all times, and there is very little overland flow because the surface soil is very porous, the surface topography is very rough (pit and mound, mostly from windthrown trees), and normally there is little soil frost (Pierce 1967). 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).

Soil depths are highly variable but average about 0.5 m from surface to bedrock or compacted till in these headwater watershed-ecosystems. In general, they are shallow at high elevations and increase in depth with decreasing elevation (Lawrence et al. 1986). The average soil depth to the C horizon within the experimental watersheds is ~57 cm (Johnson et al. 1991a). Recent measurements using ground-penetrating radar show scattered pockets of deeper (2–3 m) till at all elevations within the gauged watersheds (Scott W. Bailey, personal communication). A well-developed and well-drained surface organic layer (O horizon or forest floor) is 3–15 cm in thickness. Soil on the ridges may consist of a thin accumulation of organic matter resting directly on the bedrock. In some places and at varying depths, impermeable pan layers restrict vertical water movement and root development.

Soils are acidic and generally infertile (e.g., Johnson et al. 1991b). The average pH of soil is difficult to measure, particularly at the watershed scale. Early results indicated that HBEF soils had a pH \geq 4.5. Currently, soils appear to be significantly more acidic, pH 3.5 for W7 (Ross et al. 2009) and pH 3.5–3.7 for W1 prior to Wollastonite treatment in 1998 (Peter M. Groffman, personal communication).

Vegetation and Fauna

The vegetation of the HBEF is part of the northern hardwood forest ecosystem, an extensive forest type that extends with variations from Nova Scotia to the western Lake Superior region and southward along the Blue Ridge Mountains (Braun 1950; Kühler 1964; Oosting 1956). Classification of mature forest stands as northern hardwood ecosystems rests on a loosely defined combination of deciduous and

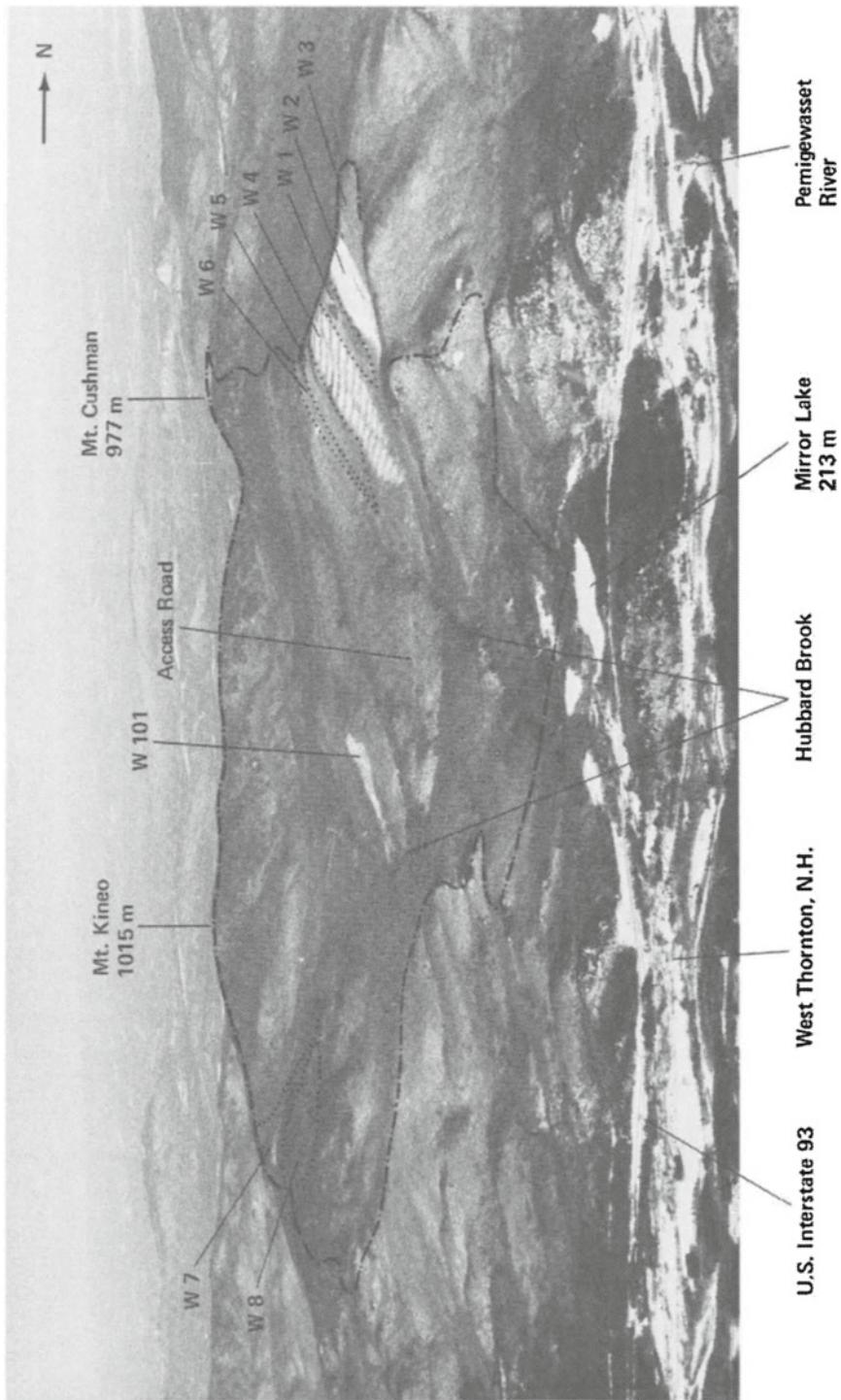
coniferous species that may occur as deciduous or mixed deciduous–evergreen stands (Photograph 1).

The forest is unevenly aged and well stocked, primarily with sugar maple (*Acer saccharum*), American beech (*Fagus grandifolia*), and yellow birch (*Betula alleghaniensis*). Red spruce (*Picea rubens*), balsam fir (*Abies balsamea*), white birch (*B. papyrifera* var. *cordifolia*), and hemlock (*Tsuga canadensis*) are prominent on north-facing slopes, on ridge tops, on rock outcrops, and along the main channel of Hubbard Brook. Logging in the valley began in the 1800s, with heavy cutting between 1906 and 1919; the forest was damaged by a hurricane in 1938 and a large ice storm in 1998, but there is no evidence of major fire in the history of these stands (Bormann et al. 1970; Likens 1972b; Davis 1985; Merrens 1988; Merrens and Peart 1992; Peart et al. 1992; Rhoads et al. 2002; Likens et al. 2004b; van Doorn et al. 2011; Charles V. Cogbill, personal communication).

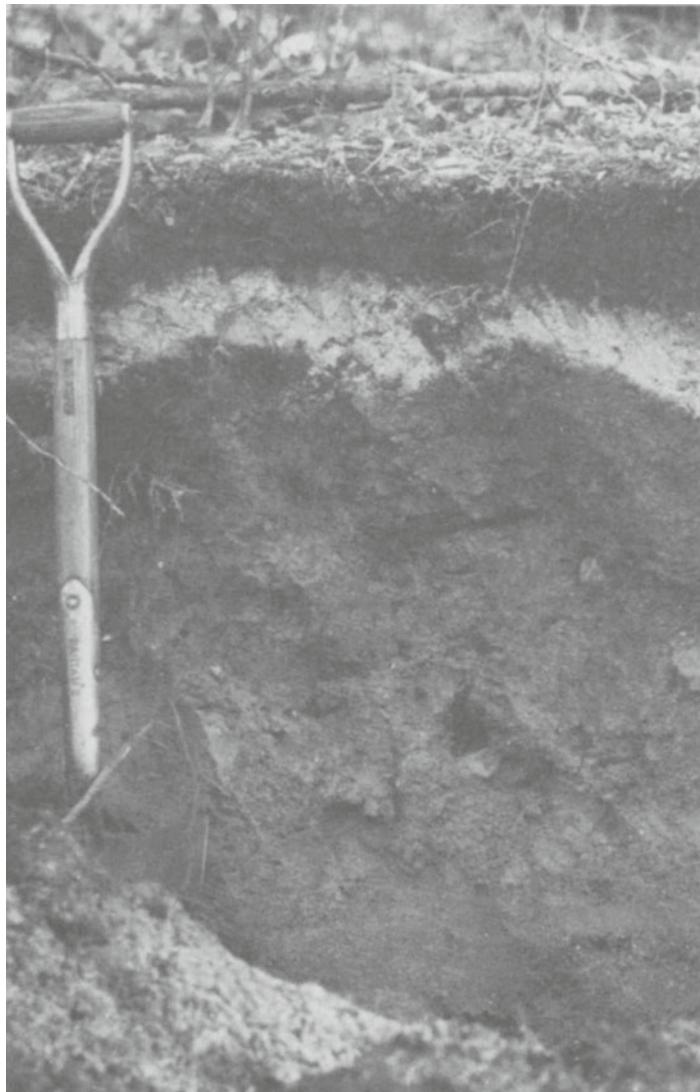
The forest in W6 had a basal area of about 23 m²/ha in 1965 (Bormann et al. 1970) and 28 m²/ha in 2007 (Siccama et al. 2007). Total (above- and belowground) live-tree biomass (~245 mg/ha for trees \geq 10 cm dbh) throughout the Hubbard Brook Valley did not change significantly between 1995 and 2005 (van Doorn et al. 2011). Aboveground biomass accumulation for the forest on W6 averaged about 4.85 Mg/ha-year during 1965–1977 but declined to 0.89 Mg/ha-year during 1987–1992 (Likens et al. 1994) and recently has declined even further (Lindenmayer and Likens 2010, p. 123).

Other regional components of the northern hardwood ecosystem, such as white ash (*Fraxinus americana* L.) and red maple (*Acer rubrum*), are common in the experimental watersheds; white pine (*Pinus strobus*) is rare except in the valley floor, and red oak (*Quercus rubra*), basswood (*Tilia americana*), and elm (*Ulmus americana*) are absent from the HBEF. About 26 species of trees and some 100 species of shrubs and herbs have been identified in the Hubbard Brook Valley (Holmes and Likens 1999).

Fauna common to northern hardwood forests occurs within the Hubbard Brook Valley. More than 125 species of birds have been observed (Likens 1973; Holmes and Likens 1999), and snowshoe hare (*Lepus americanus*), beaver (*Castor canadensis*), red fox (*Vulpes fulva*), black bear (*Ursus americanus*), moose (*Alces americana*), and white-tailed deer (*Odocoileus virginianus*) are present. The White Mountains generally have a low population density of deer because of severe winters and hunting pressure (Siegler 1968; Pletscher 1982; Pletscher et al. 1989). The northern, red-backed salamander (*Plethodon cinereus*) is a dominant vertebrate in these forests with regard to numbers and biomass (Burton and Likens 1975). Currently, total bird abundances in the HBEF are about half of what they were in 1970 (Holmes 2011), and terrestrial salamander abundances are about one-third. Native (unstocked) brook trout (*Salvelinus fontinalis*) populate Hubbard Brook and the reaches of some of its major tributaries (Warren et al. 2008) (Photograph 2).



Photograph 1 Aerial view of the Hubbard Brook Experimental Forest, North Woodstock, New Hampshire, during winter—1973 (area within *dash dotted lines*, approximately 32 km²). Experimental watersheds shown by *dotted boundaries* (see Fig. 2). Watershed 2 was cleared of all woody vegetation in 1965 and sprayed with herbicides for three successive summers to prevent regrowth. No forest products were removed. Watershed 4 was cut in 25-m-wide alternating strips in 1970, 1972, and 1974. Picture shows Watershed 4 when two-thirds of the strips were cut and harvested. Watershed 101 was cleared and products were removed in one operation in 1970. Watershed 5 was cut (whole-tree harvest) in 1983–1984 after this photograph was taken. Watershed 1 was treated with Wollastonite (CaSiO₃) in 1999 to test the effects of acid rain on soil calcium pools. All other watersheds are untreated as yet and serve as references to these watershed manipulations. *Dark areas* on the ridges and peaks generally are conifers, and the *lighter areas* are deciduous northern hardwoods



Photograph 2 A typical spodosol soil developed on till at the HBEF. The *uppermost dark layer*, an organic layer called the forest floor, rests on the mineral soil. Immediately below the forest floor is a bleached and chemically leached horizon, which grades into zones of accumulated organic matter and iron and aluminum oxides. At still lower depths, organic matter declines and the soil varies from partially weathered to unweathered mineral components. The presence of an obvious leached horizon is intermittent within the HBEF.

Drainage Streams

Headwater streams draining the watershed-ecosystems are small and perennial. Flow ranges from zero during infrequent summer droughts to hundreds of m³/ha-day during snowmelt and storm events. Five of the watersheds—3, 4, 7, 8, and 9—are larger and typically maintain flow during summer (Fig. 2).

From June to October, the streams are heavily shaded by the forest vegetation. As a result, daily water temperatures do not vary more than a degree or two Celsius during that time of year. Maximum streamwater temperatures (~21 °C) occur just before leaf out of the forest canopy. The annual temperature range in these streams is about 0 °C to about 18 °C, with a mean of about 7 °C. The mean annual temperatures in two of the south-facing streams (W3 and W6) declined ~2 °C from 1966 to 1983 and then increased by ~1 °C and became more variable thereafter (Likens 2011). The stream water is normally saturated or supersaturated with dissolved oxygen, and the pH is less than 6 in the headwaters (Likens and Buso 2006).

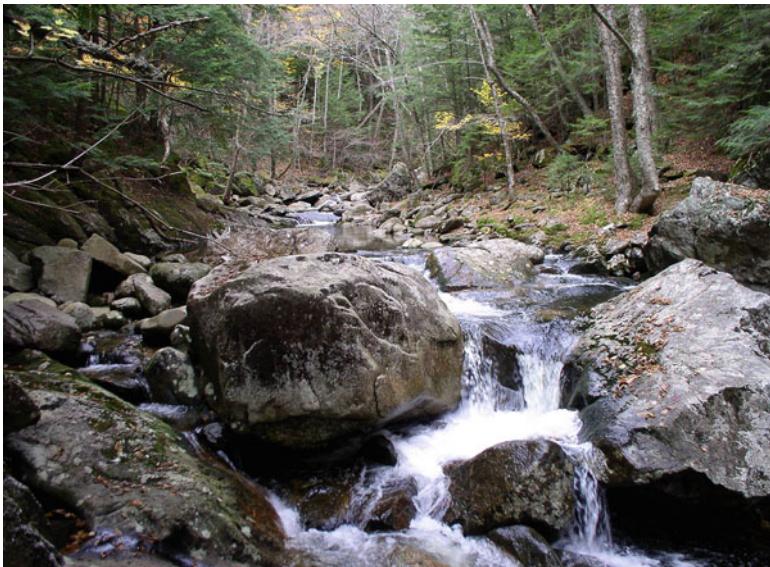
The streambed is covered by organic debris, fine sand, gravel, cobbles, and small boulders. There are occasional bedrock exposures in the steam channel, and these are preferred sites for gauging weirs. Numerous dams of organic debris occur throughout the length of the stream; the headwater streams therefore have a stair-step appearance of alternating “waterfalls” and pools. The stream channel comprises about 1–2 % of the area of each watershed-ecosystem. Areas of localized seepage are common, but not numerous (Photographs 3 and 4).

Concluding Thoughts

Additional details concerning the topography, climate, geology, and biology of the HBEF are given elsewhere (e.g., Likens et al. 1967; Johnson et al. 1968; Bormann et al. 1970; Holmes and Sturges 1973; Likens 1973, 1985; Bormann and Likens 1979; Siccama et al. 1970, 2007; Whittaker et al. 1974; Holmes and Likens 1999; Holmes 2011; <http://www.hubbardbrook.org>). A large number of papers have been published on the biogeochemistry of the Hubbard Brook Valley including eight monographs (Bormann et al. 1974; Whittaker et al. 1974; McDowell and Likens 1988; Likens et al. 1994, 1998, 2002a; Fahey et al. 2005; Lovett et al. 2005). By coupling results from long-term biogeochemical monitoring with process-level research, detailed mass balances have been developed for many elements (e.g., Likens et al. 1994, 1998, 2002a, b; Likens 2004; Lovett et al. 2005; Fahey et al. 2005; Likens and Buso 2010a; Bernal et al. 2012). Element mass balances in combination with the small, watershed-ecosystem approach provide an excellent conceptual framework to investigate the ecology, hydrology, and biogeochemistry of forest watershed-ecosystems and associated aquatic ecosystems, as well as to evaluate the response of ecosystems to disturbance. However, assessing the response of complicated and interrelated ecosystem processes to environmental change often requires more than monitoring and mass balances. Long-term monitoring has been



Photograph 3 Hubbard Brook at an elevation of about 215 m. The characteristic boulder substrate and “stair-step” nature of this fifth-order stream are evident



Photograph 4 Hubbard Brook at elevation of about 425 m. Photo by D.C. Buso

supplemented with plot and whole-ecosystem manipulations, long-term synthesis, as well as modeling efforts in the HBES to generate and test hypotheses concerning change in ecosystem structure and function and response to disturbance (some recent HBES examples include Aber et al. 1997, 2002; Berger et al. 1997; Driscoll et al. 1998, 2001; Christ et al. 1999; Groffman et al. 1999, 2001, 2006; Rosenberry et al. 1999; Hall et al. 2001; Gbondo-Tugbawa et al. 2001, 2002; Peters et al. 2004; Fitzhugh et al. 2001, 2003; Likens et al. 2004b; Likens and Buso 2006, 2010a, 2012; Bernhardt et al. 2005; Blum et al. 2002; Kobe et al. 2002; Dittman et al. 2007; McLauchlan et al. 2007; Judd et al. 2007, 2011; Warren et al. 2007; Conley et al. 2008; Bernal et al. 2012).

In addition to providing fundamental data on ecosystem function and the ecological relationships between structure and function, these biogeochemical data provide a baseline for judging the effects of human manipulations and disturbance of forest landscapes as well as information useful to managers wrestling with these problems (e.g., Likens et al. 1970; Pierce et al. 1972; Bormann and Likens 1979; Likens and Franklin 2009; Lindenmayer and Likens 2010; Bernal et al. 2012; Likens and Buso 2012).

The next chapters, Hydrology through Nutrient Cycles and Mass Balances, present detailed information about the long-term biogeochemistry of the HBEF. These sections summarize our current understanding of the flux and cycling of chemicals in the watershed-ecosystems at the HBEF in the context of the long-term changes that have occurred. An attempt is made to synthesize results and to interpret and comment on outstanding problems, solved and unsolved.

Chapter 2

Hydrology

Because of the vital role of water as a transporting agent, chemical solvent, weathering agent, and catalyst, quantitative data on hydrology are of paramount importance in understanding the biogeochemistry of a forest ecosystem. The U.S. Forest Service has monitored and maintained accurate records of precipitation and streamflow for numerous gauged watersheds of the HBEF since 1956 (Federer et al. 1990; A. Bailey et al. 2003; <http://www.hubbardbrook.org>). The HBEF was established in 1955 to study forest hydrology in New England utilizing a paired watershed approach (see McGuire and Likens 2011).

The Water-Year

Selection of a suitable water-year is a primary consideration for analysis of interannual hydrology. The ideal water-year begins and ends for a period that shows little interannual change in watershed water storage, often a point in the year of lowest water storage. One way to identify a water-year is to find that successive 12-month period that most consistently, year after year, gives the highest correlation between precipitation and streamflow and negligible changes in storage (i.e., soil water and snow). In watersheds of the HBEF, streamflow is largely dependent on (1) precipitation, (2) the capacity for water storage in the soil and thereby the amount of water stored in the soil at any time, and (3) the amount of water stored in the snowpack.

After a large array of linear regressions for successive 12-month periods of precipitation and streamflow had been examined, the water-year beginning on 1 June and ending on 31 May was chosen, with correlation coefficients of about 0.99 (see Federer et al. 1990). We repeated Federer's calculations for the period 1963–2010 and concluded that a water-year beginning 1 June was still valid based on the highest regression coefficient (r^2 0.95) and a regression slope closest to one. The high correlation coefficients indicate that water storage in the watershed is consistently at its seasonal low, which can be explained by seasonal water storage

dynamics: (1) Evapotranspiration each summer leaves the soil with relatively depleted water content; (2) autumn rains usually completely replenish water depleted during the summer; and (3) the addition of between 20 and 30 cm of water as snowpack, followed by spring soil recharge during melting of the snowpack. The selection of a water-year starting on 1 June also is advantageous because this corresponds to the period when foliage is getting established in the HBEF and allows for a separation of the water-year into periods essentially coincident with growing and dormant seasons for the vegetation. The effects of climate change on phenology and components of the water cycle, such as snowmelt, have the potential to change the water-year in the future.

Precipitation

Because precipitation serves as a major vehicle of nutrient input into an ecosystem, its accurate measurement is of prime importance in an evaluation of any biogeochemical cycle. Precipitation amount is measured at the HBEF by a fixed network of standard U.S. Weather Bureau volumetric precipitation gauges sited in cleared areas, approximately one for every 13 ha within the areas of the experimental watersheds. The Thiessen polygon method (Thiessen 1911) is used to calculate amounts of areal precipitation for discrete watersheds (see Federer et al. 1990).

On average, 143.4 cm of water falls on each unit area of Watershed 6 (W6) annually within the HBEF (1963–2009). Of this amount 65 %, or 92.6 cm, becomes streamflow, and the remainder, about 51 cm, is lost as vapor through evapotranspiration (Table 1, Fig. 3). The evapotranspiration is estimated as the difference between precipitation and streamflow for the water-year because the geologic base of the watershed is essentially watertight (see the section on “Deep Seepage” below).

There are on average 170 precipitation days (>trace) per year at HBEF or about three per week (Table 2). Dividing the average annual precipitation of 143.4 cm by 170 days gives an average intensity of 0.8 cm per precipitation day.

The seasonal effects of temperature on precipitation (rain or snow), as well as the structure and function of the biomass (e.g., interception of raindrops by the forest canopy and litter on the forest floor), are important in lowering the erosive potential

Table 1 The average annual hydrologic budget for Watershed 6 of the Hubbard Brook Experimental Forest

W6, 1963–2009 (period of biogeochemical study)	cm/unit area \pm SD	Percent of input
Input (precipitation)	143.4 \pm 20.0	100
Output (streamflow)	92.6 \pm 20.6	64.6
Output (evaporation plus transpiration) ^a	50.8 \pm 5.0	35.4

^aCalculated (Input–Output)

Fig. 3 Average hydrologic budget for Watershed 6 of the Hubbard Brook Experimental Forest with standard deviations (SD) during 1963–2009

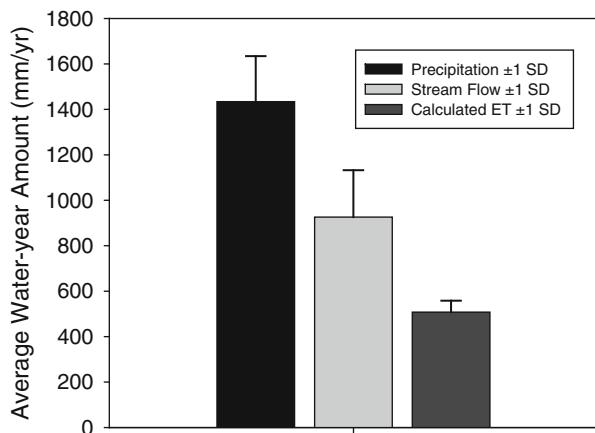


Table 2 Annual input of water as snow, rain, or mixed snow and rain for the Hubbard Brook Experimental Forest during 1974–2010^a

Precipitation type	Average number (days/year)	Percent of average annual water input (if applied to W6, 143.4 cm)
Snow	42	12 (17.2 cm)
Rain	106	71 (101.8 cm)
Mixed	20	17 (24.4 cm)

^aData are from calendar-year summations of USFS Daily Precipitation volume (mm) at the Robert S. Pierce Ecosystem Laboratory (RSPEL) and matched with daily field notes. Precipitation is recorded about 170 days per year on average or about 47 % of the time. There was no significant trend in the percent of precipitation volume as rain

of precipitation and to biogeochemical flux and cycling. Precipitation that falls as snow has a much smaller potential energy of impact, and once a snowpack is established, it acts as a “sponge” for any nonfrozen precipitation.

The form of precipitation at HBEF is being altered by climate change. Some 29 % of the annual precipitation amount falls as snow or mixed snow and rain at HBEF (Table 2). Decreasing proportions of snow and increasing amounts of mixed snow and rain have been occurring during the winter months since 1974 at the HBEF (Fig. 4). During the period (1974–2010), there was a 7 % decline ($p < 0.01$) in amount of precipitation that fell as snow (42 days/year and 12 % of annual volume) and an 8 % increase ($p < 0.01$) in precipitation that fell as a mixture of rain and snow (~20 days/year and 17 % of annual volume). These changes in type of precipitation track well with other measures of climate change at HBEF (e.g., Hamburg and Cogbill 1988; Campbell et al. 2007; Huntington et al. 2009; Likens 2011; Hamburg et al. 2013; Groffman et al. 2012). Climate change in the future will undoubtedly change various components of the hydrologic budget, including effects on chemical budgets at the HBEF, and may have wide-ranging ecological and

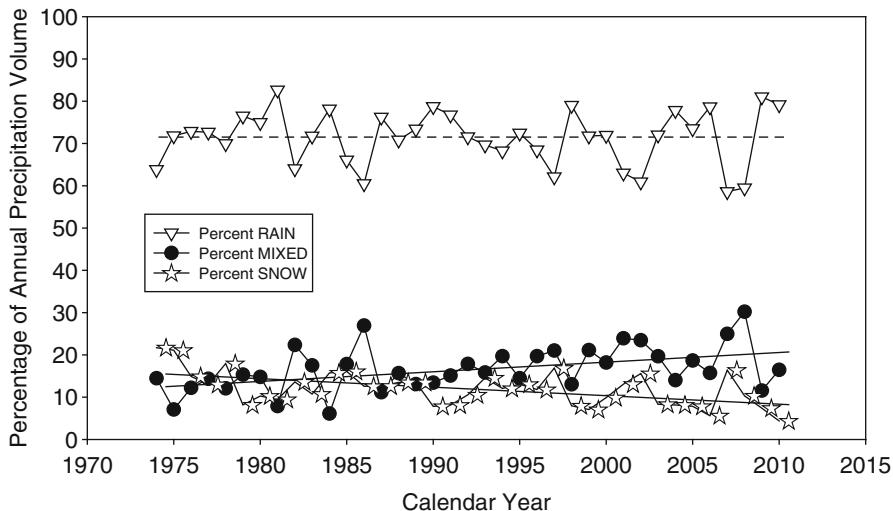


Fig. 4 Percent of total annual precipitation volume as rain (\triangledown), snow (\star), or mixed (\bullet) in Watershed 6 of the Hubbard Brook Experimental Forest during 1963–2009. Rain trend (ns), snow decline ($p < 0.001$), mixed increase ($p < 0.004$)

biogeochemical consequences. Documenting and predicting these hydrologic and concurrent biogeochemical changes are difficult but ongoing at the HBEF (e.g., Campbell et al. 2011; Judd et al. 2011).

The concept of a normal or average water-year is of limited utility because interannual variation of precipitation is high. Although the long-term average was 143.4 ± 20.0 cm/yearss ($\bar{x} \pm SD$) during 47 years of record (1963–2009), in only 2 year has precipitation been within ± 10 cm of this value. The mean deviation from the average annual precipitation is 13.9 % at HBEF (W6) and is less than the expected mean variability, about 16 %, for similar rainfall areas of the world (Conrad 1941). In the driest water-year on record, 1964–1965 at HBEF, precipitation was 97.5 cm (streamflow, 49.6 cm), whereas in the wettest year, 1973–1974, it was 188.8 cm (streamflow, 140.1 cm). These values represented the extremes of wet and dry conditions relative to precipitation; they were 34 % less and 32 % greater, respectively, than the long-term average at the HBEF (W6). This range of 91.3 cm emphasizes the need for a long-term record to understand the ecosystem's hydrologic flux (Fig. 5). If the biogeochemistry for these ecosystems were based upon either of these years alone, estimates of meteorologic input and streamwater output of nutrients would have been quite misleading. Despite the occurrence of both “extreme” wet and dry years during the period of our study (1963–2009), the range of annual precipitation varied by less than twofold. This relative “stability” in the amount of precipitation for the HBEF imparts stability to the chemical budgets as well because the two are interdependent.

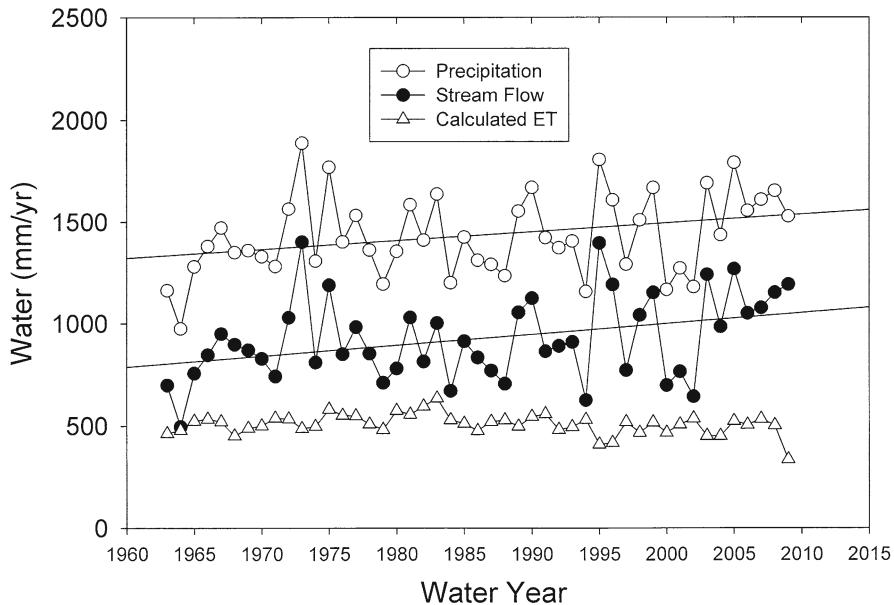


Fig. 5 Annual precipitation (P), streamflow (RO), and evapotranspiration (ET) for Watershed 6 of the Hubbard Brook Experimental Forest. The regression lines indicate significant trends during 1963–2009. $ET = P - RO$. Each water-year is from 1 June to 31 May

Based on linear regression, amount of annual precipitation in the HBEF (W6) has increased significantly during 1963–2009 ($p=0.043$), but the variability is large ($r^2=0.09$). Likewise, streamflow has also increased during this period ($p=0.015$; $r^2=0.12$) (Fig. 5; see below). Campbell et al. (2011) found essentially the same result using nonparametric, Mann–Kendall statistics, but Hamburg et al. (2013) reported nonsignificant trends for a shorter period (i.e., through 2005). Precipitation amount and streamflow during 1963–2009 in W6 are distributed normally (Kolmogorov-Smirnov, $p>0.20$).

Historically, quantitative measurements of precipitation at the HBEF began in 1958. Nevertheless, records can be extended back in time by comparison with nearby weather stations. A comparison of monthly records of precipitation from W6 with monthly data from nearby Bethlehem, NH, where records exist since 1895, gave an r^2 of 0.55 (Fig. 6a). Using this relationship, the precipitation record for W6 at HBEF was extended back to 1895 (Fig. 7). Based on this extrapolation, several features of the precipitation amount over this 115-year period (1895–2010) become clear:

- (a) On average, the HBEF (W6) has become significantly wetter since 1964 (~64-mm increase between 1964 and 2009 and ~167-mm increase between 1985 and 2009).

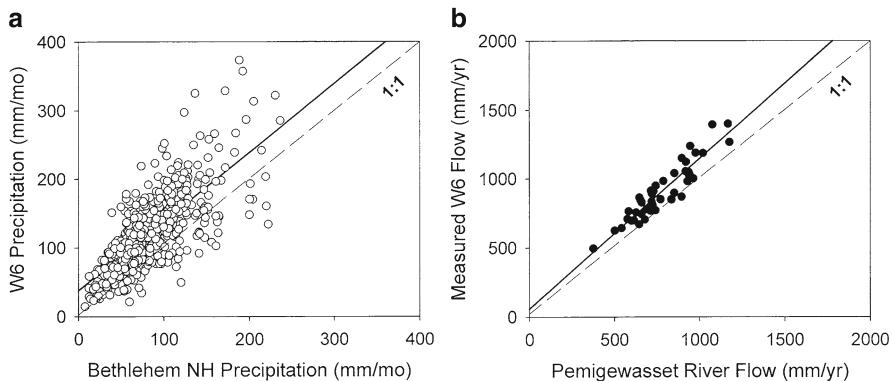


Fig. 6 Correlation between (a) average monthly precipitation for Watershed 6 of the Hubbard Brook Experimental Forest and precipitation at nearby Bethlehem, NH (NOAA Historical Climate Network) during 1963–2009 ($r^2 = 0.55$), (b) correlation between annual streamflow for Watershed 6 and the Pemigewasset River USGS gauging station in nearby Plymouth, NH ($r^2 = 0.86$)

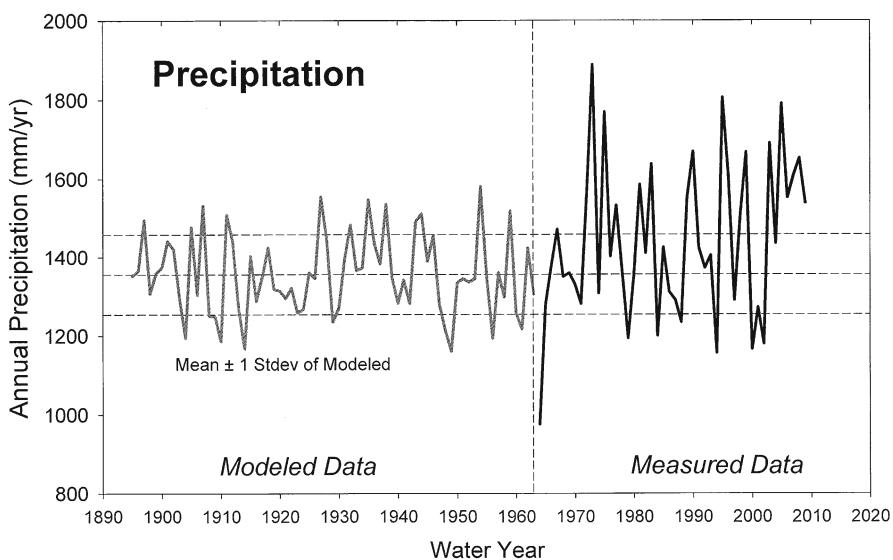


Fig. 7 Average annual precipitation for Watershed 6 of the Hubbard Brook Experimental Forest extended to 1895 based on a regression with nearby Bethlehem, NH. Dashed lines represent the mean ± 1 SD

- (b) Year-to-year variability in amount of precipitation has increased since ~1964 (the standard deviation for the annual mean value during 1964–2010 was more than two times higher than during 1895–1963; 1 standard deviation of the mean was exceeded in 22 years out of 48—5 below the mean and 17 above the mean).
- (c) The wettest and driest years occurred during the period of the HBES (1963–2010).

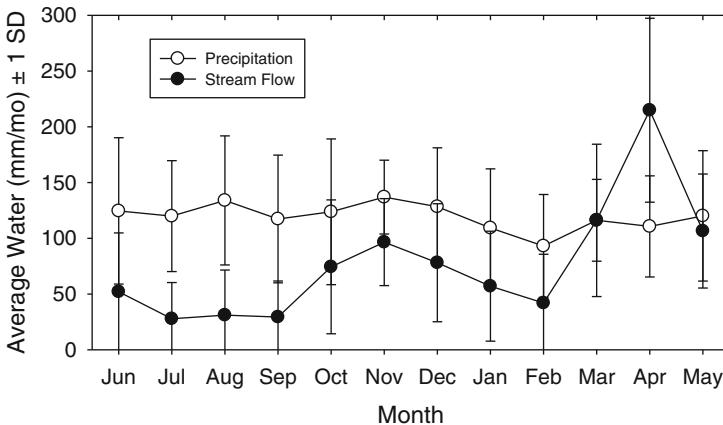
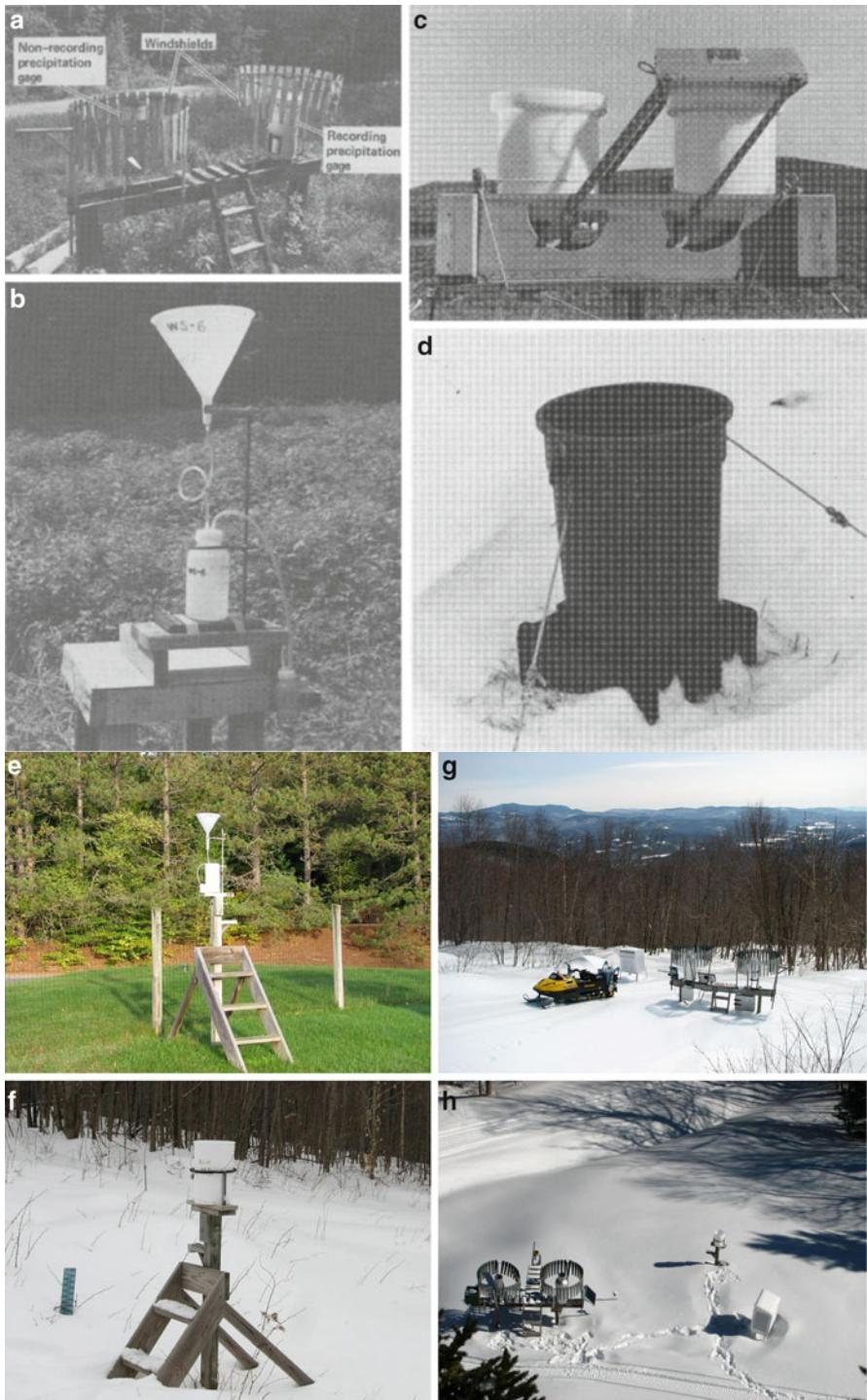


Fig. 8 Average monthly precipitation (open circle) and streamflow (filled circle) for Watershed 6 of the Hubbard Brook Experimental Forest during 1963–2009. The vertical bars are ± 1 standard deviation of the mean

In any particular year, monthly amounts of precipitation may show random variation, but for the longer term, the monthly pattern becomes quite regular (Fig. 8). The average amount of monthly precipitation shows very little seasonal variation. On average, November (13.7 ± 3.9 cm/month) is the wettest month and February (9.3 ± 4.7 cm/month) is the driest, but no month deviates widely from the overall monthly average of 11.9 ± 1.2 cm. Nevertheless, long-term data show that both precipitation and streamflow have significantly increased during the summer period, June through September (Photograph 5).

Streamflow and Evapotranspiration

Streamflow is measured continuously throughout the year by automatic recorders at stream-gauging stations, which include either a V-notch weir or a combination of V-notch and San Dimas flume (see Federer et al. 1990). The stream-gauging stations are anchored to the bedrock at the base of each watershed. Heating units in the ponding basin above the V-notch or in the flumes permit accurate measurements of streamflow during the coldest weather. In contrast to the monthly uniformity of precipitation, nearly half of the streamflow at the HBEF occurs in spring when the accumulated snowpack melts (Fig. 8). Some 47 % of the annual streamflow from W6 occurs during March, April, and May, with more than 23 % in April alone. During the summer months, streamflow is very low, particularly during July, August, and September (Fig. 8). During summer, water loss from the ecosystem occurs primarily through evapotranspiration. A secondary, minor peak in streamflow occurs in November and December when transpiration has virtually ceased after the loss of

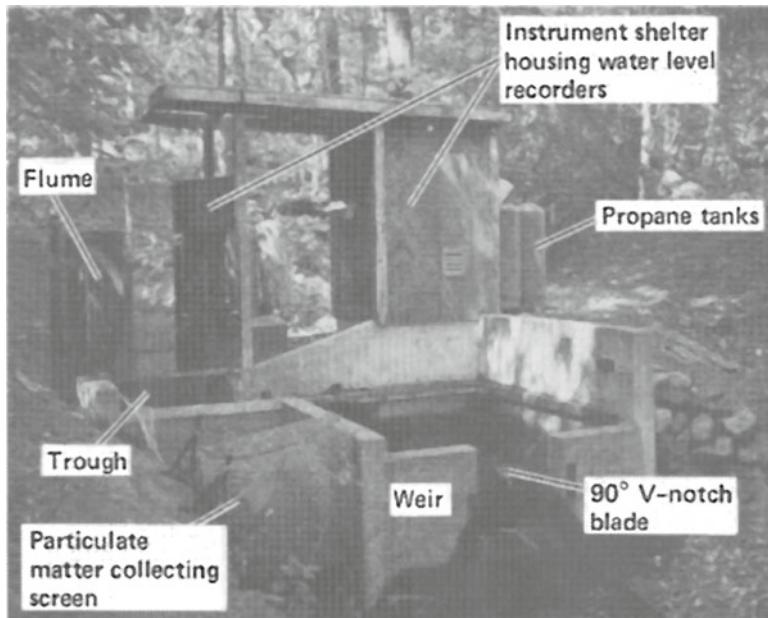


the deciduous leaves and with somewhat greater autumn rainfall. At that time, soil-water content increases and most of the rain moves through the soil and into the streams (Federer et al. 1990). Winter streamflow is diminished as precipitation accumulates as a snowpack of approximately 10 % density (water weight) with a capacity for storage of rain to a maximum of ~50 % density depending on snowpack conditions, such as temperature. Thus, when the snowpack finally melts, the runoff is a mixture of both melted snow and stored rain (Photograph 6).

On an annual basis, evapotranspiration in W6 has remained relatively constant (~51 cm/year) despite major fluctuations and a long-term increase of ~4.5 % ($p \leq 0.05$) in precipitation (Fig. 5). This result is in contrast to annual streamflow, which is highly correlated with the amount of annual precipitation (Fig. 9). New precipitation is generally subjected to evapotranspiration first, and once evapotranspiration demand is satisfied, the remainder of the precipitation leaves the watershed as streamflow. In a general way, this appears to be true, but a more detailed analysis suggests a more complex situation.

Streamflow during the months of June through September is linearly correlated with amount of precipitation ($r^2=0.75$). Calculating evapotranspiration during the growing season, June through September, shows that evapotranspiration is relatively constant (35–45 cm) until precipitation falls below ~50 cm. Below 50 cm, the seasonal evapotranspiration can fall as low as 20 cm as trees shut down their transpiration demand. Calculated evapotranspiration cannot match potential evapotranspiration when precipitation falls below ~40–50 cm (water limited), and evaporation is energy limited (sensu Budyko 1974) when precipitation is above ~45 cm (Fig. 10). Interestingly, evapotranspiration seems to peak at a maximum of ~45 cm during the growing season, and streamflow is zero at precipitation of ~30 cm (Fig. 10). Although these data are approximate, because we do not account

Photograph 5 (a–d) Precipitation collectors. Various types of precipitation collectors used at the HBEF circa 1960s and 1970s. Collectors are located in clearings within the forest to avoid contamination. No overhead obstruction is allowed above an angle of 45° from the opening of the collector. Collectors are positioned at least 2 m above the ground. (a) Gauges for quantitatively monitoring amounts of precipitation (rain and snow). *Left:* Standard United States Weather Bureau nonrecording gauge with 20.3-cm orifice. *Right:* Weight-activated recording gauge. Alter-type windshields reduce wind velocity around gauge opening to provide a sample equivalent to deposition on ground. A mixture of ethylene glycol and methanol is added to gauges in winter to convert snow to liquid state. (b) A polyethylene apparatus used for collecting bulk precipitation for chemical analysis consisting of a 28-cm diameter funnel, tubing, 2-L reservoir, and vapor barrier. Samples are retrieved and a clean apparatus installed at 1-week intervals. (c) An automatic sampler for the collection and separation of wet and dry deposition for chemical analysis. Water on heated sensor activates the mechanism to move the lid from one bucket to the other at the beginning of wet and dry periods. (d) Plastic garbage can used to collect snow for chemical analysis. Samples are retrieved and a clean collector installed at 1-week intervals. (e–h) Precipitation collectors used at HBEF currently. (e) A PVC pipe shielded bulk precipitation collector in fenced clearing at the Robert S. Pierce Ecosystem Laboratory, (f) a 21-L polyethylene bulk precipitation collector for use during winter, (g, h) winter scenes showing weather stations in the Hubbard Brook Experimental Forest (g–h, photos by D.C. Buso)



Photograph 6 Stream-gauging weir. Tandem arrangement of modified San Dimas flume and V-notch weir for monitoring streamflow on Watershed 6. The metal flume on the *left* measures high flows; the 90° sharp-edged, V-notch weir on the *right* measures low flows. The gauging station is built on bedrock so that all streamflow is channeled first through the flume and then into the weir. Recording instruments in shelters for both flume and weir monitor streamflow continuously. Propane burners are used during the winter to prevent freezing at the notch. Large particulate matter transported by the stream during high flows is caught either in the screen as the flow cascades from the flume over the trough, bypassing the V-notch, or in the ponding basin behind the V-notch. This particulate matter is removed annually and weighed. Gauging stations similar to this one or utilizing a V-notch weir only have been established on nine experimental watersheds in the HBEF (see Fig. 2)

for changes in stored soil water, they suggest a certain reasonable logic about the hydrologic behavior of these watershed-ecosystems.

Obviously, the vast majority of the transpiration for this northern hardwood forest ecosystem occurs during the growing season from about 15 May to 15 September. The seasonal importance of transpiration was demonstrated experimentally by a deforestation experiment on Watershed 2 of the HBEF (see Hornbeck et al. 1970; Likens et al. 1970; Bormann and Likens 1979). Transpiration may account for about 60–70 % of the evapotranspirational water loss on an annual basis at HBEF (C.A. Federer, personal communication), but transpiration is difficult to quantify at large scales like a watershed. There is a major need for additional quantitative measurements to partition evapotranspiration into evaporation from the forest canopy and the ground and transpiration. The relationship between annual precipitation input and streamflow continues to be quite robust in the long-term record ($r^2=0.94$; $p<0.001$) even though there has been a statistically significant increase in both

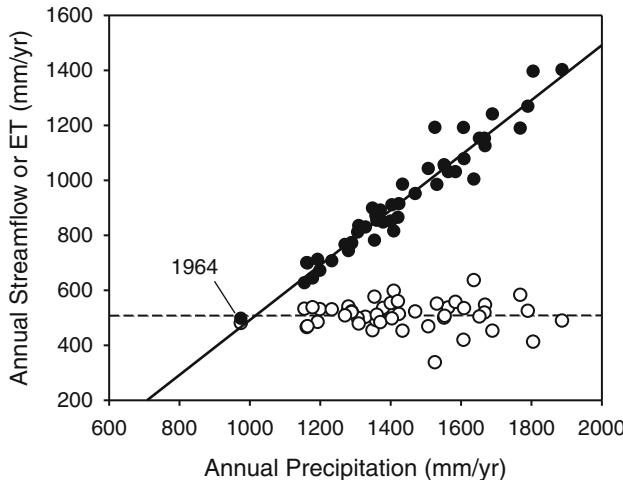
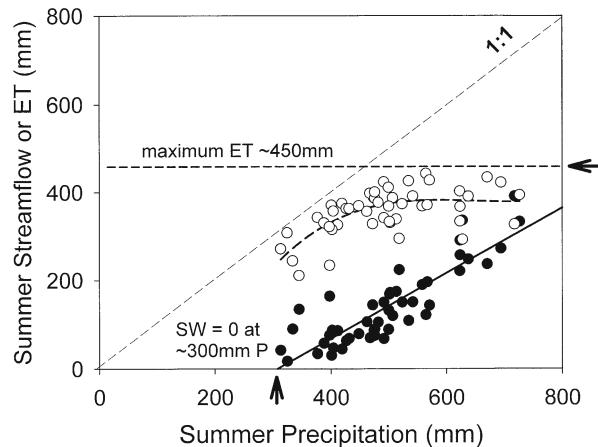


Fig. 9 Relationship between annual precipitation and annual streamflow (*filled circle*) and annual evapotranspiration (*open circle*) for Watershed 6 of the Hubbard Brook Experimental Forest during 1963–2009. Calculated evapotranspiration is determined as the difference between the amount of precipitation and streamflow. The relation between streamflow and precipitation has a slope of 0.99, $r^2=0.94$, $p<0.001$

Fig. 10 Relationship between precipitation and streamflow (*filled circle*) and evapotranspiration (*open circle*) during June through September for Watershed 6 of the Hubbard Brook Experimental Forest during 1963–2009



precipitation ($p=0.043$) and streamflow ($p=0.015$) during the period 1963–2009 (Fig. 9). The relationship of precipitation to annual evapotranspiration appears to be changing during the wetter years of 2003 through 2009, with calculated evapotranspiration (336 mm) in 2009–2010 being the lowest on record (Fig. 5).

The relationship between evapotranspiration and precipitation underscores the powerful regulating role that the living components of the ecosystem play in the hydrologic cycle. During the active growing season, evapotranspiration (mostly

Table 3 Annual hydrologic budget for four watershed-ecosystems of the Hubbard Brook Experimental Forest during 1979–1980^a

watershed-ecosystem	Area (ha)	Precipitation (cm)	Streamflow (cm)	Evapotranspiration ^b (cm)
W1	11.8	113.7	71.4	42.4
W3	42.4	113.9	69.3	44.6
W5	21.9	115.5	70.2	45.3
W6	13.2	119.3	70.8	48.5
Mean		115.63	70.41	45.21
Standard error of the mean		1.30	0.45	1.27
% of the total	100		61	39

Data prior to watershed manipulations applied to W1 (1999) and W5 (1983–1984)

^aModified from Likens et al. (1985)

^bPrecipitation minus streamflow; such estimates of annual evapotranspiration do not consider differences in soil–water storage from year to year. Estimates of such storage differences between years, based on the BROOK model (Federer and Lash 1978), rarely exceed 4 cm and commonly are less than 1 cm. Neglecting changes in soil–water storage could lead to errors of up to 7 % in estimating annual evapotranspiration

transpiration) is an important factor in regulating the amount of streamflow. Evapotranspiration then not only acts as a regulator for the hydrologic cycle but also contributes to tighter nutrient cycles by (1) diminishing streamflow that can carry nutrients out of the ecosystem, (2) by effectively concentrating the inputs from precipitation, and (3) increasing nutrient uptake as a function of transpiration.

Seasonal streamflow varies by orders of magnitude, whereas interannual streamflow varies by no more than twofold and is usually less. Because the chemical flux is so intimately tied to the hydrologic cycle, seasonal hydrologic events have corresponding effects on the seasonal chemical budgets (see Chap. 4). In contrast, the annual hydrologic budget, with its relatively small variability, imparts long-term stability to the associated annual chemical budgets, as is shown in subsequent chapters.

Some differences in hydrology exist between the experimental watersheds (W1–W6) largely related to east–west orientation. On average, about 78 mm/year or 5.4 % more precipitation falls on the westernmost experimental watershed, W6, in comparison with the most easterly south-facing watershed, W3 (see Fig. 2; Federer et al. 1990). Overall, however, differences between these south-facing watersheds of the HBEF are small (Table 3), which further demonstrates the utility of the paired small watershed approach at the HBEF.

In general, erosion rates are low and relative soil stability is high at the HBEF since glacial retreat from this area (M. Davis et al. 1985; Bormann and Likens 1979; Kaste et al. 2007). A factor of prime importance in regulating erosion and streamwater chemistry is that the HBEF soils have a high infiltration capacity. Because the surface soil is very porous, virtually all incident precipitation, rain or snowmelt, percolates through the soil even during the largest storms. Overland flow, where infiltration rate is exceeded, is not manifested at HBEF except in a few saturated boggy areas and in channels (Pierce 1967) or temporarily during extreme rainfall

events or extreme soil frost events. The downhill flow of water toward stream beds is by lateral subsurface interflow (Detty and McGuire 2010b). The soil usually remains unfrozen during the coldest months because of the thick humus layer and a deep snow cover (Hart et al. 1962). There is long-term potential, however, for increasing soil frost because of changing climate (e.g., Groffman et al. 2001, 2006; Judd et al. 2011). The surface topography is rough (pit and mound), which also facilitates infiltration rather than overland flow. Because the geologic substrate is essentially watertight, losses of water by deep seepage are minimal, and areas of non-vegetated, exposed bedrock ledge are minimal, almost all water has intimate contact with the biologic and inorganic components of the soil and subsoil as it moves downhill toward the stream channel. Frozen conditions in the stream channels add still further to the control of particulate matter losses in stream water as erodibility in winter months normally is less than that during the growing season (Bormann et al. 1974). There have been two incidents of midwinter channel erosion, in 1980 and 2011, when rain on snow caused “slush” avalanches in several streams. In these exceptional situations, these streams had a thick ice layer that permitted a snow/ice slurry to build up momentum and scour the channel.

The actual path that water follows as it flows through the soil and/or downslope is of great importance biogeochemically. Much effort has been expended at HBEF to quantify these relationships. For example, Stresky (1991) found that macropores, or “pipes,” were common in the soils of the experimental watershed-ecosystems at HBEF. He found that the average macropore was 2.5 cm in diameter (0.5–7.5 cm) and was 16 cm deep in the soil (2–130 cm) but comprised only about 0.2 % of the area of soil profiles examined. Patterns of hillslope hydrology have been studied at HBEF by Shattuck (1991), Mau (1993), and Detty and McGuire (2010a, b), which have provided new insight about streamflow and solute generation. Lawrence and Driscoll (1990) suggested that a combination of factors, including spatial variability in soil type and depth, modification of soil profiles adjacent to stream channels because of lateral flow patterns, macropore flow, and vegetation type, determines the spatial and temporal patterns of streamwater chemistry observed at HBEF. The work of Detty and McGuire (2010a, b) demonstrates the presence of shallow ground water at HBEF, and the importance of soil moisture and groundwater thresholds that must be met before hillslopes can contribute substantially to streamflow. Recent work by Zimmer et al. (2012) has shown that lateral flow paths can have a major affect on soil development and streamwater chemistry, particularly in the headwaters.

Deep Seepage

One of the key features of the HBEF that enables a close accounting of water budgets is the relatively watertight bedrock. Precipitation entering a watershed must leave by three avenues: (1) evaporation from leaf and soil surfaces, or both, to the atmosphere; (2) deep seepage, including lateral transfer through soil and bedrock

across watershed boundaries and vertical movement through deep geologic strata; and (3) streamflow. Direct measurement and quantification of evapotranspiration via eddy covariance methodology in steep terrain like HBEF and deep seepage and lateral transfer loss of water are extremely difficult to accomplish. Streamflow, however, can be measured readily and with a fair degree of accuracy in many watersheds.

When there are strong indications that a given watershed has relatively impermeable bedrock such that deep seepage is minimal and streamflow can be measured quantitatively, then the other major component of the water budget, evapotranspiration, can be calculated as the difference between streamflow and precipitation. Reasonable determinations of these components of the water budget for an entire water-year are feasible provided the water-year begins when storage of soil water is consistent each year (see above).

There is substantial evidence suggesting that the south-facing experimental watersheds at the HBEF have reasonable watertight bedrock and therefore have negligible water loss through deep seepage. Findings from a report of a geologic survey conducted at the HBEF by Bradley and Cushman (1956) point out that piezometric surface divides tend to coincide with the shape of the topography. Unconsolidated deposits lie entirely within valleys, which are rimmed by walls of bedrock. The Littleton formation (an intensely metamorphosed rock, currently mapped as the Rangeley Formation) is crossed by several sets of joints although openings are not large. These may extend one to a few meters below the surface, but their size and number decrease with depth. Only relatively small quantities of water occur in and move through these cracks. Based on these findings, Bradley and Cushman concluded that it is improbable that measurable quantities of ground water move from one watershed to another or that measurable quantities of ground water escape from the watershed through major fault zones or solution openings.

Further evidence for minimal deep seepage comes from comparison of the experimental watersheds. Assuming that two small adjacent watersheds have reasonably similar precipitation, vegetative cover, soil, and evapotranspiration, then streamflow on a unit area basis should also be similar. If there were considerable deep seepage, however, then streamflow from the two watersheds would likely be widely dissimilar. A comparison of streamflow among Watersheds 1, 3, 5, and 6 (11.8, 42.4, 21.9, and 13.2 ha, respectively) for 12 water-years was made using an analysis of variance. The forest on Watersheds 2 and 4 was cut in 1965–1966 and 1970–1974, respectively, and therefore these two watersheds cannot be used in the long-term simultaneous comparisons of streamflow with Watersheds 1, 3, 5, and 6 (Watershed 5 was whole-tree harvested in 1983–1985). In spite of wide variability in yearly streamflow during the period, e.g., 496 mm to 1,401 mm, there was no significant difference in streamflow among Watersheds 1, 3, 5, and 6. Because streamflow was virtually the same for each watershed, we conclude that the chances of deep seepage are negligible.

As stated previously, if water loss through deep seepage were negligible, then evapotranspiration should approximate precipitation minus streamflow (runoff) for the common water balance equation: $ET = P - RO \pm \Delta S$, where ET is evapotranspiration, P is precipitation, RO is streamflow, and ΔS is the change in storage of soil

water. Over the course of an entire year, we assume that the change in storage of soil water is zero as discussed above. Hart (1966) compared $P - RO$ values for Watersheds 1 and 3 (HBEF) for 5 years with calculated values of potential evapotranspiration based on the method by Thornthwaite (1948). Potential evapotranspiration, PE, is defined as the evaporation that would occur from a large fully wetted surface, that is, one with an unlimited water supply (Sellers 1965). The average water-year values for Watersheds 1 and 3 for a 5-year period (1958–1963) were 56.2 cm for PE and 53.2 cm for $P - RO$. There are several empirical methods for estimating PE (Thornthwaite 1948; Penman 1956; Hamon 1961), and PE calculations by each of these vary slightly; in general, however, such values of PE for HBEF are reasonably close to 56 cm. Actual evapotranspiration should be slightly less than PE except in rare cases. For practical purposes, the values of $P - RO$ at the HBEF can be considered as close approximations of actual evapotranspiration. The remarkable closeness of the values of $P - RO$ and PE indicates that water loss from deep seepage is not a significant factor in the water balance at the HBEF (see Fig. 9).

Chloride has not accumulated in sizeable quantities within these watershed-ecosystems in aggrading living or dead biomass since 1982 (~32 mol Cl/ha-year; Lovett et al. 2005). Moreover, chloride-bearing rocks in the HBEF are minor and release of chloride via weathering is thought to be small (~2.5 mol Cl/ha-year; Lovett et al. 2005; Chap. 5). Therefore, if losses by deep seepage were negligible, then inputs in wet and dry deposition should be observed quantitatively in the streamwater outputs from the ecosystem. In fact, annual mass balances, particularly since 1982 show small net ecosystem losses, and analyses do not suggest significant “hidden” losses (see Chap. 4 and 6).

Finally, if there were significant inputs or outputs of groundwater, then streamwater chemistry should change during low-flow periods. Such changes are not observed in the long-term record (see Chap. 3). Also, spatially dispersed chemical hot spots associated with groundwater seeps have been observed and measured for a long time at the HBEF (e.g., Dominski 1971; Mulder 1980; Likens and Buso 2006). Recently, Zimmer et al. (2012) looked more closely at ephemeral and intermittent channels, and groundwater seeps in headwaters of W3 and suggested that the high levels of solutes found there might indicate water moving through deep glacial till or fractured bedrock. Pockets of glacial till can be relatively thick in these watersheds and where compacted has lower permeability to water. Undoubtedly there is some deep seepage (in and out) in these watersheds, but the robust trend toward extremely dilute conditions in stream water observed currently (Chap. 3; Likens and Buso 2012) would be very difficult to explain at the watershed scale if deep seepage were sizeable in W6.

Thus, based on the long-term record, we have no basis to reject our assumption about the relatively watertight nature of the experimental watershed-ecosystems of the HBEF (Federer et al. 1990). This feature of these watershed-ecosystems is of great importance for calculating quantitative mass balances of water and chemicals, as will be done in subsequent chapters.

Certainly some small amount of deep seepage, in or out, must occur but is negligible relative to the errors involved (Verry 2003) and to the watershed mass balances obtained for W6 of the HBEF.

Quantifying uncertainty of hydrologic measurements at HBEF is currently being reevaluated by computer simulations and sensitivity analyses of rain gauge networks and stream calibration data (e.g., Yanai et al. 2012). Here, the uncertainty for precipitation volume and streamwater discharge is estimated at $\pm 5\%$ on an annual basis (Hornbeck et al. 1970; Hornbeck 1973; Winter 1981; Bailey et al. 2003a, b). Any deep seepage gains or losses are likely to be much smaller.

Detailed and extensive studies of groundwater flow have been done in the watershed for Mirror Lake (e.g., Winter 1985; Paillet et al. 1987; Winter et al. 1989; Winter and Likens 2009). This large watershed, at lower elevation in the Hubbard Brook Valley and with deeper till and fracture-flow systems (Powers et al. 1999), has different hydrologic characteristics than those of the experimental watersheds. Nevertheless, groundwater inputs to Mirror Lake comprised only $\sim 16\%$ of the annual water inputs to the lake (Rosenberry and Winter 2009).

Representativeness of the Hydrology of the Hubbard Brook Experimental Forest for Northern New England

One of the main concerns about small experimental watersheds is whether the research results obtained can be interpreted and extended to other, larger watersheds. Climate, soil, geologic formation, topography, vegetative cover, and past land use all vary from place to place, yet they play important roles in the behavior of water fluxes through a watershed. In light of the influences of these watershed features on water flow, the question arises: How representative is the hydrology of the HBEF to other areas of northern New England? Fortunately, there is one watershed characteristic that integrates the influences of most landscape features into a single measurable characteristic—streamflow. Considerable insight into the inner workings of a watershed-ecosystem can be obtained by continuously monitoring the flow from that watershed over long periods of time.

In a comprehensive study of streamflow characteristics of watersheds in northern New England, Sopper and Lull (1965, 1970) addressed the question of representativeness of small experimental watersheds. They compared streamflow from eight watersheds in Maine, New Hampshire, Vermont, and Massachusetts with Watershed 1 (W1) at the HBEF.

Data adapted from Sopper and Lull are presented in Table 4. The eight watersheds were chosen on the basis of being less than 259 km^2 (100 mi^2) in size, being 90 % or greater forest covered, having streams that were undisturbed by diversion or regulation, and having relatively complete records of precipitation and streamflow—the latter having simultaneous periods of records from 1 December 1956 to 30 November 1962. Annual and seasonal streamflow at the HBEF were very close to the average of the eight regional watersheds and fell within the maximum and minimum values for all periods.

Direct streamflow (that portion of the annual streamflow that rapidly leaves the watershed during and after storms, as opposed to prolonged base flow) for W1 of

Table 4 Hydrologic characteristics for selected watersheds in northern New England^a

Stream and location	Area (km ²)	Forest cover (%)	Precipitation (cm)	Average annual and seasonal water yield (cm)					Direct runoff, % of annual		
				Annual	Spring	Summer	Fall	Winter			
Austin Stream, ME	236	95	120.7	72.3	36.0	9.4	14.8	12.1	28.5	43.8	16.4
Swift River, ME	249	97	126.0	72.0	37.3	9.2	15.9	9.6	33.1	38.9	22.5
Ashuelot River, NH	184	94	113.2	58.4	32.7	3.6	10.5	11.6	15.7	42.7	11.0
N. Br. Contoocook R., NH	142	95	129.8	66.8	34.0	3.9	13.8	15.1	18.7	48.1	8.5
Otter Brook, NH	109	93	114.2	57.7	31.5	3.9	10.5	11.8	15.6	42.1	8.4
Smith River, NH	223	95	119.0	56.3	32.1	4.6	9.1	10.5	16.6	39.7	11.8
Saxtons River, VT	186	92	118.1	52.2	30.5	3.4	8.2	10.1	13.2	39.0	14.4
N. Br. Hoosic River, MA	104	90	155.5	74.8	38.9	6.3	13.2	16.4	20.6	54.2	23.8
Regional average	179	94	124.5	63.8	34.1	5.5	12.0	12.2	20.2	43.6	14.6
HBEF, WI	0.12	100	124.6	70.4	36.9	3.5	15.3	14.7	16.7	53.7	21.3

^a After Sopper and Lull (1965, 1970)

the HBEF was high, as expected, but was less than direct streamflow from two other watersheds, one of which was much larger in size, 249 km².

Additional comparisons made by Sopper and Lull (Table 4) indicated close similarities in streamflow characteristics between experimental and regional watersheds, such as (1) number and amount of mean daily discharge above a given volume of flow and (2) flow duration (percent of time flow was equaled or exceeded).

In general, streamflow in small watersheds tends to have sharper peaks, higher storm levels, and shorter periods of sustained flow than it does in large watersheds. Such streamflow characteristics in small watersheds may be accentuated in steep, mountainous terrain with shallow soils. Watersheds at the HBEF have these characteristics, but it is remarkable and reassuring that streamflow at HBEF, e.g., in a watershed (W1) of 0.12 km², closely approximates flow from watersheds that are more than three orders of magnitude greater in size! Further, the HBEF watersheds show behavior that is similar to the river they feed. Comparing the flow in the Pemigewasset River into which Hubbard Brook drains, with flow from W6 on a unit area basis (Fig. 6b), showed a strong correlation during 1963–2006 ($p \leq 0.001$, $r^2 = 0.86$). The much larger Pemigewasset River drains an area of 1,611 km² at the U.S. Geological Survey gauging station in Plymouth, NH (Slack et al. 1997). This strong relationship provides an excellent proxy for long-term streamflow from HBEF, as the Bethlehem precipitation station provides a proxy for precipitation prior to 1958, because the Pemigewasset River gauge has been operating since 1886.

The close relationships between streamwater quantity for streams in the HBEF and larger streams throughout northern New England add considerable support to the contention that HBEF streams are representative in many ways and that research results from the HBEF can be useful in extension and application to other areas for management purposes and for increasing ecological understanding at larger spatial scales.

Chapter 3

Chemistry

Samples of precipitation and stream water are obtained from the experimental watersheds for chemical analysis. Rain and snow are sampled with continuously open plastic collectors, i.e., bulk precipitation samples (Likens et al. 1967; Buso et al. 2000) collected at weekly intervals. Samples of stream water are collected by hand each week and during high-flow events approximately 10 m upstream from each weir in clean polyethylene bottles. This location is necessary because water collected from the ponding basin above the weir could be contaminated by calcium and carbonate from the cement in the weir itself. The concentrations of dissolved chemicals characterizing a period of time are reported as volume-weighted averages. These averages are computed by summing the amount of chemical from individual samples of precipitation or stream water during the period and then dividing this value by the total amount of water during the period. Nutrient flux (see Chap. 4) across ecosystem boundaries is determined by two methods. Precipitation inputs are calculated by multiplying the measured concentration of dissolved chemicals in the accumulated composite sample of precipitation by the daily amounts of precipitation during the interval; the daily values (g/ha-day) are summed to provide mass inputs by week, month, or year (e.g., g/ha-month). Streamwater outputs are calculated by multiplying the measured concentrations of dissolved chemicals in streamwater samples taken at the beginning and at the end of the interval by the streamflow on those dates. For dates between samples, the average of the beginning and ending concentrations is multiplied by the daily flows. We have tested other approaches for determining streamwater export, but the approach described here gives the most accurate and reproducible results for the HBEF. Daily values (g/ha-day) are summed on a weekly, monthly, or yearly basis to derive mass streamwater outputs (e.g., g/ha-month).

It has been shown that sampling according to a standard time series may seriously underestimate or overestimate a highly variable parameter (e.g., Claridge 1970); however, most of the dissolved chemicals in stream water at the HBEF fluctuate relatively little in concentration so that serious errors are not produced by weekly sampling in most cases (Fig. 11; Likens et al. 1967; Johnson et al. 1969;

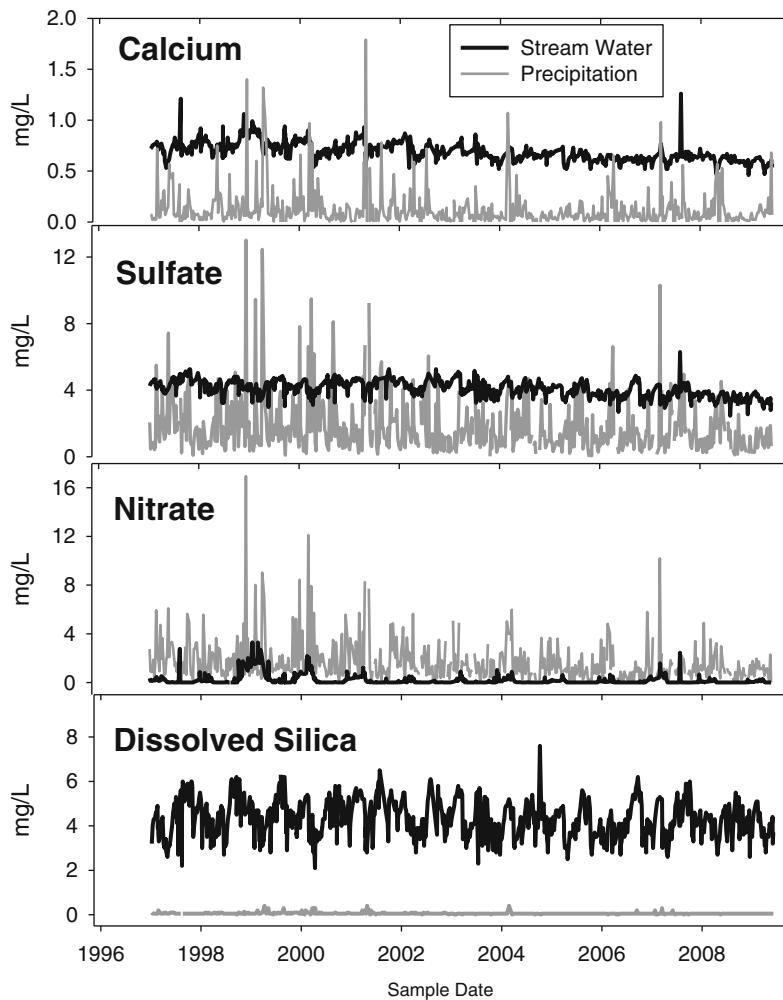


Fig. 11 Measured weekly, measured concentrations in bulk precipitation (gray) and stream water (black) for Watershed 6 of the Hubbard Brook Experimental Forest during 1996–2009

Buso et al. 2000). Concentrations of dissolved organic carbon, nitrate, hydrogen ion, and dissolved silica are more variable with instantaneous streamflow, but still show only several-fold change in concentration over >5 orders of magnitude change in instantaneous streamflow (Fig. 12).

As standard practice, we do not include data from bulk precipitation samples that contain fresh leaves, bird feces, bud scales, insects, or any other significant foreign particles. Such contamination can represent a serious problem, because a variety of substances can leach from these materials as the water comes in contact with them in the collector. Our intent is to have enough collectors in position to provide at least one “clean” sample per interval. This procedure normally works very well at our site.

From June 1963 to May 2010, 4 % of samples collected were rejected because of obvious contamination and 9 % failed QA/QC protocols. Considering the problems of contamination and biogeochemical transformations that can occur in the reservoir of a bulk precipitation collector, experience has shown that sampling intervals of not longer than a week are highly desirable, if not necessary, to obtain quantitative data on atmospheric deposition.

Details concerning the routine methods used in collecting samples of precipitation and stream water and analytical and data-management procedures have been given by Bormann and Likens (1967), Likens et al. (1967), Fisher et al. (1968), Bormann et al. (1969), and Buso et al. (2000).

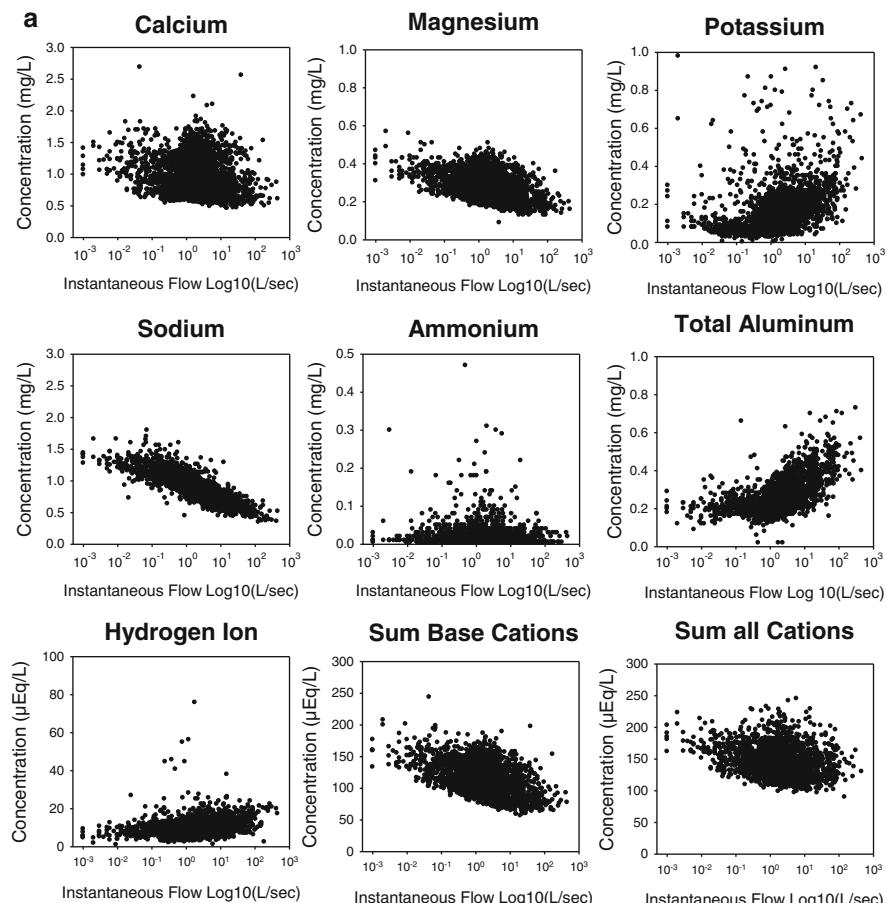


Fig. 12 Relation between (a) cation concentration in stream water and instantaneous streamflow during 1963–2010 and (b) anion concentrations in stream water and instantaneous streamflow during 1964–2010 for Watershed 6 of the Hubbard Brook Experimental Forest

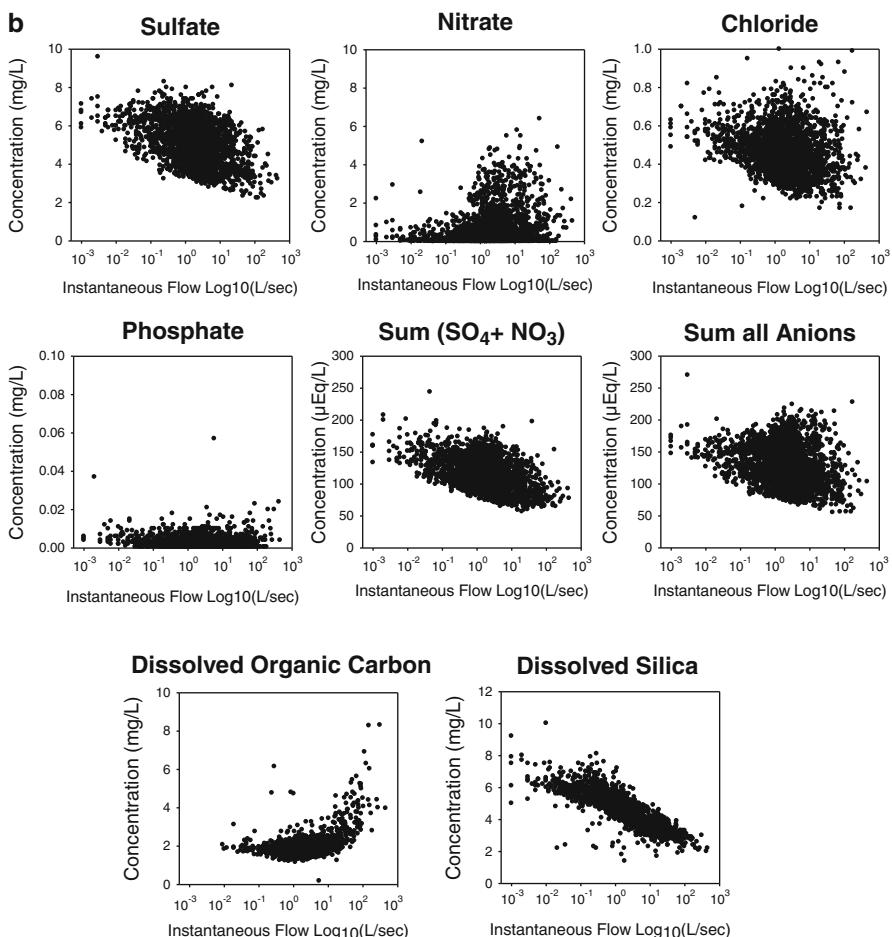


Fig. 12 (continued)

Precipitation Chemistry

Precipitation chemistry has been monitored at the HBEF since 1963. To our knowledge this unbroken series is the longest comprehensive record of precipitation chemistry in the world.

Annual Volume-Weighted Concentrations

The chemical concentration of precipitation has been dominated by hydrogen ions since 1963, constituting 67 and 48 % of the total cationic strength in 1965–1966 and 2009–2010, respectively. The remaining cationic charge is shared among

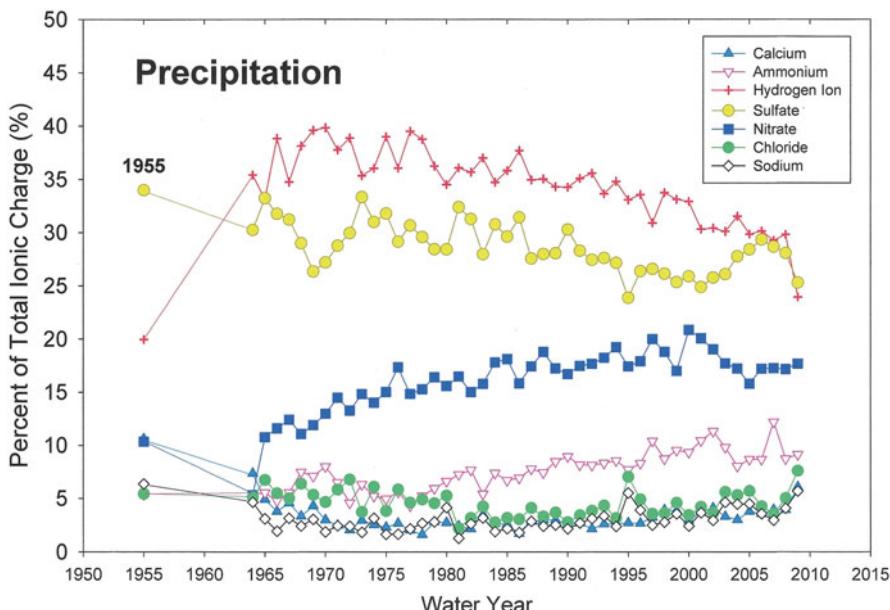


Fig. 13 Percent of total ionic charge in bulk precipitation for Watershed 6 of the Hubbard Brook Experimental Forest during 1963–2009. The values for 1955–1956 were extrapolated from isopleth maps produced by Junge (1958) and Junge and Werby (1958) (modified and extended from Likens and Bormann 1974b)

ammonium, calcium, sodium, magnesium, potassium, and aluminum, in that order (Fig. 13; Tables 5 and 6). Aluminum is found only in trace amounts. Bulk precipitation has become much more dilute since 1963, but the relative contribution of the various cations has remained the same (Likens and Buso 2012).

Although decreasing with time, sulfate and hydrogen ion are the most prevalent inorganic ions in bulk precipitation at the HBEF on an equivalent basis (Fig. 13; Tables 5 and 6). The relative importance of nitrate in precipitation on an equivalence basis has been generally increasing since 1964 (Fig. 13). Essentially, then, the incident precipitation at HBEF may be characterized as a solution of sulfuric and nitric acids at a pH < 4.6. Small errors (~0.05 pH unit) in the determination of pH, which has been used to estimate the concentration of hydrogen ion, are sufficient to explain the small discrepancy in the cation–anion balance of bulk precipitation (Tables 5 and 6), particularly in the early years of the study. Considering that these long-term averages include the various sampling and analytical errors over a 49-year span, the agreement in cation–anion equivalents is quite good.

Surprising concentrations of dissolved organic carbon are found in rain and snow at HBEF (Tables 5 and 6). Precipitation falling on the watersheds of the HBEF contains an average total organic carbon concentration of about 1 mg/L of which 84 % is dissolved (Likens et al. 1983). Only a small fraction of this organic matter is dissociated organic acids (Likens et al. 1976, 1983; Galloway et al. 1976) and does not

Table 5 Arithmetic means of volume-weighted average annual concentrations for Watershed 6 of the Hubbard Brook Experimental Forest during 1963–2009^a

A	Bulk precipitation			B			Stream water		
	Mean (μEq/L)	±SE (μEq/L)	n (obs) (years)	C of E (%)	Substance	Mean (μEq/L)	±SE (μEq/L)	n (obs) (years)	C of E (%)
Calcium	4.8	0.38	47	7.9	Calcium	48.4	2.15	47	4.4
Magnesium	2.3	0.21	47	9.1	Magnesium	21.5	0.70	47	3.3
Potassium	1.3	0.11	47	8.5	Potassium	5.2	0.15	47	2.9
Sodium	4.2	0.22	47	5.3	Sodium	31.5	0.41	47	1.3
Aluminum ^b	—	—	—	—	Aluminum	33.7	1.50	41	4.5
Ammonium	10.6	0.38	46	3.6	Ammonium	1.1	0.02	46	1.5
Hydrogen Ion	51.5	2.56	46	5.0	Hydrogen Ion	11.7	0.40	47	3.4
pH	4.29				pH	4.93			
Sulfate	42.3	1.98	46	4.7	Sulfate	102.1	2.83	46	2.8
Nitrate	22.8	0.77	46	3.4	Nitrate	14.4	1.94	46	13.5
Chloride	6.8	0.44	46	6.5	Chloride	12.8	0.39	46	3.0
Phosphate	0.4	0.04	38	11.5	Phosphate	0.1	0.01	38	12.0
Bicarbonate ^c	—	—	—	—	ANC ^d	-10.6	1.7	46	15.7
Dissolved organic carbon	—	—	—	—	Dissolved organic carbon	12.4	3.2	15	25.8
Dissolved silica (μmol/L)	—	—	—	—	Dissolved silica (μmol/L)	63.9	0.66	46	1.0
Total cations	74.7				Total cations	153.0			
Total anions	72.2				Total anions	141.8			
Organic carbon has a charge of μEq/L per mg C in stream water ^e					Aluminum assumed to have +3 valence state				

^aMeans in μEq/L (or μmol/L) ± 1 Standard Error of the Mean and the percent Coefficient of Error of the Mean (±SE/Mean)

^bOnly trace aluminum or dissolved silicon in clean precipitation

^cNo Bicarbonate at pH <5 (-ANC)

^dANC calculated from difference of sum (C_B) and sum (AA)

Table 6 Volume-weighted mean concentrations of dissolved substances in bulk precipitation for Watershed 6 at the Hubbard Brook Experimental Forest

Bulk precipitation	Decade 1964–1973		Bulk precipitation	Decade 2000–2009			
	Conc (mg/L)	Conc ($\mu\text{Eq}/\text{L}$)		Substance	Conc (mg/L)		
Water (mm/ha-year)	1,388		Water (mm/ha-year)	1,488			
Ca	0.15	7.5	Ca	0.07	3.5		
Mg	0.04	3.5	Mg	0.02	1.5		
K	0.06	1.5	K	0.04	1.0		
Na	0.12	5.1	Na	0.08	3.5		
NH_4	0.22	12.1	NH_4	0.16	8.9		
Al ^a	0	0	Al ^a	0	0		
H^+	0.073	73.1	H^+	0.028	27.6		
SO_4	2.85	59.3	SO_4	1.19	24.8		
NO_3	1.47	23.8	NO_3	1.07	17.2		
Cl	0.38	10.7	Cl	0.15	4.4		
PO_4^{b}	0.009	0.3	PO_4	0.003	0.1		
ANC (bicarbonate) ^c	0.0		ANC (bicarbonate) ^c	0.0			
Cations	102.7		Cations	46.0			
Anions	94.1		Anions	46.4			
DOC ^d	1	91.6	= $\mu\text{mol}/\text{L}$	DOC	0.8	68.4	= $\mu\text{mol}/\text{L}$
Silicon ^a	0	0	= $\mu\text{mol}/\text{L}$	Silicon ^a	0	0	= $\mu\text{mol}/\text{L}$
pH	4.14		pH	4.56			

^aAl and Si found in trace amounts in clean precipitation^b PO_4 based on 1971–1973^cBicarbonate = 0 at pH < 5^dDOC based on 1976–1977 (Likens et al. 1983)

contribute significantly to the ionic balance. The composition of the dissolved organic carbon in precipitation is undoubtedly a complex mixture of many organic species, most of which are present in trace amounts. During 1976–1977 particulate plus dissolved macromolecular (>1,000 MW) organics accounted for 51 %, and carboxylic acids represented 14 %, aldehydes 11 %, carbohydrates 8 %, and tannin/lignin 8 % of the total organic carbon in precipitation (Likens et al. 1983). Dissolved organic carbon in precipitation represents an additional energy source for the ecosystem and thus may be important ecologically and biogeochemically.

Origin of Ions in Bulk Precipitation

Cations and anions in precipitation originate from a variety of sources, including oceanic spray, terrestrial dust, gaseous and particulate pollutants, and volcanic emissions. How ionic materials find their way into a precipitation collector is an

important enigma. The solubility of atmospheric gases, such as CO₂, from either natural or anthropogenic origin, in atmospheric water is obvious, but the origin of nonvolatile constituents, such as sodium, magnesium, calcium, and potassium in precipitation is not so obvious. The dispersion of sea salts, such as NaCl and MgSO₄, in atmospheric aerosols is a well-known process (Junge 1963; MacIntyre 1974). Nevertheless, only a part of the calcium and potassium in precipitation can be reasonably attributed to marine sources, and the “excess” is customarily assigned to unknown “continental sources” (Junge 1963; Granat 1972; Cogbill and Likens 1974). At the HBEF the molar ratio for Cl:Na in bulk precipitation averaged ~2.3 prior to 1975 (peaking at 3.5 in 1976) or roughly double that anticipated from transported sea salt (1.2), suggesting transport of chloride to the HBEF from distant anthropogenic sources (Gorham 1958; Junge 1963; Lovett et al. 2005). Since ~1980 the Cl:Na ratio has approximated or been slightly higher than the sea-salt ratio (cf. Table 6; Junge 1963; Juang and Johnson 1967; Lovett et al. 2005). In contrast, the ionic Ca:Mg ratio for these periods is representative of continental precipitation (Eriksson 1952; Eaton et al. 1973).

One explanation for the excess cations in precipitation is that soil particles and industrially generated aerosols in the atmosphere may be chemically altered to produce cations. The ubiquitous hydrogen ions in precipitation may react with these entrained particles and release cations into solution (see subsequent sections). Therefore, some of the cations found in solution in a precipitation collector may have been derived from an “artificial weathering” reaction within the continuously open (bulk) collector such as used at HBEF. Such “weathering reactions” that occur within the precipitation collection reservoirs would not change the total amount of cations input to the ecosystem but might alter their chemical form or underestimate the input of hydrogen ion in precipitation.

It is important relative to quantitative meteorologic inputs to determine whether the dissolved and particulate materials in a bulk precipitation sample have originated outside the ecosystem’s boundaries or whether they have merely been circulating within the boundaries. Because the HBEF watersheds and the surrounding region (1) are almost entirely forested or have other vegetational ground cover, (2) have a long period of snow cover, and (3) have generally humid conditions during other seasons, we conclude that relatively little dust arises from within the ecosystem and that our bulk precipitation collectors measure dissolved and particulate matter that has largely originated outside the ecosystem’s boundaries. Consistent and rigorous application of our QA/QC protocols is an important constraint on this assumption.

Dry Deposition

Early in our studies, we were aware of the dry deposition of particles and gases from the atmosphere, but had little quantitative information relative to such fluxes for the ecosystems at HBEF (e.g., Eaton et al. 1976). Because dry deposition represents a potentially important input of nutrients and pollutants to forest ecosystems, much

effort has been expended to quantify this flux at HBEF. Bulk precipitation collectors may be very inefficient in collecting dry deposition, particularly aerosols smaller than 1 μm . Estimates, based on measurements of aerosol concentrations and a reasonable deposition velocity, suggest that the dry deposition of calcium, magnesium, sodium, and potassium, as measured in bulk precipitation, probably contributes a relatively small fraction (<~20 %) of total deposition inputs at HBEF (e.g., Likens et al. 1998). This is not necessarily the case for nitrogen and sulfur. Small aerosol particles and gases of nitrogen and sulfur may be generated from biogenic activity and from the combustion of fossil fuels. Both gases and small aerosols of these elements may be transported long distances in the atmosphere. These chemicals therefore exist in the atmosphere at HBEF in much higher concentrations than that expected from the local environment, and their dry deposition is seriously underestimated by bulk precipitation collectors. Using the long-term record and a mass-balance approach, Likens et al. (1990a) initially estimated that for sulfur, some 37 % of the total (wet plus dry) deposition annually occurred as dry deposition. Later work using stable isotopes (Alewell et al. 1999, 2000) showed that the mass-balance approach was not directly suitable for estimating dry deposition of sulfur for the HBEF.

Lovett et al. (1992) compared the results of three independent methods for estimating dry deposition of sulfur at HBEF: the mass-balance approach, a throughfall approach, and an inferential method using measured atmospheric concentrations and assumed deposition velocities. The results of these approaches give annual values that differed by about fourfold, with the mass-balance approach producing the largest value (Lovett et al. 1992). Likens et al. (2002a) considered various factors affecting the dry deposition estimates of sulfur at HBEF and the effect of uncertainties in these estimates on mass balances. They estimated dry deposition as 21 % of bulk deposition. More recently, the dry deposition of sulfur was estimated by using four different models based on regional values of SO₂ emissions. This approach gave dry deposition values for 2002 ranging from ~0.5 to 2.5 kg S/ha-year at the HBEF (Mitchell et al. 2011). Each of these approaches has assumptions and errors associated with it, and dry deposition remains an extremely complicated flux to measure quantitatively in forest ecosystems, particularly in mountainous terrain.

Currently, we operate an EPA-funded air quality and dry deposition monitoring site as part of the Clean Air Status and Trends Network (CASTNET). This site has been operational (at 250-m MSL, mean sea level) at HBEF since 1988. It uses an inferential method for estimating dry deposition, i.e., dry deposition fluxes are calculated as the product of measured ambient concentration and modeled deposition velocity (http://www.epa.gov/castnet/epa_jsp/sites.jsp).

Elevational Effects

There is no significant difference in the concentration of calcium, magnesium, sodium, or potassium in bulk precipitation at different elevations (from 545- to 758-m MSL) within the south-facing experimental watersheds of the HBEF (Likens

et al. 1967). Furthermore, a study done in 1971–1972 indicated no significant difference between the concentration of calcium, magnesium, sodium, potassium, ammonium, or chloride in bulk precipitation samples from the south-facing experimental watersheds at 610-m MSL and those from the U.S. Forest Service’s Robert S. Pierce Ecosystem Laboratory at 252-m MSL. However, based upon an analysis of paired samples from these two locations, the concentrations of sulfate and nitrate were significantly higher ($p < 0.01$ and $p < 0.05$, respectively) at the lower elevation. In a later, more comprehensive 10-year study done between 1978 and 1989, Martin et al. (2000) found no statistical difference for any ions collected with bulk precipitation collectors at the two elevations. The source of the higher values in the earlier study may have been related to human activity at the lower elevations, but this was not confirmed.

A recent analysis (2000–2009) of volume-weighted average monthly concentrations in three bulk precipitation collectors located at 252-m MSL, 550-m MSL (W6), and 640-m MSL (W9) showed no significant ($p > 0.05$) differences in any solute measured. Nevertheless, the largest differences observed were between 252-m MSL and the higher elevations demonstrating the importance of using bulk precipitation collectors co-located with the watershed ecosystems being studied.

Acid Precipitation

One of the more interesting and environmentally important discoveries from the Hubbard Brook Ecosystem Study was finding high acidity in rain and snow at HBEF (Likens et al. 1972; Likens 2010). The first sample of rain collected at the HBEF in July 1963 had a pH value of 3.7. The average annual weighted pH from 1964 to 1965 was 4.03 (Fig. 14); the lowest value recorded for a storm at HBEF during 1963–2009 was pH 2.85, and the highest value was 5.85 during 1963–2009. During the early years of the study (1963–1974), no value for weekly precipitation exceeded a pH of 5.0. Such acidic precipitation is decidedly abnormal chemically because pure water in equilibrium with atmospheric concentrations of CO₂ should have a pH of not less than about 5.6 (Barrett and Brodin 1955). In other words, the precipitation at HBEF had a hydrogen ion concentration 50–500 times greater than expected during this early period.

The increased acidity of precipitation is the result of anthropogenic emissions of SO₂ and NO_x from the combustion of fossil fuels, which are hydrolyzed and oxidized to strong acids (H₂SO₄, HNO₃) in the atmosphere (Bolin 1971; Likens et al. 1972; Likens and Bormann 1974a; Likens 2010). The occurrence of acid precipitation at HBEF, which is >100 km distant from any large urban-industrial area, emphasizes that one of the major ways humans can influence natural ecosystems is through pollution of the atmosphere and that these effects are not limited to areas adjacent to sources of pollution (Likens et al. 1979; Likens 1984).

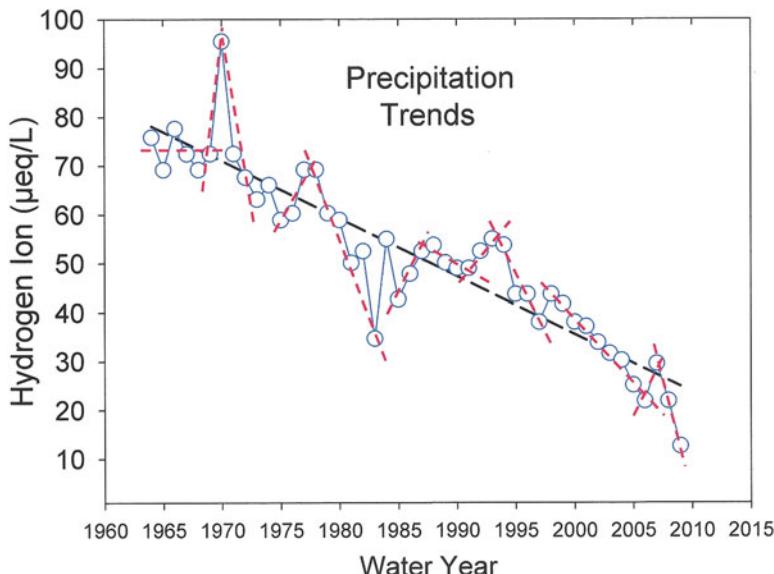


Fig. 14 Volume-weighted annual concentration of hydrogen ion in bulk precipitation for Watershed 6 of the Hubbard Brook Experimental Forest from 1963 to 2009. The linear regression is highly significant ($p < 0.01$, $r^2 0.84$). The shorter *dashed lines* are fitted by eye

During the 1970s and 1980s, the acid rain debate in the USA and Europe was in full swing (Likens 2010). The First International Symposium on Acid Precipitation and the Forest Ecosystem was held in 1975 at Ohio State University. We helped to organize this Symposium and participated in it. Numerous studies of the ecological impact of acid rain were underway at the HBEF by 1975, but the backbone of our research on this important environmental problem was the developing long-term record of precipitation and streamwater chemistry. Partly on the basis of this long-term record of precipitation chemistry at HBEF, the U.S. Congress enacted amendments in 1990 to the 1970 Clean Air Act, which for the first time explicitly included provisions for regulating acid rain. Both of these regulations reduced emissions of SO_2 and particulates and impacted precipitation concentrations at HBEF. The 1990 Amendments to the Clean Air Act called for a reduction of 10 million tons (9.1 million metric tons) in SO_2 emissions/year and reductions of 1.2 million tons (1.1 million metric tons) in NO_x emissions/year below 1980 levels by the year 2000. Additional reductions in NO_x emissions were required after 2000 (see <http://www.epa.gov/airmarkets/progsregs/arp/nox.html> and <http://www.epa.gov/airmarkets/progsregs/arp/reductions.html>). Acidity of bulk precipitation decreased during this period, but some 18 years of continuous monitoring were required before we could report that the acidity at the Hubbard Brook Experimental Forest was significantly reduced (Fig. 14; Likens 1989). During the past 45 years, hydrogen ion has decreased 54 $\mu\text{Eq/L}$ ($r^2 0.84$; Fig. 14).

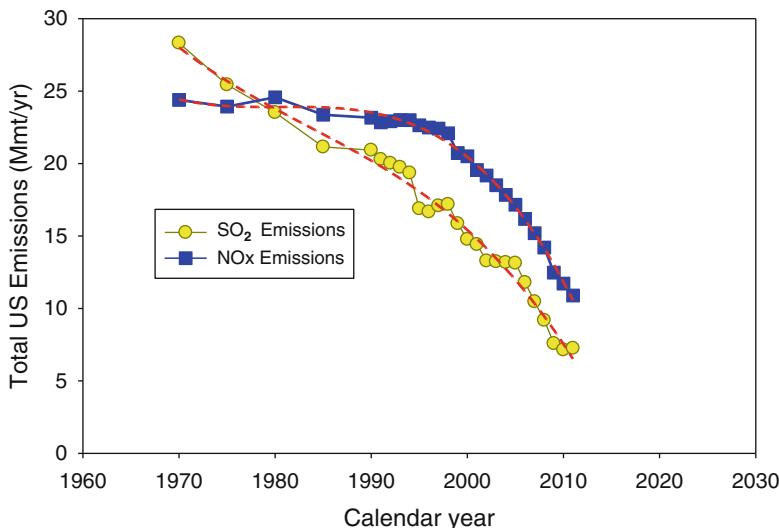
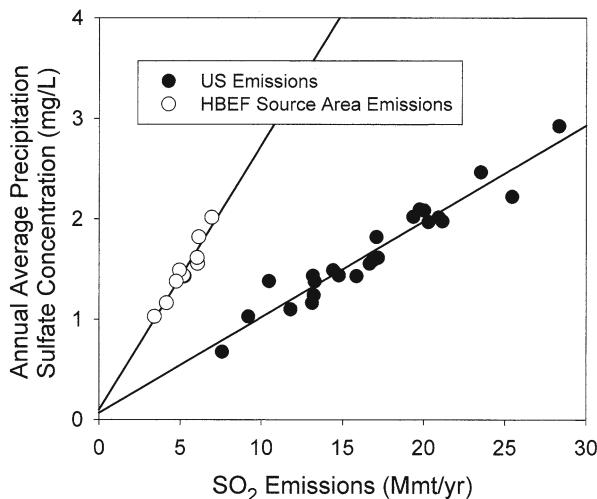


Fig. 15 Total US emissions of SO₂ and NO_x for calendar years from 1970 to 2010. The third-order polynomial regressions have r^2 of 0.99. Data from U.S. Environmental Protection Agency

The sources, distribution, and ecological effects of acid rain have been studied in North America during the past four decades, and much has been learned (e.g., Likens et al. 1972, 1979, 2001, 2012; Cogbill and Likens 1974; Likens and Bormann 1974a; Schindler et al. 1985; Charles 1991; Likens 1998, 2010; Driscoll et al. 2001; Weathers et al. 2007). The HBEF is an important site for monitoring atmospheric pollutants in the northeastern USA because of the long record, location “downwind” of major sources, and lack of local, major pollution sources. An extremely important finding from the long-term data is that bulk precipitation concentrations and both streamwater concentrations and output of sulfate at HBEF are significantly correlated with emissions of SO₂ from the source area for HBEF (Likens et al. 2001, 2002a, 2005). For example, US total emissions of SO₂ and NO_x have markedly declined since 1970 (Fig. 15). Correlated with this decrease, long-term data from HBEF showed a striking relationship ($p < 0.01$, $r^2 = 0.92$) between emissions of SO₂ from the source area for HBEF (24-h back trajectory) (Fig. 16) and sulfate concentrations in bulk precipitation at HBEF (see also Likens et al. 2005). A similar relationship was observed for national SO₂ emissions and sulfate concentrations in bulk precipitation at the HBEF (Fig. 16; $r^2 = 0.93$).

Like sulfate, atmospheric deposition of nitrate is directly correlated with NO_x emissions (both $p < 0.001$; Butler et al. 2003, 2005), but ammonium deposition is not correlated with ammonia emissions ($p > 0.10$) as changes in both emissions and deposition have been small. Annual deposition of sulfate has been declining rapidly (-0.5 kg/ha-year , $p < 0.001$) for several decades, and recently declines in nitrate, as

Fig. 16 Annual average bulk precipitation sulfate concentrations for Watershed 6 of the Hubbard Brook Experimental Forest related to annual SO_2 emissions from the 24-h back trajectory, source area for the Hubbard Brook Experimental Forest ($r^2 = 0.92$) and to annual US SO_2 emissions, $r^2 = 0.93$ (also see Likens et al. 2005)



well as DIN ($\text{NH}_4^+ + \text{NO}_3^-$) deposition have declined in concordance with the most recent NO_x emissions declines. The EPA estimated that US emissions of NO_x declined from 24.2 million tons in 1998 to 11.3 million tons in 2012 (Fig. 15; <http://www.epa.gov/ttnchiel/trends/>). Unfortunately, the US EPA has changed their methodology and timeframe for calculating state and national emissions repeatedly, which has led to much frustration and difficulty in attempts to establish these important relationships, particularly over the long term (see Likens et al. 2005).

There is a strong correlation ($r^2 = 0.81$) between the decrease in streamwater sulfate and sum of base cation (C_B) concentrations at HBEF, but the nitrate concentration drives the major annual fluctuations in acid-neutralizing capacity (ANC) (as determined by the difference between C_B and $[\text{SO}_4^{2-} + \text{NO}_3^-]$) (Fig. 17). It is expected that the ANC of stream water in W6 will continue to increase as SO_2 and NO_x emissions decrease and the ecosystems recover from acidification (Fig. 17). Also, it is expected that as sulfur deposition declines, sulfate concentration in stream water will decline less in W6 because of the release of stored sulfur in soil (Kerr et al. 2012).

In 2005–2009, the estimated sulfur loading from the atmosphere at HBEF wet plus dry (~7 kg/year) was still much higher than values recommended for protection of sensitive forest and associated aquatic ecosystems like those found at HBEF (see Likens 1992, 2010). Moreover, declining concentrations and inputs in atmospheric deposition of base cations, particularly calcium and magnesium at HBEF (Fig. 18b; Driscoll et al. 1989a; Hedin et al. 1994; Likens et al. 1996, 1998) and loss of base cations from the soil (Chaps. 4 and 5), are causing forest and associated aquatic ecosystems at HBEF to become even more sensitive to atmospheric inputs of acidic substances (Driscoll et al. 1989a; Likens et al. 1996, 1998; Likens 2010; Likens and Buso 2012).

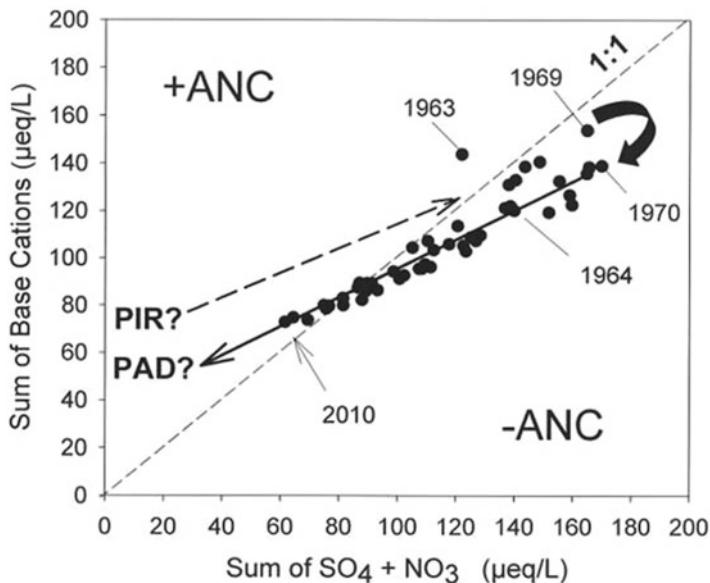


Fig. 17 Acidification and recovery of acid-neutralizing capacity in stream water of Watershed 6 in the Hubbard Brook Experimental Forest. PIR preindustrial revolution, PAD post-acid deposition (modified from Likens and Buso 2012)

Acid rain continues to have major environmental impact on terrestrial and aquatic ecosystems of the HBEF despite large decreases in emissions of SO_2 and NO_x from the source area (Likens et al. 2002a, 2005; Likens 2010) and declines in bulk precipitation acidity of 80 % since 1963. Undoubtedly, emissions will continue to change in the future as a result of economic recovery, changing energy demand, and federal and state actions, both within the USA and internationally.

Acid Rain and Base Cation Depletion

Long-term mass-balance analyses (see Chap. 4) led to the discovery that calcium and other base cations had been depleted from watershed-ecosystems of the HBEF by decades of acid deposition (Likens et al. 1996, 1998). It had been generally assumed that annual changes in the storage of base cations within available nutrient pools of forest soils like those at HBEF were negligible (see Likens and Bailey 2013; Chap. 5), but Reuss and Johnson (1986) on theoretical grounds, and detailed studies of terrestrial ecosystems at various locations (e.g., Likens et al. 1996, 1998; S. Bailey et al. 2003, 2005; Fernandez et al. 2003, 2010; Long et al. 2009; Warby

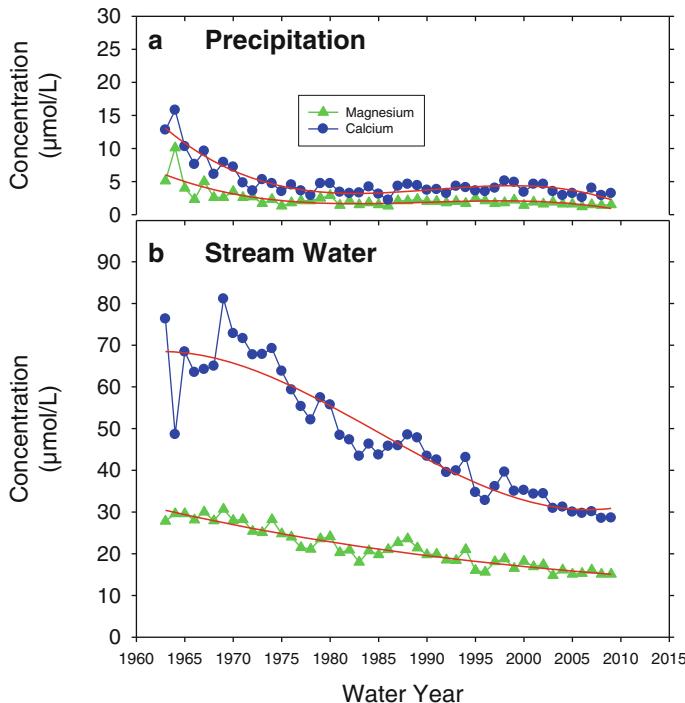


Fig. 18 Annual volume-weighted mean concentrations of calcium and magnesium in (a) bulk precipitation and (b) stream water for Watershed 6 of the Hubbard Brook Experimental Forest during 1963–2009

et al. 2009; Watmough and Dillon 2001, 2004) and in aquatic ecosystems (e.g., Buso et al. 2009; Jeziorski et al. 2008; Korosi et al. 2012), surprisingly showed significant, widespread calcium depletion resulting from acid rain. Moreover, long-term data from W6 of the HBEF showed sizeable declines in calcium (~50 %) and magnesium (~30 %) concentrations in stream water (Fig. 18b) and even larger relative declines in precipitation concentrations (~75 % and ~80 %, respectively) (Fig. 18a; see “Dilution” section below; Likens and Buso 2012; Likens and Bailey 2013).

Johnson et al. (1981) proposed a 2-step process in the neutralization of acid rain where atmospheric inputs of hydrogen ion are first neutralized by the dissolution of reactive alumina in the soil zone, and then both hydrogen ion and aluminum acidity are neutralized by chemical weathering of primary silicate minerals. Increased loss of base cations results in reduced aluminum neutralization. This study was important for demonstrating the neutralization of acid rain and for showing the role of this process in generating toxic dissolved aluminum in the rooting zone of the soil and in stream water. Thus, mineral weathering is the dominant process that neutralizes acidity, and its rate is governed largely by (1) presence of soil water, (2) types of

minerals present, (3) distribution of soil particle sizes, and (4) depths of soils and unconsolidated deposits (Likens and Bailey 2013; see Chap. 5). Because upland forests in the northern Appalachian Mts., like HBEF, have silicate minerals that decompose slowly, have relatively coarse soils with high sand and low clay content (small surface area), and have shallow depths to bedrock (Bailey 2000), neutralization of incoming acids is limited and the impact of acid rain on these sensitive systems is relatively large.

Because the podzol soils at HBEF were generally quite acidic ($\text{pH} < 4.7$), the geochemical effects of acid deposition were thought early in the HBES to be minimal (Johnson et al. 1972). Krug and Frink (1983) suggested that acid deposition was not responsible for the observed acidification of surface fresh waters, rather suggesting it was due to changes in land use, and that anthropogenic sulfate deposition merely replaced the organic acidity in fresh waters with little or no change in pH. Other scientists concluded that Krug and Frink were partly correct (e.g., R. Davis et al. 1985; Driscoll et al. 1989b) but not offsetting. The ecosystem response is much more complicated (see below and Chap. 5), and there are harmful ecological effects from the anthropogenic acidification and mobilization of dissolved aluminum. Over the long term, acid deposition has had several important effects on a variety of soil processes, e.g., reduction in nitrogen fixation, loss of base cations, and loss of buffering capacity. Theoretically, 1 m of rain at pH 4 could leach 20 kg/ha of CaCO_3 from the system in drainage water.

Acid precipitation apparently has been falling on much of the eastern USA since the early 1950s (Cogbill and Likens 1974; Likens and Bormann 1974a; Butler et al. 1984; Cogbill et al. 1984). There have been many upward and downward short-term trends in annual volume-weighted average concentrations of hydrogen ion between 1964–1965 and 2009–2010; however, no long-term trend in hydrogen ion concentration was statistically significant until 18 years of continuous data had been obtained (Likens 1989; Fig. 14). Such findings auger strongly for the value of long-term studies.

Sulfuric acid is the dominant acid in precipitation at HBEF. Based on a stoichiometric formation process in which a sea-salt anionic component is subtracted from the total anions (Cogbill and Likens 1974), sulfate contributed more than 65 % of the acidity in precipitation during the early years of our study. Although sulfuric acid dominated bulk precipitation at HBEF and accounts for most of the hydrogen ion in precipitation, the increase in input of hydrogen ion during the first decade of our study was caused by an increase in the annual nitric acid content of precipitation falling on these watershed-ecosystems.

Precipitation chemistry has changed both qualitatively and quantitatively at HBEF during the past five decades, including absolute concentrations (Fig. 19a) and relative proportions of the component chemicals (Fig. 20; Tables 5 and 6). Based upon the acid anion composition, the sulfate contribution to acidity dropped from 75 to 50 % and nitrate increased from <15 to 35 % from 1964–1965 to 2009–2010. Annual inputs reflect these changes in complex ways. In a further attempt to resolve the relative importance of the various factors controlling annual hydrogen ion inputs during the early years when acidity was high, a stepwise multiple

regression analysis was done to relate the annual hydrogen ion input to a variety of independent variables. An analysis of five independent variables indicated that 86 % of the variability in annual hydrogen ion input during the decade 1964–1974 was related to annual nitrate input. Six percent of the variability was caused by annual sulfate input, 5 % by the input of the sum of all cations minus hydrogen ion, 2 % by year, and <0.01 % by the annual amount of precipitation. A multiple linear regression of annual volume-weighted average concentrations during 1964–2009 showed that hydrogen ion concentrations could be predicted from sulfate concentrations ($p<0.001$) and chloride concentrations ($p<0.01$) but not by sum of base cations, ammonium, nitrate concentrations, or precipitation volume ($p>0.19$).

The sources and changing concentrations of many of these ions in precipitation illustrate how economic decisions and activities far removed from this region can

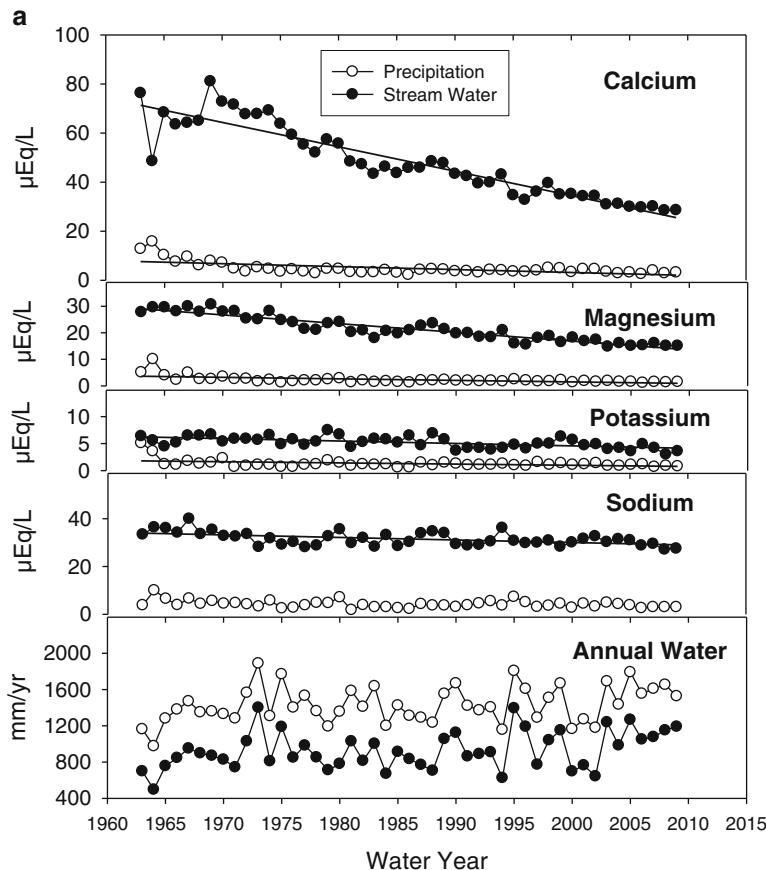


Fig. 19 Annual volume-weighted mean concentrations in (a) bulk precipitation and (b) stream water for Watershed 6 of the Hubbard Brook Experimental Forest during 1963–2009. Linear regressions shown when correlations are significant ($p<0.05$)

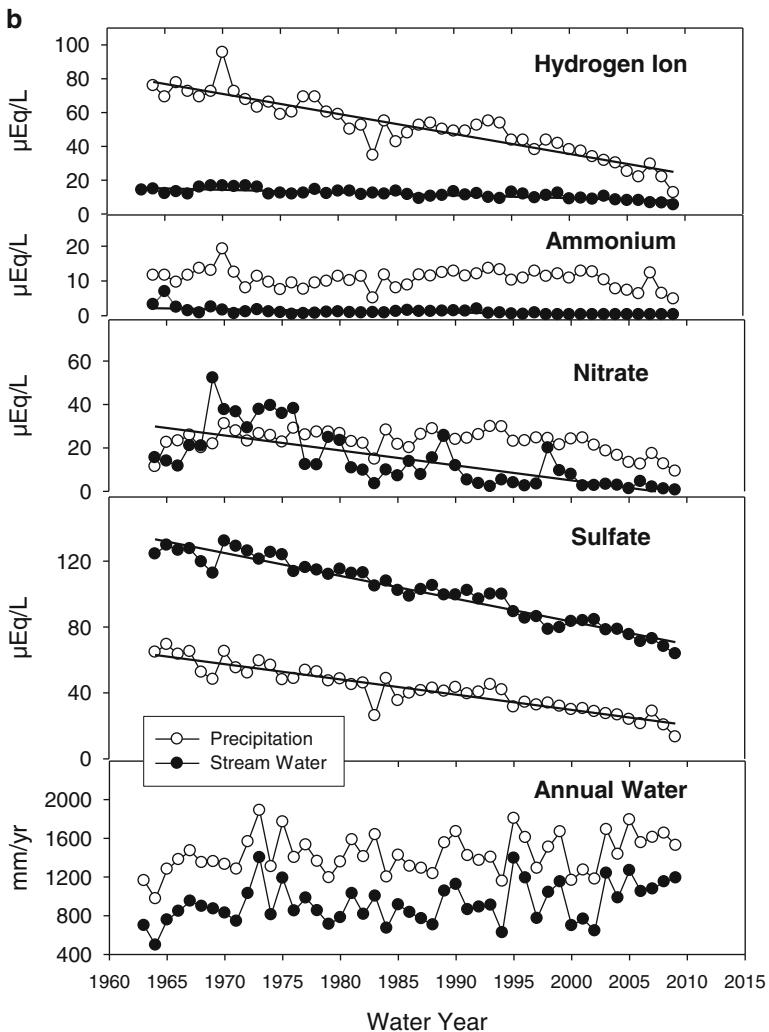


Fig. 19 (continued)

influence the dynamics of the northern hardwood forest and associated aquatic ecosystems. Several decades ago, changes in atmospheric chemistry resulting from changes in fossil fuel consumption, disposal of gaseous effluents into the atmosphere, and reduction of alkaline particulates in the atmosphere resulted in decreased pH of precipitation over the northeastern USA. Initially, increases in hydrogen ion concentration were related to increases in sulfur emissions (Likens et al. 1972, 2005). However, later in the long-term record of precipitation chemistry at HBEC, significant changes in the concentration of hydrogen ion were caused by changes in emissions of both nitrogen oxides and sulfur dioxide (Figs. 13 and 15).

Because precipitation is weakly buffered, the presence of small amounts of strong mineral acids, such as H_2SO_4 and HNO_3 , can greatly depress the pH value. Even though only relatively small amounts of acid are involved, the potential effect of increased amounts of hydrogen ions on biologic and chemical systems can be large.

Fish kills of major proportions and diminished reproduction of salmonoid-type fish have been observed and attributed to acid precipitation in areas of similar geology in the Adirondack Mountains of New York (Schofield 1976), in Canada (Beamish 1976), and in Scandinavia (Wright et al. 1976). No fish occur in the small headwater streams of the HBEF, but Eastern brook trout (*Salvelinus fontinalis*) occur in the streams at lower elevations in the HBEF (Warren et al. 2008). This pattern of distribution is thought to be the result of extreme acidification of headwaters and from physical barriers within the drainage network.

Some charge equivalence changes and biotic responses: Appreciable amounts of dissolved organic matter are found in the undisturbed tributaries to Hubbard Brook. Fisher (1970) reported an average dissolved organic matter concentration of 2.34 mg/L during 1968–1969 in Bear Brook (downstream of W6). This amount would be 1.05 mg of dissolved organic carbon per liter if the dissolved organic matter were 45 % carbon. Hobbie and Likens (1973) found an average annual weighted concentration of 1.0-mg dissolved organic carbon (DOC) per liter in stream water from W6. Most of the streamwater carbon values ranged between 0.3 and 2.0 mg/L, but a maximum carbon value of 4.8 mg/L was observed during an extremely high streamflow event (29 July 1969, 34×10^4 L/ha-day). McDowell and Likens (1988) reported an average DOC concentration of 1.8 mg/L in Bear Brook stream water during 1976–1977 and 3.1 mg/L in 1978–1979. Lawrence et al. (1986) measured an average DOC concentration of 1.8 mg/L in 1984. Systematic weekly measurement of DOC began in W6 in 1995. During 1995–2010, the mean DOC concentration was 2.2 ± 0.30 SD mg/L (range 0.18–8.31 mg DOC/L) with no temporal trend. Values during the fall tend to be higher than at other times of the year, probably because of rewetting of the stream channel. Moreover, there is an inverse relation between DOC concentrations and pH of stream water (greater in W9, pH 3.9–5.7) and a direct relation with instantaneous flow.

Several authors have reported recent increases in DOC concentrations in surface waters of North America and Europe. Suggested causes for this increase include reduction in acid deposition and recovery from acidification, land-use change, climate change, and changes in atmospheric deposition, e.g., nitrogen (e.g., Findlay 2005; Roulet and Moore 2006; Montieth et al. 2007; Erlandsson et al. 2011; Evans et al. 2006, 2012). Unfortunately, the record of measurement in the HBEF is not continuous from the early 1960s and analytical methods have changed, but available data do not provide a convincing case for an increase in DOC concentration in stream water during the past 3+ decades.

Watershed 9 is the most acidic (current average pH~4.5) and humic (average DOC ~10 mg/L) watershed in HBEF (Likens and Buso 2006). It is fishless, likely due to low pH and high dissolved aluminum concentrations (Driscoll et al. 1980), but brook trout (*Salvelinus fontinalis*) are present in Hubbard Brook at the confluence with W9 (Warren et al. 2008). Watershed 9 is typical of coniferous-dominated

(spruce/fir) headwater streams in New England. There has been a 20 % decline in ionic strength (based on total dissolved cations and anions) in W9 since 1995—a decrease of $\sim 5 \mu\text{S}/\text{cm}$ in average electrical conductivity. Average sulfate concentration has declined by $\sim 37 \mu\text{Eq/L}$ (87–50 $\mu\text{Eq/L}$) (Fig. 21) during this period or $\sim 58 \%$ lower than measured in 1989 (Hedin et al. 1990). The DOC concentrations and exports from W9 have not increased as expected (e.g., Erlandsson et al. 2011) during this time ($p > 0.10$), but may in the future if the current sulfate decline were to level off because of the release of sulfate from large reservoirs of absorbed sulfate in the humic soils and wetlands of W9. Changes in DOC export have important implications for watershed carbon budgets and stream biota. For example, with decreasing ionic strength and lower competition from sulfate (De Wit et al. 2007; Montieth et al. 2007), the charge density of DOC probably will continue to increase, surpassing sulfate contributions to charge density in the next decade or so. As a result of these changes, brook trout may return to W9 in the foreseeable future.

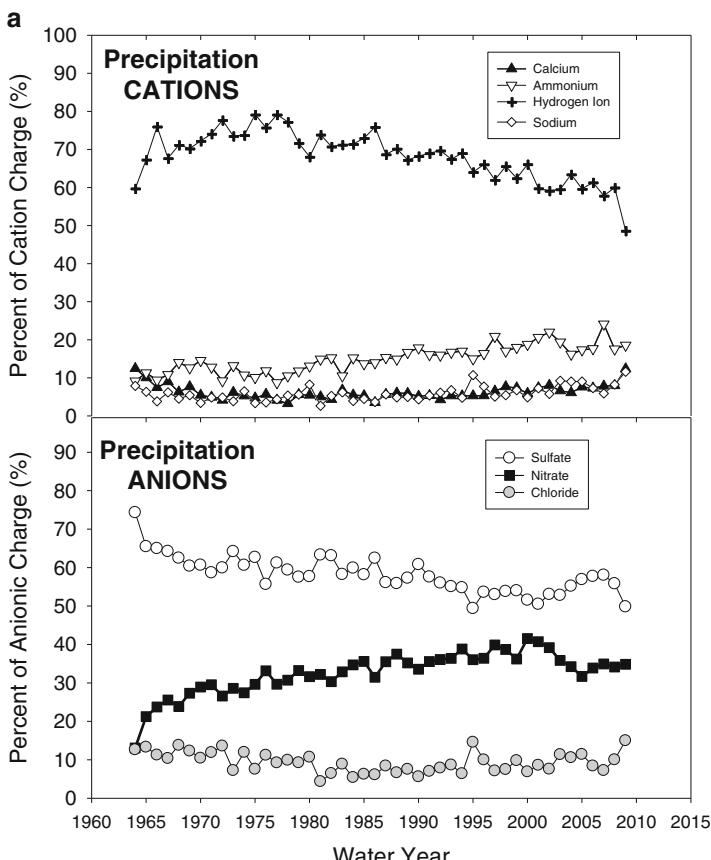


Fig. 20 Percent of ionic charge for cations and anions in bulk precipitation (a) and stream water (b) for Watershed 6 of the Hubbard Brook Experimental Forest during 1963–2009

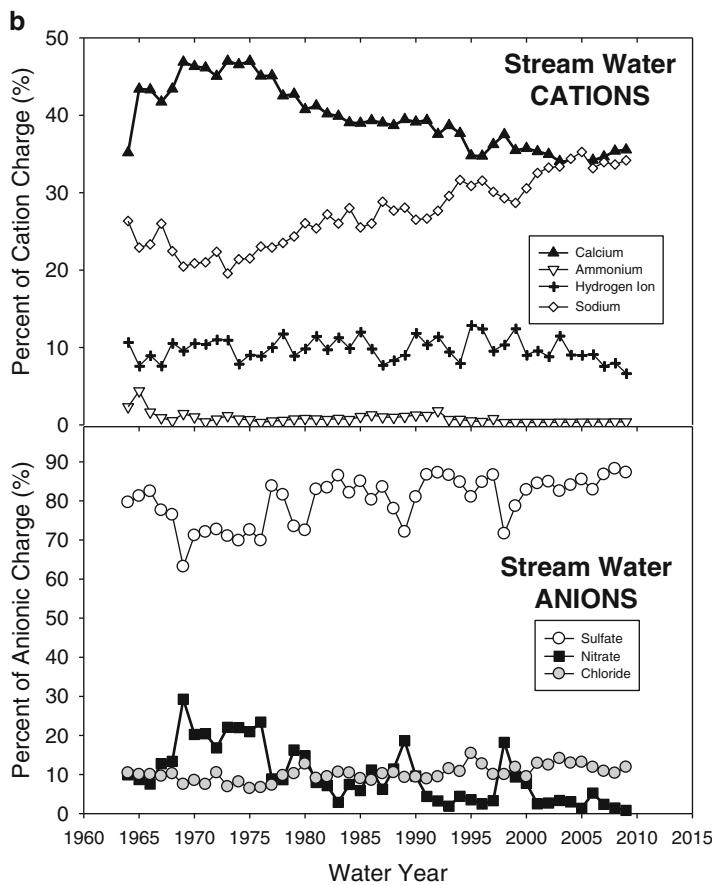


Fig. 20 (continued)

Headwater results scaled to Hubbard Brook and beyond: Watershed 6, a headwater stream, has an area of 13.2 ha and drains into Hubbard Brook, a fifth-order river, with a drainage area of $\sim 32 \text{ km}^2$. Because of the 2-order magnitude difference in size of these drainage areas, discharge differs widely: high flows in W6 approach $0.1 \text{ m}^3/\text{s}$, whereas high flows in Hubbard Brook can reach an estimated $200 \text{ m}^3/\text{s}$. Hubbard Brook is a tributary to the Pemigewasset River ($2,644 \text{ km}^2$ drainage area) that, in turn, drains into the Merrimack River ($12,200 \text{ km}^2$ catchment area), a major source of drinking water in an area of New England with nearly 200 communities and over two million inhabitants. The Merrimack River watershed has also been designated for anadromous fish reintroduction, including Atlantic salmon (*Salmo salar*), a species requiring high-quality headwater streams, such as in the upper Pemigewasset River system, for spawning. Atlantic salmon fry are found in the lower part of Hubbard Brook.

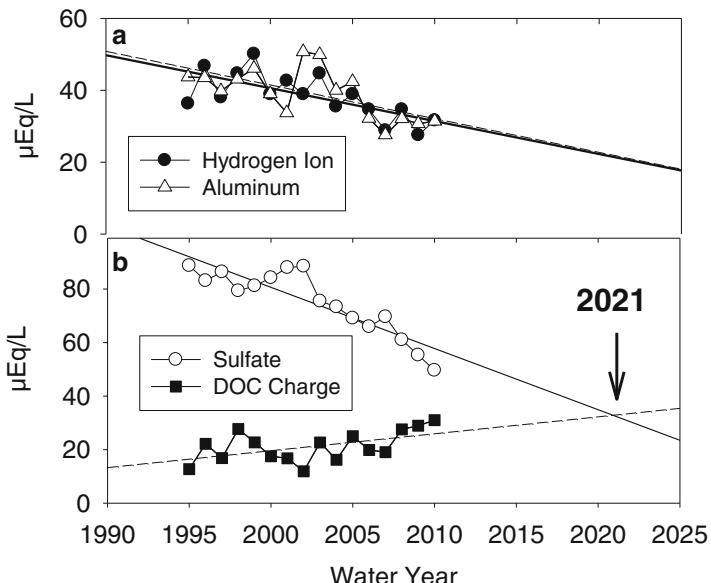


Fig. 21 Trends in hydrogen ion ($r^2 = 0.48$, $p = 0.003$), monomeric aluminum ($r^2 = 0.40$; $p = 0.009$), sulfate ($r^2 = 0.79$; $p = 0.01$), and DOC charge ($r^2 = 0.27$; $p = 0.039$) in W9 stream water of the Hubbard Brook Experimental Forest. Anionic charge for DOC is projected to exceed sulfate in 2021

Both W6 and Hubbard Brook represent the headwaters of this important Merrimack River watershed, and research into the impacts of disturbances on these smaller catchments is essential to understand and manage the larger system. Maintaining high water quality with water processing plants downstream is prohibitively expensive compared to maintaining pristine natural catchments upstream. Yet, because they are small in area and dilute, headwater streams are among the most sensitive of aquatic resources to pollutants (e.g., Lowe and Likens 2005).

Unfortunately, acidic deposition has thoroughly permeated W6 and Hubbard Brook (and all of New England). Concentrations of strong acid anions (AA: sulfate and nitrate) are very similar in these different-sized drainages (Fig. 22). The slopes of the time-series trends are slightly different (-1.93 ± 0.08 se for Hubbard Brook; -2.30 ± 0.12 se for W6), although the median AA values are not statistically different. Evidently, W6 is releasing AA about 19 % faster than Hubbard Brook. Both these streams are recovering from acidic deposition and should achieve similar, low AA values in the near future (11 $\mu\text{Eq/L}$ is the target baseline within three decades if deposition rates were to continue to fall) (see “Dilution” below and Likens and Buso 2012). The full impact of strong acid anions depends on the availability of neutralizing base cations in the soil and till and on the hydrologic pathways where the dissolved ions are generated. The sensitivity of these two watersheds to acid deposition is high, but differs. Hubbard Brook has on average 14 $\mu\text{Eq/L}$ more base cations

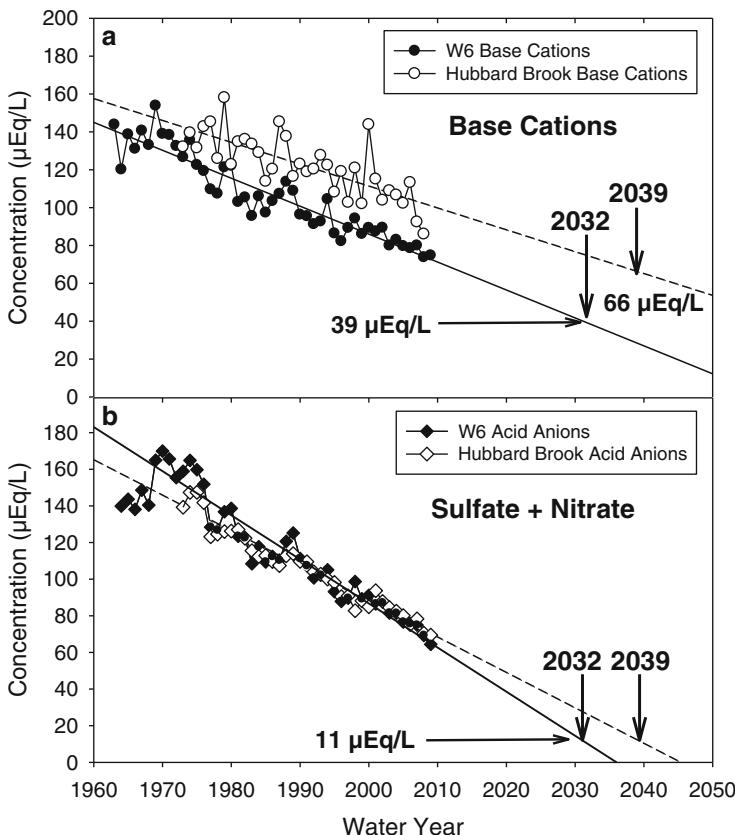


Fig. 22 (a) Trends in the sum of base cation concentrations for Watershed 6 (W6) and Hubbard Brook (HB) stream water from 1963 to 2009. Slopes significant at $p < 0.01$; W6 slope $-1.48 \mu\text{Eq/L-year}$; HB $-1.15 \mu\text{Eq/L-year}$. (b) Strong acid anion concentration (sulfate + nitrate) trends are highly significant ($p < 0.001$) and rigorous, $r^2 > 0.90$ for both W6 and HB. Baseline target values explained in text

than W6, and the medians are statistically different. However, annual base cation values fluctuate more in Hubbard Brook than in W6 ($r^2 = 0.56$ in Hubbard Brook; $r^2 = 0.87$ in W6 for linear regressions shown in Fig. 22), reflecting a broader range of water pathways from long-contact times at low flows (high base cations) to “short-circuiting” at high flows (low base cations) and more variable geologic substrates in the much larger Hubbard Brook drainage. Larger, more complex watersheds probably will be slower to release acid anions, even with reduced acid deposition (Mitchell and Likens 2011).

These findings have important ramifications for setting and maintaining water quality standards downstream. Moreover, the requirement of young salmonids to live in relatively uniform chemical conditions is compromised in Hubbard Brook, where shifts in pH can range from pH 6.5 to pH 5.0, mobilizing toxic aluminum at



Photograph 7 Winter conditions at the HBEF ca. 1969. Note that the snowpack has mostly buried the instrument shelter for the gauging weir on Watershed 6 (see page 26)

the lower pH values (Johnson et al. 1981). Any changes (\pm) in acidic deposition will be realized sooner in W6 than in Hubbard Brook, but both will react relatively quickly because they have been sensitized by decades of acidic inputs and consequent depletion of base cations.

The biogeochemistry in the Hubbard Brook Valley is poised for large and significant biogeochemical changes in the upcoming decade or two—this situation provides compelling motivation for the maintenance of a continuing and adaptive monitoring program (sensu Lindenmayer and Likens 2009, 2010).

Snow and Snowpack Chemistry

The chemistry of the considerable amount of snow that frequently accumulates as snowpack during the winter at HBEF (see Photograph 7) may have little similarity to the chemistry of the snow that falls (Hornbeck and Likens 1974) but can significantly affect the chemistry of stream water during snowmelt (e.g., Johnson et al. 1981; Hooper and Shoemaker 1985; Hooper 1986). For example, potassium concentrations tend to be up to two orders of magnitude higher in the snowpack than in ambient snowfall. In addition to concentration effects due to sublimation, much of this increase comes from the leaching of potassium from plant parts also incorporated in the snowpack (Hornbeck and Likens 1974). In sharp contrast, amounts of nitrate and ammonium in the snowpack tend to be lower than amounts input in ambient snowfall.

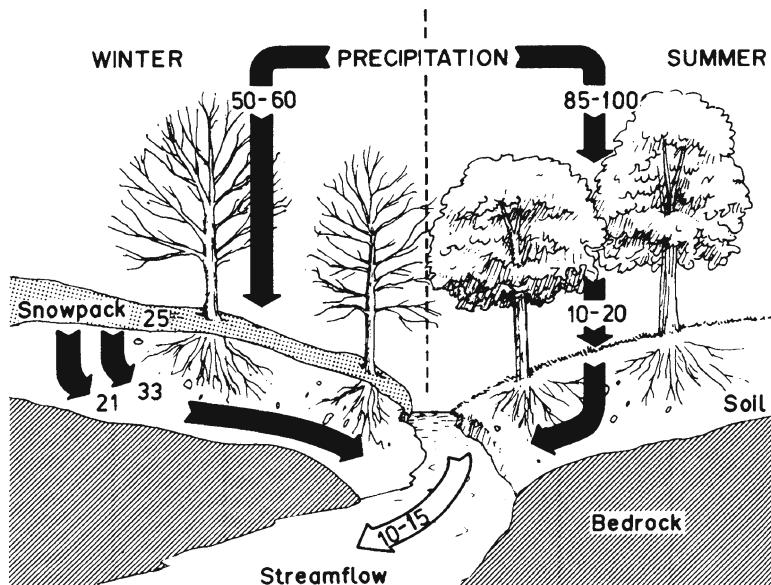


Fig. 23 General relationships for two seasonal periods in Watershed 6 at Hubbard Brook Experimental Forest. The values are hydrogen ion concentrations in $\mu\text{Eq/L}$ (modified from Hornbeck et al. 1976)

The first portions of meltwater (~20 %) from the snowpack may be significantly more acidic than subsequent portions (Hornbeck et al. 1976; Johannessen et al. 1976). This phenomenon may cause a sharp drop in the pH of drainage streams and lakes during the spring and has been blamed for fish kills in Scandinavia (e.g., Wright et al. 1976) and eastern North America. This seasonal change in pH also has been observed in streams and in Mirror Lake within the Hubbard Brook Valley, but it is a very temporal condition of variable intensity. During the winter and with intermittent melting, the snowpack becomes less acidic than the incident precipitation (Hornbeck et al. 1976). When the snow melts rapidly, there may be a flush of highly acidic water into the stream channels; however, when the snowpack melts more slowly, the reduction of pH in stream water is much less pronounced.

Despite seasonal and long-term differences in acidity of precipitation, effects of snow accumulation and melt, and variations in residence time of soil water, the acidity of stream water at the HBEF at the level of the gauging weirs is remarkably constant throughout the year (Fig. 23). Even though the average monthly concentration for hydrogen ion in bulk precipitation for W6 ranged from ~40 to ~70 $\mu\text{Eq/L}$, average monthly concentrations in stream water from W6 only changed from ~8 to ~12 $\mu\text{Eq/L}$ during 1964–2009 (Fig. 24). The uniformity of streamwater acidity indicates a strong buffering action of the terrestrial ecosystem (Fig. 23). The terrestrial ecosystem is therefore very effective in ameliorating the short-term impact of acid precipitation on the associated aquatic ecosystems. An exception is the acid pulse

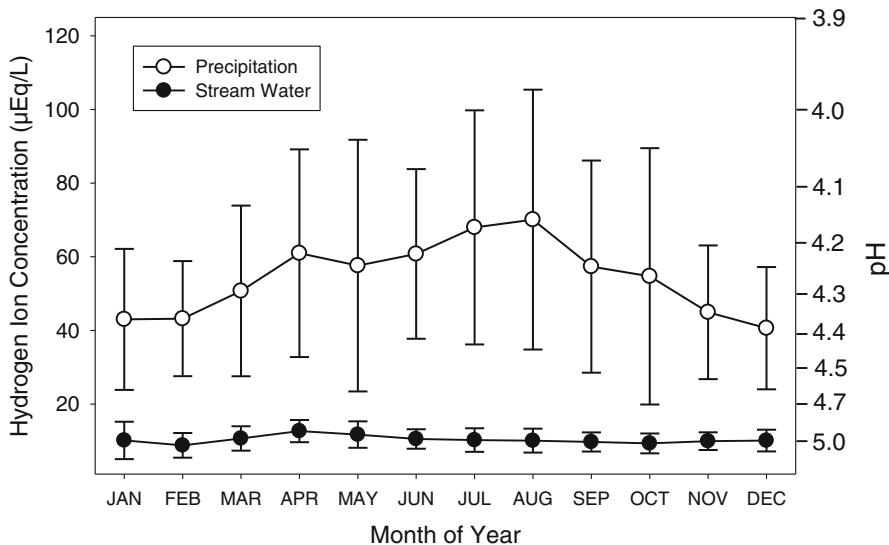


Fig. 24 Volume-weighted mean monthly hydrogen ion concentration and pH for bulk precipitation and stream water for Watershed 6 of the Hubbard Brook Experimental Forest during 1965–2009. The vertical lines for each month represent 1 standard deviation from the mean

during snowmelt in the upper headwaters. Because of the long-term nature of this acid deposition problem, the buffering capacity of the ecosystem has been slowly, but relentlessly, depleted (Likens et al. 1998; Likens 2010; Likens and Buso 2012).

Dilution and Effect of Acid Rain on Baselines

Long-term records (>10 years) provide a unique opportunity for new insights and for developing realistic temporal trends. As shown repeatedly in this little book, short-term records, e.g., <6 years, can be quite misleading regarding biogeochemical patterns and trends (e.g., Fig. 14).

Using our long-term data now approaching five decades, it is apparent that the chemistry of both precipitation and stream water in the Hubbard Brook Valley has moved from what we may have thought to be “normal” conditions when we initiated the Hubbard Brook Ecosystem Study in 1963 to very dilute conditions today. In fact, based on electrical conductivity, concentrations in W6 are projected to approach demineralized water in 2015 (bulk precipitation) and 2025 (stream water) (Fig. 25; Likens and Buso 2012). Because such dilute chemistry is unrealistic for natural waters, theoretical baseline values of $3 \mu\text{S}/\text{cm}$ and $5 \mu\text{S}/\text{cm}$ were calculated for bulk precipitation and stream water, respectively.

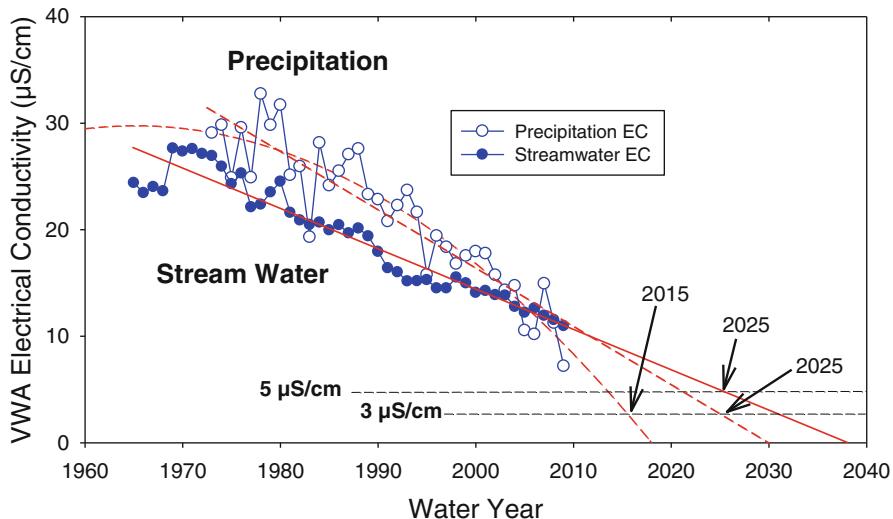


Fig. 25 Volume-weighted annual electrical conductivity in bulk precipitation and stream water for Watershed 6 of the Hubbard Brook Experimental Forest during 1964–2009 (modified from Likens and Buso 2012)

The projected baseline values for sum of base cations (calcium, magnesium, potassium, sodium) and acid anions (sulfate and nitrate) in bulk precipitation and stream water are lower (Table 7; post-acid deposition, PAD) than predicted earlier (Likens et al. 1996) for preindustrial revolution (PIR) conditions and the result of federal air pollution regulations reducing inputs and of excessive leaching of base cations from the watershed-ecosystems by decades of acid rain (Likens and Buso 2012). Rapid dilution of surface waters to very low values has important ecological, biogeochemical, and natural resource management implications (Likens and Buso 2012).

Projected PAD baseline concentrations have been calculated for precipitation and stream water at electrical conductivity of 3 and 5 $\mu\text{S}/\text{cm}$, calcium of 2 and 11 $\mu\text{Eq}/\text{L}$, magnesium of 1 and 6 $\mu\text{Eq}/\text{L}$, potassium of 1 and 3 $\mu\text{Eq}/\text{L}$, sodium of 3 and 19 $\mu\text{Eq}/\text{L}$, sulfate of 8 and 10 $\mu\text{Eq}/\text{L}$, nitrate of 2 and 1 $\mu\text{Eq}/\text{L}$, chloride of 3 and 8 $\mu\text{Eq}/\text{L}$, and pH 5.4 and 5.5, respectively (Likens and Buso 2012). We assume that stream water in PIR was dominated by $\text{Ca}(\text{HCO}_3)_2$, but now is moving toward NaHCO_3 because of preferential calcium depletion from soils due to acid rain (Likens and Buso 2012).

Although such long-term data are indispensable in order to think about baseline conditions, there are many pitfalls, including the following: (1) Are the records long enough to make accurate projections and (2) can simulation models be used to improve these extrapolations? Given the difficulty in describing baseline conditions, the effort is important because of the cost of implementing federal regulations and the biological imperative to manage and protect sensitive ecosystems.

Table 7 Post acidic deposition (PAD) models for bulk precipitation and streamwater concentrations in Watershed 6 of the Hubbard Brook Experimental Forest (modified from Likens and Buso 2012)

Precipitation			Stream water		
PAD Model for 2015			PAD Model for 2025		
Ion	Conc (mg/L)	Charge (μEq/L)	Ion	Conc (mg/L)	Charge (μEq/L)
Calcium	0.04	2.0	Calcium	0.22	11.0
Magnesium	0.01	1.0	Magnesium	0.07	6.0
Potassium	0.04	1.0	Potassium	0.12	3.0
Sodium	0.07	3.0	Sodium	0.44	19.0
Aluminum	0.000	0.0	Aluminum	0.001	0.1
Ammonium	0.036	2.0	Ammonium	0.002	0.1
H ⁺ (pH)	5.40	4.0	H ⁺ (pH)	5.52	3.0
<i>sum C_B</i>		7.0	<i>sum C_B</i>		39.0
CATION sum		13.0	CATION sum		42.2
Sulfate	0.38	8.0	Sulfate	0.48	10.0
Nitrate	0.12	2.0	Nitrate	0.06	1.0
Chloride	0.11	3.0	Chloride	0.28	8.0
Phosphate	0.001	0.1	Phosphate	0.001	0.1
Bicarbonate (ANC)	0	0.1	Bicarbonate (ANC)	NA	15.0
DOC	1.0	0.0	DOC	1.5	8.0
<i>sum AA</i>		10.0	<i>sum AA</i>		11.0
ANION sum	NA	13.2	ANION sum	NA	42.1
IMBALANCE		-0.2	IMBALANCE		0.1
Theoretical		3.0	Theoretical		5.4
Electrical conductance (μS/cm)			Electrical conductance (μS/cm)		

Impact of Acid Rain on Accumulation of Forest Biomass

Our model of the forest ecosystem (Fig. 1) suggests a number of functions internal to the forested ecosystem that may be affected by acid precipitation. For example, leaching of substances from the canopy can be accelerated and, in fact, that seems to be the case. Eaton et al. (1973) found that 90 % of the hydrogen ions striking the summer canopy of the forest were consumed within the canopy, presumably releasing an equivalent amount of base cations. Laboratory studies of seedlings of major tree species at HB EF (Wood and Bormann 1974, 1975) indicated increased leaching of cations as the hydrogen ion content of artificially applied mist increased.

The forest ecosystem is regulated by a large number of environmental factors such as the amount and distribution of precipitation; temperature; the length of growing season; unusual meteorologic events, such as ice and wind storms; the availability of nutrients; insect and disease outbreaks; and pollutants such as acid rain and ozone. Significant effects of acid rain on forest growth are difficult to detect. Moreover, it is extremely difficult to separate the effects of acid rain from other variables. It is entirely possible, however, that acid rain is reducing forest growth or tree survival over wide areas by small, but persistent impacts, or by

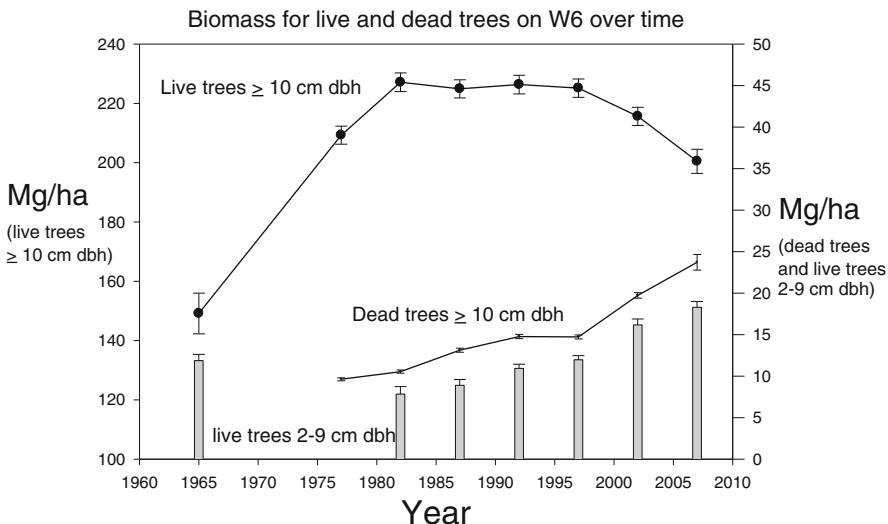


Fig. 26 Biomass accumulation for live and dead trees, above- and belowground in Watershed 6 of the Hubbard Brook Experimental Forest from 1965 to 2007 (Data from Whittaker et al. 1974; Likens et al. 1994; Siccama et al. 2007; van Doorn et al. 2011)

upsetting ecological conditions so as to reduce the capacity of certain species to resist insect or disease attacks or by reducing the ecosystem's buffering capacity through excessive leaching of base cations. Slow but cumulative effects over many years may result in serious deterioration of the forest ecosystem, particularly as acid deposition is but one of an array of pollutants affecting the landscape (e.g., Bormann 1974). We (Likens et al. 1996) suggested that some 840 kg Ca/ha had been depleted from W6 soil pools during 1940–1995 by acid rain, but our recent models of long-term streamwater losses from the ecosystem suggest a value closer to 300 kg Ca/ha during this period (see Chap. 6). Nevertheless, 300 kg Ca/ha per 55 years is still a large loss from the ecosystem.

How has the forest ecosystem in W6, the reference watershed, responded to acid rain? Whittaker et al. (1974) and Cogbill (1976) reported a decline in forest growth on south-facing slopes of the HBEF during the 1960s and 1970s, but total forest biomass in W6 increased rapidly until ~1982 and then leveled off (Likens et al. 1994; Fahey et al. 2005; Siccama et al. 2007; Lindenmayer and Likens 2010, p. 123; Fig. 26). Recent measurements, 2007, showed that the forest is now declining in biomass (Lindenmayer and Likens 2010, p. 123; van Doorn et al. 2011). Soil carbon is a very large pool at the HBEF; annual changes are small and difficult to measure (Huntington et al. 1988, 1989; S. P. Hamburg, personal communication). Nevertheless, the forest in W6 is probably no longer accumulating biomass, but now may be emitting carbon to the atmosphere rather than sequestering it (Fig. 26; Likens and Franklin 2009; Lindenmayer and Likens 2010; Likens and Bailey 2013).

There are several possible explanations for this decrease in living forest biomass at the HBEF. It could be a natural pattern; a response to climate change (e.g.,

Campbell et al. 2007; Likens 2010); an effect of air pollution, such as ozone (e.g., Ollinger et al. 1997) or a direct effect of acid rain; or possibly disease was a major causal factor (e.g., Lovett et al. 2006); perhaps it is nutrient limitation such as by nitrogen (e.g., LeBauer and Treseder 2008) or calcium. Applying a hallmark HBES approach to this complicated question, a watershed-scale manipulation was initiated in 1999 whereby Wollastonite (CaSiO_3) was added experimentally to W1 of the HBEF. The calcium added (1,189 kg calcium/ha) was roughly equivalent to the amount calculated to have been leached from the ecosystem by acid rain in the previous 50 years or so (Likens et al. 1996). The early results of the experiment are encouraging regarding the important role of calcium in this ecosystem (e.g., Juice et al. 2006; Halman et al. 2008). The seedlings, germinants, and canopy of sugar maple (*Acer saccharum*) are responding positively to the addition of the wollastonite, in comparison with sugar maple in adjacent, untreated areas. Likewise, red spruce (*Picea rubens*) showed less winter injury in the treated area in comparison to the reference area (Hawley et al. 2006).

A number of researchers have linked the decline in sugar maple in Pennsylvania, New York and New England to changes in base cations and aluminum availability in the soil, e.g., Horsley et al. (2002), Bailey et al. (2004, 2005), Hallett et al. (2006), Long et al. (2009), Likens and Bailey (2013). In the Duchesnay Experimental Forest near Quebec City, Quebec, Moore et al. (2012) evaluated the effect of a dolomitic lime addition on sugar maple 15 years after the application. They found that a single addition had long-term beneficial effects on soil chemistry and sugar maple nutrition, vigor, growth, and regeneration. To obtain maximum information useful to policy makers and those responsible for the management of the northern hardwood forest, efforts such as this must be integrated and interpreted fully within an ecosystem framework. A program mounted in this way is the highest socially responsible investment of research funds for helping to resolve a potentially critical environmental problem.

Trace Metals

Another component of regional air pollution impact on the HBEF is from atmospheric input of various trace metals, including copper, lead, cadmium, mercury, and zinc, to these watershed-ecosystems (Siccama and Smith 1978; Siccama et al. 1980; Smith and Siccama 1981; Johnson et al. 1995; Driscoll et al. 2007). Here we will briefly report on the biogeochemistry of lead in the HBEF. Sizeable concentrations of lead were found in bulk precipitation input to W6 during 1975–1985, leading to significant inputs and accumulation of this toxic metal within the ecosystem (Fig. 27). Concentrations in bulk precipitation during this period often exceeded the US drinking water standard of 25 $\mu\text{g/L}$ (Johnson et al. 1995).

Much of the lead in rain and snow came from the combustion of leaded gasoline by automobiles and buses. In the 1970s, legislation was passed to restrict the sale of leaded gasoline (gasoline with alkyl-lead additives) in the USA. As a result of

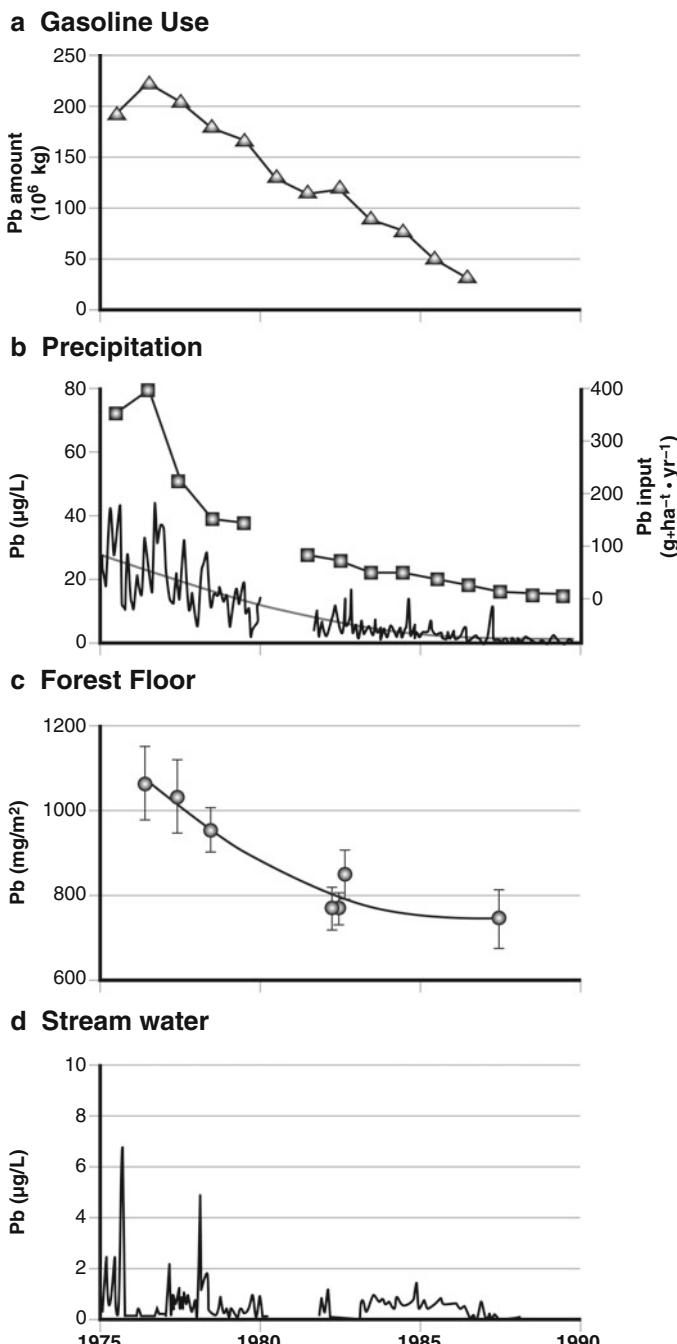


Fig. 27 Lead (Pb) use in gasoline and lead in precipitation, forest floor, and stream water at Watershed 6 of the Hubbard Brook Experimental Forest. Data for Pb consumed in gasoline (a) are from Nriago (1990). Squares (b) are estimates of Pb input to the HBEF, based on volume-weighted average Pb concentrations in bulk precipitation. Forest floor Pb pool sizes (c) are computed as the average Pb content in $15 \times 15\text{-cm}$ block samples; sample size varied from 58 to 119. Error bars show 1 standard error. Streamwater concentrations (d) from weekly samples of stream water in Watershed 6. (Redrawn from Johnson et al. 1995)

Table 8 Ecosystem budgets of lead (Pb) for two time periods: high atmospheric deposition of Pb (1975–1977) and low Pb deposition (1985–1987) (adopted from Johnson et al. 1995)

	1975–1977 (g/ha-year)	1985–1987 (g/ha-year)
Bulk precipitation input	325	29
Streamwater output	6	4
Net plant uptake	33	1
Weathering release	7	7

decreased use of leaded gasoline, concentrations and inputs of lead in bulk precipitation, accumulation in the forest floor, and outputs in stream water of W6 declined precipitously (Fig. 27). Johnson et al. (1995) determined some ecosystem fluxes for lead during a period of high atmospheric deposition (1975–1977) and during a period of low atmospheric deposition (1985–1987) (Table 8).

Similar to the acid rain situation, pollutants generated some distance from the HBEF were transported through the atmosphere to be deposited at HBEF. Also as with acid rain, legislation restricting the release of lead to the atmosphere was reflected in improving environmental conditions relative to this toxic metal in areas like HBEF remote from the source(s).

Throughfall and Stemflow

The water that reaches the forest floor is of vastly different chemical content than the incident precipitation. Only about 85 % of the incident precipitation actually reaches the ground of the northern hardwood forest ecosystem during the growing season. The remainder is evaporated (or absorbed) directly from the surface of leaves, branches, and stems (Leonard 1961; Lovett et al. 1996). As the precipitation passes through the forest canopy, its chemistry is altered significantly (Table 9). Throughfall and stemflow (about 5 % runs down the stems of deciduous trees) during the growing season are greatly enriched in potassium (about 91 times), phosphorus (18 times), magnesium (15 times), and calcium (10 times). All other dissolved substances also increase, with the exception of hydrogen ion, which is retained within the canopy by cation exchange reactions.

Based on an average DOC concentration of bulk precipitation of 1.1 mg/L (1973–1974; Likens et al. 1983) and an average, long-term precipitation of 1,440 mm, some 15.8 kg/ha-year of dissolved organic carbon would be added to the ecosystems of the HBEF each year in direct precipitation. As the precipitation passes through the forest canopy, it is enriched in organic carbon (Table 10; McDowell and Likens 1988). Throughfall and stemflow during the growing season contain some 52 kg carbon per hectare (Eaton et al. 1973), so an additional 36 kg carbon/ha must be leached from the forest canopy and added to that already present in the precipitation. These relationships probably are much more complicated than

Table 9 Weighted average chemical composition of incident precipitation and throughfall under different size classes of sugar maple, yellow birch, and American beech trees of Watershed 6 during the growing season (values in mg/L, except H)

Solutes	Precipitation under canopy					
	Precipitation above canopy		Throughfall and stemflow		Net change	
	(a)	(b)	(a)	(b)	(a)	(b)
Ca	0.16	0.11	1.59	0.72	+1.43	+0.61
Mg	0.03	0.02	0.45	0.20	+0.42	+0.18
K	0.07	0.06	6.37	1.98	+6.30	+1.92
Na	0.06	0.07	0.14	0.10	+0.08	+0.03
NO ₃ -N	0.22	0.32	0.67	0.41	+0.45	+0.09
NH ₄ -N	0.21	0.23	1.21	0.225	+1.00	-0.005
Total N	0.44	—	2.44	—	+2.00	—
PO ₄ -P	0.0026 ^c	—	0.15	—	+0.147	—
SO ₄ -S	0.9	0.84	5.4	1.15	+4.5	+0.31
Cl	0.45	0.15	1.46	0.28	+1.01	+0.13
H (μ Eq)	86.3	74.6	0.010	30.4	-0.077	-44.2
Organic C	2.4 ^d	3.41	12	8.75	+10	+5.34

^(a)Modified from Eaton et al. (1973) for 1969

^(b)Modified from Lovett et al. (1996) for 1989–1992

^cWeighted average for 1972–1974

^dWeighted average for 1973–1974

shown by this simple calculation, because the microflora of the leaf and bark surfaces of the vegetation may metabolize the more labile, dissolve organic substances in precipitation, and in turn secrete other organic substances.

There are various sources for the dissolved substances in throughfall and stemflow, but their relative importance is not entirely clear (e.g., Eaton et al. 1973): (1) Some nutrients are contained in the incident precipitation and (2) some of the nutrients may have been impacted aerosols that are washed off by the incident precipitation. These two portions should be considered as a part of the chemical flux from outside the ecosystem. Similarly, (3) nutrients with a normal gaseous phase, which were incorporated directly on or into the plant (e.g., fixation of carbon by photosynthesis, absorption, and reaction with SO₂ or NH₃) and then removed from tissues by incident precipitation, should be considered as meteorologic inputs in the watershed-ecosystem balance. The remaining nutrients in throughfall and stemflow, which have been leached from the vegetational tissues or associated microflora, are nutrients cycling primarily within the intrasystem cycle of the ecosystem (Fig. 1) and should not be considered part of the meteorologic flux. We have not been able to quantify the amounts of chemicals transported along each of these pathways long term for the ecosystems at HBEF. Some specific data are presented later in the discussion of nutrient cycles at HBEF (Chap. 6).

Table 10 Volume-weighted mean concentrations of dissolved substances in stream water of Watershed 6 of the Hubbard Brook Experimental Forest

Stream water	Decade 1964–1973		Stream water	Decade 2000–2009	
	Conc (mg/L)	Conc (μEq/L)		Substance	Conc (mg/L)
Water (mm/ ha-year)	882		Water (mm/ ha-year)	1,006	
Ca	1.36	67.8	Ca	0.62	30.8
Mg	0.34	28.0	Mg	0.19	15.8
K	0.23	5.8	K	0.16	4.2
Na	0.78	33.9	Na	0.69	29.8
NH ₄	0.04	2.1	NH ₄	0.01	0.3
Al	0.32	35.7	(@+3)	Al ^e	0.23
H ⁺	0.015	15.0		H ⁺	0.008
SO ₄	6.0	124.6		SO ₄	3.60
NO ₃	1.8	28.7		NO ₃	0.16
Cl	0.5	15.0		Cl	0.38
PO ₄ ^b	0.002	0.1		PO ₄ ^b	0.001
ANC (bicarbon- ate) ^a	0	0.0		ANC (bicarbon- ate) ^a	8.0
DOC ^c	1.8	10.8	DOC ^c	2.1	12.6
Cations	188.3		Cations	113.7	
Anions	179.2		Anions	108.9	
DOC ^{c, d}	1.8	149.9	=μmol/L	DOC ^d	2.1
Dissolved silica	4.1	144.5	=μmol/L	Dissolved silica	3.6
pH	4.82		pH	5.10	=μmol/L

^aBicarbonate = 0 at pH < 5^bPO₄ based on *n* = 3 years (1971–1973)^cDOC based on 1976–1977 (Likens et al. 1983)^dDOC charge is assumed at -6 μEq/L per mg/L C^eAluminum is assumed at +3 valence

Streamwater Chemistry

The chemistry of stream water has been monitored on a weekly basis in Watersheds 1–6 of the HBEF since 1963 and in Watershed 7–9 since 1995. Base cations were measured during 1963–1964 in W7 and a full suite of chemistry in W8 during 1974–1978. Experiments that involved cutting of the forest vegetation were undertaken in Watershed 2, starting in November of 1965; in Watershed 4, starting in October of 1970; and in Watershed 5, starting in 1983. An experimental addition of Wollastonite was added to Watershed 1 in 1999. Only long-term data on streamwater chemistry from W6, the biogeochemical reference watershed at the HBEF, are presented here.

Concentrations of Dissolved Substances

The HBEF forest ecosystem brings about both qualitative and quantitative chemical changes in rain and snowmelt water as it passes through the system (Tables 5, 6, and 10). Water enters the system as a dilute solution of sulfuric and nitric acid ($\text{pH} < 5$) but leaves the system containing primarily neutral sulfates ($\text{pH} \sim 5$). Calcium and sulfate dominate the streamwater chemistry, but sodium, magnesium, and aluminum also are relatively important cations on an equivalent basis. Sulfate is seven times more abundant than the next most abundant anion, currently chloride, in stream water. The balance between cations and anions in stream water is good over a 47-year span (Tables 5 and 10). The ionic charge assigned to aluminum and to DOC is problematic. The charge for aluminum can be modeled using pH, but the DOC charge is the residual, although the anionic charge per mg carbon is typical of values in the literature (Buso et al. 2000).

Although there have been 40–50 % declines in ionic strength of both precipitation and stream water (Tables 5, 6, and 10), stream water ionic strength is still about twice that of the incoming bulk precipitation. A principal factor here is the concentration effect (distillation) of evapotranspiration. As water is lost from the system by evapotranspiration, chemicals in solution tend to be concentrated into a smaller volume of water. Based upon an average annual evapotranspiration loss of 36 % (Table 3), the concentration factor would be 1.6, which would fall short of the observed concentration factor for chemicals (2.2 times during 1964–1973; 1.7 times during 2000–2009; Table 11). However, the concentration factor is not so straightforward as it appears, for not only do concentrations in stream water change but the proportions of ionic or dissolved species change as well, indicating important internal chemical and biologic reactions (Fig. 20b). Concentration factors (stream water $out \div$ precipitation in) vary from ~2 times for DOC and 7–10 times for calcium, magnesium, and sodium to 0.3 times for hydrogen ion and 0.2 times for nitrate and phosphate (comparing early and recent decades; Table 11). These factors are relatively stable for individual solutes, but over the long term the concentration factor is decreasing for the combined sums of all ions (Table 11). In any case, an additional quantity of dissolved salts is acquired by the water from within the ecosystem's boundaries. This process is related to chemical weathering reactions (Johnson et al. 1968; Likens et al. 1994, 1998, 2002a; S. Bailey et al. 2003) and is discussed separately in Chap. 5.

In general, the measured streamwater concentrations of most dissolved substances vary within a narrow range (less than a factor of 2–4), even though discharge of water may fluctuate over five orders of magnitude during an annual cycle at the HBEF (Figs. 12 and 48 below). This relation is particularly true for calcium, magnesium, and sulfate, which decrease with increasing streamflow. Sodium and dissolved silica concentrations may be diluted up to fourfold during periods of high streamflow, whereas aluminum, hydrogen ion, dissolved organic carbon, nitrate, and potassium concentrations are increased with increased discharge. Biotic activity within the ecosystem plays an important role in determining these relationships

Table 11 Concentration factors for all solutes across two decadal periods in Watershed 6 of the Hubbard Brook Experimental Forest

	Decade 1964–1973		Decade 2000–2009			Conc factor = S/P
	Precipitation ($\mu\text{Eq/L}$)	Stream water ($\mu\text{Eq/L}$)	Conc fac- tor = S/P	Precipitation ($\mu\text{Eq/L}$)	Stream water ($\mu\text{Eq/L}$)	
Ca	7.5	67.8	9.1	3.5	30.8	8.9
Mg	3.5	28.0	8.0	1.5	15.8	10.3
K	1.5	5.8	4.0	1.0	4.2	4.1
Na	5.1	33.9	6.6	3.5	29.8	8.5
NH ₄	12.1	2.1	0.2	8.9	0.3	0.0
Al	0.0	35.7	NA	0.0	25.0	NA
H ⁺	73.1	15.0	0.2	27.6	7.9	0.3
SO ₄	59.3	124.6	2.1	24.8	74.9	3.0
NO ₃	23.8	28.7	1.2	17.2	2.6	0.2
Cl	10.7	15.0	1.4	4.4	10.7	2.5
PO ₄	0.27	0.06	0.2	0.09	0.03	0.3
DOC	91.6	166.6	1.8	68.4	174.9	2.6
dSi	0.0	65.9	NA	0.0	61.1	NA

dSi is dissolved silica in $\mu\text{moles/L}$.

for potassium and nitrate in stream water. Nitrate and potassium are quite sensitive indicators of biologic activity; therefore, streamwater concentrations for these two nutrients are markedly reduced during periods of plant growth (growing season) and increased during periods of vegetation dormancy. Ammonium and phosphate show no relationship with discharge.

To describe these variations in streamwater chemistry empirically, we developed a model that predicts streamwater concentration in relation to stream discharge (Johnson et al. 1969). The model is based on some rather simple and intelligible assumptions. First of all, we assume that two discrete water types exist in our watershed-ecosystem: one is represented by relatively dilute water recently added to the system in rain or snowmelt, and the other is older, more concentrated, subsurface water (mostly soil water). Second, we assume that stream water at a given point at any time is some mixture of these two water types. Last, we assume that subsurface water is added to the stream at a constant rate, whereas rainwater or snowmelt water is added on a variable, day-to-day basis. Essentially, then, stream water becomes a variable mixture between pure rainwater or snowmelt water and pure subsurface water, the proportions of which vary from day to day and season to season. During flood periods, say during the spring snowmelt, stream water is composed primarily of snowmelt water. During drought periods, say in midsummer, stream water is composed of subsurface drainage water. In spite of these tightly prescribed and perhaps simplistic assumptions, the model does in fact work and serves to describe both reliably and accurately quantitative fluctuations in streamwater chemistry on a

day-to-day or season-to-season basis (Johnson et al. 1969). Within an undisturbed watershed, the model predicts quite precisely the changes in streamwater chemistry elicited by a given storm or a given dry period. The simple premises of the model testify to the remarkable chemical stability and chemical controls inherent in these forested ecosystems. This model was developed when concentrations were significantly higher (1964–1973), but still applies today despite major dilution of precipitation and streamwater chemistry. It also is significant that the model completely breaks down when the watershed is disturbed, such as by clear-cutting (e.g., Likens et al. 1970).

The maintenance of relatively constant streamwater chemistry is in part a result of the yearlong high infiltration capacity and permeability of the forest soils at the HBEF and in part of a high rate constant for the chemical reactions manifested in the soil zone. Apparently, chemical equilibria between aqueous and solid phases are achieved rapidly through various geologic and biologic reactions in the soil. As a consequence, streamwater chemistry is essentially established in the soil zone or the interflow drainage passages within the upper reaches of each watershed-ecosystem (Johnson et al. 1981; Likens and Buso 2006; Zimmer et al. 2012). This is an excellent example of the way in which both the form and rate of chemical flux are modified and tightly regulated by a forest ecosystem. Similar constancy of streamwater chemistry also has been observed for the major cations in the Coweeta Experimental Forest of North Carolina (Johnson and Swank 1973).

These examples suggest that the relative independence of streamwater chemistry from streamwater discharge is a rather general feature of eastern deciduous forest ecosystems on weathering resistant granitic and schistic substrates. The importance of this result should not be underestimated, for it demonstrates that the chemistry of regional headwater streams is the product of the natural ecosystem, the control of which may be altered by disturbance. For example, in disturbed forested areas and agricultural lands, concentrations of chemicals in stream water usually increase but vary markedly with discharge (e.g., Powell 1964, pp. 18–19; Likens et al. 1970; Likens and Bormann 1974b).

Despite long-term trends, the concentration of most ions in stream water varies little from year to year (Fig. 19), because gradual change is a characteristic of undisturbed watershed-ecosystems of the HBEF. In contrast, the annual weighted concentration of nitrate, generally increasing from 1964 to 1970, suddenly doubled from 1969 to 1976 (water-years) and then sharply declined (Fig. 28). For example, the average weighted concentration during 1964–1967 was 0.92 mg/L; during 1967–1969 it was 1.40 mg/L, in 1969–1972 it was 3.14 mg/L, and in 1992–1993 it was 0.23 mg/L. An explanation for this initial rise in the nitrate concentration is primarily circumstantial, and there are several possibilities. A severe drought in 1963 and 1964 may have “primed” the ecosystem for a nitrate release triggered by rewetting and soil frost (see Bernal et al. 2012). The snow cover formed very late in the winter of 1969–1970, and widespread freezing of the soils was observed. Annual streamwater concentration of nitrate rose markedly that year (Fig. 28). Then, in 1973–1974, widespread freezing of the forest soils occurred again, and again nitrate concentration increased. Various workers have reported that the freezing and

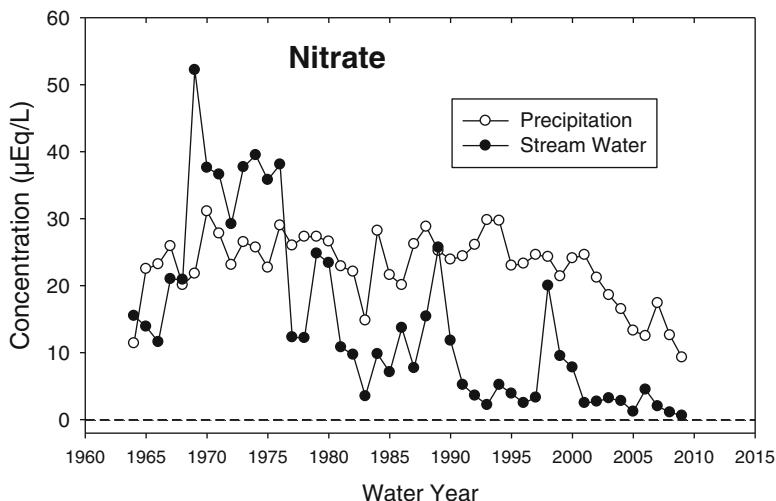


Fig. 28 Volume-weighted annual concentration of nitrate in bulk precipitation and stream water for Watershed 6 at the Hubbard Brook Experimental Forest during 1964–2009

thawing of soils promotes nitrification and the mobilization of nitrate to drainage waters (Arefyeva and Kolesnikov 1964; references cited in McGarity and Rajaratnam 1973). Therefore, freezing and thawing of the HB EF soils may have induced nitrification and the subsequent loss of relatively large amounts of nitrate in stream water. However, we have no explanation for the very slow rate of recovery (residual effect) observed during the 2 years after the freezing occurred in 1969–1970. It might have been expected that if soil frost enhanced nitrification, the nitrate would have been flushed rapidly from the system and in subsequent years nitrate concentrations in stream water would have returned to “normal.” Then, after ~1978 nitrate concentrations dropped to low values, barely above detection limits during summer after 1980. Soil freezing in December 1989 and 1997 may have increased nitrate concentration again in stream water of W6 (Fig. 28; see Mitchell et al. 1996). However, following a severe soil freezing event during winter of 2006, Judd et al. (2011) observed only minimal export of nitrate in stream water. Because it is difficult to differentiate among the many factors that could cause such different ecosystem responses, Judd et al. (2011) suggested that other changes over the past decades (e.g., acid rain impacts) may have combined to reduce the effects of frost events on nitrogen fluxes (see also Bernal et al. 2012).

Initially (1964–1974), an inverse relationship between nitrate and sulfate concentration in stream water was observed, but the long-term record shows the opposite (Fig. 29a; Likens et al. 1970). The relationship between nitrate and sulfate in precipitation also has changed with time (Fig. 29b). Streamwater concentrations of nitrate generally reach a maximum during the late winter (Fig. 30), whereas concentrations of sulfate at that time are at a minimum.

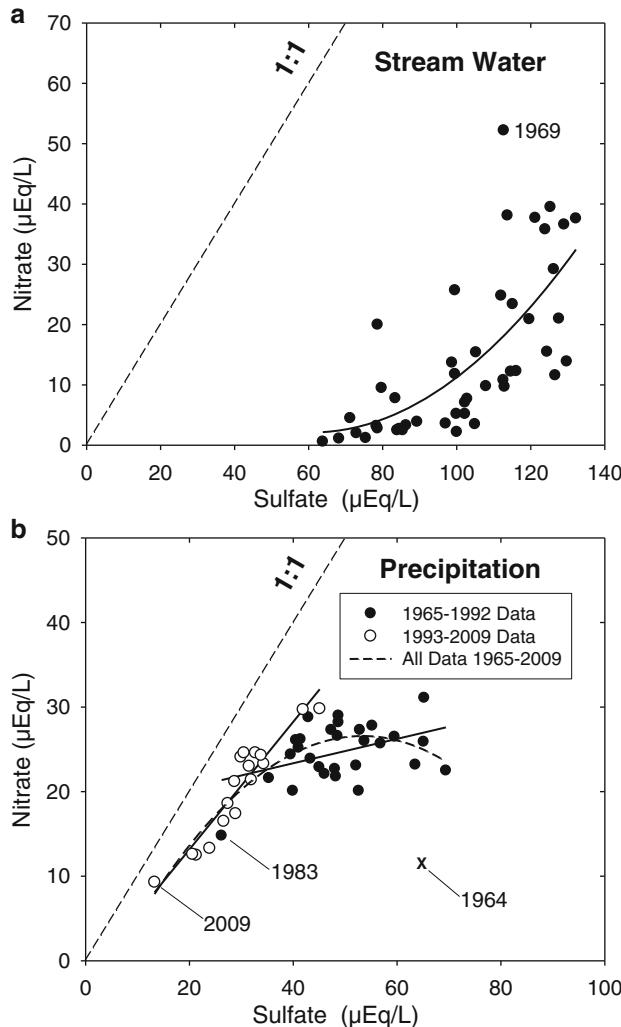


Fig. 29 Relationship between annual volume-weighted nitrate and sulfate concentrations in (a) stream water and (b) bulk precipitation of Watershed 6 of the Hubbard Brook Experimental Forest during 1964–2009. The second-order regression for (a) is significant ($p < 0.001$; $r^2 0.48$) and for (b) the dashed line is significant ($p < 0.001$; $r^2 0.59$); regression for 1965–1992 is not significant, but regression for 1993–2009 is significant ($p < 0.001$; $r^2 0.89$)

There is very poor correlation between the pattern for annual values of ammonium and/or nitrate in precipitation and in stream water (Fig. 19b) range in seasonal.

A final complicating factor is that some larger (untreated) watersheds show a larger range in seasonal nitrate concentrations in stream water than smaller watersheds (see below; Likens and Buso 2006), but there are differences in flow paths

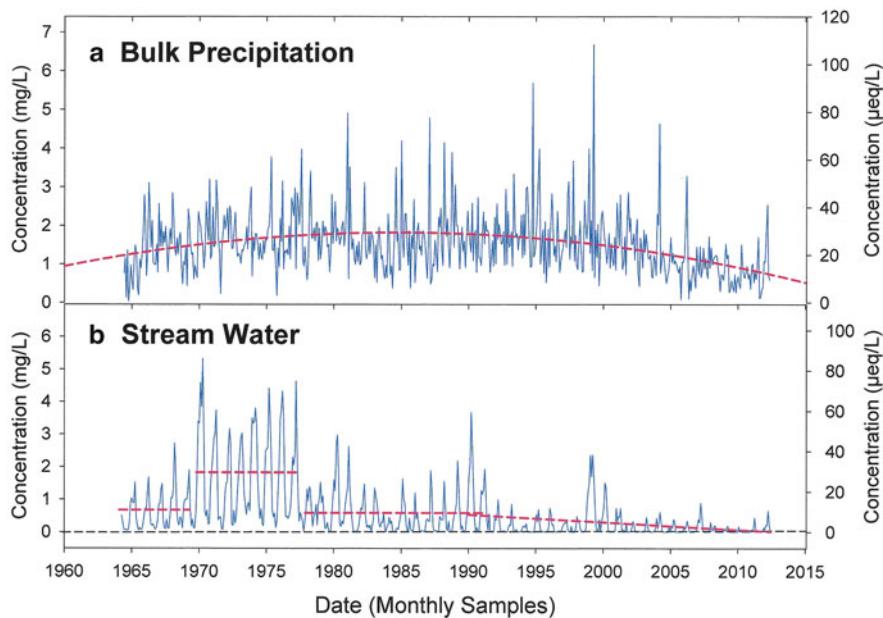


Fig. 30 Monthly volume-weighted concentrations of nitrate in bulk precipitation (a) and stream water (b) for Watershed 6 of the Hubbard Brook Experimental Forest during the period 1964–2012

(seeps) and geology; even so, a causal relationship is not clear. In particular, W1 (the 1999 Wollastonite-treated watershed) has recently begun to export significantly more nitrate, even during the dormant season, but an explanation for this response is elusive. Surface seeps tend to have a much higher nitrate concentration than nearby streams (Likens and Buso 2006).

Valleywide Streamwater Chemistry: A Synoptic View

In spring and fall of 2001, streamwater chemistry was measured at 100-m intervals in all streams of the Hubbard Brook Valley (Fig. 31; Likens and Buso 2006). The chemistry of streams varied throughout this large drainage network according to elevation, channel length, size of area drained, and type of drainage. Relatively large longitudinal differences were observed for elements like hydrogen ion, dissolved aluminum, and dissolved organic carbon throughout the drainage network, whereas other elements like sodium, chloride, and dissolved silica changed little. The chemistry of Hubbard Brook, a fifth-order river draining the valley, was

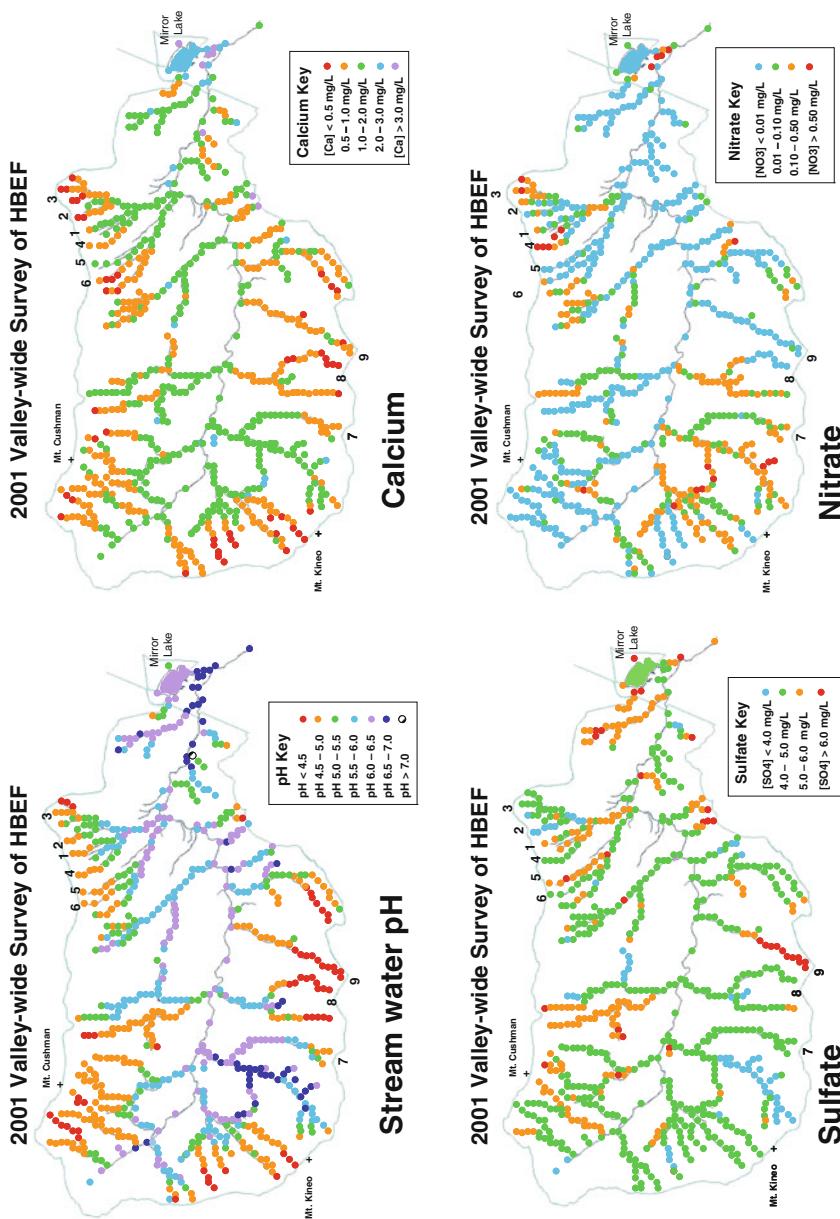
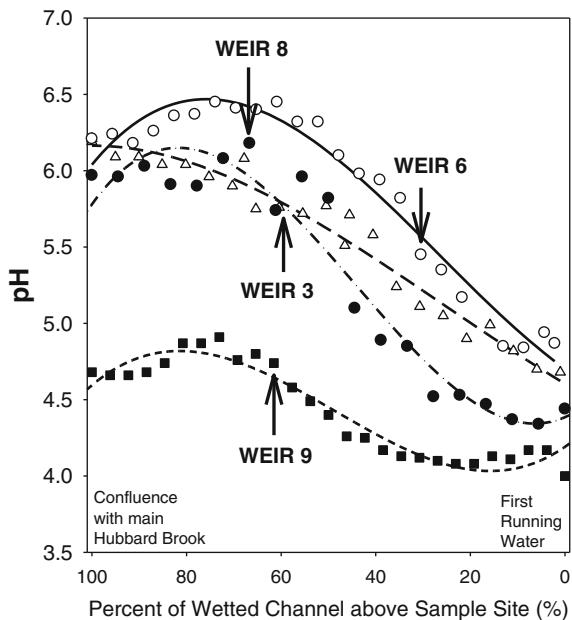


Fig. 31 Streamwater concentrations for pH, calcium, sulfate, and nitrate throughout the Hubbard Brook Valley (Adapted from Likens and Buso 2006)

Fig. 32 Distribution of pH concentrations along the longitudinal distance for Bear Brook (W6), Canyon Brook (W8), Paradise Brook (W3), and Cascade Brook (W9) of the Hubbard Brook Experimental Forest. Gauging stations are marked with arrows. The third-order polynomial regressions have r^2 of 0.97 for Bear Brook (W6), 0.97 for Paradise Brook, 0.94 for Canyon Brook, and 0.93 for Cascade Brook (modified from Likens and Buso 2006)



remarkably constant throughout its length in spite of different chemistry of inflowing tributaries (Likens and Buso 2006). Such synoptic view of streamwater chemistry at close intervals throughout and entire, large drainage system is unusual, but quite informative, as the larger scale adds new insights about patterns and dynamics of streamwater chemistry. For example, using streamwater pH as a critical diagnostic biogeochemical variable in the Hubbard Brook Valley, we learned that it was highly fortunate that the gauging weirs in the experimental watersheds had been sited at or near the pH inflection points along the longitudinal distance of the headwater streams being studied (Fig. 32).

As described elsewhere in this book, streamwater samples are collected routinely for chemical analysis from fixed locations above the gauging weirs. This approach is based on the assumption that the chemistry from these sites integrates the diverse biogeochemical processes occurring throughout the watershed-ecosystem above the sampling point (Bormann and Likens 1967; Likens and Buso 2006; Chap. 1). This synoptic study helped to clarify this assumption. Moreover, this study helped us to understand the temporal and spatial dynamics within the entire drainage network (Likens and Buso 2006). Likens and Buso (2006) review several previous, smaller-scale attempts to evaluate longitudinal/elevational changes in streamwater chemistry, but the effort in 2001 was the first, high-density, valleywide, synoptic study at HBEF.

The gauging stations had been situated in the HBEF on the basis of hydrologic, not biogeochemical, considerations, primarily whether bedrock was exposed for

attachment of the weir to prevent significant leakage of water around or under the gauging station. As it turns out, these locations are close to optimal for measuring stream chemistry because change is most obvious and pronounced at the inflection points along the stream channel in the longitudinal distribution of data (Fig. 32).

A variety of factors influence streamwater chemistry including soils, till, bedrock, vegetation, and hydrologic flow paths. For example, almost all tributaries had obvious pH trends along their longitudinal channels until they became fourth- to fifth-order streams. In contrast, the pattern of pH in Hubbard Brook was subdued, rather constant and quite different than the headwater streams (Fig. 31). As such, it is much more interesting and informative to study the biogeochemistry of the headwater streams. Moreover, the unprotected nature of Hubbard Brook in the vicinity of Mirror Lake leads to higher concentrations of various pollutants, e.g., road salt (Likens and Buso 2010b).

Seasonal Variations in Bulk Precipitation and Streamwater Concentrations

As noted elsewhere, climate and biologic activity at HBEF are distinctly seasonal, and much of the biogeochemistry reflects these climatic patterns. Normally the snowpack persists from about mid-November until mid-April (Table 2). The trees start to produce leaves during May, with full canopy closure by mid- to late May, and major leaf fall occurs in mid-October. These phenological events are changing, however, because of climate change (Campbell et al. 2007; Richardson et al. 2006; Hayhoe et al. 2007; Huntington et al. 2009; Vadeboncoeur et al. 2009; Groffman et al. 2012; Hamburg et al. 2013). Some organisms of the ecosystem, such as stream algae, have adapted to utilize the favorable environmental conditions of the transition periods between seasons (see Muller and Bormann 1976; Bernhardt et al. 2005).

The year has been divided into four seasons to investigate the short-term variations in chemistry of bulk precipitation and stream water: summer from 1 June to 30 September, autumn from 1 October to 30 November, winter from 1 December to 28 February, and spring from 1 March to 31 May. Although these periods are arbitrary, they correspond well with actual observed conditions and biologic activity at HBEF. Given the strong temporal trends in bulk precipitation and streamwater chemistry that have emerged during this long-term study, the seasonal data are presented here as means for both the entire period (1963–2009; Table 12) and for two decades (based on water-years): one early in the study 1964–1973, and one late, 2000–2009 (Tables 13–16).

Fall precipitation (+34 %) and especially streamflow (+71 %) have increased between the decades (Tables 13 and 15). It is unknown how ecosystem water storage has changed during this period. The weighted concentrations of various ions in bulk precipitation are highly variable on a storm or weekly basis, but several

Table 12 Seasonal volume-weighted average (a) bulk precipitation and (b) streamwater concentrations for entire period (1963–2009) for Watershed 6 of the Hubbard Brook Experimental Forest

Obs	Summer		Fall		Winter		Spring	
	Years	June–September	October–November	December–February	March–May			
		mg/L	μEq/L	mg/L	μEq/L	mg/L	μEq/L	mg/L
(a) Bulk precipitation concentration								
Calcium	47	0.08	4.0	0.08	4.0	0.06	3.0	0.14
Magnesium	47	0.02	1.6	0.03	2.5	0.02	1.6	0.04
Potassium	47	0.05	1.3	0.07	1.8	0.03	0.8	0.06
Sodium	47	0.05	2.2	0.14	6.1	0.11	4.8	0.11
Aluminum ^a	34	0.00	0.0	0.00	0.0	0.00	0.0	0.00
Ammonium	46	0.217	12.0	0.151	8.4	0.119	6.6	0.244
Hydrogen ion ^b	47	0.061	60.5	0.045	44.6	0.039	38.7	0.054
pH			4.22		4.35		4.41	4.27
Sulfate	46	2.62	54.5	1.59	33.1	1.20	25.0	2.19
Nitrate	46	1.27	20.5	1.33	21.4	1.44	23.3	1.60
Chloride	46	0.18	5.1	0.30	8.5	0.25	7.1	0.26
Phosphate	39	0.011	0.3	0.007	0.2	0.007	0.2	0.021
DOC ^c	15	1.3	0.0	0.6	0.0	0.4	0.0	0.8
Dissolved silica ^a	38	0.00	NA	0.00	NA	0.00	NA	0.00
	Totals	5.81 (mg/L)		4.36 (mg/L)		3.70 (mg/L)		5.54 (mg/L)
	Cations	81.6 (μEq/L)		67.3 (μEq/L)		55.5 (μEq/L)		83.7 (μEq/L)
	Anions	80.4 (μEq/L)		63.1 (μEq/L)		55.5 (μEq/L)		79.4 (μEq/L)
(b) Streamwater concentration								
Calcium	47	0.91	45.4	0.94	46.9	0.98	48.9	0.96
Magnesium	47	0.24	19.8	0.26	21.4	0.27	22.2	0.25
Potassium	47	0.11	2.8	0.21	5.4	0.19	4.9	0.23
Sodium	47	0.76	33.1	0.77	33.5	0.77	33.5	0.66
Aluminum ^d	40	0.27	20.3	0.29	21.8	0.30	22.5	0.33
Ammonium	46	0.020	1.1	0.023	1.3	0.017	0.9	0.016
Hydrogen ion ^b	47	0.011	11.3	0.010	10.0	0.011	10.8	0.013
pH			4.95		5.00		4.97	4.91
Sulfate	46	4.94	102.8	5.01	104.2	4.82	100.3	4.75
Nitrate	46	0.17	2.7	0.27	4.4	1.08	17.5	1.25
Chloride	46	0.39	11.0	0.50	14.1	0.48	13.5	0.44
Phosphate	38	0.003	0.1	0.002	0.1	0.003	0.1	0.003
DOC ^c	15	2.8	16.9	2.5	14.9	1.9	11.6	2.0
Dissolved silica	46	1.94	NA	1.95	NA	1.88	NA	1.63
	Totals	12.57 (mg/L)		12.72 (mg/L)		12.74 (mg/L)		12.55 (mg/L)
	Cations	133.7 (μEq/L)		140.2 (μEq/L)		143.7 (μEq/L)		141.1 (μEq/L)
	Anions	133.4 (μEq/L)		137.7 (μEq/L)		143.0 (μEq/L)		143.6 (μEq/L)

^aAluminum and dissolved silica are trace in precipitation

^bHydrogen ion in μg/L VWA-concentration

^cDOC has no charge in precipitation

^dAluminum valence assumed to be +2 (Buso et al. 2000)

^eDissolved organic carbon at 6 μEq/mg-C

Table 13 Seasonal volume-weighted average concentrations in bulk precipitation for Watershed 6 of the Hubbard Brook Experimental Forest for decades 1964–1973 and 2000–2009

	Decade (10-year block)	Precip (mm/ha)	Ca (mg/L)	Mg (mg/L)	K (mg/L)	Na (mg/L)	Al (mg/L) ^a	NH ₄ (mg/L)	H ⁺ (μEq/L)	SO ₄ (mg/L)	NO ₃ (mg/L)	Cl (mg/L)	PO ₄ (mg/L) ^b	dSi (mg/L) ^a
Summer	1964–1973	120.5	0.14	0.04	0.06	0.08	0.00	0.25	0.1	3.75	1.30	0.38	0.013	0.00
	2000–2009	128.3	0.06	0.02	0.04	0.05	0.00	0.19	0.0	1.55	0.92	0.10	0.005	0.00
Fall	1964–1973	114.9	0.16	0.07	0.08	0.21	0.00	0.20	0.1	2.43	1.51	0.50	0.009	0.00
	2000–2009	153.5	0.05	0.02	0.04	0.09	0.00	0.12	0.0	0.95	0.93	0.19	0.002	0.00
Winter	1964–1973	114.9	0.10	0.03	0.03	0.11	0.00	0.15	0.0	1.64	1.44	0.32	0.010	0.00
	2000–2009	108.2	0.05	0.02	0.02	0.11	0.00	0.10	0.0	0.80	1.17	0.21	0.002	0.00
Spring	1964–1973	110.5	0.21	0.05	0.06	0.12	0.00	0.26	0.1	3.08	1.74	0.36	0.034	0.00
	2000–2009	114.4	0.12	0.03	0.06	0.06	0.00	0.23	0.0	1.37	1.21	0.16	0.009	0.00
Years of observations (<i>n</i>)	47	47	47	47	47	34	46	47	46	46	46	39	38	

Years are water-years: 1 June–31 May

^aAluminum and dissolved silica (dSi) are trace only in precipitation

^bPhosphate data N/A in 1964–1968; early data based on 1971–1980 decade

Table 14 Seasonal water and volume-weighted average concentration changes in bulk precipitation for Watershed 6 of the Hubbard Brook Experimental Forest between decades 1964–1973 and 2000–2009

	Past to present	Precip	Ca	Mg	K	Na	Al ^a	NH ₄	H ⁺	SO ₄	NO ₃	Cl	PO ₄	dSi ^a
Summer	%Change	6	-54	-57	-29	-43	NA	-25	-65	-59	-29	-74	-59	NA
Fall	%Change	34	-71	-74	-48	-54	NA	-37	-65	-61	-38	-62	-78	NA
Winter	%Change	-6	-46	-46	-39	3	NA	-33	-46	-51	-18	-35	-83	NA
Spring	%Change	4	-43	-39	-9	-54	NA	-12	-63	-56	-30	-55	-75	NA

^aAluminum and dissolved silica (dSi) are trace only in precipitation

seasonal trends have emerged. In general, average cation concentrations are mostly lower during winter and somewhat higher during spring; sulfate concentrations are lowest in winter, but nitrate and chloride are lowest during summer. Highest average sulfate concentrations occur during summer, nitrate in spring, and chloride in fall (Table 12a; Fig. 33).

Seasonal bulk precipitation chemistry concentrations are much lower in the recent pentad (Fig. 33) reflecting the long-term trends in annual bulk precipitation chemistry (see Fig. 19). The total ionic concentration of bulk precipitation during the winter at HBEF is about 68 % that of the spring season of the year (Table 12a). Currently, this trend is reflected in the long-term concentrations, particularly of calcium, magnesium, hydrogen ion, chloride, and sulfate. Early in the record, a peak in concentration for sodium, potassium, and magnesium occurred in the autumn, but this increase has disappeared in the more recent pentad (Fig. 33; Table 13). As expected, all base cations in bulk precipitation have decreased in all seasons, except for sodium in the winter (+3 % increase). Inexplicably, there is no similar increase in winter chloride. Annual patterns for many of the elements may result in part from the origin of air masses and in part from lower aerosol scavenging efficiency by raindrops as compared to snowflakes. Herman and Gorham (1957) suggested from studies in Nova Scotia that snowflakes may be less efficient than raindrops in removing materials from the atmosphere. Nitrate concentrations in bulk precipitation tend to increase in winter and spring, whereas sulfate and ammonium tend to increase in spring and summer (Fig. 33; Tables 12a and 13). Higher sulfate concentrations in the spring and summer are usually attributed to more rapid oxidation of SO₂ to sulfate in the warmer months. Likewise, SO₂ concentrations in the atmosphere are usually higher in the winter because SO₂ is not being converted to sulfate as rapidly. Ammonium is higher in the spring and summer because there are greater NH₃ emissions from increased volatilization (followed by conversion to ammonium) from the soil during these warmer months.

Other unexplained variations include that calcium equivalent concentrations in bulk precipitation were much greater than (almost double) sodium values during the spring and summer but are less than sodium during the autumn and winter during 1964–1973 (Table 13). The relatively high concentrations of sodium and chloride in autumn rains relative to other seasons may reflect a larger influence from marine aerosols from coastal storms at this time in the eastern USA (e.g., Likens et al. 1990b).

Table 15 Seasonal volume-weighted average concentrations in stream water for Watershed 6 of the Hubbard Brook Experimental Forest between decades 1964–1973 and 2000–2009

Season	Decade (10-year block)	Flow (mm/ha)	Ca (mg/L)	Mg (mg/L)	K (mg/L)	Na (mg/L)	Al (mg/L) ^a	NH ₄ (mg/L)	H ⁺ (μEq/L)	SO ₄ (mg/L)	NO ₃ (mg/L)	Cl (mg/L)	PO ₄ (mg/L) ^b	dSi (mg/L)
Summer	1964– 1973	31.5	1.26	0.31	0.15	0.82	0.19	0.045	0.0	6.37	0.42	0.47	0.004	4.45
	2000– 2009	42.6	0.85	0.26	0.12	0.98	0.26	0.007	0.0	4.88	0.02	0.45	0.002	5.28
Fall	1964– 1973	63.6	1.37	0.37	0.23	0.90	0.34	0.074	0.0	6.50	0.70	0.60	0.004	4.77
	2000– 2009	108.9	0.62	0.20	0.19	0.71	0.24	0.005	0.0	3.65	0.04	0.43	0.001	3.74
Winter	1964– 1973	52.3	1.43	0.37	0.22	0.85	0.27	0.037	0.0	5.92	2.21	0.56	0.002	4.29
	2000– 2009	67.7	0.63	0.20	0.14	0.72	0.21	0.005	0.0	3.69	0.21	0.41	0.001	3.87
Spring	1964– 1973	157.2	1.36	0.33	0.25	0.71	0.35	0.026	0.0	5.76	2.29	0.52	0.003	3.50
	2000– 2009	138.5	0.61	0.19	0.19	0.24	0.005	0.0	3.52	0.26	0.36	0.001	3.44	
Years of observations (<i>n</i>)	47	47	47	47	40	46	47	46	46	46	46	38	38	46

Years are water-years: 1 June–31 May
^aSi dissolved silicate

^bAluminum data N/A 1971–1975; data from 1964–1970 (7-years) and 1976–1978 (3-years) used for early decade
Phosphate data N/A in 1964–1971; early data based on 1972–1983 decade

Table 16 Seasonal water and volume-weighted average concentration changes in stream water for Watershed 6 of the Hubbard Brook Experimental Forest between decades 1964–1973 and 2000–2009

	Past to present	Flow	Ca	Mg	K	Na	Al	NH ₄	H ⁺	SO ₄	NO ₃	Cl	PO ₄	dSi
Summer	%Change	35	-32	-18	-19	19	36	-84	-27	-23	-95	-5	-54	19
Fall	%Change	71	-55	-48	-18	-22	-31	-93	-36	-44	-95	-29	-78	-22
Winter	%Change	29	-56	-45	-34	-15	-22	-87	-51	-38	-91	-26	-69	-10
Spring	%Change	-12	-55	-43	-26	-74	-31	-80	-48	-39	-89	-31	-66	-2

dSi dissolved silica

Overall, large declines in average concentrations occurred for almost all solutes between 1964–1973 and 2000–2009 decades, especially for calcium, hydrogen ion, sulfate, nitrate, and chloride. The least amount of change occurred between winter and the largest change occurred between fall decades (Tables 13 and 14). The fall precipitation volume increased by 63 % between these decades.

Concentrations of most ions in stream water are much less variable seasonally than in bulk precipitation (Figs. 34 and 35; Table 12b). Like seasonal precipitation values, seasonal streamwater concentrations are consistently lower in the recent pentad than the earlier one (Figs. 34 and 35; Table 15). Concentrations in stream water are slightly lower in the summer, in part because of the intense biologic utilization (uptake) of potassium and nitrate during the growing season (Fig. 34). Both dissolved silica and sodium concentrations in stream water have increased in summer between decades (Tables 15 and 16). Is this because of deeper flow paths?

In general, nitrate concentrations in stream water begin to rise in the autumn when there is a reduction in biologic activity and attain a maximum concentration in the winter or early spring (Figs. 30 and 34; Likens 2004). As streamwater nitrate concentrations have declined with time (Fig. 28), the seasonal pattern also has become more subdued (Figs. 30 and 34). US Geological Survey Water Resources data show a similar pattern for rivers and streams throughout New England and New York State. This pattern also has been observed in the surface waters of Mirror Lake (Buso et al. 2009, p. 122) and in other freshwater lakes where nitrate concentrations reach maximum levels in winter and early spring. The increase in non-anthropogenic nitrate concentrations in lakes has been attributed to increased nitrification during the winter (Hutchinson 1957, p. 871), but at HBEF the early spring maximum may be the result of decreased plant uptake by terrestrial deciduous vegetation and increased soil production (and retention) during winter (e.g., Judd et al. 2007).

At HBEF, we initially observed that nitrate concentrations increased markedly with increased streamflow (Johnson et al. 1969). However, this may have been a fortuitous relationship since the late winter–early spring period of maximum streamflow is potentially also a time for relatively high nitrification in the soil (see Judd et al. 2007). With time and changing conditions, e.g., reduced winter snowpack, however, this relationship has all but disappeared. Even though there may be no causal relationship between high nitrate concentration and increased streamflow, the fact that the late winter–early spring period of high nitrate concentrations also is

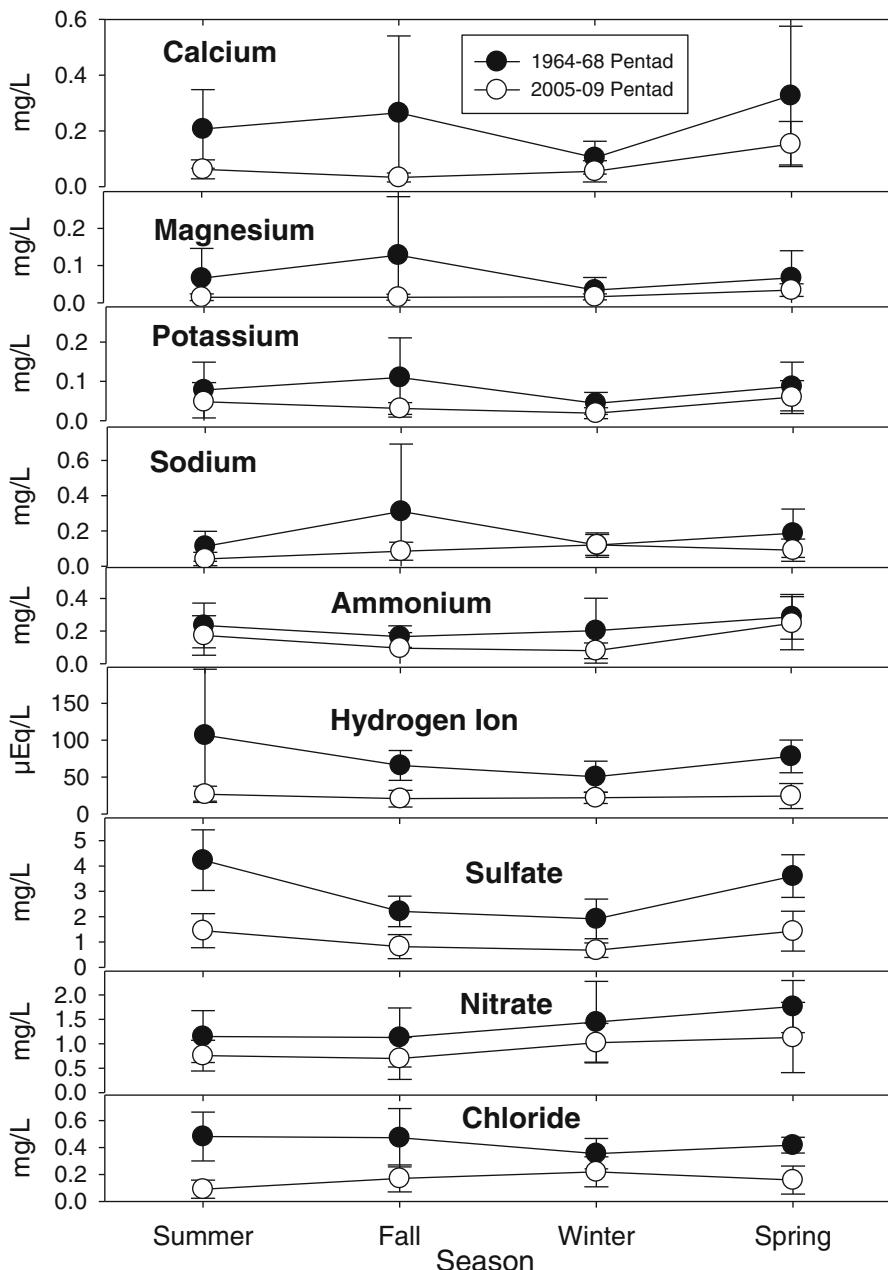


Fig. 33 Mean seasonal bulk precipitation concentrations \pm 1 SD for calcium, magnesium, potassium, sodium; ammonium, hydrogen ion, sulfate, nitrate, and chloride during two pentads, 1964–1968 and 2005–2009, in Watershed 6 of the Hubbard Brook Experimental Forest

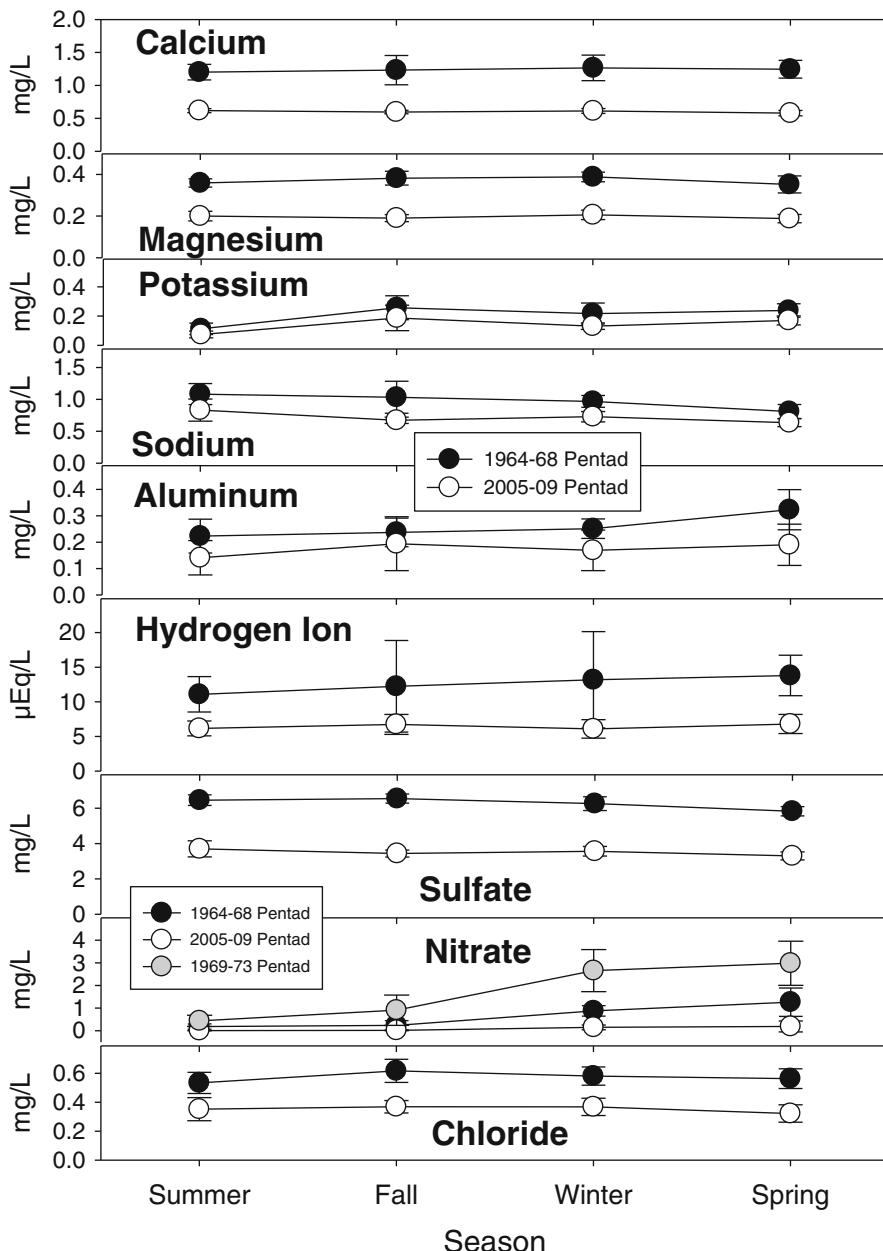


Fig. 34 Mean seasonal streamwater concentrations ± 1 SD for calcium, magnesium, potassium, sodium; aluminum, hydrogen ion, sulfate, nitrate, and chloride during two pentads, 1964–1968 and 2005–2009, in Watershed 6 of the Hubbard Brook Experimental Forest

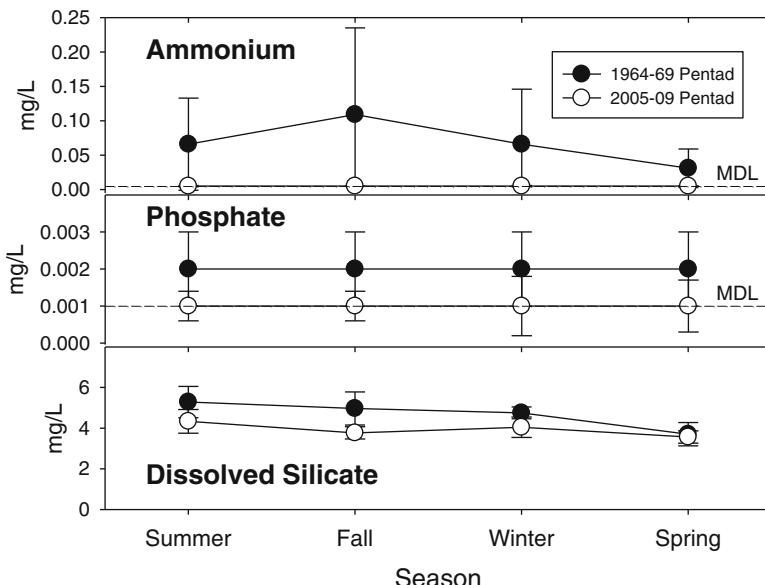


Fig. 35 Mean seasonal streamwater concentrations ± 1 SD for dissolved silica, ammonium, and phosphate during two pentads, 1964–1968 and 2005–2009, in Watershed 6 of the Hubbard Brook Experimental Forest

characterized by large discharge remains of prime importance to nutrient budget calculations.

The seasonal pattern for ammonium concentrations in stream water is quite interesting. During the early pentad (1964–1968; Fig. 35; Table 15), there was a clear peak in ammonium concentration during the autumn, which probably reflects increased decomposition of organic matter in the forest floor after leaf fall. In the current period (Table 15), however, streamwater concentrations of ammonium consistently are very low throughout the year and show no distinct seasonal pattern (Fig. 35). Most solutes have an individual pattern of seasonal change between the two decades (Tables 15 and 16). Patterns are not necessarily in synchrony for bulk precipitation and stream water, raising many intriguing biogeochemical questions.

Long-Term Trends in Bulk Precipitation and Streamwater Chemistry

Longer-term biogeochemical records, now spanning some 49 years, have revealed some remarkable trends in the chemistry of bulk precipitation and stream water at HBEF. Notably, annual volume-weighted concentrations of hydrogen ion, sulfate, and calcium in bulk precipitation decreased by 80 %, 75 %, and 66 %, respectively,

since 1963 or 1964 (Fig. 19). Since the amount of annual precipitation increased only 14 % during this period (Fig. 19), the annual inputs of these ions also decreased significantly (see Chap. 4; Likens 1992; Likens and Buso 2012). The decline of acid anions and base cations in surface waters recorded at HBEF since 1963–1964 has also been found more widely in the eastern USA and in northwest-Europe, although the length of record at these other locations is shorter (e.g., Hedin et al. 1994; Watmough et al. 2005; Clair et al. 2010; Navrátil et al. 2010). Most of the decline in base cations at HBEF was due to a decline in calcium concentrations, and most of this decline occurred prior to about 1975 (Figs. 18 and 19a). By 1969 it appeared that the annual nitrate concentration in bulk precipitation was on an upward trend (Fig. 19b), but the longer-term record indicates that between about 1972 and 2002 nitrate concentrations were relatively flat, and now concentrations have declined and are similar or lower than values in the mid-1960s (Figs. 19b, 28, and 30).

The long-term record for concentration of hydrogen ion in bulk precipitation is particularly interesting (Fig. 14). Clearly the average precipitation at HBEF is not as acidic today as it was in the 1960s, but it required 18 years of measurement to fit a statistically significant linear regression ($p < 0.05$) to these temporal data (Likens 1989). A close examination of this long-term record, however, shows periods when several years of data give contrasting trends (Fig. 14). Obviously, short-term (3–6 years) records can be misleading relative to the overall trend. This is an important finding not only for interpreting results from the HBES, but also for general ecological studies and state and national monitoring programs of management relevance (see Lindenmayer and Likens 2010).

Coincident with the declines in annual volume-weighted concentrations in bulk precipitation were declines in the chemistry of stream water at HBEF (Table 10; Likens and Buso 2012). Average calcium, sulfate, and hydrogen ion concentrations declined by 64 %, 52 %, and 59 %, respectively, during 1963 or 1964–2009 (Fig. 19). Calcium concentrations in stream water actually increased from 1963–1964 to 1969–1970 and then decreased steadily thereafter. The decline in annual sum of base cations and sulfate concentrations in stream water was closely correlated with the decline in atmospheric inputs of gaseous and particulate pollutants (e.g., Driscoll et al. 1989a, b; Likens 1992; Likens et al. 1998, 2002a, 2005). The decrease in annual concentration of hydrogen ion in stream water was relatively small in the long-term record (Fig. 19b), primarily because the decline in sum of base cations was paralleled by the decline in sulfate concentration (Fig. 19a; Driscoll et al. 1989a, b).

It has been suggested that a few streamwater samples can serve as a biogeochemical baseline for a terrestrial ecosystem. This assumption is tenuous at best given the long-term data presented in this chapter. For example, from a monthly sample effort over 18 years, Palmer et al. (2004) did not detect the long-term trends in streamwater chemistry we observe from our systematic, weekly sampling extending over 48 years in the same watershed. Moreover, the marked and often unexplainable changes in the intensively sampled stream water of the HBEF suggest caution in attributing baseline characteristics to a few samples that unwittingly may

characterize a high or low period in the history of the site. It would be misleading to generate different conclusions about the biogeochemistry of W6 from two different decadal-long data sets for precipitation and streamwater chemistry separated by nearly three decades. Clearly, the most useful biogeochemical baseline is one of sufficient length to allow trend analyses, and even then the baseline may be elusive (Likens and Buso 2012).

Chapter 4

Input–Output Budgets

Because our ecosystems are watersheds, the flux of chemicals into the system may be simplified to that in atmospheric deposition (meteorologic vector) and the output to that in drainage waters (geologic vector), at least for those nutrients without a prominent gaseous phase (Bormann and Likens 1967; Likens and Bormann 1972). Theoretically, then, the difference between annual hydrologic input (I) and output (O), the Net Hydrologic Flux (NHF) for a given chemical constituent, shows whether that constituent is being accumulated within the ecosystem, $I > O$; is being lost from the system, $I < O$; or is quantitatively passing through the system, $I = O$. By this definition, the release of weathering products does not represent an input to the ecosystem per se; instead, weathering is considered as a process internal to the ecosystem and a part of the intrasystem cycle (Fig. 1; Bormann and Likens 1967; Likens and Bormann 1972). Likewise, uptake and long-term storage of nutrients by plants are internal ecosystem processes and not outputs, per se. On the other hand, complete mass-balance calculations or NEF (Net Ecosystem Flux), on the time frame of the HBES (about 50 years), considers annual weathering release or net soil release as an input and annual biomass storage as an output (see below and Chap. 6).

Explicit boundaries for an ecosystem (a watershed in our case) are necessary to make quantitative measures of flux when determining input–output budgets. Because ecosystem boundaries usually are determined by the investigator to make these quantitative measures of flux, rather than on the basis of some known or obvious functional discontinuity, between ecosystems, such as the shoreline of a lake, has raised criticism about this ecosystem approach (e.g., see Likens 1998; Fitzsimmons 1996; Currie 2011). Nevertheless, the theoretical and methodological components and constraints for establishing ecosystem boundaries are given in Bormann and Likens (1967, 1979); Likens and Bormann (1972); Likens (1975, 1992, 2001); Likens and Bormann (1985); and Wiens et al. (1985). Using watershed boundaries, when topographic and phreatic boundaries are the same and when the geologic substrate is relatively watertight, as at HBEP, alleviates this problem as water is the primary transport vector in humid areas (Bormann and Likens 1967; Likens and Bormann 1972).

Mass Meteorologic Input of Dissolved Substances

The long-term average annual input of dissolved inorganic substances in rain and snow was calculated to be 23 kg/ha or 2,081 Eq/ha during 1963–2009 (see Tables 17 and 19). Characterizing the “dilution effect” (see above), the atmospheric input of total solutes during an early wet year (1973–1974) was 3,377 Eq/ha-year, whereas the input during a similar wet year in 1995–1996 (6 % less water input) was 2,390 Eq/ha (29 % less than the solute input in 1973–1974). Nevertheless, even with this gradual “dilution effect,” the input of chemicals in bulk precipitation to these forested ecosystems is substantial, both as nutrients and as weathering agents.

Annual Variation in Net Hydrologic Budgets

There now are, depending on the chemical constituent, almost 50 years of quantitative annual net hydrologic budgets (NHF) for precipitation (P) input and streamwater (S) output at the HBEF. Over the long term, there has been considerable change but relatively small uncertainty in mean annual budgets for most of the major ions (Tables 17 and 18). Comparing medians, there has been hydrologic net loss (S>P) of calcium (6.9 times), magnesium (6.5 times), potassium (2.9 times), sodium (4.9 times), sulfate (1.6 times), chloride (1.3 times), DOC (1.9 times), aluminum, and dissolved silica and net gain (P>S) of ammonium (21.6 times), nitrate (4.3 times), hydrogen ion (7.1 times), and phosphate (6.6 times) from these watershed-ecosystems (Tables 17 and 18; Likens 2004). The long-term averages show a small net gain in phosphate and a small net loss of chloride each year, but there is no statistical difference ($p>0.05$) between mean annual inputs in bulk precipitation and streamwater outputs (Table 18).

There are two separate considerations in evaluating annual hydrologic input minus output budgets: (1) the direction of the net change, whether input is greater or less than output, and (2) the magnitude of the net change, i.e., the difference in amount between input and output. These parameters may vary from year to year for the individual chemical elements (Figs. 36a–c and 37). For some elements, data from a single annual cycle ($n = 1$) are sufficient to establish the direction of net change; for others, data from several years ($n>1$) are necessary. Similarly, a variable number of years are required to characterize the magnitude of net change with meaningful confidence limits. Based on almost 50 years of study at the HBEF, it is possible to make some generalizations about the annual budgets for the various ions. Generally, the direction of net change for budgets of bulk precipitation input minus streamwater output for calcium, magnesium, sodium, aluminum, ammonium, hydrogen ion, sulfate, and dissolved silica was predictable from only a few years (1–3) of data (Table 17; Fig. 36a–c). For these ions, the direction of the budget difference is not in doubt, but the magnitude may be. For potassium, nitrate, phosphate, and chloride, one or a few years were likely to give unreliable results for both

Table 17 Inputs in bulk precipitation (IN) and outputs in stream water (OUT) for Watershed 6 of the Hubbard Brook Experimental Forest during 1963–2009

Water-year	Ca	Ca	Ca	Mg	Mg	Mg	K	K	K
	IN	OUT	NET	IN	OUT	NET	IN	OUT	NET
1963	3.0	10.7	-7.7	0.7	2.4	-1.6	2.3	1.8	0.6
1964	3.1	4.8	-1.7	1.2	1.8	-0.6	1.4	1.1	0.3
1965	2.6	10.4	-7.7	0.6	2.7	-2.1	0.6	1.3	-0.8
1966	2.1	10.8	-8.7	0.4	2.9	-2.5	0.6	1.7	-1.1
1967	2.8	12.2	-9.4	0.9	3.5	-2.6	1.0	2.4	-1.4
1968	1.6	11.7	-10.1	0.4	3.0	-2.6	0.7	2.3	-1.6
1969	2.2	14.1	-12.0	0.4	3.2	-2.8	0.8	2.3	-1.5
1970	1.9	12.1	-10.1	0.6	2.8	-2.3	1.2	1.7	-0.6
1971	1.2	10.7	-9.4	0.4	2.5	-2.1	0.3	1.7	-1.4
1972	1.1	14.0	-12.8	0.5	3.2	-2.7	0.6	2.4	-1.8
1973	2.0	19.0	-17.0	0.4	4.3	-3.9	0.8	3.1	-2.3
1974	1.2	11.2	-10.0	0.4	2.8	-2.4	0.5	2.1	-1.6
1975	1.2	15.2	-14.0	0.3	3.6	-3.3	0.5	2.3	-1.8
1976	1.3	10.1	-8.8	0.3	2.5	-2.2	0.4	1.9	-1.5
1977	1.1	10.9	-9.8	0.4	2.6	-2.2	0.7	1.8	-1.2
1978	0.8	8.9	-8.1	0.3	2.2	-1.8	0.6	1.8	-1.2
1979	1.1	8.2	-7.0	0.4	2.0	-1.7	0.9	2.1	-1.2
1980	1.3	8.7	-7.4	0.5	2.3	-1.8	0.8	2.0	-1.2
1981	1.1	10.0	-8.9	0.3	2.5	-2.3	0.6	1.8	-1.2
1982	0.9	7.7	-6.8	0.3	2.1	-1.7	0.7	1.7	-1.0
1983	1.1	8.7	-7.6	0.3	2.2	-1.9	0.7	2.3	-1.6
1984	1.0	6.2	-5.2	0.3	1.7	-1.4	0.6	1.5	-0.9
1985	0.9	8.0	-7.1	0.3	2.2	-1.9	0.4	1.9	-1.5
1986	0.6	7.6	-7.1	0.2	2.1	-1.9	0.3	2.1	-1.8
1987	1.1	7.1	-6.0	0.3	2.1	-1.8	0.7	1.4	-0.7
1988	1.1	6.9	-5.7	0.3	2.0	-1.7	0.5	1.9	-1.4
1989	1.4	10.1	-8.7	0.4	2.7	-2.3	0.9	2.4	-1.5
1990	1.2	9.8	-8.5	0.4	2.7	-2.3	0.8	1.6	-0.8
1991	1.1	7.4	-6.3	0.3	2.1	-1.7	0.6	1.4	-0.8
1992	0.9	7.0	-6.1	0.3	2.0	-1.7	0.6	1.5	-0.9
1993	1.2	7.3	-6.0	0.3	2.0	-1.7	0.6	1.4	-0.8
1994	1.0	5.4	-4.4	0.2	1.6	-1.3	0.6	1.0	-0.4
1995	1.3	9.7	-8.4	0.5	2.7	-2.2	0.7	2.6	-1.9
1996	1.1	7.8	-6.7	0.4	2.2	-1.9	0.6	1.9	-1.3
1997	1.0	5.6	-4.5	0.3	1.7	-1.4	0.8	1.5	-0.7
1998	1.5	8.3	-6.7	0.3	2.4	-2.0	0.7	2.0	-1.4
1999	1.7	8.1	-6.4	0.5	2.3	-1.8	0.9	2.9	-1.9
2000	0.8	4.9	-4.1	0.2	1.5	-1.3	0.5	1.6	-1.1
2001	1.2	5.3	-4.1	0.3	1.6	-1.3	0.6	1.4	-0.8
2002	1.1	4.4	-3.4	0.2	1.4	-1.1	0.6	1.2	-0.6
2003	1.2	7.7	-6.5	0.4	2.2	-1.8	0.6	1.9	-1.3
2004	0.8	6.1	-5.3	0.3	1.9	-1.6	0.5	1.6	-1.1
2005	1.2	7.6	-6.5	0.3	2.3	-2.0	0.8	1.8	-1.0

(continued)

Table 17 (continued)

Water-year	Ca	Ca	Ca	Mg	Mg	Mg	K	K	K
	IN	OUT	NET	IN	OUT	NET	IN	OUT	NET
2006	0.8	6.2	-5.4	0.2	2.0	-1.7	0.7	2.0	-1.3
2007	1.3	6.5	-5.2	0.3	2.1	-1.8	0.5	1.8	-1.3
2008	1.0	6.6	-5.6	0.3	2.1	-1.8	0.6	1.4	-0.8
2009	1.0	6.8	-5.8	0.3	2.2	-1.9	0.5	1.7	-1.2
SUM	63.4	414.5	-351.1	18.2	111.0	-92.8	32.9	87.1	-54.2
AVG	1.3	8.8	-7.5	0.4	2.4	-2.0	0.7	1.9	-1.2
±SD	0.6	3.0	2.8	0.2	0.6	0.5	0.3	0.4	0.5
Water-year	Na	Na	Na	Al	Al	Al	NH ₄	NH ₄	NH ₄
	IN	OUT	NET	IN	OUT	NET	IN	OUT	NET
1963	1.0	5.4	-4.3	0.0	0.9	-0.9	na	na	na
1964	2.2	4.1	-1.9	0.0	1.4	-1.4	2.0	0.29	1.8
1965	1.9	6.3	-4.4	0.0	2.4	-2.4	2.7	0.94	1.7
1966	1.2	6.7	-5.4	0.0	2.8	-2.8	2.4	0.37	2.0
1967	2.2	8.7	-6.5	0.0	3.0	-3.0	3.1	0.24	2.8
1968	1.4	6.9	-5.6	0.0	2.7	-2.7	3.3	0.13	3.2
1969	1.8	7.1	-5.3	0.0	3.2	-3.2	3.2	0.39	2.8
1970	1.4	6.3	-4.9	0.0	na	na	4.6	0.23	4.4
1971	1.4	5.6	-4.2	0.0	na	na	2.9	0.07	2.8
1972	1.5	7.9	-6.5	0.0	na	na	2.3	0.21	2.1
1973	1.4	9.1	-7.7	0.0	na	na	3.8	0.44	3.4
1974	1.8	5.9	-4.2	0.0	na	na	2.3	0.16	2.1
1975	1.0	8.0	-7.0	0.0	na	na	2.4	0.19	2.2
1976	0.9	5.9	-5.0	0.0	2.9	-2.9	2.4	0.07	2.3
1977	1.3	6.3	-5.0	0.0	3.8	-3.8	2.1	0.10	2.0
1978	1.5	5.6	-4.1	0.0	3.7	-3.7	2.3	0.10	2.2
1979	1.3	5.3	-4.0	0.0	2.5	-2.5	2.1	0.13	2.0
1980	2.2	6.4	-4.2	0.0	3.5	-3.5	2.8	0.16	2.6
1981	0.6	7.1	-6.4	0.0	4.2	-4.2	2.9	0.16	2.7
1982	1.3	6.0	-4.7	0.0	3.1	-3.1	2.9	0.12	2.7
1983	1.1	6.5	-5.4	0.0	3.6	-3.6	1.5	0.17	1.3
1984	0.8	5.1	-4.3	0.0	2.1	-2.1	2.5	0.10	2.4
1985	0.8	6.0	-5.2	0.0	2.9	-2.9	2.0	0.19	1.9
1986	0.7	5.8	-5.1	0.0	2.7	-2.7	2.1	0.23	1.8
1987	1.3	6.0	-4.7	0.0	2.3	-2.3	2.7	0.17	2.6
1988	1.1	5.6	-4.6	0.0	2.2	-2.2	2.5	0.15	2.4
1989	1.3	8.2	-6.9	0.0	4.2	-4.2	3.5	0.25	3.2
1990	1.2	7.6	-6.4	0.0	4.4	-4.4	3.8	0.30	3.5
1991	1.3	5.7	-4.5	0.0	1.7	-1.7	2.9	0.21	2.7
1992	1.5	6.0	-4.5	0.0	2.6	-2.6	3.0	0.31	2.7
1993	1.8	6.4	-4.6	0.0	3.0	-3.0	3.4	0.11	3.3
1994	1.0	5.2	-4.2	0.0	1.6	-1.6	2.8	0.08	2.7
1995	3.0	9.9	-6.9	0.0	4.8	-4.8	3.3	0.13	3.2
1996	1.9	8.2	-6.3	0.0	3.9	-3.9	3.1	0.08	3.0

(continued)

Table 17 (continued)

Water-year	Na	Na	Na	Al	Al	Al	NH ₄	NH ₄	NH ₄
	IN	OUT	NET	IN	OUT	NET	IN	OUT	NET
1997	0.9	5.3	-4.4	0.0	2.2	-2.2	3.0	0.11	2.9
1998	1.2	7.4	-6.2	0.0	3.6	-3.6	3.1	0.06	3.0
1999	1.7	7.5	-5.8	0.0	3.8	-3.8	3.6	0.06	3.5
2000	0.7	4.8	-4.1	0.0	1.8	-1.8	2.3	0.04	2.2
2001	1.3	5.5	-4.2	0.0	1.9	-1.9	2.9	0.04	2.9
2002	0.9	4.8	-3.9	0.0	1.6	-1.6	2.7	0.03	2.6
2003	1.9	8.6	-6.7	0.0	4.1	-4.1	3.2	0.06	3.1
2004	1.4	7.1	-5.7	0.0	2.7	-2.7	2.0	0.05	1.9
2005	1.6	9.0	-7.4	0.0	3.3	-3.3	2.3	0.06	2.3
2006	0.9	6.9	-6.0	0.0	2.7	-2.7	1.8	0.05	1.7
2007	1.1	7.3	-6.2	0.0	2.6	-2.6	3.6	0.05	3.5
2008	1.1	7.2	-6.0	0.0	1.0	-1.0	1.9	0.06	1.9
2009	1.1	7.5	-6.5	0.0	1.0	-1.0	1.3	0.06	1.3
SUM	64.0	312.1	-248.0	0.0	114.4	-114.4	125.2	7.7	117.5
AVG	1.4	6.6	-5.3	0.0	2.8	-2.8	2.7	0.2	2.6
±SD	0.5	1.3	1.2	0.0	1.0	1.0	0.7	0.2	0.6
Water-year	H ⁺	H ⁺	H ⁺	SO ₄	SO ₄	SO ₄	NO ₃	NO ₃	NO ₃
	IN	OUT	NET	IN	OUT	NET	IN	OUT	NET
1963	0.86	0.10	0.76	na	na	na	na	na	na
1964	0.74	0.07	0.67	30.4	29.7	0.7	6.9	4.8	2.1
1965	0.89	0.09	0.80	42.7	47.1	-4.5	17.9	6.5	11.4
1966	1.06	0.11	0.95	42.1	51.4	-9.3	19.8	6.1	13.7
1967	1.08	0.11	0.96	46.0	58.2	-12.2	23.6	12.4	11.2
1968	0.93	0.14	0.79	34.1	51.5	-17.4	16.8	11.6	5.2
1969	0.99	0.14	0.85	31.5	47.1	-15.6	18.4	28.2	-9.8
1970	1.28	0.14	1.14	41.7	52.6	-11.0	25.7	19.3	6.3
1971	0.92	0.12	0.80	34.0	46.0	-12.0	22.1	16.8	5.2
1972	1.05	0.17	0.88	39.1	62.4	-23.3	22.4	18.6	3.8
1973	1.20	0.22	0.97	54.0	81.5	-27.6	31.1	32.7	-1.6
1974	0.87	0.10	0.77	35.7	48.7	-13.0	20.8	19.8	1.0
1975	1.03	0.15	0.89	40.8	70.7	-29.9	24.9	26.3	-1.4
1976	0.85	0.10	0.75	32.8	46.4	-13.6	25.2	20.1	5.1
1977	1.05	0.12	0.93	39.5	54.8	-15.3	24.7	7.5	17.2
1978	0.94	0.12	0.81	34.5	46.9	-12.4	23.1	6.4	16.6
1979	0.72	0.08	0.64	27.1	38.2	-11.1	20.2	10.9	9.3
1980	0.79	0.11	0.69	31.6	43.2	-11.6	22.4	11.3	11.1
1981	0.80	0.14	0.66	34.3	55.7	-21.4	22.5	6.9	15.6
1982	0.74	0.09	0.65	31.2	44.1	-13.0	19.4	4.9	14.5
1983	0.56	0.12	0.44	20.6	50.5	-29.9	15.0	2.2	12.9
1984	0.66	0.08	0.58	28.1	34.8	-6.7	21.0	4.1	16.9
1985	0.61	0.12	0.48	24.1	44.8	-20.7	19.1	4.0	15.0
1986	0.62	0.10	0.52	25.1	39.5	-14.4	16.3	7.1	9.2
1987	0.68	0.07	0.61	25.7	38.0	-12.3	20.9	3.7	17.3

(continued)

Table 17 (continued)

Water-year	H ⁺	H ⁺	H ⁺	SO ₄	SO ₄	SO ₄	NO ₃	NO ₃	NO ₃
	IN	OUT	NET	IN	OUT	NET	IN	OUT	NET
1988	0.66	0.07	0.58	25.4	35.7	-10.3	22.0	6.7	15.3
1989	0.79	0.12	0.67	30.6	50.4	-19.8	24.3	16.8	7.5
1990	0.82	0.15	0.67	34.7	53.7	-19.0	24.7	8.2	16.5
1991	0.70	0.10	0.60	26.9	42.4	-15.4	21.5	2.8	18.7
1992	0.71	0.11	0.61	26.7	41.5	-14.8	22.2	2.0	20.2
1993	0.78	0.09	0.69	30.4	43.7	-13.3	25.9	1.2	24.7
1994	0.63	0.06	0.57	23.3	30.0	-6.7	21.3	2.0	19.3
1995	0.79	0.18	0.61	27.3	59.8	-32.5	25.8	3.4	22.4
1996	0.70	0.14	0.56	26.5	48.8	-22.3	23.3	1.9	21.4
1997	0.50	0.07	0.42	20.3	32.0	-11.7	19.7	1.6	18.1
1998	0.66	0.11	0.54	24.4	39.3	-14.9	22.7	12.9	9.8
1999	0.70	0.14	0.55	25.5	44.1	-18.5	22.1	6.8	15.3
2000	0.45	0.06	0.39	16.7	27.9	-11.2	17.4	3.4	14.1
2001	0.47	0.07	0.40	18.6	30.8	-12.2	19.4	1.2	18.2
2002	0.40	0.06	0.34	16.3	26.1	-9.8	15.5	1.1	14.5
2003	0.54	0.13	0.41	22.3	46.6	-24.4	19.5	2.4	17.1
2004	0.44	0.08	0.35	18.3	37.1	-18.8	14.7	1.7	13.0
2005	0.45	0.10	0.34	20.5	45.9	-25.3	14.8	0.9	13.8
2006	0.34	0.08	0.26	15.9	35.9	-20.0	12.0	2.9	9.1
2007	0.48	0.07	0.41	22.3	37.7	-15.4	17.3	1.3	16.0
2008	0.36	0.08	0.29	16.4	37.7	-21.3	12.9	0.8	12.1
2009	0.19	0.06	0.13	9.8	36.5	-26.7	8.8	0.4	8.4
SUM	34.44	5.05	29.39	1,325.6	2,067.4	-741.8	927.9	374.8	553.1
AVG	0.73	0.11	0.63	28.8	44.9	-16.1	20.2	8.1	12.0
±SD	0.24	0.03	0.22	9.1	11.0	7.0	4.7	8.0	7.0
Water-year	Cl	Cl	Cl	PO ₄	PO ₄	PO ₄	DOC	DOC	DOC
	IN	OUT	NET	IN	OUT	NET	IN	OUT	NET
1963	na	na	na	na	na	na	na	na	na
1964	3.8	2.9	1.0	na	na	na	na	na	na
1965	6.4	4.3	2.1	na	na	na	na	na	na
1966	5.4	4.6	0.8	na	na	na	na	na	na
1967	5.5	5.3	0.1	na	na	na	na	na	na
1968	5.5	5.1	0.5	na	na	na	na	na	na
1969	4.7	4.1	0.6	na	na	na	na	na	na
1970	5.3	4.6	0.6	na	na	na	na	na	na
1971	5.1	3.5	1.6	0.082	na	na	na	na	na
1972	6.6	6.6	-0.1	0.195	0.018	0.177	na	na	na
1973	4.5	5.9	-1.4	0.131	0.032	0.100	na	na	na
1974	5.2	4.2	1.0	0.097	0.017	0.081	na	na	na
1975	3.6	4.6	-1.0	0.148	0.031	0.117	na	na	na
1976	4.9	3.3	1.6	0.139	0.023	0.116	na	na	na
1977	4.4	3.5	0.9	0.125	0.045	0.080	na	na	na
1978	4.2	4.1	0.1	0.225	0.037	0.188	na	na	na

(continued)

Table 17 (continued)

Water-year	Cl	Cl	Cl	PO ₄	PO ₄	PO ₄	DOC	DOC	DOC
	IN	OUT	NET	IN	OUT	NET	IN	OUT	NET
1979	3.2	3.9	-0.7	0.209	0.033	0.176	na	na	na
1980	4.3	5.6	-1.3	0.561	0.017	0.545	na	na	na
1981	1.7	4.5	-2.7	0.470	0.033	0.437	na	na	na
1982	2.4	3.7	-1.3	0.246	0.025	0.221	na	na	na
1983	2.3	4.6	-2.3	0.237	0.042	0.195	na	na	na
1984	1.9	3.3	-1.4	0.174	0.027	0.147	na	na	na
1985	1.9	3.5	-1.6	0.198	0.065	0.133	na	na	na
1986	1.8	3.1	-1.3	0.256	0.069	0.187	na	na	na
1987	2.9	3.4	-0.6	0.412	0.067	0.345	na	na	na
1988	2.2	3.5	-1.3	0.166	0.020	0.145	na	na	na
1989	3.0	4.8	-1.8	0.343	0.050	0.293	na	na	na
1990	2.4	4.6	-2.2	0.385	0.080	0.305	na	na	na
1991	2.4	3.2	-0.8	0.165	0.036	0.129	na	na	na
1992	2.8	3.3	-0.5	0.101	0.023	0.077	na	na	na
1993	3.5	4.3	-0.7	0.161	0.012	0.149	na	na	na
1994	2.0	2.8	-0.8	0.201	0.009	0.191	na	na	na
1995	6.0	8.4	-2.4	0.100	0.029	0.071	15.6	32.2	-16.6
1996	3.6	5.4	-1.8	0.065	0.011	0.054	15.3	26.5	-11.3
1997	2.0	2.7	-0.7	0.153	0.012	0.141	11.7	16.4	-4.7
1998	2.5	4.0	-1.5	0.127	0.023	0.104	14.8	25.7	-10.8
1999	3.4	4.9	-1.5	0.188	0.044	0.144	12.4	33.0	-20.6
2000	1.6	2.4	-0.7	0.060	0.015	0.045	13.1	15.6	-2.5
2001	2.3	3.5	-1.2	0.140	0.012	0.128	13.3	16.5	-3.2
2002	1.7	2.8	-1.1	0.089	0.011	0.078	11.8	10.2	1.6
2003	3.5	5.9	-2.4	0.162	0.016	0.146	15.4	33.4	-18.0
2004	2.6	4.2	-1.6	0.068	0.007	0.061	11.3	22.4	-11.1
2005	3.1	5.2	-2.1	0.099	0.006	0.092	12.5	25.2	-12.7
2006	1.7	3.8	-2.1	0.008	0.005	0.003	8.4	22.0	-13.6
2007	2.1	3.5	-1.4	0.011	0.006	0.006	13.1	20.3	-7.3
2008	2.2	3.3	-1.1	0.023	0.006	0.017	14.7	24.0	-9.3
2009	2.2	3.7	-1.5	0.008	0.006	0.002	8.7	24.9	-16.1
SUM	156.3	192.5	-36.2	6.728	1.020	5.625	192.0	348.1	-156.1
AVG	3.4	4.2	-0.8	0.173	0.027	0.148	12.8	23.2	-10.4
±SD	1.4	1.1	1.2	0.123	0.019	0.114	2.2	6.7	6.3
Water-year	di Silica			di Silica			di Silica		
	IN	OUT	NET						
1963	na	na	na						
1964	0	20.9	-20.9						
1965	0	31.2	-31.2						
1966	0	36.3	-36.3						
1967	0	36.4	-36.4						
1968	0	29.2	-29.2						
1969	0	35.3	-35.3						

(continued)

Table 17 (continued)

Water-year	di Silica IN	di Silica OUT	di Silica NET
1970	0	34.7	-34.7
1971	0	31.6	-31.6
1972	0	42.8	-42.8
1973	0	50.5	-50.5
1974	0	32.3	-32.3
1975	0	47.3	-47.3
1976	0	35.3	-35.3
1977	0	38.6	-38.6
1978	0	30.1	-30.1
1979	0	29.3	-29.3
1980	0	32.6	-32.6
1981	0	43.3	-43.3
1982	0	32.3	-32.3
1983	0	35.3	-35.3
1984	0	27.0	-27.0
1985	0	33.3	-33.3
1986	0	31.8	-31.8
1987	0	30.8	-30.8
1988	0	26.1	-26.1
1989	0	40.9	-40.9
1990	0	42.2	-42.2
1991	0	32.3	-32.3
1992	0	32.7	-32.7
1993	0	32.8	-32.8
1994	0	26.5	-26.5
1995	0	47.7	-47.7
1996	0	39.8	-39.8
1997	0	29.5	-29.5
1998	0	40.4	-40.4
1999	0	42.1	-42.1
2000	0	27.2	-27.2
2001	0	28.6	-28.6
2002	0	24.3	-24.3
2003	0	43.2	-43.2
2004	0	35.3	-35.3
2005	0	44.2	-44.2
2006	0	36.7	-36.7
2007	0	40.5	-40.5
2008	0	43.2	-43.2
2009	0	46.1	-46.1
SUM	0.0	1,630.6	-1,630.6
AVG	0.0	35.4	-35.4
\pm SD	0.0	6.8	6.8

Table 18 Mean annual (arithmetic average of annual values) bulk precipitation input, streamwater output and net loss or gain, and standard deviation of the mean for dissolved substances, during 1963–2009 for Watershed 6 of the Hubbard Brook Experimental Forest^a

Substance	Inputs			Outputs			Net loss or gain ^b				
	Obs (years)	Mean kg/ ha-year)	% of total (kg) ±1 SD	Mean Eq/ ha-year)	% of total (kg) ±1 SD	Mean kg/ ha-year)	% of total (kg) ±1 SD	Mean Eq/ ha-year)	% of total (kg) ±1 SD	Mean Eq/ ha-year)	% of total (kg) ±1 SD
Calcium	47	1.35	0.58	2	67	29	3	47	8.82	2.96	7
Magnesium	47	0.39	0.18	1	32	15	2	47	2.36	0.57	2
Potassium	47	0.70	0.32	1	18	8	1	47	1.85	0.44	2
Sodium	47	1.36	0.47	2	59	20	3	47	6.64	1.28	6
Aluminum	34	0.00	0.00	0	0	0	0	40	2.79	0.98	2
Ammonium	46	2.72	0.65	4	151	36	7	46	0.17	0.15	<1
Hydrogen ion	47	0.733	0.237	1	727	235	35	47	0.107	0.035	<1
Sulfate	46	28.82	9.06	40	600	189	29	46	44.94	10.96	38
Nitrate	46	20.17	4.66	28	325	75	16	46	8.15	8.01	7
Chloride	46	3.40	3.40	5	96	96	5	46	4.18	1.14	3
Phosphate	46	0.173	0.123	<1	5.4	3.9	<1	38	0.027	0.019	<1
DOC	15	12.80	2.23	18	na	na	15	na	23.20	6.74	19
Dissolved	38	0.00	0.00	0	na	na	46	na	16.59	3.19	14
silica	Total	72.61 kg	100	2,081 Eq	100	119.83 kg	100	2,621 Eq	100	-47.22 kg	100
Cations				1,054				1,296			-401 Eq
Anions				1,027				1,325			-241
											-159

^aThese data emphasize that for some elements, data from one or a few annual cycles can give grossly aberrant estimates of long-term mean values of both direction and magnitude of change

^bThere are small rounding errors associated with some of these mean values and their calculation from gross output minus input

Table 19 Summary of average input–output (NHF) budgets for Watershed 6 of the Hubbard Brook Experimental Forest during 1963–2009^a

Element	Years of data	Inputs		Outputs				NHF + DD (kg/ ha-year)	Σ WS I–O (kg/ha-year)		
		BP		DD		Stream (kg/ ha-year)	M				
		Bulk precip (kg/ha-year)	Dry dep (kg/ ha-year)	Included in BP	Included in BP						
Calcium	47	1.35		-8.82	-0.21			-7.47	-7.68		
Magnesium	47	0.39		-2.36	-0.19			-1.97	-2.16		
Potassium	47	0.70		-1.85	-0.52			-1.15	-1.67		
Sodium	47	1.36		-6.64	-0.25			-5.28	-5.53		
Aluminum	42	<0.01		-2.79	-1.38			-2.79	-4.17		
Iron ^b	na	<0.01		-0.05	-0.64			-0.05	-0.69		
Hydrogen	47	0.73		-0.11	0.00			0.63	0.63		
Sulfur	46	9.60	2.05	-14.97	-0.03			-5.37	-3.32		
Nitrogen	46	6.76	1.40	-2.00	-0.11			4.76	6.16		
Chlorine	46	3.40	0.68	-4.18	0.68			-0.78	na		
Phosphorus	39	0.056		-0.009	-0.012			0.047	0.035		
Carbon	18	12.8		-23.20	-3.98			-10.40	-14.38		
Dissolved silica ^c	46	<0.01		-35.45	-6.19			-35.45	-41.64		

Dry deposition (DD) included with BP for elements without gaseous/aerosol phase, except carbon. Particulate losses (M) modified from Bornmann et al. (1974); particulate matter losses are from water-years 1966 through 1969. S, N, and P converted from solutes measured as SO_4 , $\text{NO}_3 + \text{NH}_4$, and PO_4 . Average value from Mitchell et al. (2011). Estimated as 1.4 kg/ha N (Lovett et al. 1997). Not estimated, but long-term balance would be equal to 0.7 kg/ha Cl (Lovett et al. 2005)

^aNot all years have data: these are from the years of continuous, systematic measurements

^bIron streamwater outputs estimated from average trace concentrations in stream water [0.005 mg/L] times average flow (see Fuss et al. 2011)

^cDissolved silica measured and expressed as SiO_2

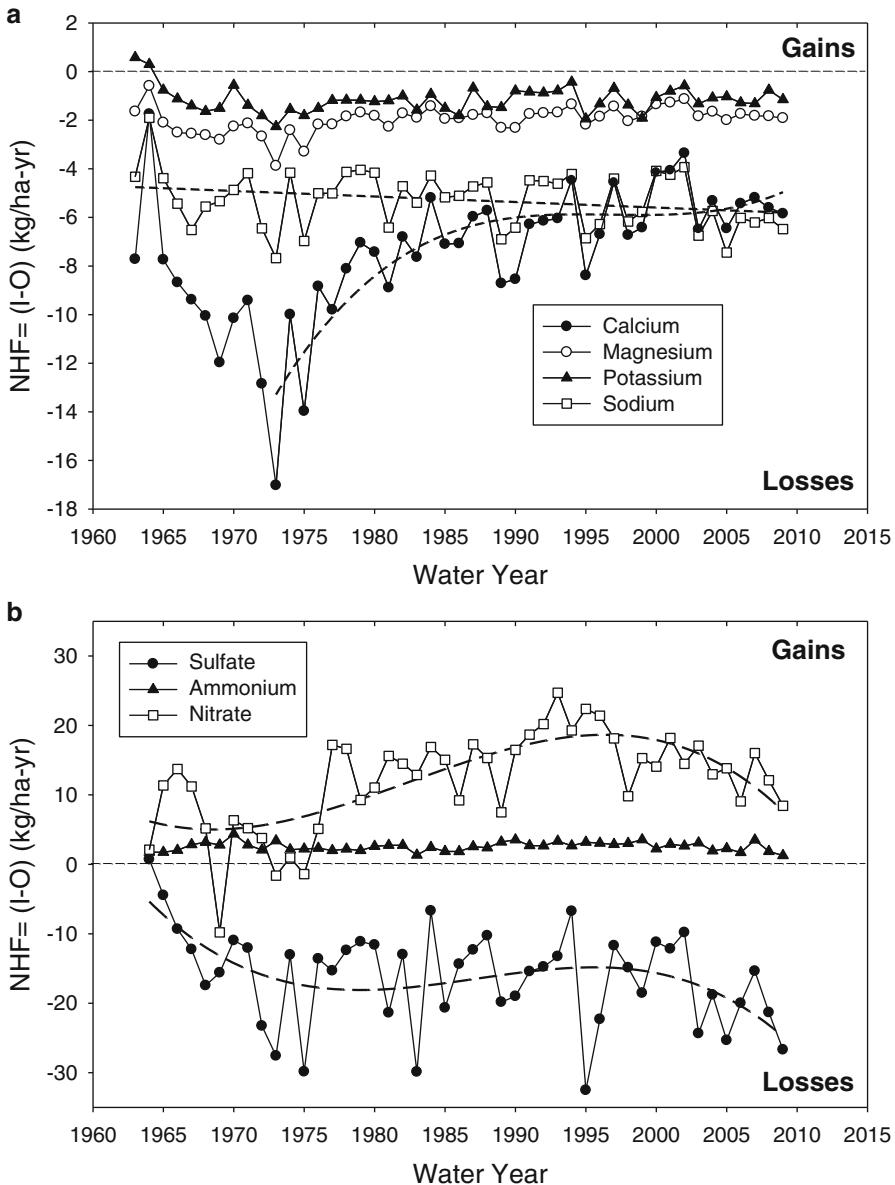


Fig. 36 Net hydrologic flux (bulk precipitation input–streamwater output) for (a) calcium (filled circle), magnesium (open circle), potassium (filled triangle), and sodium (square); (b) sulfate (filled circle), ammonium (filled triangle), and nitrate (square); and (c) dissolved silica (filled circle), in Watershed 6 of the Hubbard Brook Experimental Forest from 1963 to 2009

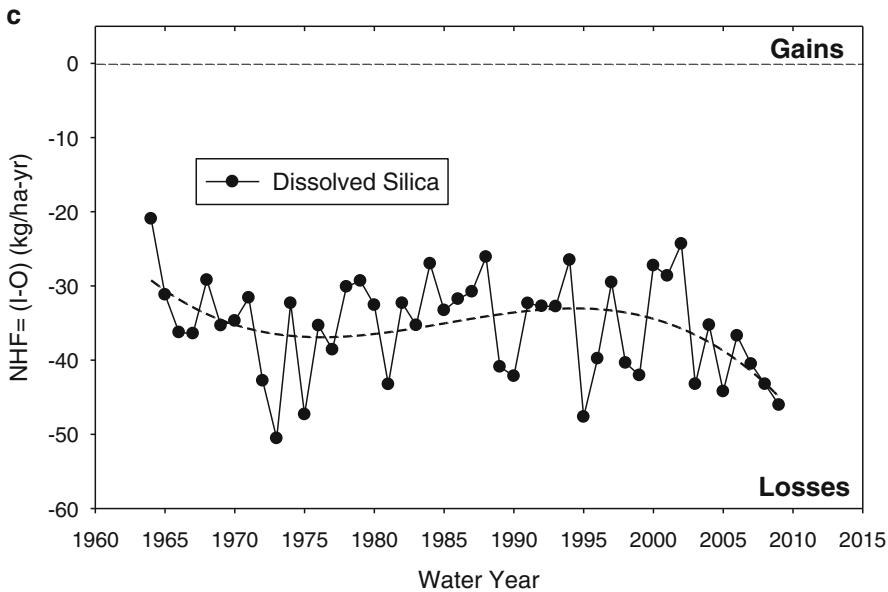


Fig. 36 (continued)

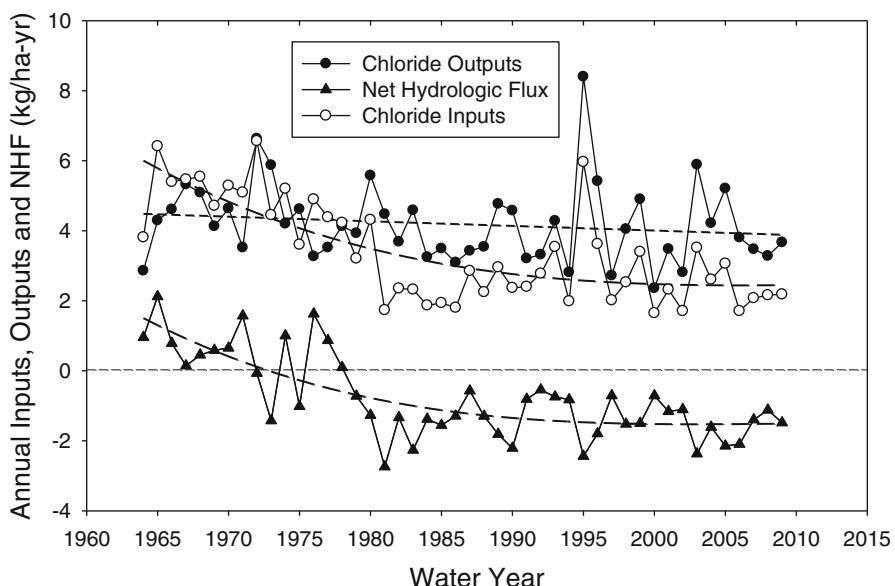


Fig. 37 Annual bulk precipitation inputs (open circle), streamwater outputs (filled circle), and Net Hydrologic Flux (filled triangle) for chloride in Watershed 6 of the Hubbard Brook Experimental Forest from 1964 to 2009. Chloride inputs ($r^2 0.51$), outputs (ns), NHF ($r^2 0.47$, $p < 0.001$)

net change and magnitude. With the standard deviation of the mean and Table 18 and Fig. 36a–c used as a guide, a few annual measurements would yield reliable estimates of magnitude of loss or gain for calcium, magnesium, sodium, aluminum, ammonium, hydrogen ion, and dissolved Si. Nitrate, chloride, and potassium also have a large range in annual magnitude of net change, but they are much more unpredictable relative to direction of net change than the other ions (Tables 17 and 18; Figs. 36b and 37). Annual bulk precipitation inputs of phosphate and chloride have been particularly variable (Table 18, Fig. 37). The standard deviation of the mean for long-term potassium inputs is 44 %; for phosphate inputs, it is 72 %; and for chloride, it is 100 % of the mean (equivalence basis). These highly variable inputs are therefore the major reason for the uncertainty in the average annual budgets for these elements.

Following an initial decline in NHF (increased losses) for calcium since ~1973, there was a significant ($r^2=0.66$) upward trend of diminished losses (Fig. 36a) as available weatherable calcium was depleted and precipitation inputs decreased (see Chaps. 3 and 5). The NHF of sodium tended (insignificantly) toward increased losses, whereas the NHF for magnesium and potassium showed no trend (Fig. 36a).

Sulfate showed highly variable but a decreasing trend toward increasing losses ($r^2=0.24$; Fig. 36b), whereas chloride hovered at NHF of zero, mostly positive prior to ~1977 and negative thereafter (Fig. 37). Nitrate, ammonium, and dissolved inorganic nitrogen were mostly positive (net gain) throughout the 47-year period (Fig. 36b). The NHF for dissolved silica was highly variable and consistently negative (Fig. 36c).

These data emphasize that for some elements data from one or a few annual cycles may give grossly aberrant estimates of long-term mean values of both direction and magnitude of change.

Some Examples of Important Components of Input–Output Budgets

Nitrogen

During the 46-year period, 1964–2009, 927.8 kg/ha of nitrate (209.7 kg/ha $\text{NO}_3\text{-N}$) were added in bulk precipitation and 374.8 kg of nitrate per hectare (84.7 kg/ha $\text{NO}_3\text{-N}$) were lost in stream water from forested, watershed-ecosystems at HBEP. Likewise, 125.2 kg of ammonium per hectare (97.4 kg/ha $\text{NH}_4\text{-N}$) have been added in precipitation, and 7.72 kg of ammonium per hectare (6.0 kg/ha $\text{NH}_4\text{-N}$) have been lost in stream water during 1964–2009. These amounts give a total dissolved inorganic nitrogen input of 307.1 kg N/ha and a total dissolved inorganic nitrogen output of 90.7 kg N/ha during this 46-year period. These long-term data show clearly that >3 times more dissolved inorganic nitrogen has been added to W6 in bulk precipitation than has been lost in stream water. This amount although

substantial did not account for the nitrogen accumulating within the ecosystem in living and dead biomass during the early years of the study, 1963–1982 (Bormann et al. 1977; Covington 1975, 1976; Whittaker et al. 1974; see Chap. 6). It was estimated that nitrogen was incorporated and stored in biomass during this early period at a rate of about 16.7 kg N/ha-year in these forest ecosystems (about 9 kg N/ha-year in living biomass and about 8 kg N/ha-year in soil organic matter; Bormann et al. 1977). Because nitrogen is essentially absent from the bedrock and till at HBEF, it can be assumed that the release of nitrogenous substances by weathering and the formation of secondary nitrogenous minerals are negligible. Therefore, the net gaseous and aerosol exchange of nitrogen across the ecosystem's boundaries was estimated (Fig. 1) from net biomass accumulation minus net hydrologic flux (bulk precipitation input minus streamwater output). The net gain in dissolved inorganic nitrogen during 1963–1974 was 2.5 kg/ha-year (bulk precipitation input minus loss of dissolved and particulate nitrogen compounds in streamflow; Bormann et al. 1977). Therefore, applying an ecosystem analysis to the small watershed approach and based on net biomass uptake (16.7 kg N/ha-year) and NHF (2.5 kg N/ha-year), it was estimated that on average about 14.2 kg of nitrogen/ha-year entered the ecosystem in a gaseous form or from impacted nitrogenous aerosols (Bormann et al. 1977). This value is almost certainly too large (see Chap. 6) as inputs of gases and particles (dry deposition) were not fully evaluated for the ecosystems at HBEF at that time. More recently, the dry deposition of N to these forest watersheds has been estimated at ~1.4 kg N/ha-year (Lovett et al. 1997). Field data indicated that microbial fixation of nitrogen occurs within these forested ecosystems, but the values are relatively small (~2 kg N/ha-year; Roskoski 1980). Denitrification, particularly chemical denitrification, may also occur, but recent estimates indicate that it also is small. Annual fluxes (losses) of N_2O ranged between 0.27 and 1.4 kg N/ha-year between 1986 and 2004 (Bowden and Bormann 1986; Groffman et al. 2006, 2009). In situ, temporal measurements of denitrification are difficult and frequently contentious, particularly at the watershed scale. Using stable isotopes, Bernal et al. (2012) found no evidence for long-term changes in denitrification rates at the HBEF. Long-term measurements of the forest floor and mineral soil have not detected any significant changes in N content, in large part because of the difficulty in detecting rather small changes within large N pools in the soil.

Inputs and outputs and the NHF for inorganic nitrogen have changed dramatically with time at HBEF (Figs. 36b and 45), and extensive work now has been done on many aspects of the nitrogen budget (see also Chap. 6). For example, Bernal et al. (2012) have shown the legacies of previous disturbance, the critical value of long-term data, and, based on an analysis of nitrogen isotopes in archived water samples, that denitrification appears to be a negligible contributor to this change. Nitrogen isotopes (^{15}N) in soil organic matter show little trend over time, whereas this isotopic signature should have increased if denitrification were to have increased (see Chap. 6). Our long-term biogeochemical record and climate dynamics showed that climate alone cannot explain the occurrence of the dramatic >90 % drop in watershed nitrate concentration and export in stream water (Fig. 19b) over the past 46 years, despite longer growing seasons and higher soil temperatures (Bernal et al. 2012).

Bernal et al. (2012) evaluated eight potential drivers/vectors of this streamwater decline in nitrate export (decreased N deposition, increased losses of DON, longer growing season, increased plant accumulation, increased denitrification, changes in soil-water flow paths/temperature, sugar maple decline, historical disturbances) and identified two capable of causing the observed change in the N cycle: altered paths of soil-water flow and historic effects of forest cutting (Bernal et al. 2012).

Chlorine

The long-term annual hydrologic budget for chloride has changed dramatically since 1964 (Table 17; Fig. 37). Initially, the chloride hydrologic budget at HB EF was thought to be in balance or net retention occurred (Juang and Johnson 1967; Lovett et al. 2005). Prior to 1981–1982, the annual hydrologic chloride budget ranged from +2.1 (1965–1966) and −2.7 (1981–1982) to −0.6 kg Cl/ha-year in 1987–1988, averaging −0.8 kg Cl/ha-year during 1964–2009 (Table 17).

Chlorine, like nitrogen, may have a gaseous phase at normal biologic temperatures; however, chlorine gas is very reactive and thus is not common in long-range atmospheric transport. Significant amounts of chloride in throughfall and stemflow (Eaton et al. 1973; Lovett et al. 1996; Berger et al. 2001) suggested that small amounts of impacted aerosols containing chloride were washed off vegetation surfaces or that chloride was leached from vegetation by incident precipitation. Experimental additions of chloride to the forest floor showed that biologic uptake and accumulation of chloride can occur in foliage (Berger et al. 2001). Also, substantial releases of chloride occurred in stream water from some internal reservoir, possibly biomass decay, after experimental disturbance by deforestation (Likens et al. 1970). Somewhat surprisingly, long-term data, experimental watershed manipulation, and experimental plot studies (Berger et al. 2001) suggest an important role for forest vegetation in the chloride cycle, which raises questions about the value of chloride as a conservative tracer in various ecosystem studies.

Lovett et al. (2005) suggested that the dominant source of chloride in the atmosphere during the 1960s and 1970s was from regional coal burning, whereas in more recent decades, chloride deposition originated primarily from marine sources. Dry deposition of chloride is difficult to evaluate but may contribute ~20 % of bulk precipitation inputs (Lovett et al. 2005). Mineralization from soil organic matter also may be an important source of chloride in stream water (Lovett et al. 2005).

Sulfur

Except for 1964, the NHF for sulfate has been consistently negative (Fig. 36b), suggesting some “missing” source. Storage (net uptake) of sulfur in the annual biomass increment occurred (above- and belowground) at a rate of about ~37 mol/ha-year



Photograph 8 Collecting a streamwater sample from Watershed 4 at the Hubbard Brook Experimental Forest (Photo by D.C. Buso)

(3.6 kg/ha-year) in 1964–1969 and 3.1 mol/ha-year (0.3 kg/ha-year) in 1993–1998 (Likens et al. 2002a). But, chemical weathering releases ~50 mol/ha-year (4.8 kg S/ha-year) within the ecosystems of the HBEF and probably more than balances the net biomass storage (Likens et al. 2002a). Sulfur also may exist as a gas or as an aerosol in the atmosphere. Unfortunately, the amount of S input from atmospheric gaseous and aerosol sources annually has high uncertainty—estimated in 1964–1969 and 1993–1998 as 85 (8.1 kg/ha-year) and 57 mol/ha-year (5.5 kg/ha-year), respectively (see Chap. 6). A new approach in 2011 for evaluating dry deposition of S gave a range of 0.5–2.5 kg S/ha-year (Mitchell et al. 2011). This amount should be added to the bulk precipitation input value in calculating the net ecosystem flux for these ecosystems (see Chap. 6). The origin, quantification, and ecological effects of gaseous and/or aerosol inputs of sulfur require detailed studies to elucidate the role of sulfur in forested ecosystems. Unfortunately, these fluxes frequently are not quantitatively or carefully evaluated in biogeochemical studies.

Dissolved Silica

Negligible amounts of dissolved silica are input in bulk precipitation to watershed-ecosystems of the Hubbard Brook Experimental Forest, so the NHF is strongly and consistently negative (Fig. 36c). These outputs in stream water are made up from weathering of silicate minerals within the ecosystem (Photograph 8).

Input–Output Budgets: Summary

Overall, during the period 1963–2009, there was an average annual net loss of total dissolved inorganic substances from W6 amounting to 47.2 kg/ha-year (Table 18). The net loss averaged 241 Eq/ha-year for cations and 159 Eq/ha-year for anions (Table 18). Organic anions make up the imbalance. The average annual net output of dissolved inorganic substances minus dissolved silica (1963–2009) was 30.6 kg/ha-year (Table 18). However, sizeable yearly variations and long-term trends have occurred during the study (Figs. 19, 27, 36, and 37; Table 17). For example, the smallest net loss of dissolved inorganic substances (27.8 kg/ha or 7.0 kg/ha for total dissolved material minus dissolved silica) occurred during 1964–1965, the driest year of our study. The largest net losses of dissolved inorganic substances occurred during the wettest year, 1973–1974 (139.7 kg/ha and 986 cationic equivalents per hectare). Hydrogen ion dominates equivalent fluxes due to its high reactivity, but because it is the lightest element, it does not significantly affect mass.

Budgets adjusted to all major sources of input and output for the entire period are presented in Table 19 and in Chap. 6. Table 19 is somewhat misleading because of strong temporal trends in inputs and outputs such as for sulfate, nitrate, and calcium. The explanation for the overall net losses lies in the biogeochemical reactions that occur within the ecosystem, notably chemical weathering, biotic uptake and net storage of nutrients, and related phenomena (see Chap. 6).

We show average inputs in bulk precipitation (Table 20) and outputs in stream water (Table 21) for two decades: one at the beginning of the long-term study (1964–1973) and one currently (2000–2009).

The pattern of average bulk precipitation solute input and streamwater solute output during the seasonal periods for the entire study (Tables 22 and 23) and for two decades (Tables 24 and 25) is similar to and driven by the monthly flux (Figs. 38, 39, 40, and 41), but the resolution is not as great. Input (on a weight basis) using the most recent decade (2000–2009) is greatest during the summer and lowest during the winter by ~41 % (Table 24). The equivalent input is lowest during the winter, largely because of the sharp decline in sulfate, ammonium, and DOC inputs. On a weight basis, sulfate, nitrate, and dissolved organic carbon provide about 80–88 % of the dissolved inorganic substances in precipitation. On an equivalent basis, hydrogen ion and sulfate dominate, as expected. In general the input of nitrate reflects more closely than any other ion the amount of water added as precipitation because nitrate concentration has remained high in precipitation until recently (Table 17, Fig. 28). Inputs of magnesium, potassium, and to a lesser extent calcium and sodium are relatively greater than expected on the basis of amount of precipitation during the autumn (enriched precipitation relative to the annual average) and less during the winter. All ionic inputs during the winter season were less than expected on the basis of amount of precipitation; in general, however, inputs of individual dissolved substances were highly variable on a seasonal basis (Table 22).

In the early decade (1964–1973), more than 55 % of the annual output of dissolved substances in stream water occurred during the spring. More recently (2000–2009), however, only 36 % of dissolved substances in stream water output occur in

Table 20 Average decadal bulk precipitation inputs for two periods (1964–1973 and 2000–2009) for Watershed 6 of the Hubbard Brook Experimental Forest

Past precipitation inputs 1964–1973 decade				Present precipitation inputs 2000–2009 decade			
Water INPUTS	Total (mm)	Average (mm/ ha-year)	VWA conc ($\mu\text{Eq/L}$)	Water INPUTS	Total (mm)	Average (mm/ ha-year)	VWA conc ($\mu\text{Eq/L}$)
Precipitation	13,880	1,388		Precipitation	14,877	1,488	
Solute INPUTS	10-year total (Eq)	10-year avg (Eq/ha-year)	% Total cations or anions	INPUTS	10-year total (Eq)	10-year avg (Eq/ha-year)	% Total cations or anions
Calcium	1,035	103.5	7.5	Calcium	514.8	51.5	7.5
Magnesium	482.0	48.2	3.5	Magnesium	229.3	22.9	3.3
Potassium	203.1	20.3	1.5	Potassium	151.8	15.2	2.2
Sodium	714.2	71.4	5.1	Sodium	523.0	52.3	7.6
Aluminum ^a	1.0	0.1	0.01	Aluminum ^a	1.0	0.1	0.0
Ammonium	1,677	167.7	12.1	Ammonium	1,326	132.6	8.9
H ⁺ ion	10,142	1,014	73.1	H ⁺ ion	4,104	410.4	27.6
Average pH			4.14	Average pH			4.56
Sulfate	8,230	823.0	59.3	Sulfate	3,689	368.9	24.8
Nitrate	3,299	329.9	23.8	Nitrate	2,459	245.9	16.5
Chloride	1,489	148.9	10.7	Chloride	649.2	64.9	4.4
Phosphate ^b	60.4	6.0	0.4	Phosphate	21.1	2.1	0.3
Bicarbonate ^c	0.0	0.0	0.0	Bicarbonate ^c	0.0	0.0	0.0
DOC ^d	0.0	0.0	0.0	DOC ^d	0.0	0.0	0.0
Total cations	1,425		102.7	Total cations	685.0	46.0	100.0
Total anions	1,308		94.2	Total anions	681.8	45.8	100.0
Imbalance	117.6		8.5	Imbalance	3.2	0.2	
Dissolved silica	0.7 (kg)	0.1 (kg/ha-year)	0.005	Dissolved silica	0.7 (kg)	0.1 (kg/ha-year)	0.005 (mg/L)
							(mg/L)

^a Aluminum and dissolved silica found only in trace amounts in precipitation (Buso et al. 2000)

^b Phosphate analysis not available for all of 1964–1973; used 1971–1980 input data

^c Bicarbonate (as ANC) not measurable below pH 5

^d DOC = dissolved organic carbon not a charged species in precipitation

Table 21 Average decadal streamwater outputs for two periods (1964–1973 and 2000–2009) for Watershed 6 of the Hubbard Brook Experimental Forest

Past streamwater outputs 1964–1973 decade				Present streamwater outputs 2000–2009 decade			
Water OUTPUTS	Total (mm)	Average (mm/ha-year)		Water	OUTPUTS	Total (mm)	Average (mm/ha-year)
Streamflow	8,817	881.7		Streamflow	10,064	1,006	
Solute OUTPUTS	10-year total (Eq)	10-year avg (Eq/ha-year)	VWA conc (µEq/L)	% Total cations or anions	10-year total (Eq)	10-year avg (Eq/ha-year)	VWA conc (µEq/L) or anions
Calcium	5,975	597.5	67.8	36.3	3,104	310.4	30.8
Magnesium	2,465	246.5	28.0	15.0	1,590	159.0	15.8
Potassium	513.9	51.4	5.8	3.1	417.7	41.8	4.2
Sodium	2,989	298.9	33.9	18.2	2,999	299.9	29.8
Aluminum ^a	3,010	301.0	34.1	18.3	1,677	167.7	16.7
Ammonium	183.6	18.4	2.1	1.1	Ammonium ^a	28.3	2.8
H+ ion (and pH)	1,324	132.4	15.0	8.0	H+ ion (and pH)	792.7	79.3
Average pH			4.82		Average pH		7.5
Sulfate	10,984	1,098	124.6	70.4	Sulfate	7,542	74.9
Nitrate	2,533	253.3	28.7	16.2	Nitrate	260.7	26.1
Chloride	1,326	132.6	15.0	8.5	Chloride	1,078	107.8
Phosphate ^b	9.0	0.9	0.1	0.1	Phosphate	2.9	0.3
Bicarbonate ^c	0.0	0.0	0.0	0.0	Bicarbonate ^c	350.0	35.0
DOC ^d	740.0	74.0	8.4	4.7	DOC ^d	1,290	129.0
Total cations	1,646		186.7	100.0	Total cations	1,061	105.4
Total anions	1,559		176.8	100.0	Total anions	1,052	104.6
Imbalance		86.9	9.9		Imbalance	8.5	0.8
Dissolved silica	348.9 (kg)	34.9	4.0	na	Dissolved silica	98.6 (kg)	9.9 (kg/ha-year)
						(mg/L)	1.0 (mg/L) na

^a Aluminum valence estimated +2.5 for pH 4.8 (1964–1973) and +2.0 for pH 5.1 (2000–2009) (Buso et al. 2000)^b Phosphate analysis not available in 1964–1973; used 1973–1982 export data^c Bicarbonate (as ANC) not measurable below pH 5; ANC measured routinely since 1990 (Buso et al. 2000)^d DOC assigned a charge of -6 µEq/mgC (Buso et al. 2000); DOC mass for 1964–1973 based on sporadic measurements and may be higher

Table 22 Seasonal volume-weighted average bulk precipitation values for Watershed 6 of the Hubbard Brook Experimental Forest during 1963–2009

Solute	Obs Years	Summer		Fall		Winter		Spring	
		mg/L	μEq/L	October–November		December–February		mg/L	μEq/L
				mg/L	μEq/L	mg/L	μEq/L		
Calcium	47	0.08	4.0	0.08	4.0	0.06	3.0	0.14	7.0
Magnesium	47	0.02	1.6	0.03	2.5	0.02	1.6	0.04	3.3
Potassium	47	0.05	1.3	0.07	1.8	0.03	0.8	0.06	1.5
Sodium	47	0.05	2.2	0.14	6.1	0.11	4.8	0.11	4.8
Aluminum ^a	34	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
Ammonium	46	0.217	12.0	0.151	8.4	0.119	6.6	0.244	13.5
Hydrogen ion ^b	47	0.061	60.5	0.045	44.6	0.039	38.7	0.054	53.6
pH			4.22		4.35		4.41		4.27
Sulfate	46	2.62	54.5	1.59	33.1	1.20	25.0	2.19	45.6
Nitrate	46	1.27	20.5	1.33	21.4	1.44	23.3	1.60	25.8
Chloride	46	0.18	5.1	0.30	8.5	0.25	7.1	0.26	7.3
Phosphate	39	0.011	0.3	0.007	0.2	0.007	0.2	0.021	0.7
DOC ^c	15	1.3	0.0	0.6	0.0	0.4	0.0	0.8	0.0
Dissolved silica ^a	38	0.00	na	0.00	na	0.00	na	0.00	na
Totals		5.81 (mg/L)		4.36 (mg/L)		3.70 (mg/L)		5.54 (mg/L)	
Cations		81.6 (μEq/L)		67.3 (μEq/L)		55.5 (μEq/L)		83.7 (μEq/L)	
Anions		80.4 (μEq/L)		63.1 (μEq/L)		55.5 (μEq/L)		79.4 (μEq/L)	

^aAluminum and dissolved silica are trace in precipitation^bHydrogen ion in μg/L VWA-concentration^cDOC has no charge in precipitation

spring, followed closely by 34 % during autumn (Table 25). This dramatic change is due to a sharp drop in sulfate and nitrate export and an overall dilution of stream water with time (Likens and Buso 2012). In contrast, only 11 % and 12 % of the output occurs during summer in the early and recent decades, respectively (Table 25). Sulfate clearly dominates the output of dissolved substances on a weight and equivalent basis. Calcium, magnesium, sodium, sulfate, chloride, and hydrogen ion losses in stream water generally reflect the amount of water lost. Phosphate losses during the early decades bore little relationship to the amount of streamflow; summer and winter losses are appreciably greater than expected, and autumn and spring losses are less than expected from the amount of streamflow. The relation to streamflow was much stronger in the recent decade. Likewise, output of nitrate during summer and autumn is less than expected and during winter and spring is more than expected on the basis of water loss. Outputs of potassium and ammonium on a seasonal basis were more variable with regard to streamflow during the early decade. Ammonium outputs are less so currently; the reduction of potassium concentration during the summer (Fig. 34) produces an obvious drop in streamwater output assumed to be from biologic utilization and storage within the forested ecosystem (Table 25).

Table 23 Seasonal volume-weighted average streamwater values for Watershed 6 of the Hubbard Brook Experimental Forest during 1963–2009

Solute	Obs	Summer		Fall		Winter		Spring	
		Years	mg/L	October–November		December–February	mg/L	mg/L	μEq/L
				June–September	μEq/L				
Calcium	47	0.91	45.4	0.94	46.9	0.98	48.9	0.96	47.9
Magnesium	47	0.24	19.8	0.26	21.4	0.27	22.2	0.25	20.6
Potassium	47	0.11	2.8	0.21	5.4	0.19	4.9	0.23	5.9
Sodium	47	0.76	33.1	0.77	33.5	0.77	33.5	0.66	28.7
Aluminum ^a	40	0.27	20.3	0.29	21.8	0.30	22.5	0.33	24.8
Ammonium	46	0.020	1.1	0.023	1.3	0.017	0.9	0.016	0.9
Hydrogen ion ^b	47	0.011	11.3	0.010	10.0	0.011	10.8	0.013	12.4
pH			4.95		5.00		4.97		4.91
Sulfate	46	4.94	102.8	5.01	104.2	4.82	100.3	4.75	98.8
Nitrate	46	0.17	2.7	0.27	4.4	1.08	17.5	1.25	20.2
Chloride	46	0.39	11.0	0.50	14.1	0.48	13.5	0.44	12.4
Phosphate	38	0.003	0.1	0.002	0.1	0.003	0.1	0.003	0.1
DOC ^c	15	2.8	16.9	2.5	14.9	1.9	11.6	2.0	12.1
Dissolved silica	46	4.15	na	4.17	na	4.02	na	3.49	na
Totals		14.78 (mg/L)		14.94 (mg/L)		14.88 (mg/L)		14.41 (mg/L)	
Cations		133.7 (μEq/L)		140.2 (μEq/L)		143.7 (μEq/L)		141.1 (μEq/L)	
Anions		133.4 (μEq/L)		137.7 (μEq/L)		143.0 (μEq/L)		143.6 (μEq/L)	

^aAluminum valence assumed to be +2 (Buso et al. 2000)

^bHydrogen ion in μg/L VWA-concentration

^cDOC=dissolved organic carbon at 6 μEq/mg-C

Monthly Variations

A greater insight into the biogeochemistry of these forest ecosystems can be gained by examining the nutrient budgets on a monthly scale. Three patterns of input–output emerge: (1) those in which input exceeds output in every month, (2) those in which output exceeds input in every month, and (3) those in which there is a crossover from input dominance to output dominance on a monthly basis. These patterns are not related to whether the elements have a gaseous component or are entirely sedimentary. For example, calcium, phosphorus, and potassium have sedimentary cycles, yet they exhibit different patterns; sulfur and nitrogen, however, both with prominent gaseous phases, exhibit two patterns. Instead of this simple assumption, a complex interaction involving such factors as input, effect of biologic activity, and annual variations in weather are determining factors.

Output Consistently Greater Than Input

Calcium exemplifies a nutrient in which the output exceeds the input each month of the year on a long-term basis (Fig. 38). The effects of increased streamflow are

Table 24 Seasonal average bulk precipitation inputs for Watershed 6 of the Hubbard Brook Experimental Forest for two decades (1964–1973 and 2000–2009)

Substance	Summer		Fall		Winter		Spring	
	June–September		October–November		December–February		March–May	
	1964–1973	2000–2009	1964–1973	2000–2009	1964–1973	2000–2009	1964–1973	2000–2009
Precipitation (mm/ha)	120.5	128.3	114.9	153.5	114.9	108.2	110.5	114.4
	g/ha	g/ha	g/ha	g/ha	g/ha	g/ha	g/ha	g/ha
Calcium	166.9	77.1	188.6	72.0	109.4	55.8	233.7	137.3
Magnesium	43.5	18.9	80.1	27.9	33.0	16.8	50.8	32.3
Potassium	75.1	53.4	89.0	62.2	38.1	22.0	67.2	63.3
Sodium	99.0	56.8	238.1	145.3	124.9	121.3	131.8	106.9
Aluminum ^a	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ammonium	304.6	229.6	226.7	190.2	167.3	105.8	284.2	258.9
Hydrogen ion ^b	107.7	37.9	83.1	39.2	54.5	27.9	84.6	32.3
Sulfate	4,519.8	1,873.8	2,795.4	1,465.7	1,882.3	866.0	3,404.9	1,564.4
Nitrate	1,566.4	1,104.7	1,731.4	1,434.5	1,653.5	1,270.2	1,920.4	1,381.7
Chloride	457.1	120.8	571.6	292.1	365.0	223.8	402.8	187.1
Phosphate ^c	15.8	6.5	10.5	3.2	11.3	1.9	37.2	9.7
DOC ^d	na	1,513.6	na	908.7	na	487.0	na	919.1
Dissolved silica ^a	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

^aAluminum and dissolved silica are trace in precipitation

^bHydrogen ion is in µg/ha

^cPhosphate data not available prior to 1971; used 1972–1981 data for early decade

^dSeasonal DOC flux not available prior to 1990

clearly shown by the peak chemical outputs in April and a smaller peak in November–December. During a specific year, the monthly input and output may be quite variable, and monthly outputs may not exceed inputs, particularly during summer. Magnesium, sodium, aluminum, and dissolved silica all have patterns similar to calcium; i.e., outputs consistently exceed inputs on a monthly basis (Fig. 38).

Input Consistently Greater Than Output

In sharp contrast to calcium, ammonium is characterized by monthly inputs that consistently exceed outputs on a long-term basis (Fig. 39). Monthly streamwater outputs of ammonium are relatively constant and low, with a small peak in April, driven by large water outputs. The pattern of ammonium inputs may be highly variable for a specific year, but it becomes much clearer and distinctly sinusoidal with long-term data. The monthly input during late autumn and winter is relatively low.

Table 25 Seasonal average streamwater exports for Watershed 6 of the HBEF for two decades (1964–1973 and 2000–2009)

Substance	Summer		Fall		Winter		Spring	
	June–September		October–November		December–February		March–May	
	1964–1973	2000–2009	1964–1973	2000–2009	1964–1973	2000–2009	1964–1973	2000–2009
Streamflow (mm/ha)	31.5	42.6	63.6	108.9	52.3	67.7	157.2	138.5
	g/ha	g/ha	g/ha	g/ha	g/ha	g/ha	g/ha	g/ha
Calcium	398.0	268.9	872.4	672.3	748.1	426.7	2,130.8	840.4
Magnesium	97.6	80.5	238.1	213.3	192.1	136.3	517.4	258.5
Potassium	46.5	37.6	147.6	207.1	113.1	97.0	396.5	259.4
Sodium	259.4	309.0	572.8	767.8	444.5	489.5	1,118.4	885.1
Aluminum ^a	59.3	80.7	216.9	256.6	140.3	142.0	546.6	332.8
Ammonium	14.1	2.2	47.0	5.5	19.4	3.4	40.9	7.1
Hydrogen ion ^b	4.7	3.4	7.6	8.3	7.7	4.9	25.2	11.4
Sulfate	2,003.3	1,534.7	4,130.3	3,974.4	3,096.6	2,499.2	9,064.0	4,880.2
Nitrate	132.5	7.1	445.5	40.8	1,156.9	140.2	3,603.4	362.0
Chloride	149.3	141.8	382.7	463.7	291.4	278.1	820.4	496.9
Phosphate ^c	1.1	0.5	2.5	0.9	1.1	0.5	4.4	1.3
DOC ^d	na	1,116.3	na	2,700.4	na	1,221.6	na	2,634.4
Dissolved silica	1,399.4	1,663.2	3,030.4	4,070.8	2,246.0	2,615.5	5,498.5	4,766.6

^a Aluminum data from 1964–1970 (7-years) and 1976–1978 (3-years) used for early decade

^b Hydrogen ion in µg/ha

^c Phosphate data not available prior to 1971: used 1973–1982 data for early decade

^d Seasonal DOC flux not available prior to 1990

This pattern may reflect a reduced rate of ammonia input into the atmosphere from decay in the soil because of the lower temperatures, or the transfer of ammonia to the atmosphere may be reduced by the presence of a snowpack. Likewise, higher inputs during the spring and summer may reflect the general increase in biologic activity of the soil and the elevated generation of ammonia. However, because ammonia may be converted rapidly to nitrate, N₂O, N₂, etc., it is difficult to interpret these monthly fluxes. The overall pattern of monthly fluxes for hydrogen and phosphate are similar to ammonium (input exceeds output) (Fig. 39). Calculated output values for ammonium and phosphate are compromised somewhat because many streamwater values are at or below method detection levels (Buso et al. 2000).

A maximum phosphate concentration in bulk precipitation often occurs in May (Fig. 39) due to pollen contamination. If pollen contamination were obvious, the sample would be rejected, but small amounts of pollen may not be visible and may decompose contributing to elevated concentrations of phosphate (and potassium).

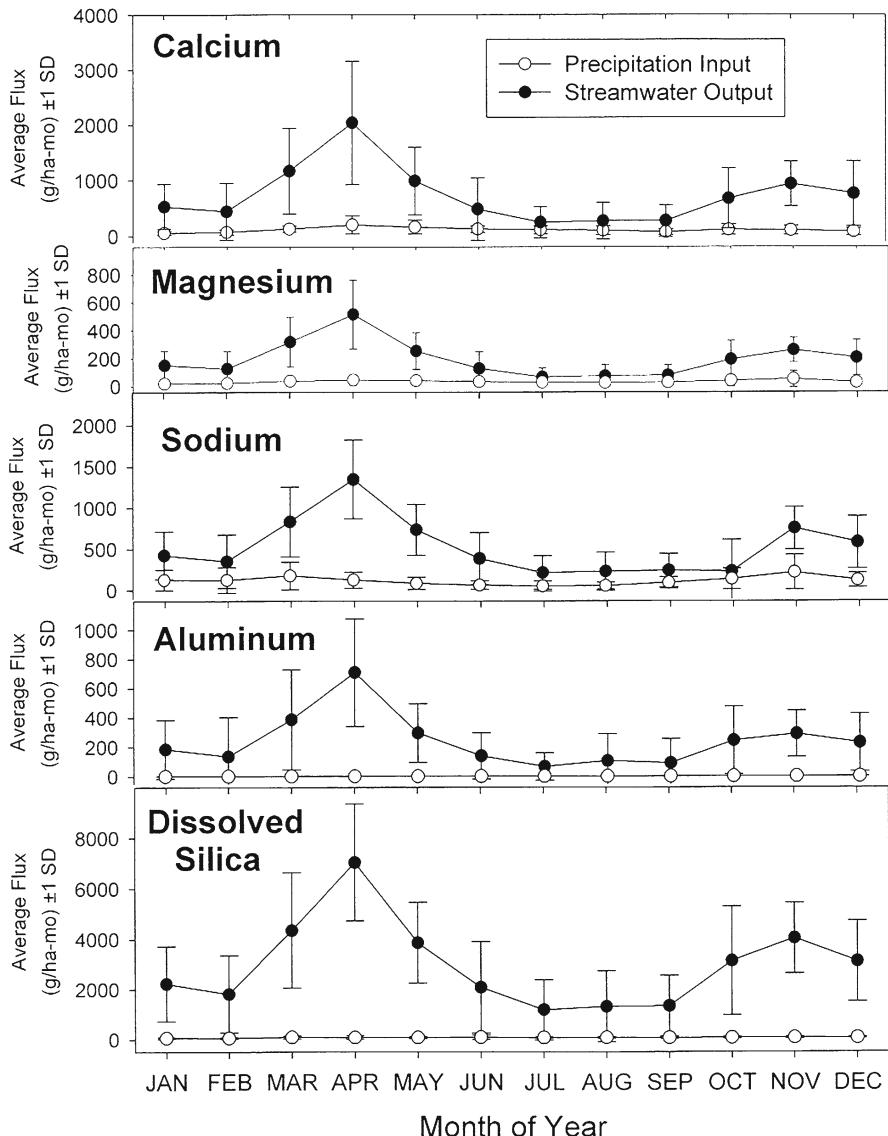


Fig. 38 Average volume-weighted monthly bulk precipitation inputs and streamwater outputs for calcium, magnesium, sodium, aluminum, and dissolved silica for Watershed 6 of the Hubbard Brook Experimental Forest during 1963–2009

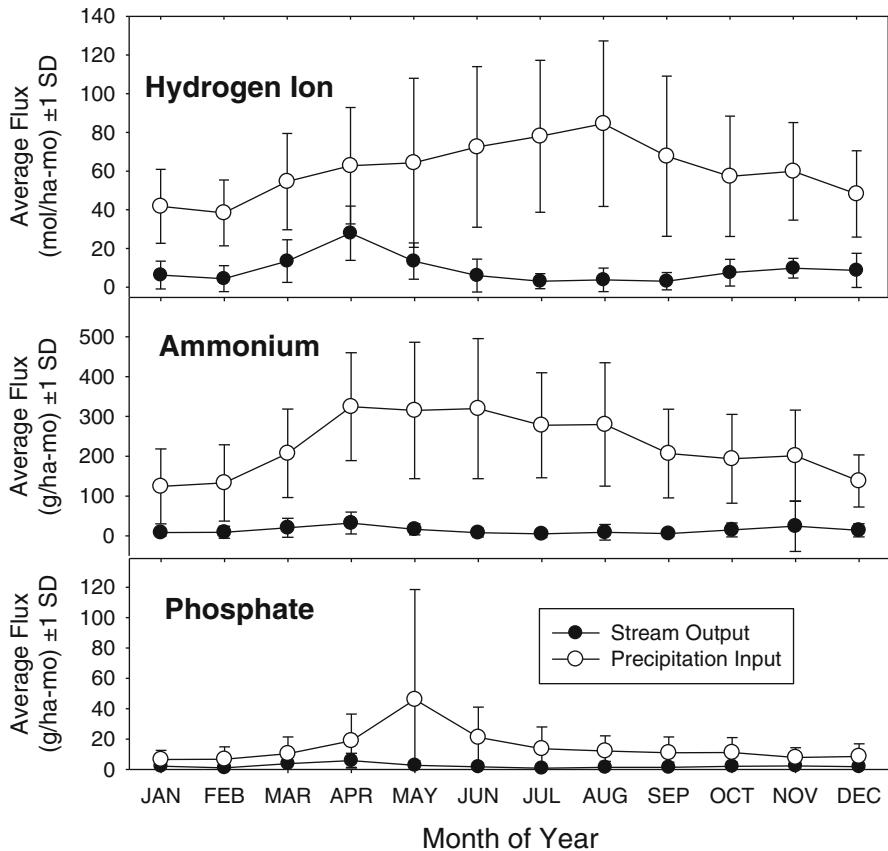


Fig. 39 Average volume-weighted monthly bulk precipitation inputs and streamwater outputs for hydrogen ion, ammonium, and phosphate for Watershed 6 of the Hubbard Brook Experimental Forest during 1963–2009

Crossover Patterns

Long-term potassium inputs barely exceed outputs from mid-June through mid-September, but during the remainder of the year, monthly outputs are larger than inputs, with a large peak in April (Fig. 40). This pattern is of interest, for as suggested earlier the potassium budget (particularly potassium in stream water) is particularly sensitive to seasonal biologic control within the ecosystem (Likens et al. 1994; Table 25; Fig. 40). As mentioned above, the forest vegetation of these watersheds normally breaks dormancy in May, and the deciduous leaves are shed about mid-October. Apparently the biotic portion of the ecosystem actively extracts potassium from the soil and drainage waters during this growing season (cf. Johnson et al. 1969). The “crossover times” separating the NHF values (Fig. 40) were not

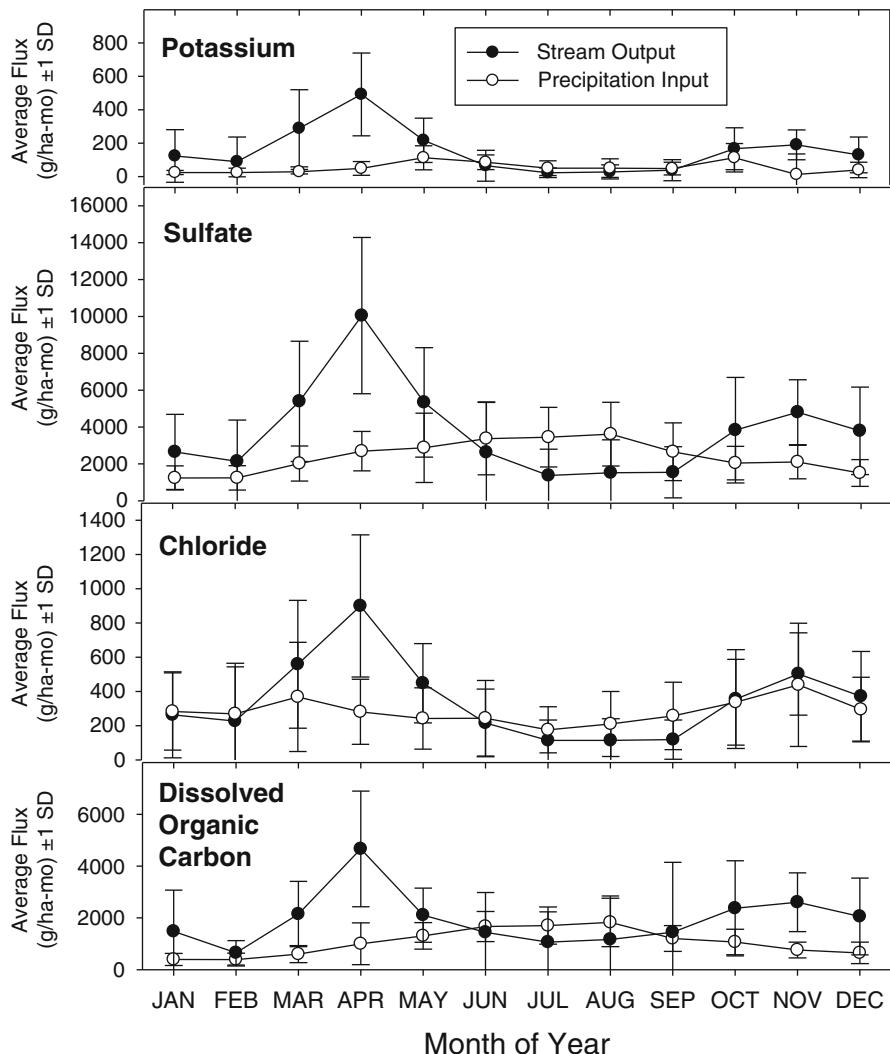


Fig. 40 Average volume-weighted monthly bulk precipitation inputs and streamwater outputs for potassium, sulfate, chloride, and dissolved organic carbon for Watershed 6 of the Hubbard Brook Experimental Forest during 1963–2009

identifiable in the “long-term” monthly budgets by 1969 (1963–1969), which presumably was a residual effect of the drought years (1963–1965) on the cumulative average (see Table 17). Longer-term data show that the large monthly export of potassium in stream water during March through May of each year generally surpasses the average annual input to these forest ecosystems (Fig. 40; Tables 18, 24, and 25). Nevertheless, the monthly pattern of potassium inputs and outputs for any

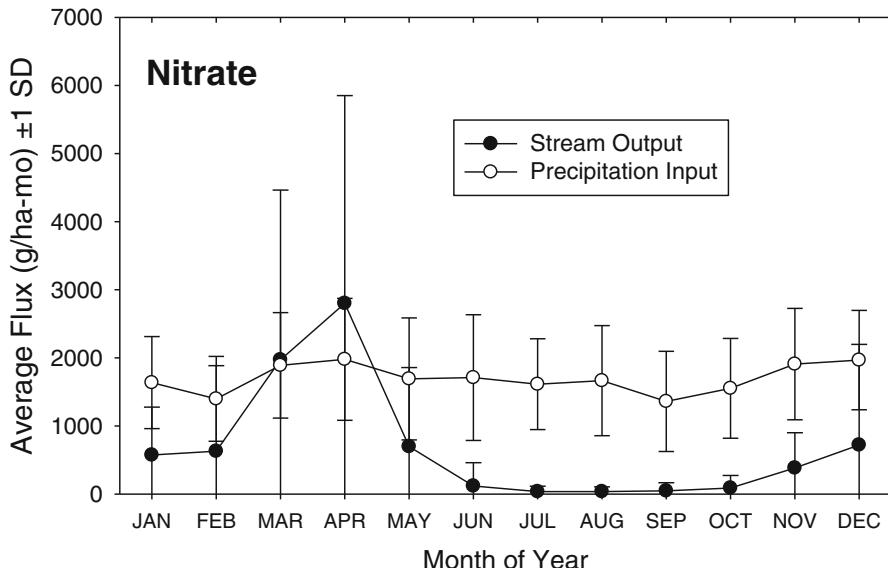


Fig. 41 Average volume-weighted monthly bulk precipitation inputs and streamwater outputs for nitrate in Watershed 6 of the Hubbard Brook Experimental Forest during 1964–2009

specific year may be highly variable. For example, as mentioned above, inputs exceeded outputs during the drought years of 1963–1965, but less dramatic, although complicated, patterns occurred in other years. Potassium has a relatively stable annual NHF pattern despite its crossover pattern on a monthly basis.

The monthly pattern for sulfate, chloride, and dissolved organic carbon is generally similar to that of potassium (Fig. 40) except that the long-term results show that the crossover from input to output dominance in sulfate, chloride, and dissolved organic carbon is more pronounced than for potassium. The monthly input of sulfate and dissolved organic carbon bulk precipitation have a damped symmetrical, sinusoidal pattern, with a peak in June–July–August and a low in January–February.

Monthly nitrate flux requires special consideration (Fig. 41). The monthly pattern is generally consistent but distinctly different than the pattern for ammonium (Fig. 39), although the annual patterns for these two nitrogenous ions are similar (i.e., inputs exceed outputs; Table 18). The pattern for nitrate after 8 years (1964–1972) showed that inputs exceeded outputs during every month except April, even though after 8 years the average output for April was 55 % higher than it was in 1968–1969. However, during 1969–1970, 1970–1971, and 1973–1974, a distinct change in the annual pattern occurred (Table 17). During these 3 years, the long-term annual relationship, where input exceeds output, was reversed. The input during August, September, October, November, and January 1969–1970 was less than the long-term average, but it was the relatively large outputs in April and to a lesser

extent in December and February that overwhelmed the long-term pattern of the annual budget. As mentioned previously, this change in pattern during 1969–1970 and 1973–1974 may have been related to the unusual occurrence of soil frost increasing streamwater losses. Other disturbances have occurred in the long-term record (e.g., Bernal et al. 2012). The long-term pattern (1964–2009) shows that inputs of nitrate exceed output during every month except March and April, although monthly values tend to be highly variable (Fig. 41).

Marked changes in concentrations of nitrate in precipitation and stream water during the period of study (Fig. 28; Tables 6 and 10) also have affected the long-term monthly and seasonal flux (e.g., Fig. 41). As a result of these perturbations in precipitation and streamwater flux, the resolution of the “average” long-term monthly pattern for nitrate is not particularly useful. Nevertheless, based on 47 years of data, monthly inputs of nitrate exceed outputs during all months except April. Inputs and outputs are essentially balanced during March (Fig. 41).

Relationship of Annual Mass Output of Dissolved Substances to Annual Streamflow

One of the major findings from the long-term Hubbard Brook Ecosystem Study is the highly significant direct relationship of annual gross output of cations to annual streamflow (Figs. 42 and 43). In retrospect, this finding should not have been too surprising since chemical concentrations are quite constant with stream discharge (Johnson et al. 1969, Fig. 48). Nevertheless, the direct relation of gross annual export of most ions to the annual streamflow is highly predictable ($r^2 = >0.95$), but because concentrations have changed dramatically with time, there are interesting but important subtleties. For example, the relation for gross output of calcium (Eq/ ha-year) to annual discharge (mm) is strongly positive and highly significant ($p = <0.01$). When this relation is partitioned into shorter temporal periods reflecting the change in streamwater chemistry with time, an interesting pattern emerges (Fig. 42a). The slope of the relations has flattened with time, and linear regressions for the three periods after 1976 no longer go through the origin (Fig. 42a). For example, based on the linear regressions for 1964–1975 and 2000–2009, more than 2 times as much calcium would have been lost during the earlier period than now at a flow of ~1,500 mm/year. This result is due primarily to the depletion of calcium from the watershed-ecosystem by decades of acid rain (see Chap. 3).

Because of the regulation effect of the forest ecosystem on chemical concentrations in stream water as it emerges from watersheds of the HBEF, even after the sizeable impact of a pollutant, such as acid rain, mass output can be predicted rather reliably simply from a knowledge of annual hydrologic output. This relationship is useful for (1) characterizing conditions in an undisturbed forest and (2) providing baseline information for evaluating biogeochemical conditions in a forest disturbed by acid rain (but, see Likens and Buso 2012). These important relations also provide critical information to land-use, hydrologic, and water-quality planners.

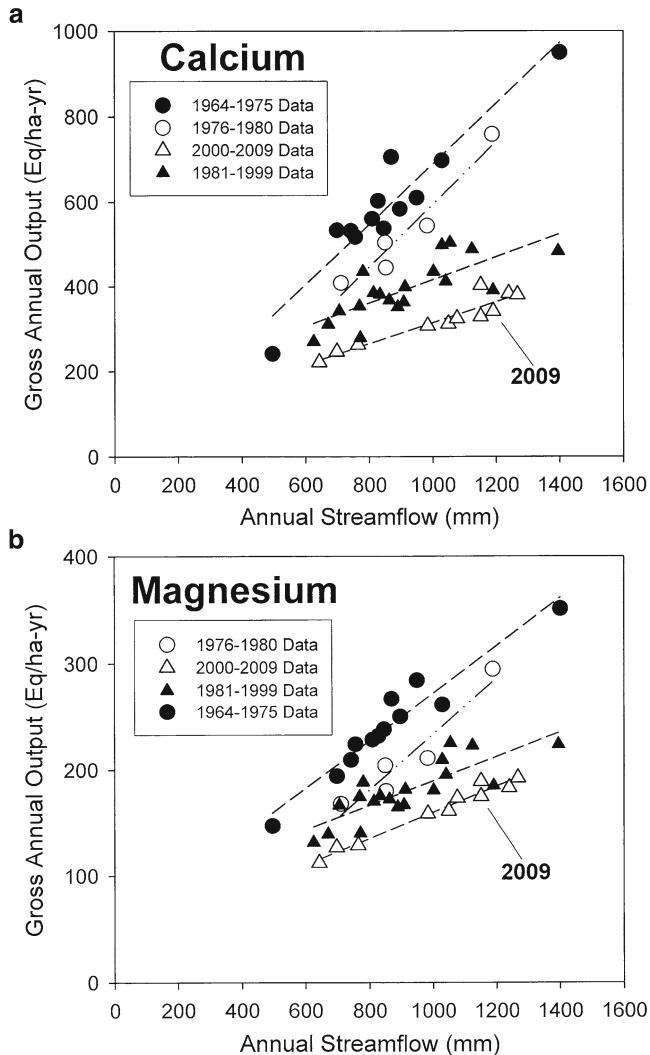


Fig. 42 Relationship between annual streamflow and annual gross outputs of (a) calcium and (b) magnesium for different periods in Watershed 6 of the Hubbard Brook Experimental Forest during 1963–2009

Annual Variation in Mass Output of Dissolved Substances

On a mass basis (kg/ha), sulfate, dissolved silica, and DOC are the dominant substances exported in stream water, whereas on an ionic basis, sulfate and calcium dominate, although both of these ions have declined markedly (see section on

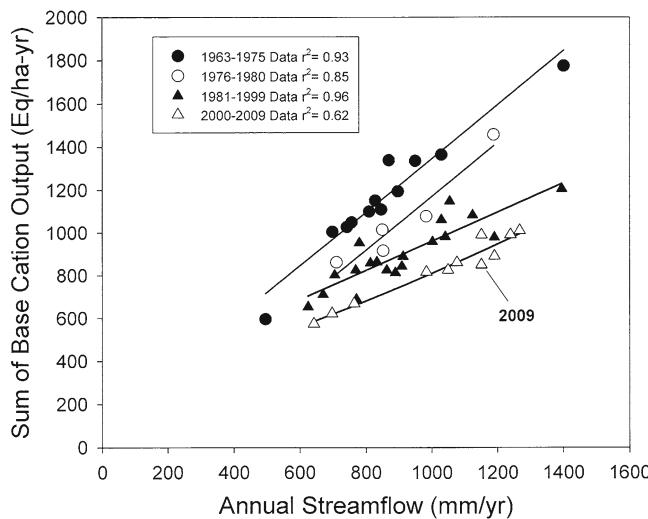


Fig. 43 Relationship between annual streamflow and annual gross output of sum of base cations during different periods in Watershed 6 of the Hubbard Brook Experimental Forest during 1963–2009

Dilution in Chap. 3). The annual gross output of total dissolved substance (excluding dissolved organic carbon) during 1963–2009 averaged 96.6 kg/ha; excluding dissolved silica, it was 80.0 kg/ha (Table 18). With time, sulfate has declined, but its predominance is still striking. In 2009–2010, the annual gross output of sulfate is 36.5 kg/ha or 759 Eq/ha, which represents 26 % of the total dissolved substances (including DOC) or 87 % of the anionic equivalency (not accounting for DOC). The annual gross output of total inorganic dissolved substances varies relatively little from year to year. Annual mass export varied by threefold and equivalency by 2.9-fold, which could be largely explained by the range (2.7-fold) in annual streamflow (Fig. 5). The largest output of dissolved solids occurred during the 1973–1974 water-year (119 % greater than the long-term average), and the drought year of 1964–1965 had the smallest output (26 % less than the long-term average). The average annual output of cations during the period 1963–2009 was calculated to be 1,296 Eq/ha, and the average annual output of anions during 1963–2009 was 1,325 Eq/ha. The poorest agreement in equivalents, 7 and 8 % (difference based on the smaller value), between cations and anions, respectively, occurred in 1964 and 1975, and the best agreement, <1 %, was in 1990 and 2008.

Hydrogen ion and nitrate inputs in bulk precipitation were not as closely correlated as hydrogen ion outputs in stream water and nitrate inputs in bulk precipitation (Fig. 44). Annual inputs of dissolved inorganic nitrogen (DIN) were more closely correlated to annual outputs of DIN in stream water (Fig. 45). The explanation for

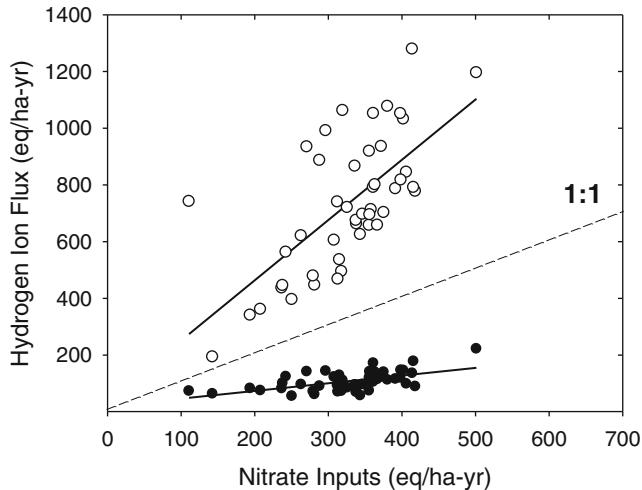


Fig. 44 Relationship between hydrogen ion inputs and nitrate inputs in bulk precipitation (*open circle*) and hydrogen ion inputs and nitrate outputs in stream water (*filled circle*) in Watershed 6 of the Hubbard Brook Experimental Forest during 1964–2009

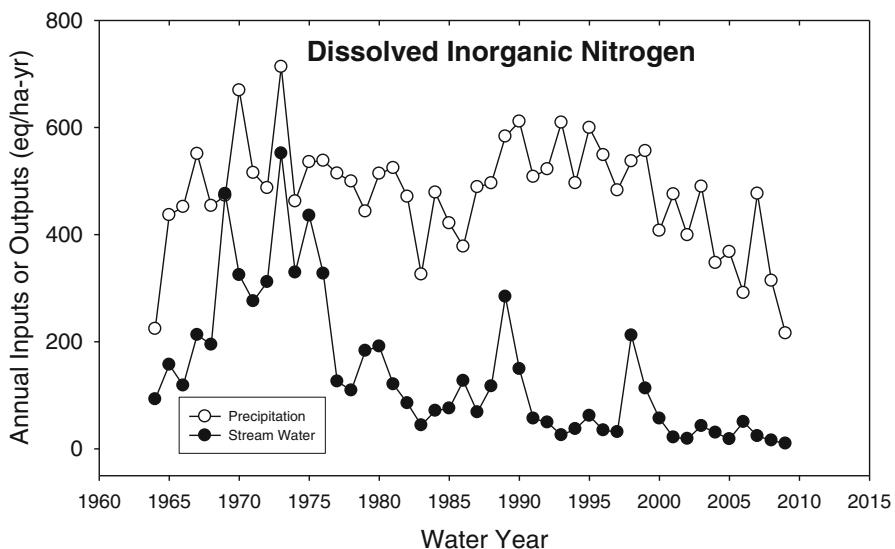


Fig. 45 Annual bulk precipitation inputs (*open circle*) and streamwater outputs (*filled circle*) of dissolved inorganic nitrogen in Watershed 6 of the Hubbard Brook Experimental Forest during 1964–2009

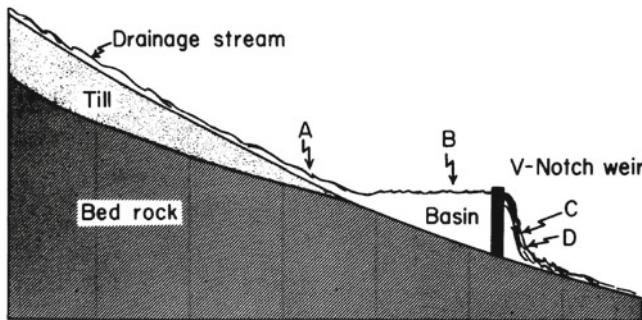


Fig. 46 Sampling procedure employed in the measurement of total nutrient losses from a watershed-ecosystem. A = water sample for dissolved substances, B = suspended and bed load dropped in basin, C = water sample filtered through a fine-meshed net, D = water sample, after filtered as C, through the finer pore of membrane filter. Total losses = dissolved substances (A) + particulate matter ($B+C+D$). Modified from Bormann et al. (1969)

the marked decline in streamwater concentrations and outputs of DIN during the long-term record (Fig. 28) currently is the subject of much research at HBEF (Likens 2004; Bernhardt et al. 2005; Judd et al. 2011; Bernal et al. 2012).

Particulate Matter

Measurement of Mass Output

In addition to dissolved chemical substances, both organic and inorganic particulate matter may be exported from ecosystems in stream water. Particulate matter is removed from the watershed as suspended load carried by turbulent water and as bed load rolled, slid, or bounced along the stream bed. Heavier particulate matter collects in the ponding or stilling basin behind the weir where, over an 8-year period, it was periodically dug out, weighted, proportionally sampled, oven dried, and analyzed for dry weight and organic and inorganic content (Bormann et al. 1969, 1974). Suspended particulate matter that passed over the weir was periodically sampled using a 1-mm mesh net and by passing a sample of water through the net and then filtering it through a 0.45- μm pore Millipore filter at 40 psi. Samples were then analyzed for dry weight and organic and inorganic content and expressed as concentrations per unit volume of water. These concentrations were used in combination with the hydrologic discharge record to determine the export of materials over the weir. These three components, basin, netted, and filtered, were combined to give total particulate export from the ecosystem (Fig. 46).

It is noteworthy that this estimate of total particulate export includes both suspended particulate matter and bed load, whereas most reports of particulate export from ecosystems are concerned with suspended load alone. If the heavier inorganic

material that collects behind the weir were considered as a measure of bed load, then bed load constitutes about 55 % of the total particulate export.

Annual Loss

Erosion and transport of particulate matter from these forested watersheds are relatively low even though the watersheds are on steep slopes ($12\text{--}13^\circ$) and are subject to large amounts of precipitation (1,434 cm/year). Although the glacial till in these watersheds is relatively resistant to erosion (Hunt 1967), it is primarily the living and dead biomass that minimizes the loss of particulate matter by regulating the amount, timing, and effect of moving water within the undisturbed ecosystem. Organic debris dams in the stream channels of these headwater ecosystems apparently play a major role in minimizing the export of particulate matter (Bilby and Likens 1980).

The undisturbed ecosystems tightly regulate erosion and transport and lose only about 33 ± 13.4 kg/ha of particulate matter with annual runoff (Table 26). This material averages about 33 ± 4 % (standard error) organic, but the organic–inorganic proportion is strongly influenced by flow rate of the stream, with higher organic proportions associated with higher flow rates (Fig. 47; Bormann et al. 1974).

Seasonal Variation in Erodibility

Although the maximum output of particulate matter occurs during high-discharge periods, summer flows are more effective in exporting particulate matter than are flows of about the same velocity when vegetation is dormant (Bormann et al. 1974). The 30 % greater erodibility during the summer is probably related to increased biologic activity and decomposition within the ecosystem. In winter, the stream channels are often stabilized by ice and snow, and in addition, precipitation generally falls as snow, with low potential energy of impact. Rarely (twice in 50 years), there have been ice flows that scour the stream channel and move large amounts of organic and inorganic bed load materials.

Particulate Matter Versus Dissolved Substance Export

There is a sharp contrast in the response of dissolved substance and particulate matter export to discharge rate of the stream. Concentrations of dissolved substances are relatively little affected by flow rates, whereas particulate matter concentrations are directly and exponentially related to stream discharge (Figs. 47 and 48). As a consequence, the bulk of particulate matter is moved during storms. Output of dissolved substances is therefore closely related to annual output of water, whereas removal of particulate matter is more of a stochastic process, strongly related to the occurrence of random storms. This pattern is reflected in the fact that during the

Table 26 Annual particulate matter output in kilograms of oven-dry weight organic and inorganic materials per hectare for Watershed 6^a circa 1970

	Source of output	Organic	Inorganic	Total
1965–1966	Ponding basin	2.12	1.77	3.89
	Net	0.34	0.01	0.35
	Filter	1.37	1.28	2.65
	Total	3.83	3.06	6.89
1966–1967	Ponding basin	13.41	17.07	30.48
	Net	0.39	0.01	0.40
	Filter	2.72	2.95	5.67
	Total	16.52	20.03	36.55
1967–1968	Ponding basin	3.83	5.93	9.76
	Net	0.43	0.01	0.44
	Filter	2.61	2.82	5.43
	Total	6.87	8.76	15.63
1968–1969	Ponding basin	4.61	8.31	12.92
	Net	0.42	0.01	0.43
	Filter	2.57	2.81	5.38
	Total	7.60	11.13	18.73
1969–1970	Ponding basin	11.28	30.67	41.90
	Net	0.40	0.01	0.41
	Filter	3.30	3.69	6.99
	Total	14.98	34.37	49.30
1970–1971	Ponding basin	2.70	2.75	5.45
	Net	0.39	0.01	0.40
	Filter	1.77	1.78	3.55
	Total	4.86	4.54	9.40
1971–1972	Ponding basin	3.66	2.52	6.18
	Net	0.37	0.01	0.38
	Filter	1.76	1.80	3.56
	Total	5.79	4.33	10.12
1972–1973	Ponding basin	17.88 ^b	77.40	95.28
	Net	0.60	0.01	0.61
	Filter	10.09	13.61	23.70
	Total	28.57	91.02	119.59
8-Year average	Ponding basin	7.44	18.30	25.74
	Net	0.42	0.01	0.43
	Filter	3.27	3.84	7.11
	Total	11.13	22.15	33.28

^aPonding basin output = particulate matter collected in a ponding basin of the weir upstream from the V-notch; net output = suspended particulate, >1 mm, that passes over the V-notch of the weir; filter output = suspended particulate matter, >0.45 µm <1 mm, that passes over the V-notch of the weir

^bUnderestimate

period 1965–1973, particulate matter output ranged from 7 to 120 kg/ha-year and was highly correlated with the occurrence of individual storms in a particular year. An analysis of more than 4 years of data indicated that 86 % of the total particulate matter was exported in 1.6 % of the total time in the period and with 23 % of the

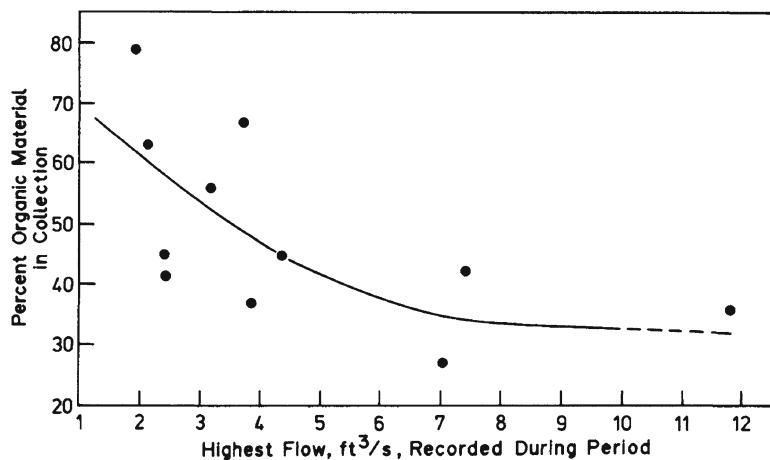
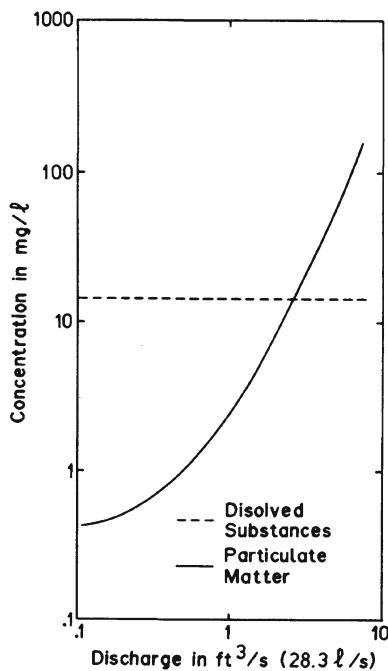


Fig. 47 Percent organic material in basin collections from Watershed 6 plotted against the highest flow recorded during the period. $1 \text{ ft}^3/\text{s} = 28.3 \text{ L/s}$. After Bormann et al. (1974). Circa 1974

Fig. 48 General relationships between the concentration of dissolved substances and particulate matter and stream discharge in the Hubbard Brook Experimental Forest. After Bormann et al. (1969)



water, whereas 16 % was exported in 0.0025 % of the total time and with 0.2 % of the water (Bormann et al. 1974).

These relationships have important implications for the export of certain elements. Most of the chemical elements with a sedimentary cycle are exported from

Table 27 Average annual gross output of some elements as dissolved (D) and particulate (P) substances from Watershed 6 of the Hubbard Brook Experimental Forest during 1966–1967 to 1969–1970^a

Element	Particulate + dissolved element total, kg/ha	Particulate		Dissolved	
		kg/ha	% of P+D element total	kg/ha	% of P+D element total
Aluminum	3.37	1.38	40.9	1.99	59.1
Calcium	13.93	0.21	1.7	13.7	98.3
Chloride	4.58	—	0	4.58	100
Iron	0.89	0.64	72	0.25 ^b	28
Magnesium	3.34	0.19	5.7	3.15	94.3
Nitrogen	4.01	0.11	2.7	3.90	97.3
Phosphorus	0.019	0.012	63.2	0.007	36.8
Potassium	2.40	0.52	21.7	1.88	78.3
Silicon	23.8	6.19	26.0	17.6 ^c	74.0
Sodium	7.48	0.25	3.3	7.23	96.7
Sulfur	17.63	0.03	0.2	17.6	99.8
Carbon ^d	12.3	3.98 ^e	32.4	8.35 ^f	67.5

^aParticulate matter losses during 1966–1967 to 1969–1970 are modified from Bormann et al. (1974). Dissolved substance losses are averages during the period 1963–1974

^bAverage of Smith et al. (1986) and Fuss et al. (2011)

^cAssuming that dissolved silica is in the form of SiO₂

^dOrganic only

^eAssuming organic matter is 40 % C

^fAssuming an average carbon concentration of 1 mg/L (Hobbie and Likens 1973)

the watershed-ecosystem primarily in the dissolved form, as shown above; however, the majority of the iron and phosphorus is lost in the form of particulate matter (Table 27). In contrast to other elements, therefore, the total output of iron and phosphorus is more directly related to stream discharge rate and is less predictable from annual streamflow. Moreover, phosphorus in particulate form is mostly unavailable to aquatic microorganisms and plants within the stream ecosystem unless it first undergoes decomposition or mineralization.

Our data show that in the forest ecosystems at HBEF, solution losses are the major force in the geologic process of fluvial denudation. In terms of gross export of mass, dissolved substances—about 119 kg/ha, including dissolved organic matter during 1964–2009—are about eight times greater than particulate matter losses (Tables 26 and 27).

The Role of Debris Avalanches in Landscape Denudation

Our data suggest that headwater watersheds, with their well-developed forests, are gradually lowered in place by the action of solution coupled with slow mass movements. Both of these actions deliver material to the stream, where it is removed by

erosion and transportation. The possibility that infrequent debris avalanches play an equal or greater role in moving material downslope in headwater watersheds should also be considered. For example, Hack and Goodlett (1960) have shown in the Appalachian Mountains of Virginia and West Virginia that infrequent but catastrophic landslides play a major role in removing material from low-order watersheds and that this activity is independent of any restraining influence by the biota. Flaccus (1958a, b) has shown essentially the same thing for the White Mountains of New Hampshire. Our data on stream losses allow a rough comparison of these very different denudational processes.

Flaccus (1958a, b) mapped 543 debris avalanches on aerial photos of the White Mountains. His study area, most of which is heavily forested, is adjacent to the Hubbard Brook Valley and contains extensive stretches of the Littleton formation (now mapped as the Rangeley Formation in our watershed). The mapped avalanches occur in about equal proportions on slopes of the Littleton formation and slopes underlain by plutonic rocks. Flaccus examined in detail a range of avalanches, thought to be a fair sample of the total, and calculated the average weight of material moved downslope as 21,800 metric tons. In those slides fresh enough to permit location of the topmost elevation, it was found that 100 % occurred above the 610-m elevation contour. Within his study, we have calculated an area of about 128,000 ha above the 610-m elevation. Using Flaccus' data for numbers and dates of avalanches and average amounts of material moved in each event, we have estimated that 462 kg/ha-year are moved downslope by debris avalanches occurring above 610 m in the White Mountains (Bormann et al. 1969). This estimate is about triple our estimate of 200 kg/ha-year for dissolved plus particulate export from headwater watersheds of the HBEF. This comparison suggests that debris avalanches are at least equivalent to the combined action of solution and slower mass movements in lowering the surface of low-order watersheds in the White Mountains.

However, two additional factors must be considered: (1) Disturbances that destroy the biotic stability of the ecosystem, such as fire, can lead to greatly increased losses by solution, mass wasting, and erosion; and (2) the incidence of avalanches per unit area increases sharply with increasing elevation and increasing slope (Flaccus 1958a, b). In the White Mountains, only 18 % of the recorded avalanches occur wholly below 910 m.

In the Hubbard Brook Valley, it seems unlikely that debris avalanches have occurred within recent times in the area currently occupied by northern hardwood forest. With minor exceptions, elevations within the Hubbard Brook Valley are below 910 m, and except for a few sites of very restricted area, our slopes do not meet Flaccus' minimum slope requirement of 25° or is there any evidence of recent or old debris avalanches. It seems safe to conclude that debris avalanches have not played a significant role in the denudation of the relatively gentle slopes of the HBEF, at least during the last millenium.

Apparently, denudation in the area of the Hubbard Brook Valley is primarily a result of the less dramatic action of solution and erosion in combination with slower mass movements, such as creep, which may deliver materials to the streambeds. This result, in turn, suggests that the weathering rind in our watersheds is fairly old.

Locally, this is shown by well-developed soil profiles; however, in some places, the surface is subject to shallow stirring by burrowing animals and from trees uprooted by the wind or during ice storms.

Long-Term Changes in Input–Output Budgets

Because of long-term changes in the chemistry of precipitation and stream water, there have been associated changes in the input–output budgets for the watershed-ecosystems at HBEP. In general, the overall patterns for the input–output relations have remained remarkably the same with time, but there are some important differences in detail. The long-term data for watershed-ecosystems at HBES show significant net gains in NHF (precipitation input minus streamflow output) for dissolved inorganic nitrogen, hydrogen ion, and phosphate. The discrepancy between the sum of anions and cations is small for bulk precipitation and streamwater fluxes in two decades spanning the long-term study (Tables 20 and 21).

Importantly, current streamwater concentrations of nitrate in Watershed 6 are the lowest on record (Fig. 28), even though forest biomass accumulation is very low or negative (Fig. 26; Likens 2004; Lindenmayer and Likens 2010; Bernal et al. 2012). Significant net losses of calcium, magnesium, sodium, potassium and sulfate, aluminum, organic carbon, and dissolved silica occur, but streamwater outputs of calcium, magnesium, and sodium are appreciably smaller than during 1964–1973 and, as a percentage of total cation loss, have become smaller (Tables 18 and 21). Chloride shows a very small long-term net loss, but annual values are highly variable as discussed above (Tables 18 and 19).

The balance between the sum of cations and the sum of anions for streamwater outputs in the earlier decade (Table 21) is not good, but assigning a charge for the organic anion and dissolved aluminum simultaneously was problematic. Making such adjustments, if data were available, probably would reduce the discrepancy to a smaller error.

Chapter 5

Weathering

Both the qualitative and the quantitative changes in water chemistry elicited during the passage of water through a forest ecosystem are related in part to the process of chemical weathering. The bulk ionic composition of water entering the ecosystems of the HBEF in precipitation is characterized by acid salts, primarily H_2SO_4 and HNO_3 . In contrast, water leaving these systems is characterized mainly by neutral salts, such as CaSO_4 and Na_2SO_4 , and to a lesser extent by nitrates and chlorides. This qualitative change in chemistry exemplifies the general chemical weathering reactions. This reaction and some of the chemical pathways in an open system, such as the watershed-ecosystems of the HBEF, are shown in Fig. 49. As described in Chap. 1, chemicals generated from weathering may not quickly cross the ecosystem boundary as they may be taken up by vegetation, participate in cation exchange reactions in the soil, etc., and, therefore, are referred to as “weathering release.” Nevertheless, the release of ionic substances from primary minerals by chemical weathering is an important source of nutrients in soils, soil water, and output flux in stream water from forest ecosystems (e.g., Likens et al. 1967, 1994, 1998, 2002a; Mast and Drever 1990; Williams et al. 1986; Yuretich and Batchelder 1988; Johnson et al. 1994; S. Bailey et al. 2003; Houle et al. 2012). These chemicals also are important contributors to the ecosystem mass balance, but often these contributions are difficult to quantify, especially since the amounts may be “masked” by biotic uptake and long-term storage (see below). Mineral weathering is a one-way reaction, and HBEF soils are composed of minerals derived from igneous and metamorphic bedrock. The soil environment is much different, however, than the igneous and metamorphic environments where these minerals formed. Hence, the minerals are inherently unstable tending to decompose on reaction with water and enhanced by the action of acids, both mineral and organic.

As H^+ is consumed within the system, base cations (M^+) may be leached from various components of the system, and primary minerals (M^+X) are converted into soluble ions and left behind as secondary minerals or coatings on soil surfaces (Fig. 49). When mechanical erosion or other disturbance is sufficiently slow, the glacial drift and to a lesser extent bedrock interact with organic substances to form soil.

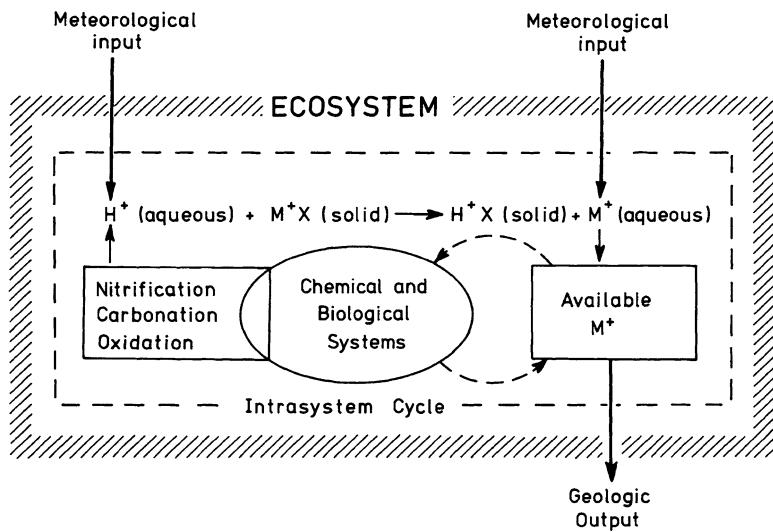


Fig. 49 M^+ represents a base cation, such as calcium, and X is an ionic exchange substrate, usually a primary silicate mineral but also includes such derivatives as soil minerals or soil humates. The above diagram illustrates that as H^+ is added to the system from external and internal sources, base cations (M^+) are leached from the system, and primary silicate minerals (M^+X) are transformed into secondary minerals (H^+X)

The rate at which the chemical weathering reaction proceeds may be operationally defined as the rate at which hydrogen ion is supplied to the system (see Figs. 49 and 50; Driscoll and Likens 1982).

Following the final retreat of the Pleistocene continental glacier some 14,000 years ago in the Hubbard Brook Valley, chemical and physical weathering of freshly exposed rock and mineral surfaces was thought to be relatively high (Likens and Moeller 1985, p. 397). With time, however, chemical weathering flux declined as labile, relatively easily weatherable minerals were depleted or reduced, and the climate/soil/vegetation complex became more stable. Currently, weathering fluxes are relatively quite low, even with recent increased acidity of atmospheric deposition. These fluxes are difficult to measure quantitatively, particularly at the watershed scale. Efforts to extrapolate results of laboratory studies of weathering to a watershed scale have not been successful (e.g., Nezat et al. 2004). Initially, one of the ideas of the Hubbard Brook Ecosystem Study was that very difficult to measure, large-scale ecosystem processes, such as weathering, could be estimated from mass balances generated by the small watershed-ecosystem approach (Bormann and Likens 1967). This approach proved to be difficult, however, for weathering at the watershed scale because of uncertainty in other components of the mass balance and gradually morphed into a somewhat broader concept for ecosystem analysis, net soil release (see Likens et al. 1994, p. 79). Some estimates of weathering and net soil release are compared in Table 28.

Meteorologic Inputs				
	Bulk Precipitation	+960		
	Dry Deposition	+362		
Weathering Reactions				
			Net Forest Accumulation	
			Forest Biomass	Forest Floor
				Total
Ca	-1055	Ca	+ 405	+ 70
Mg	- 288	Mg	+ 57	+ 17
Na	- 252	Na	+ 7	< 1
K	- 182	K	+ 147	+ 9
S	+ 25	S	- 75	- 50
Al	- 211	Fe	+ 40	+ 63
Fe	- 78	NO₃⁻	-----	-----
P	+ 83	NH₄⁺	-----	+ 144
		P	- 74	- 16
TOTAL -1957			TOTAL	+ 697
Stream Exports				
Stream pH (H ⁺)		- 100		
Stream alkalinity (HCO ₃ ⁻)		+ 126		
Discrepancy in charge balance (organic anions, hydroxide ligands)		+ 26		
SUMMARY				
Hydrogen Ion Sources		+ 2541		
Hydrogen Ion Sinks		- 2428		
Budget Discrepancy		+ 113		

Fig. 50 Hydrogen ion budget for Watershed 6 of the Hubbard Brook Experimental Forest circa 1982 (modified from Driscoll and Likens 1982). Hydrogen ion flux is in Eq H⁺/ha-year. Positive values indicate hydrogen ion generation (source); negative values indicate consumption (sink). It was not possible to distinguish dissolved inorganic nitrogen accumulation in the forest floor and forest biomass

Initially at HB EF, we attempted to estimate weathering as the long-term cationic denudation rate, i.e., the rate at which cations are exported from the system (Reynolds and Johnson 1972). A major insight gained from the ecosystem approach relative to this estimate was that net sequestration of cations by the biomass must be included in the mass-balance calculation. Moreover, the role of cation exchange and secondary mineral formation was identified, but could not be quantified or differentiated. Recent data on the biogeochemistry of potassium

Table 28 Some estimates of chemical weathering fluxes and net soil release rates in Watershed 6 of the Hubbard Brook Experimental Forest (mol/ha-year)

Element	Weathering	Net soil release	References
K	–	179 in 1964–1969; 60 in 1987–1992	Likens et al. (1994)
Na	250–370	207–241	Likens et al. (1998), S. Bailey et al. (2003)
Ca	50–80; 54–132	175–701	Likens et al. (1998), S. Bailey et al. (2003)
S	50 (max)	44 in 1964–1969; 128 in 1993–1998	Likens (2002a)
Cl	1.7–3.4	–	Lovett et al. (2005)

(Likens et al. 1994), calcium (Likens et al. 1998), and sulfur (Likens et al. 2002a) suggested that secondary minerals (particularly vermiculite for potassium), the cation exchange complex for potassium and calcium, soil adsorption for sulfate, and the biota play important roles in regulating the loss of these elements in stream water on an annual basis at HBEF.

The full, mass balance for the calculation of cationic denudation on an annual basis is

$$P_i + W_i = S_i + \Delta B_i \pm \Delta O_i \pm \Delta X_i \pm \Delta M_i \quad (1)$$

where P_i is atmospheric input of element i , W is the weathering release from primary minerals, S is dissolved loss in stream water, ΔB is net storage in biomass, ΔO is net long-term storage in the soil organic matter pool, ΔX is the net change in the exchangeable pool, and ΔM is the net change in the secondary mineral pool.

Bailey et al. (1996) used a detailed analysis of the isotopic composition of strontium, coupled with a mass-balance analysis of both calcium and strontium at the Cone Pond watershed, some 7 km from the HBEF, in an attempt to distinguish between weathering release and net exchange with various ecosystem pools (e.g., cation exchange complex, forest floor). They estimated the weathering flux for calcium to be only about 30 % of the value estimated by a standard mass balance. Hyman et al. (1998) found a similar value for weathering using a different technique involving the estimation of mineral weathering rinds on rock fragments.

Sources of Hydrogen Ion in the Weathering Reaction

Hydrogen ion, which is a major driver of the chemical weathering reaction, is supplied from two sources at HBEF: one external to the ecosystem's watershed boundaries and the other internal (Fig. 50). The external source is from acids supplied in

bulk precipitation and dry deposition (meteorologic input); the internal source is from various biologic and chemical processes and transformations occurring within the ecosystem. Currently, the meteorologic input of hydrogen ion at HBEF is mainly in the form of H_2SO_4 and HNO_3 (Tables 18 and 19). This external input of hydrogen ion at HBEF has been decreasing over the past decades, but the long-term average in bulk precipitation is 0.727 ± 0.24 (SD) $\times 10^3$ Eq/ha-year (Table 18). If this were the only source of hydrogen ions at HBEF (and the ecosystem were in a steady state, which it is not), we might expect this value for consumption of hydrogen ion to be more or less balanced by the mean net rate at which ionic calcium, magnesium, potassium, sodium, and aluminum have been leached from the system in stream water. In fact, more of these cations are removed from the ecosystem each year on average (1.19×10^3 Eq/ha) in stream water than there are external hydrogen ions to replace them (Table 18). The difference (0.462×10^3 Eq/ha-year) implies the action of internally generated hydrogen ion. By this definition “internal” is taken to mean everything that is not sensibly added by meteorologic input.

Under prevailing biologic and chemical conditions circa 1982, external and internal generation of hydrogen ions play about equal roles in driving the weathering reaction at HBEF (Fig. 50). This conclusion is based on the assumption that most of the hydrogen ions entering the ecosystem from both external and internal sources are consumed in the weathering reactions. This hydrogen ion balance was done in 1982, but biotic and chemical conditions have changed significantly during the period 1963–2009. For example, net forest biomass accumulation since 1982 has been small or negative (Siccama et al. 2007; Lindenmayer and Likens 2010; van Doorn et al. 2011), and both precipitation inputs and streamwater outputs of several dissolved solutes have declined significantly since 1982 (Likens and Buso 2012).

Some of the major internal sources of hydrogen ion at HBEF are as follows.

Carbon

Reduced carbon in the form of CHO compounds is continually oxidized in the soil zone with the production of CO_2 at partial pressures normally greatly exceeding (thousands of $\mu\text{L/L}$) those found in the atmosphere (Fernandez et al. 1993; Brady and Weil 2008). Some CO_2 reacts with the soil water to form carbonic acid, which has a potential to generate hydrogen ions. However, the soils at HBEF, at least in the upper soil horizons, (Johnson et al. 1991b) are quite acidic ($\text{pH} < 4.7$). Under these conditions H_2CO_3 dissociates only very slightly, and hence carbonation weathering reactions (Carroll 1970) are inhibited. An additional potential source of hydrogen ion at HBEF is from the production of organic acids by biologic activity within the soil zone, such as citric, tartaric, tannic, and oxalic acids (McDowell and Likens 1988). The role of such organic acids in chemical weathering has undoubtedly been important over the long term in ecosystems of the HBEF. However, the effects of

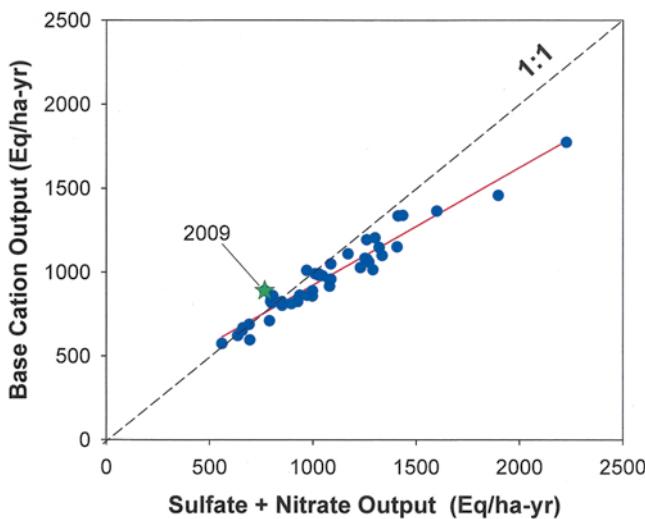


Fig. 51 Long-term relationship between sum of base cations (calcium, magnesium, sodium, and potassium) output and sum of acid anions (sulfate, nitrate) input in stream water of Watershed 6 of the Hubbard Brook Experimental Forest (r^2 0.93)

these organic acids have not been quantitatively assessed at the HBEF. There is no obvious signature of organic acids in the charge balance between streamwater acid anion and base cation exports from W6 (Figs. 17 and 51).

Nitrogen

Another aspect of the chemical weathering reaction at HBEF is the role of the ammonium ion. It is well known to agriculturalists that additions of ammonium have an acidifying effect on soils (e.g., Reuss 1976; Brady and Weil 2008). When ammonium ion is fully oxidized to nitrate ion, two hydrogen ions are produced. Ammonium is added to the ecosystem both by meteorologic input and by biological decomposition within the system. The actual acidifying effect of ammonium in the HBEF soils is unknown; however, it is estimated that only about 10–20 % of the soil ammonium is oxidized (Melillo 1977). The rest is apparently taken up directly by plants, which may release additional hydrogen ions (Reuss 1976). In the long term, $\text{NH}_4\text{-N}$ contributes some 32 % (weight basis) of dissolved inorganic nitrogen (DIN) in bulk precipitation inputs, but only 7 % of the DIN in streamwater outputs (Table 18) reflecting the biogeochemical transformations occurring within the ecosystem. Although nitrification represents a substantial source of hydrogen ion, it is not sufficient by itself to make up the observed deficit between cationic output and external, meteorological hydrogen ion input (Fig. 50; Groffman et al. 1999, 2001; Fitzhugh et al. 2003; Judd et al. 2007; Ross et al. 2012).

Sulfur

Although sulfur concentrations in bedrock at HBEF can be high, even much higher concentrations than average crustal rocks (Bailey et al. 2004), due to small amounts of sulfide minerals, such as pyrite, Bailey et al. (2004) show that soil C horizon concentrations of sulfur are low. This result is probably due to both low sulfur-bearing rocks in the glacial drift and early postglacial depletion of iron sulfides. These minerals, which are extremely reactive, are subject to oxidation in the soil zone with the concomitant production of sulfuric acid (Carroll 1970; Likens et al. 2002a). In addition, microbially liable organic sulfur compounds, such as carbon-bonded sulfur and ester sulfates, are subject to oxidation with the production of sulfuric acid or sulfates (Mitchell et al. 1992; Zhang et al. 1999). Oxidation may occur by strict chemical reactions, but most sulfur oxidation occurring in the soil profile is thought to be biochemical in nature (e.g., Brady and Weil 2008).

Estimates of Ecosystem Weathering Flux

As mentioned above, the cationic denudation during 1963–1974 in the HBEF ecosystem was estimated at 2.0×10^3 Eq/ha-year, comparable to that calculated for New England (2.2×10^3 Eq/ha), but substantially less than the average (3.8×10^3 Eq/ha) for the North American continent (Reynolds and Johnson 1972). This low value is reasonable given the relatively resistant nature of the silicate-based material at HBEF to weathering. Estimating weathering flux is more complicated, however, because we know that both living and dead biomass have been accumulating and soils have been developing within the forest ecosystems at HBEF for the past 14,000 years (Likens and Davis 1975; M. Davis et al. 1985). In effect, this net accretion of biomass represents a long-term sink for some of the nutrients supplied from weathering release, and for an ecosystem mass balance, estimates of weathering must be added to that actually removed from the system as dissolved and particulate matter export. This disposition of cations within the ecosystem allows some important conclusions: (a) Cations stored within the biomass and soil cation exchange pools must be included in calculations of contemporary weathering; (b) the rate of storage is a consequence of the ecosystem's current state of forest succession and, therefore, it changes with time; and (c) existence of the forest and its state of development must be considered in mass-balance estimates of weathering. Thus, cationic denudation values during the first two decades of the HBES, including biomass accumulation, were about twice those reported previously (Johnson et al. 1972). Currently, annual biomass storage is minimal or declining (Chap. 3). Thus, the biological demand for weathering products is currently greatly reduced.

Weathering flux is not uniform across the watershed. Nezat et al. (2004) examined the effect of elevation and vegetation on long-term weathering flux in Watershed 1 of the HBEF. Coniferous vegetation is much more abundant in the upper third of south-facing watersheds, and soils and glacial till are thinner (see Chap. 1).

Using titanium mineral depletion in the soil profile, they found that the weathering flux of base cations decreased by twofold from this coniferous zone (a decrease in elevation of 260 m) to lower elevation hardwood dominated zones in this watershed over the period since glacial retreat.

Net Soil Release

Since direct estimates of W_i , ΔX_i , ΔM_i , and ΔO_i currently are quantitatively unknown or poorly known at HBEF, we recently proposed the use of “net soil release” rather than “weathering” or “cationic denudation” in our ecosystem analysis of these systems (see Likens et al. 1994, 1998, 2002a), and it is calculated as

$$\text{Net soil release} = W_i \pm M_i \pm \Delta X_i \pm \Delta O_i = S_i + \Delta B_i - P_i \quad (2)$$

[symbols as in Eq. (1)].

Net soil release includes mobilization of an element, e.g., calcium, via chemical weathering, cation exchange, and mineralization, in response to watershed inputs, exports, and net biomass uptake (Likens et al. 1994, p. 79).

The long-term comprehensive data collected in the HBES allow us to compensate for the changing effects of precipitation chemistry, biologic activity, hydrologic dilution, and seasonal variation in characterizing streamwater chemistry. Our experience suggests that the most important factor in this regard is the growth status of the forest and how that affects net storage in biomass. This factor may mask the actual rate at which rocks are chemically decomposing within the system. Changing precipitation inputs also are critical to these reactions and mass balances, for example, weathering flux is likely to increase if climate change were to produce warmer and wetter conditions at the HBEF (Chap. 2).

An example is provided by the case for calcium weathering. Several Ca-bearing minerals at the HBEF like plagioclase, biotite, garnet, and hornblende could release calcium to soil water through chemical weathering (Likens et al. 1998). Plagioclase, a calcium–sodium silicate mineral, is relatively abundant and thought to be a major source of weatherable calcium at HBEF, but inputs from bulk precipitation and estimates of weathering release are less than calcium outputs in stream water plus biomass storage over the long term (see Chap. 6). Thus, release from soil exchange sites and organically bound calcium also must be occurring (Likens et al. 1998). Blum et al. (2002) suggested that another source of calcium for the ecosystem is from fungal mycorrhizal weathering (“mining” sensu van Breeman et al. 2000) of apatite inclusions in silicate minerals in deeper soil horizons. Release of calcium from calcium oxalate crystals may be an unaccounted source of enhanced leaching of calcium in the HBEF, driven by hydrogen ion release from root uptake processes (S. Bailey et al. 2003).

S. Bailey et al. (2003) used net sodium output (streamwater loss minus bulk precipitation inputs) as an indicator of weathering fluxes at HBEF because sodium is

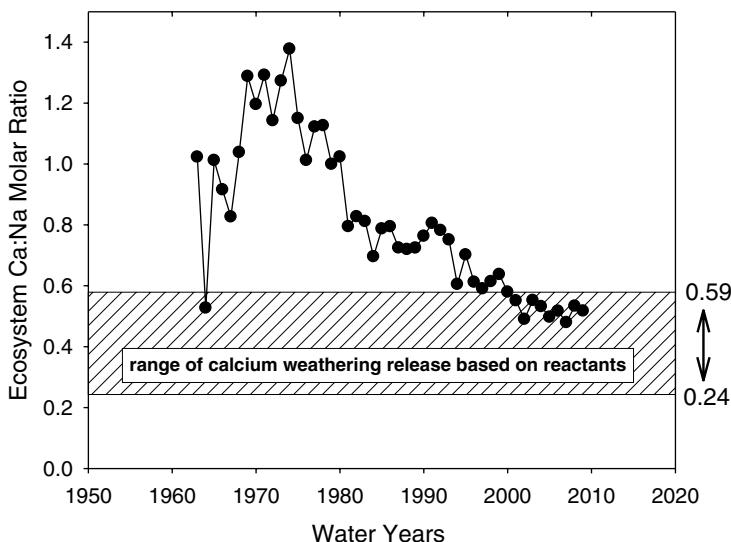


Fig. 52 Net ecosystem Ca:Na ratios (streamwater outputs minus bulk precipitation inputs) for Watershed 6 of the Hubbard Brook Experimental Forest (modified and extended from S. Bailey et al. 2003)

negligible as a component of the soil exchange complex (Johnson et al. 1991b), in soil organic matter and in secondary minerals (Likens et al. 1998), and long-term storage is minimal in biomass of the HBEF. Thus, weathering release of sodium may be estimated simply as the difference between streamwater loss and bulk precipitation inputs (Eq. 1). Assuming that weathering release of calcium and sodium is stoichiometrically related, weathering release of calcium can be estimated by multiplying the weathering release of sodium by the Ca:Na ratio of the weathering reactants. At HBEF these range from 0.24 for available soil plagioclase to 19.0 for calcic plagioclase in the Rangeley Formation (Likens et al. 1998; S. Bailey et al. 2003), to even higher ratios for trace minerals such as epidote and apatite.

S. Bailey et al. (2003) suggested that the streamwater–bulk precipitation ratio for Ca:Na in W6 would stabilize between 0.24 and 0.59 based on the release from the principal weathering reactants. In fact, this ratio now may have stabilized as it has hovered near 0.50 since 2000 (Fig. 52). S. Bailey et al. (2003) further argued that the sodic plagioclase Ca:Na ratio of 0.24 gives the lower bound to weathering release of calcium, whereas the minimal ecosystem Ca:Na ratio they observed (0.59) provided an upper bound. These values are equivalent to a calcium weathering rate of 54 and 132 mol/ha-year, respectively, thereby constraining this release of calcium to the ecosystem. Higher ratios prior to ~1975 reflect much larger amounts of calcium input to the HBEF in bulk precipitation (Likens et al. 1998, p. 97) and depletion of labile soil exchange pools (S. Bailey et al. 2003). The current ratio also shows the depletion of calcium in proportion to the availability of weatherable minerals, such as plagioclase, hornblende, and apatite, and that major ecosystem pools (exchange,

vegetation) may be relatively stable, where weathering release is dominated by sodic plagioclase, with minor contributions from calcic plagioclase, hornblende, and apatite.

The Ca:Na ratio also can be used to assess various ecosystem dynamics. For example, evaluating retention and leaching of calcium within and from the ecosystem suggest that (1) depletion of exchangeable calcium pools, (2) decomposition in the forest floor, and (3) changes in mineral weathering do not appear to be important sources of calcium in streamwater outputs following major disturbance, such as clear-cutting (S. Bailey et al. 2003). As mentioned elsewhere, net release of hydrogen ion from various internal ecosystem processes (Fig. 49) may contribute significantly to increased calcium leaching.

There are a number of calcium-bearing minerals in the bedrock of the HBEF, including slowly weathering plagioclase and biotite and intermediate-weathering minerals like amphibole (hornblende and actinolite), pyroxenes (mostly diopside), and clinozoisite. These are also present in the glacial till of the valley, which is the parent material for soil in the watershed-ecosystems (Likens et al. 1998). It is believed, however, that most calcium comes from weathering of the relatively abundant plagioclase in the HBEF (Likens et al. 1998; Nezat et al. 2004). Finally, calcium is also released from soil exchange sites and mineralization of soil organic matter.

Weathering generally accounts for <<50 % of the net soil release value for calcium in the HBEF (Likens et al. 1998). Likens et al. (1998) estimated that total calcium lost from exchange sites and soil organic matter between 1965 and 1992 was 9.9–11.5 kmol/ha. This amount is greater than the entire exchangeable pool measured in 1983, is 53–61 % of the living biomass pool in 1992, and is 2.0–2.4 times greater than the forest pool of calcium in 1969–1970 (Likens et al. 1998).

The calcium minerals of the bedrock obviously are the most prone to weathering, and calcium compromises some 1.4 % abundance in bedrock (Table 27; Johnson et al. 1968). If this were the only source, then some 1.5 metric tons per hectare of bedrock must undergo weathering every year to provide the requisite net soil release of calcium to the system (Table 28). If we were to assume that this calcium-based value (1.5 tons of rock per hectare year) was the lower limit for the rate of rock weathering, we could then calculate the fraction of each element extracted by the weathering process (Table 29). These estimates seem to be compatible with what is known about the vulnerability of various silicate minerals to chemical attack (Goldich 1938; Marshall 1964; White and Brantley 1995); i.e., calcium-rich minerals are the least stable and potassium-rich minerals are the most stable in the bedrock of the HBEF exposed to an acidic chemical regime.

Secondary minerals (especially vermiculite) and exchangeable pools probably play an important role in regulating streamwater losses of potassium from watershed-ecosystems of the HBEF (Likens et al. 1994). Biotite and muscovite are primary potassium-bearing minerals in bedrock, till, and soil with some potassium feldspar; mixed-layer biotite/vermiculite and illite are the dominant secondary minerals at the HBEF (Likens et al. 1994). Biotite is probably the most weatherable of this group (Sverdrup and Warfvinge 1988). In the acidic soils of the HBEF, weathering of

Table 29 Chemical composition of bedrock and glacial till at the Hubbard Brook Experimental Forest

Element	Abundance in bedrock ^a , %	Amount contained in 1,500 kg of bedrock, kg	Mean composition of glacial till ^b
Ca ²⁺	1.4	21.1	8.7
Na ⁺	1.6	24.1	14.7
Mg ²⁺	1.1	16.5	3.9
K ⁺	2.9	43.6	21.6
Al ³⁺	8.3	124.8	57.5
S ^c	0.2–0.8	7.5	—
Si ⁴⁺	30.7	461.7	394.2

^aTaken from Johnson et al. (1968)^bUnpublished data from S. Bailey^cBailey et al. (2004)

potassium feldspar, muscovite, and biotite to kaolinite and hydroxyl-interlayered vermiculite are ultimate sources of dissolved potassium, but on short timescales, potassium may be sequestered in interlayers providing a sink (Douglas 1989; Likens et al. 1994). With declining inputs of mineral acid deposition from the atmosphere (Chap. 3), is weathering now rebuilding exchange pools in HBEF soils?

A Final Point: When compared with the usual published chemical analyses for large, high-order streams in New England (Johnson et al. 1972), the headwater streams of the HBEF appear to be rather unusual in chemical makeup; i.e., they are dominated by strong acids (sulfuric and nitric). Significantly, the sulfate content of New England stream water is fixed at ~4–6 mg/L, and it stays essentially at this concentration during the remainder of its transit to the sea (Johnson et al. 1972; Pearson and Fisher 1971). Because of its physiographic location, the HBEF (Fig. 2) represents the incipient stages of drainage water, i.e., precipitation that recently percolated through the soil zone and is appearing in variable source areas or first-order stream channels. These acids, however, are in the process of being neutralized by chemical weathering reactions. The rate of neutralization varies somewhat as a function of local streamflow rate and local bedrock chemistry, but our experience at HBEF suggests that the major chemical composition of stream water is determined within a few meters of the initiation of soil water flow and at most the first few hundred meters of streamflow (e.g., Hall and Likens 1980; Likens and Buso 2006; Zimmer et al. 2012).

The relatively low pH typical of headwater streams at HBEF (pH 4–5) precludes the presence of significant quantities of ionized carbonic acid (bicarbonate) (Stumm and Morgan 1996). As the water moves downstream and through longer flow paths from the headwaters, it is progressively neutralized by weathering reactions (e.g., Johnson et al. 1981). As the pH rises above 5, carbonic acid can dissociate and carbonation weathering reactions may proceed. Clear evidence for this is that bicarbonate alkalinity increases downstream as shown by chemical analyses in the mainstream of Hubbard Brook itself.

Chapter 6

Nutrient Cycles and Mass Balances

Chemical elements without a prominent gaseous phase at normal biologic temperature, such as calcium, magnesium, and potassium, have what is referred to as a sedimentary biogeochemical cycle (Odum 1959). That is, flux and cycling are affected primarily by hydrologic factors (including dissolution, erosion, and sedimentation), landslides, vulcanism, and biologic agents. At some places, for example, arid regions, calcium, magnesium, sodium, potassium, and phosphorus have relatively large airborne fluxes of particulates, which complicate quantitative measurement of their fluxes and cycles. The presence of a prominent gaseous component in the biogeochemical cycle (e.g., C, N, and S) greatly complicates measurement and analysis at the ecosystem scale, as discussed previously. To illustrate a sedimentary cycle, the average biogeochemical relationships for calcium and potassium at HBEF will be summarized for two pentads: one near the beginning of the long-term record and one nearer the end. The cycle for sulfur will be used to show relationships for an element with a major meteorologic component. “Average” is somewhat misleading in this regard because of the large temporal changes that have occurred since 1963, as discussed in previous chapters. Nevertheless, summarizing and synthesizing long-term data into a conceptual diagram for various nutrients provides new understanding and insights.

The Calcium Cycle

This synthesis for calcium will be done for two 5-year periods, 1964–1969 and 1987–1992 (Fig. 53). In addition, mass-balance diagrams will be presented below showing annual values for bulk precipitation input, net soil release, streamwater output, and biomass storage to allow the calculation of a net ecosystem flux (NEF) annually throughout the period 1963–2009.

Bulk precipitation contributed 1.5 kg/ha (61 mol/ha) of calcium to the ecosystem each year during the initial pentad (1964–1969), but less than half that amount,

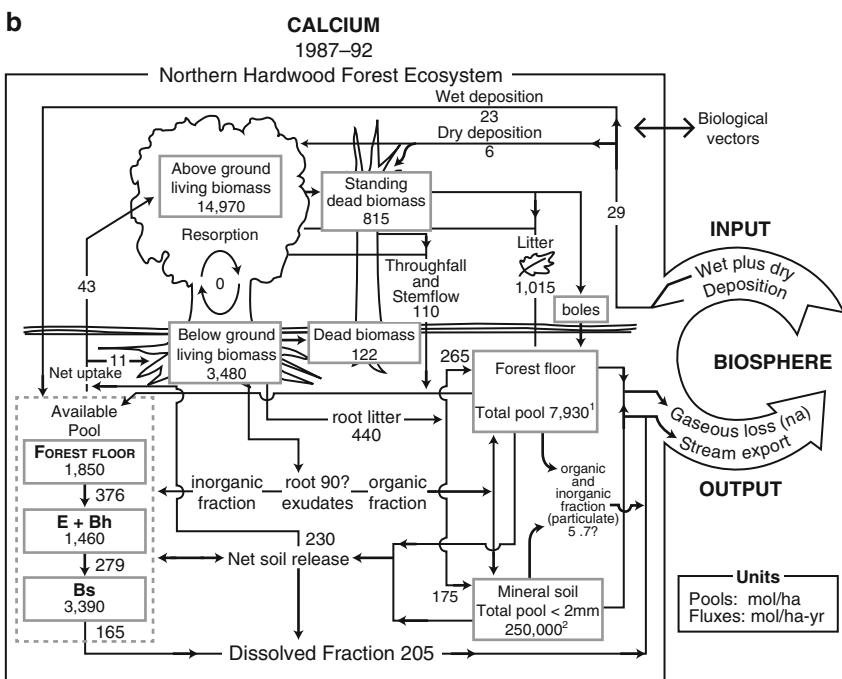
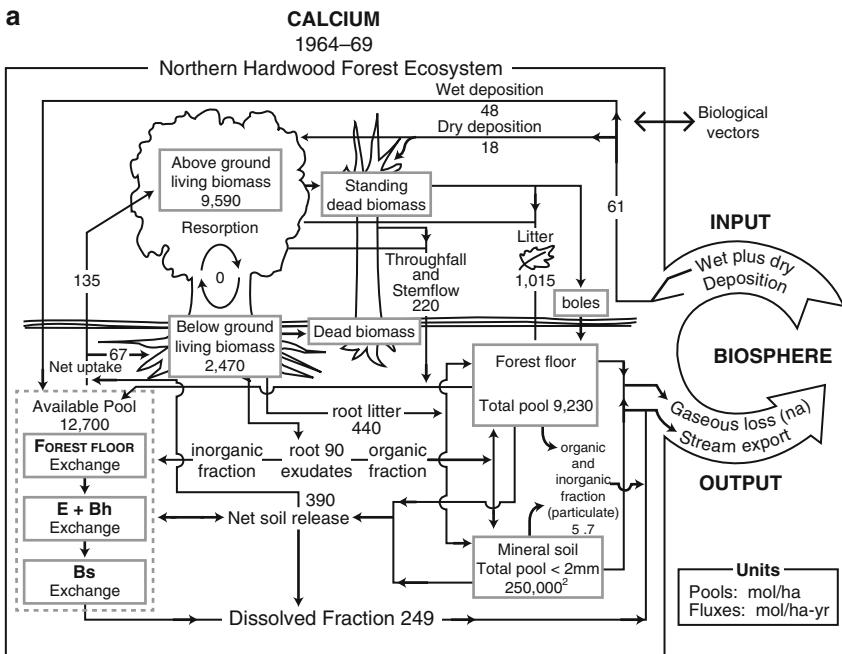


Fig. 53 Ecosystem pools (boxes) and fluxes (arrows) for calcium for Watershed 6 at the Hubbard Brook Experimental Forest. Average values in mol/ha or mol/ha-year for periods specified. Values for 1964–1969 (a) are modified from Likens et al. (1977); and values for 1987–1992 (b): above- plus belowground biomass is average of 1987 and 1992 values, belowground assumed to be 20 % of aboveground; net uptake values are based on the difference in biomass storage between 1982 and 1992; (1) root and aboveground litter, root exudates, and mineral soil assumed to be same as 1964–1969; total forest floor pool from Johnson (1989); (2) total mineral soil pool from Federer et al. (1989) (from Likens et al. 1998). Reprinted with permission of Kluwer Publishers

0.7 kg/ha (29 mol/ha), during the later one (1987–1992). Estimated dry deposition contributed 0.3 and 0.1 kg Ca/ha-year, respectively, during these two pentads. In addition, some 9.7 and 5.7 kg of Ca/ha-year, respectively, were generated within the ecosystem by net soil release. Initially (1964–1969), the 55-year-old forest was strongly accumulating biomass, so 3.4 kg of Ca/ha-year was stored aboveground and 1.7 kg/ha-year belowground in the annual vegetation growth increment. Since 1982, however, above- and belowground biomass accumulation has been small with only 1.3 kg Ca/ha-year stored in total (Fig. 53b). Approximately 25.3 kg Ca/ha-year is returned to the soil via aboveground litter, 11.0 kg/ha-year in belowground litter, and 6.7 kg/ha-year in fine root turnover; throughfall and stemflow decreased by half from the earlier to later pentad. The remainder is lost from the system in drainage water and decreased from 6.2 to 5.1 kg Ca/ha-year from 1964–1969 to 1987–1992. Most (97 %) of this loss is in the dissolved form. The more recent (1987–1992; Fig. 53b) annual net loss from the ecosystem (5.2 kg/ha) in streamwater is only 3 % of the exchangeable pool of calcium (~161 kg/ha) in the soil and about 3.8 times greater than the amount currently stored annually by the biomass (1.3 kg/ha). The exchangeable pool of calcium has been depleted markedly during the past 50 year or so, primarily through mobilization by acid rain (Likens et al. 1996, 1998; Likens and Buso 2012). Annual gross uptake of calcium by trees is about 26–30 % of the exchangeable pool, and some 7–8 times more calcium is cycled through the vegetation than is lost in streamwater annually (Likens et al. 1998).

Most of the calcium in the ecosystem, or more than 93 %, is present in the soil complex, whereas only about 7 % (460 kg/ha) is bound in the vegetation. Nevertheless, currently <1 % of the net biomass storage is provided by the available nutrient pool each year. Meteorologic input supplies an amount of calcium equivalent to about 50 % of all calcium taken up (net) by vegetation annually, whereas net soil release generates about four times more than the annual net vegetation uptake. Annually, calcium stored by vegetation is returned to the forest floor by litter, stemflow, throughfall, and root exudates. More recent (1987–1992) inputs to the available nutrient pool come from net soil release, 50 %; leaching from the canopy, 24 %; root exudates, 20 %; and atmospheric deposition, 6 % (Fig. 53b; Likens et al. 1998). Interestingly, root exudates from living vegetation release ~20 % as much calcium as is lost as root litter. Gosz et al. (1973) calculated that some 17.3 kg Ca/ha was released by decomposition and leaching of current litter each year at HBEF.

Comparing calcium dynamics from 1964–1969 to 1987–1992, net annual biomass storage decreased by ~75 %, atmospheric deposition by >50 %, throughfall and stemflow by ~50 %, stream output of dissolved calcium by ~20 %, and net soil release by ~40 % (Fig. 53).

The Potassium Cycle

Potassium is another element with a sedimentary cycle. Potassium is an important nutrient in forest ecosystems (Tripler et al. 2006), and although cycled relatively rapidly in the forest floor, it is strongly retained within the ecosystem against losses

in streamwater (Likens et al. 1994). Comparing an ecosystem analysis in 1964–1969 (Fig. 54a) with one done more recently in 1987–1992 (Fig. 54b) showed the same loss in streamwater and similar inputs in bulk precipitation for these different periods. There were decreases in biomass storage, throughfall flux, and net soil release with time, correlating with decreases in biomass accretion during this period. Potassium in precipitation inputs, in streamwater outputs, and in the exchange complex of the mineral soil is relatively small compared to rock and biomass pools (Fig. 54). Annual net hydrologic flux (NHF) was negative (streamwater output > precipitation input) for all years except 1963–1965, drought years at the HBEF (Likens et al. 1994). Following these drought years, annual NHF values varied, but tended to fluctuate between ~ -0.4 and -1.4 kg/ha-year.

Because of changes in the long-term chemistry of bulk precipitation and particularly because of the decline in biomass accumulation at HBEF, significant changes in the flux and cycling of potassium occurred between the early (1964–1969) period of study and the current (1987–1992) period (Likens et al. 1994). For example, storage of potassium in biomass, net soil release, and throughfall all decreased, whereas resorption increased from the earlier pentad to the later one (Fig. 54).

An elevational gradient of biotic and abiotic conditions in W6 provided an opportunity to assess effects on the biogeochemistry of the watershed-ecosystem. Different patterns in pools and fluxes of potassium were evident along this gradient. There were higher concentrations and fluxes of potassium in vegetation, aboveground litter, throughfall, forest floor, and soil water in the lower, more deciduous zones than in the higher, more spruce–fir dominated zone. Abiotic patterns included elevational decreases in soil cation exchange capacity (as a function of reduced soil organic matter) and soil/till depth at higher elevations (Likens et al. 1994). These abiotic patterns tended to increase the relative impact from strong acid anions like sulfate and nitrate in atmospheric deposition.

The Sulfur Cycle

Elements like carbon, sulfur, and nitrogen have a prominent gaseous phase at normal biologic temperatures, and this greatly complicates quantitative measurements of the biogeochemical flux and cycling because the flux of gases and airborne particles are difficult to measure quantitatively, particularly at the watershed scale. To provide an example of this type of biogeochemical cycle, sulfur will be used (Fig. 55).

Sulfur plays a key role in the biogeochemical and ecological function of forested watershed-ecosystems at HBEF. Even though it has been declining since 1964, sulfate is the dominant anion in both precipitation and streamwater (see Table 5, Chap. 3). Sulfate represented 71 % and 53 % of anions in bulk precipitation and 80 % and 87 % of anions in streamwater in 1964–1965 and 1997–1998, respectively. More than 95 % of the sulfur in the ecosystem at any one moment is found in the soil complex, and the remaining 5 % occurs in living biomass (Fig. 55).

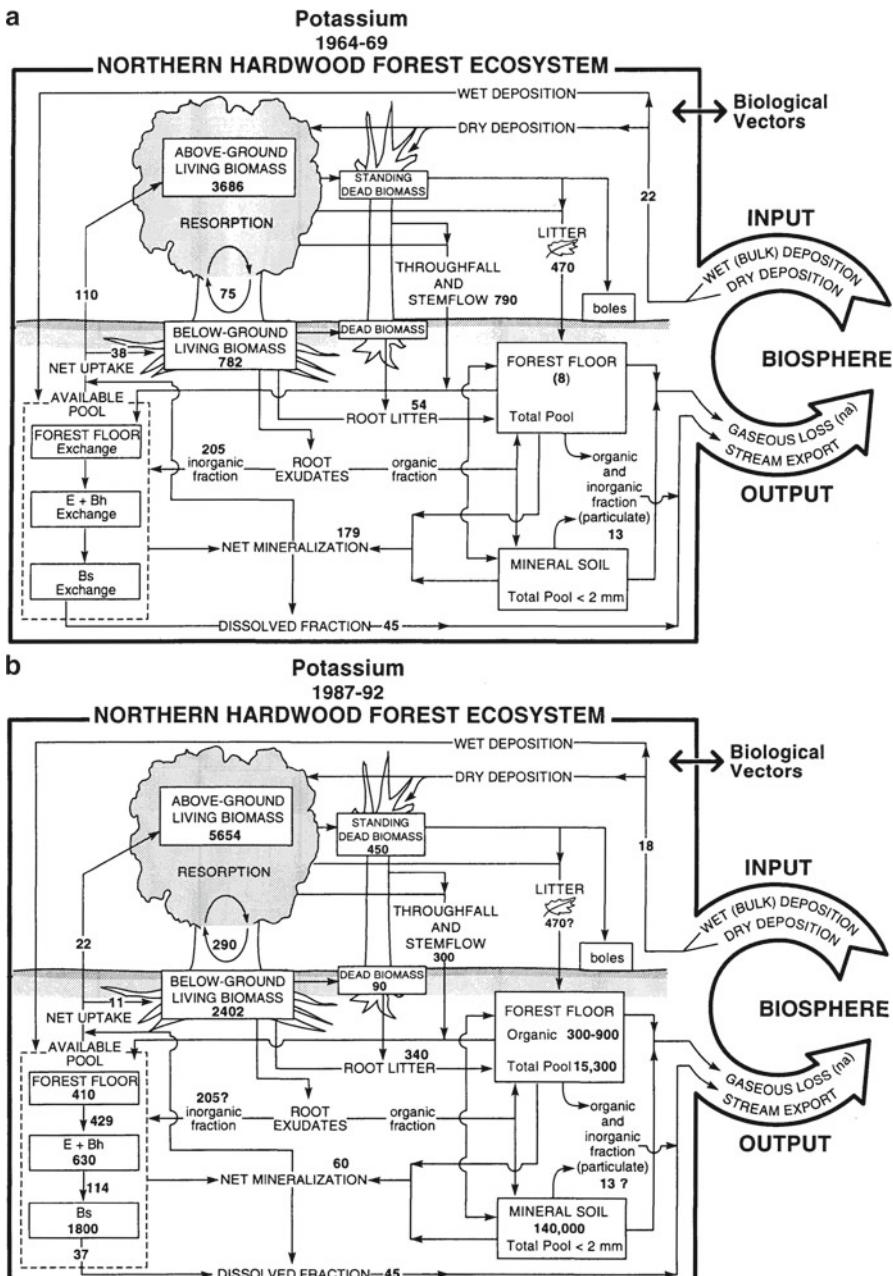


Fig. 54 Ecosystem pools (boxes) and fluxes (arrows) for potassium for Watershed 6 at the Hubbard Brook Experimental Forest. Average values in mol/ha or mol/ha-year for periods specified. Values for 1964–1969 (a) and for 1987–1992 (b). From Likens et al. (1994). Reprinted with permission of Kluwer Academic Publishers

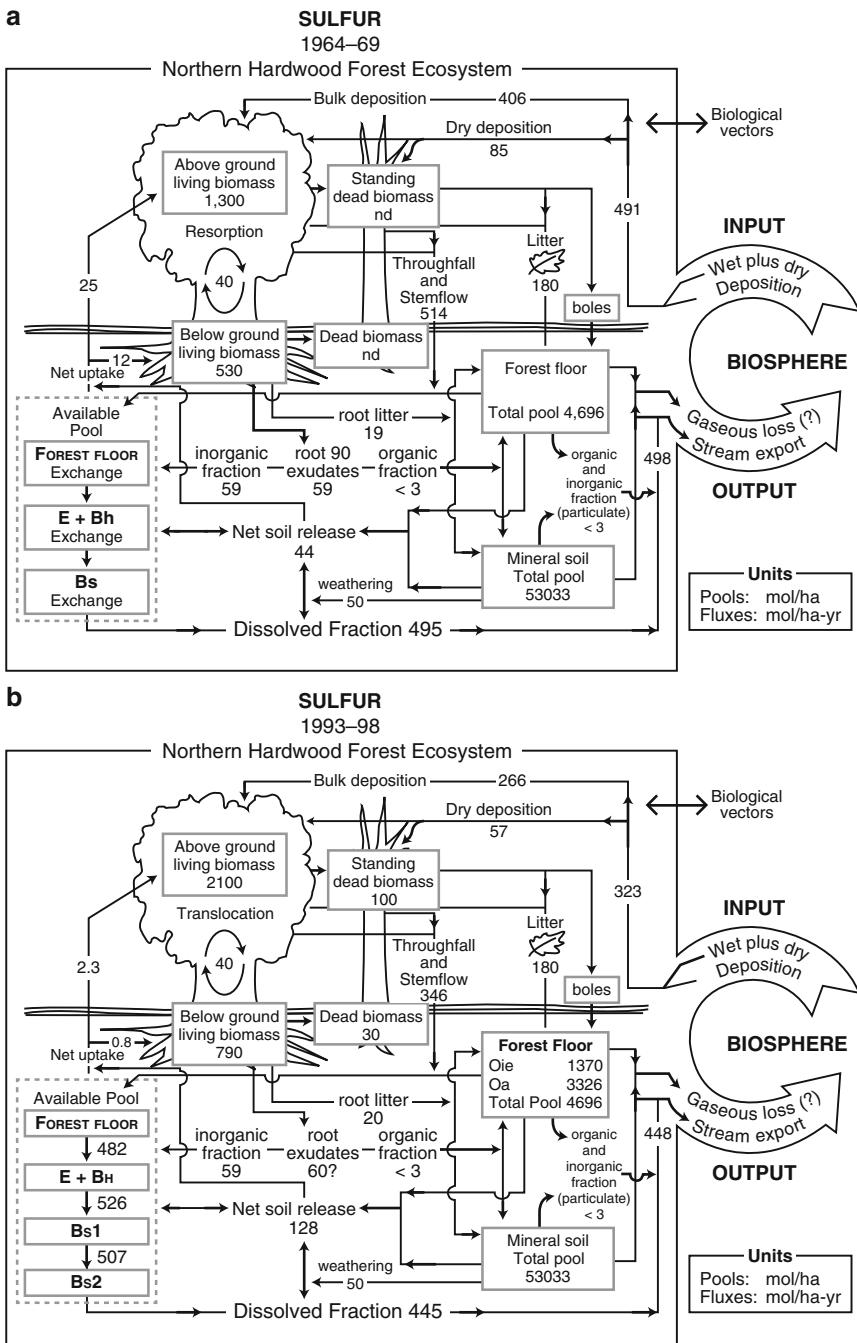


Fig. 55 Ecosystem pools (boxes) and fluxes (arrows) of Sulfur for Watershed 6 at the Hubbard Brook Experimental Forest. Average values in mol/ha or mol/ha-year for periods specified. Values for 1964–1969 (a) and for 1993–1998 (b). Above-plus belowground biomass is for 1997; root and aboveground litter and root exudates assumed to be same as in 1964–1969; net uptake values based on difference in biomass storage between 1982 and 1998; Forest floor pools and total mineral soil pool for both periods from Zhang et al. (1999) as estimated for W5 in 1983. From Likens et al. (2002a) and reprinted with permission of Kluwer Academic Publishers

In a recent pentad (1993–1998), vegetation stores sulfur at a rate of 0.1 kg/ha-year. Net soil release is 4.1 kg S/ha-year, and mineral weathering generates an amount of sulfur equivalent to about 16 times the sulfur stored annually by vegetation. Meteorologic input is approximately 100 times the annual vegetation storage (Fig. 55). The sulfur budget of the forest ecosystems at HBEF is therefore dominated by meteorologic inputs (i.e., wet and dry deposition).

In 1993–1998, gross uptake of S in trees was estimated at ~9.2 kg S/ha-year, based on estimates of root exudates, root litter, canopy litterfall, canopy leaching, and net biomass storage (Fig. 55; Likens et al. 2002a). Only ~1 % of gross uptake of S is accrued, whereas 99 % is returned to the soil. Gross uptake during 1964–1969 was ~11 % more than in 1993–1998, and net biomass storage of sulfur was ~12 % of gross uptake (Fig. 55; Likens et al. 2002a). Loss of sulfate via streamwater decreased significantly from the earlier to the later pentad, but net biomass storage decreased even more. Because annual net biomass storage of sulfur decreased by more than an order of magnitude from the earlier to the later pentad, streamwater loss of S was >13 times than net biomass storage in 1964–1969 and 145 times greater in 1993–1998 (Fig. 55; Likens et al. 2002a).

Recent (1993–1998) inputs to the available nutrient compartment are partitioned as follows: atmospheric bulk precipitation (50 %), net soil release (24 %), dry deposition (11 %), root exudates (11 %), and canopy leaching (4 %) (Fig. 55).

It is well known that plants can utilize SO₂ directly from the atmosphere (Hill 1971; Hoeft et al. 1972; Cowling et al. 1973), and various authors have suggested input from aerosols and dust impacted on vegetation surfaces (Eriksson 1952; Tamm and Troedsson 1955; Duvigneaud and Denayer-DeSmet 1964; Carlisle et al. 1967; White and Turner 1970). Our throughfall and stemflow data (Table 9) suggest that sulfurous aerosols may be impacted on vegetation surfaces in large amounts during the summer. We do not know the actual proportions of these two meteorologic sources of sulfur at HBEF, but we estimate that the net gaseous input is about fivefold greater than the aerosol deposition on an annual basis (Lovett et al. 1997). Currently (1993–1998), the combination of net gaseous uptake and aerosol deposition accounts for about 18 % of the total meteorologic input or 13 % of the annual hydrologic export (Fig. 55). Obviously such inputs must be carefully assessed in biogeochemical studies.

A summation of the values for biomass accretion, weathering release, precipitation input, and streamwater output shows a sulfur imbalance, suggesting some additional source(s) of sulfur for the ecosystem. Because net hydrologic fluxes (precipitation inputs–streamwater outputs) for S are consistently imbalanced at the HBEF, with streamwater outputs exceeding bulk precipitation inputs (Chap. 4; Likens et al. 2002a), dry deposition of sulfur needs to be added to this balance. One exception occurred during the drought year of 1964–1965, when precipitation inputs exceeded streamwater outputs.

Dry deposition of S is difficult to measure quantitatively in forest landscapes in mountainous terrain. During 2002, dry deposition was estimated to be 0.5–2.5 kg S/ha-year using a new approach (Mitchell et al. 2011), as compared to an estimate of 1.8 kg/ha-year during 1993–1998 (Likens et al. 2002a). Adding dry deposition reduced the overall imbalance. Both unmeasured desorption and mineralization of

sulfur stored in the soil also probably contributed to this imbalance. In the long term, annual balances were both positive and negative (Likens et al. 2002a).

Nutrient Cycle Relationships at the HBEF

The allocation of budgetary items for the major nutrients at HBEF circa ~1974 is given in Tables 30 and 31. This was a time when forest biomass was strongly aggrading and meteorologic inputs of acid, sulfate, and nitrate were high. These values, along with those of Tables 17, 18, and 19, suggest several important conclusions regarding the biogeochemistry of the northern hardwood ecosystem. These are the following: (a) In relation to gross losses, nutrient inputs in bulk precipitation represent a significant addition to the ecosystem. Such inputs can be the major source of nutrients in terrestrial ecosystems low in weathering substrates (e.g., Art et al. 1974); (b) for some elements, such as nitrogen, sulfur, and chloride, dry deposition or biologic gaseous fixation can provide significant input to forest

Table 30 Standing stocks and annual biogeochemical fluxes for a 55-year-old forested ecosystem at the Hubbard Brook Experimental Forest (circa 1974)

Component	Chemical element								
	Ca	Mg	Na	K	N	S	P	Cl	
<i>Standing stock (kg/ha)</i>									
Aboveground biomass	383	36	1.6	155	351	42	34	a	
Belowground biomass	101	13	3.8	63	181	17	53	a	
Forest floor	372	38	3.6	66	1256	124	78	a	
<i>Annual flux (kg/ha-year)</i>									
Bulk precipitation input	2.2	0.6	1.6	0.9	6.5	12.7	0.04	6.2	
Gaseous or aerosol input	a	a	a	a		6.1	a	?	
Weathering release ^b	21.1	3.5	5.8	7.1	0	0.8	?	a	
Streamwater output									
Dissolved substances	13.7	3.1	7.2	1.9	3.9	17.6	0.01	4.6	
Particulate matter	0.2	0.2	0.2	0.5	0.1	<0.1	0.01	a	
Vegetation uptake	62.2	9.3	34.8	64.3	79.6 ^c	24.5 ^c	8.9	a	
Litter fall	40.7	5.9	0.1	18.3	54.2	5.8	4.0	a	
Root litter	3.2	0.5	0.01	2.1	6.2	0.6	1.7	a	
Throughfall and stemflow	6.7	2.0	0.3	30.1	9.3	21.0	0.7	4.4	
Root exudates	3.5	0.2	34.2	8.0	0.9	1.9	0.2	1.8	
Net mineralization	42.4	6.1	0.1	20.1	69.6	5.7	?	?	
Aboveground biomass accretion	5.4	0.4	0.03	4.3	4.8	0.8	0.9	a	
Belowground biomass accretion	2.7	0.3	0.12	1.5	4.2	0.4	1.4	a	
Forest floor accretion	1.4	0.2	0.02	0.3	a	0.8	0.5	a	

^aSmall, unmeasured

^bCurrently calculated as net soil release; see Chap. 5

^cRoot uptake

Table 31 Allocation of budgetary items in percent for watershed-ecosystems of the Hubbard Brook Experimental Forest (circa 1974)

	Ca	K	Mg	Na	N	S
<i>Source</i>						
Bulk precipitation input	9	11	15	22	31	65
Net gas or aerosol input	—	—	—	—	^a	31
Weathering release ^b	91	89	85	78	—	4
<i>Storage or loss</i>						
Biomass accumulation						
Vegetation	35	68	17	2	43	6
Forest floor	6	4	5	<1	37	4
Streamflow						
Dissolved substances	59	22	74	95	19	90
Particulate matter	<1	6	5	3	<1	<1

^aSee Table 30^bCurrently calculated as net soil release; see Chap. 5

ecosystems; (c) although variable and changing with time, hydrologic-driven budgets for the forest watershed-ecosystems currently show gains in carbon, hydrogen ion, nitrogen, phosphorus, and chloride and losses in sulfur, dissolved silica, calcium, sodium, aluminum, magnesium, and potassium (Likens 2004; Chap. 4). Losses of the latter substances from the intrasystem nutrient cycle are made up by weathering of primary minerals/net soil release, dry deposition, and mineralization of soil organic matter (Fig. 1); (d) net soil release is the major source of calcium, potassium, magnesium, and sodium in the ecosystem; (e) a dramatic decrease in net biomass uptake since 1982 has greatly decreased the NEF for calcium and magnesium, and a decrease in net biomass uptake and streamwater output increased the NEF for nitrogen. The forest floor is a particularly effective storage site for nitrogen. In contrast, <10 % of the sodium and sulfur added to the ecosystem from meteorologic sources is stored in the biomass, and the remainder, more than 90 %, is lost in streamflow annually; (f) root exudates are very important to the intrasystem cycle of sodium, whereas stemflow and throughfall are particularly important for cycling sulfur and potassium, and litter plays a major role in the cycling of phosphorus, nitrogen, magnesium, and calcium.

Annual Watershed-Ecosystem Mass Balances (“Budgets”)

Another informative way to summarize and synthesize long-term biogeochemical dynamics is to measure or estimate the full range of ecosystem fluxes and organize this information into annual mass balances (“budgets”) in order to calculate Net Ecosystem Flux (NEF). This is done here for calcium, sodium, potassium, sulfur, dissolved inorganic nitrogen, and chlorine (Figs. 56, 57, 58, 59, 60, and 63), which provides a sampling of elements with and without a prominent gaseous phase.

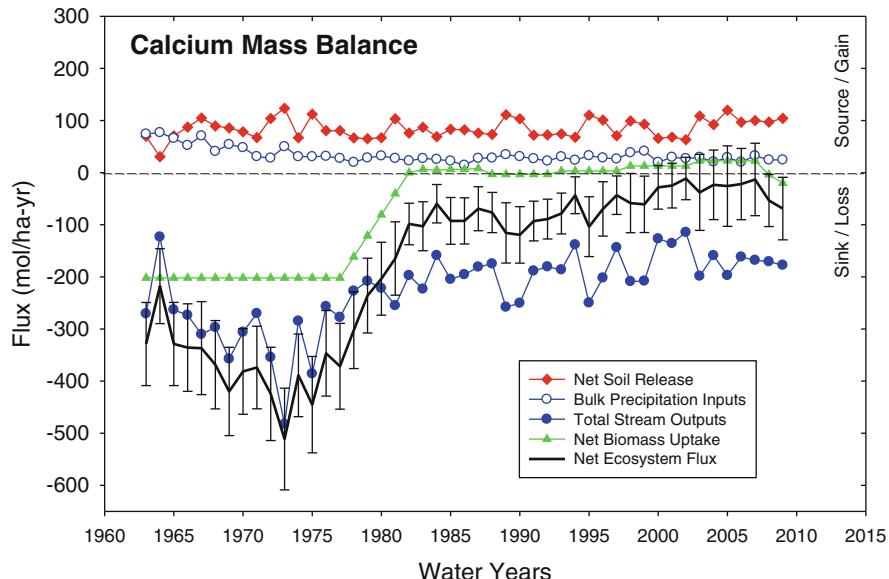


Fig. 56 Annual ecosystem mass balances for calcium in Watershed 6 of the Hubbard Brook Experimental Forest during 1963–2009. Bulk precipitation input, including dry deposition (*open circle*); *filled diamond* is net soil release based on midrange reaction rate (of $0.37 \times \text{NHF}$ for sodium; see Chap. 5); *filled circle* is streamwater output; *filled triangle* is net biomass storage; and is net ecosystem flux obtained by difference (*straight line*) Net Ecosystem Flux is obtained by difference [modified and extended from Likens (1996, 1998)]

Displaying these long-term budgetary data in this way helps to put the detailed, biogeochemical data for the watershed-ecosystem for selected pentads into perspective and provides new insights about the biogeochemical dynamics of these elements. The inputs to the mass balance shown are bulk precipitation, dry deposition, and net soil release. The outputs are streamwater exports, net biomass storage, and net gas flux. The difference, annually, between inputs and outputs is net ecosystem flux, NEF (or NHF when only the hydrologic components are known).

These long-term data on inputs and outputs allow mass balances to be constructed and compared over time. The values in these mass balances are updated and modified from those published previously (e.g., Likens et al. 1994). The uncertainty bars on the NEF term in these mass-balance diagrams are root mean squares for estimated errors for the other components of the mass balance: bulk precipitation = measured with $\pm 5\%$ uncertainty; dry deposition = included in bulk precipitation for calcium, sodium, and potassium; sulfur, nitrogen, and chlorine estimated as a % of bulk precipitation with 50 % estimated uncertainty (the uncertainty in S dry deposition, Mitchell et al. 2011); net soil release = estimated as $\pm 50\%$ uncertainty (based on S. Bailey et al. 2003); streamwater output = measured with $\pm 5\%$ uncertainty; net biomass uptake = for above-plus belowground; the range was 27 to 150 %, uncertainty from high to low uptake (based on Yanai et al. 2012);

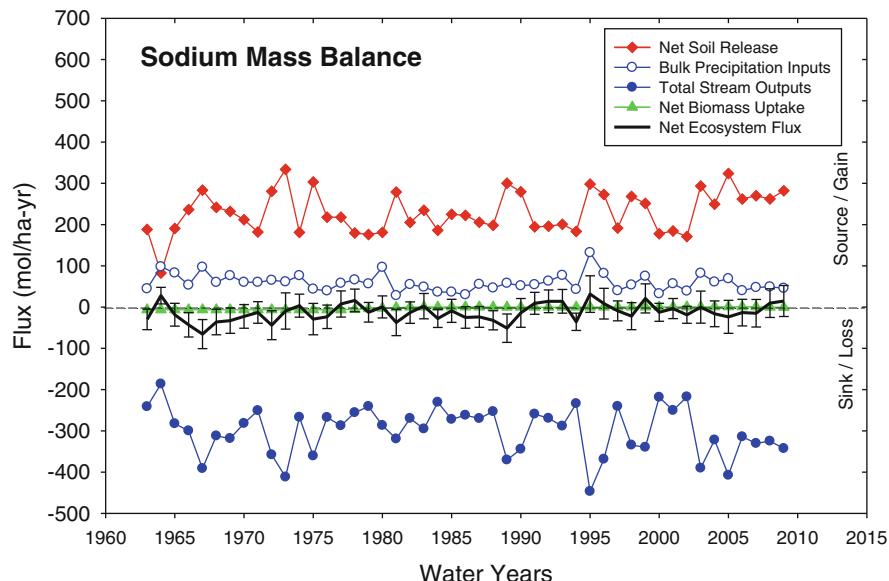


Fig. 57 Annual ecosystem mass balances for sodium in Watershed 6 of the Hubbard Brook Experimental Forest during 1963–2009. *Open circle* is bulk deposition input, including dry deposition; *filled diamond* is net soil release (net soil release approximates NHF for sodium); *filled circle* is streamwater output; *filled triangle* is net biomass storage; and (*straight line*) is Net Ecosystem Flux obtained by difference

see element-by-element details in figure legends; mass balances—further explanations [see page 160–161].

Annual budgets of this sort over almost five decades are a unique contribution from the long-term biogeochemical studies at the HBEF. Long-term budgetary patterns have changed, are often individualistic for each element in adjacent watershed-ecosystems, but provide key insights regarding the important drivers of change, such as hydrology, biomass aggradation, air pollution, and climate change. Examples for six elements are given below.

Calcium

The long-term annual mass budgets for calcium in W6 are shown in Fig. 56. This figure is extended some 15 years beyond that published in Likens et al. (1998); this recent period occurs when biomass uptake and storage in W6 are minimal (Likens et al. 1994; Lindenmayer and Likens 2010; van Doorn et al. 2011).

In this current analysis (Fig. 56), we adopted the conservative assumption of Likens et al. (1998) that bulk precipitation collectors sample both wet and dry

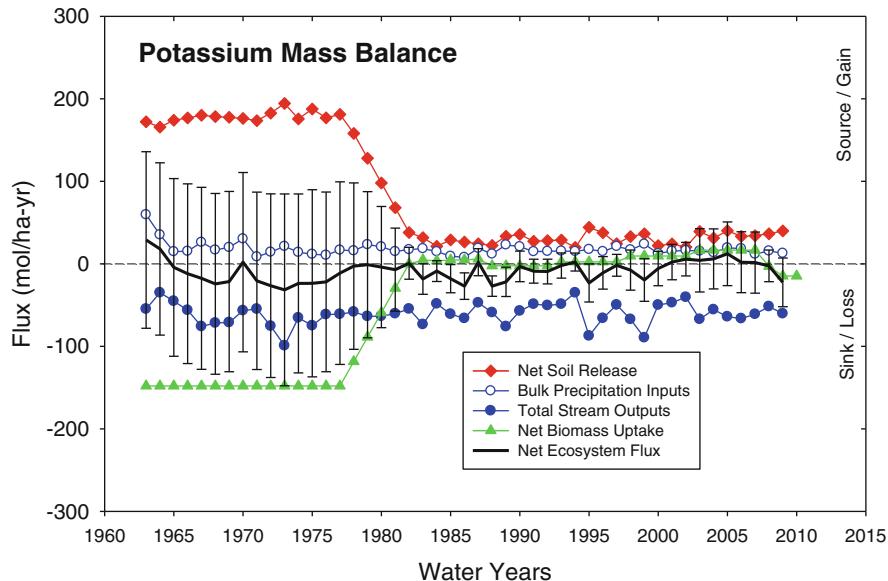


Fig. 58 Annual ecosystem mass balances for potassium in Watershed 6 of the Hubbard Brook Experimental Forest during 1963–2009. Open circle is bulk deposition input including dry deposition; filled diamond is net soil release; (filled circle) is streamwater output; (filled triangle) is net biomass storage; and straight line is Net Ecosystem Flux obtained by difference [modified and extended from Likens et al. (1994)]

deposition of calcium. With annual streamwater output of calcium decreasing from ~1973 to ~1985 and then relatively constant, bulk precipitation inputs decreasing since the mid-1950s (Fig. 19; Likens and Bailey 2013), net biomass storage minimal since ~1982 and net soil release (based on sodium biogeochemistry, S. Bailey et al. 2003) similar to bulk precipitation inputs and rather constant, net ecosystem flux (NEF) of calcium is much smaller after ~1982 (Fig. 56). Streamwater outputs have dominated the fluxes of calcium throughout the study. Nevertheless, the striking result shown by this long-term record is the marked loss of calcium ($-NEF$) from the watershed-ecosystem, particularly prior to ~1985. It was calculated earlier that these watershed-ecosystems lost ~840 kg Ca/ha or approximately 50 % of the available nutrient pool during the period 1940–1995 (Likens et al. 1996, 1998; but see p. 63). These net losses have been attributed to the impact of acid rain during this period (Likens et al. 1996, 1998; Likens and Bailey 2013). The NEF during 1963–2009 was -8.3 kmol Ca (207 kg Ca) (Fig. 56; Table 32). Total streamwater losses of calcium were larger than NEF during this 47-year period (Table 32).

The acid-neutralizing capacity in streamwater became positive in W6 for the first time in our study ~2000 (Fig. 17), but acid rain continues, albeit at a smaller amount (Fig. 14), and the NEF continues to be negative, but not significantly different than zero (Fig. 56). An increase in acidic input in bulk precipitation and/or net biomass uptake (forest recovery) would increase NEF losses.

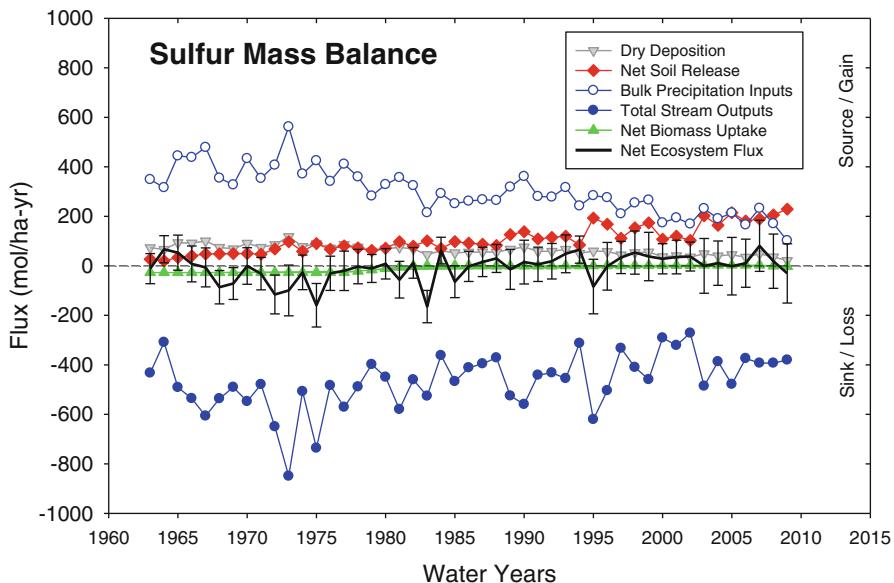


Fig. 59 Annual ecosystem mass balances for sulfur for Watershed 6 of the Hubbard Brook Experimental Forest during 1964–2009. Open circle is bulk deposition input; filled diamond is net soil release; filled circle is streamwater output; filled triangle is net biomass storage; and inverted filled triangle is dry deposition based on Mitchell et al. (2011), and straight line is net ecosystem flux obtained by difference [modified and extended from Likens et al. (2002a)]

Sodium

As is typical of an element with a sedimentary cycle, streamwater outputs greatly exceeded bulk precipitation inputs of sodium (Fig. 57) throughout the long-term study (1963–2009). In these mass balances, dry deposition inputs were included as a part of bulk precipitation inputs, and net soil release was calculated as a function of annual streamflow and a variable annual NHF for sodium. Net soil release and streamwater exports dominate the annual, long-term mass-balance values for sodium. The uncertainty for net soil release of sodium is estimated at $\pm 10\%$. Because net soil release plus bulk precipitation input approximately equal streamwater output on an annual basis, net storage of sodium in biomass is very small even before biomass stopped accumulating in ~1982. NEF is approximately in balance (-0.6 kmol/ha) in the long-term record, particularly given the uncertainties (Fig. 57). Sodium concentrations are slightly decreasing in both bulk precipitation and streamwater, so the recent increasing amount of precipitation and streamflow are the primary drivers in these fluxes (Figs. 19a and 57). Streamwater output and net soil release/weathering are the dominant fluxes in these long-term mass balances for sodium at the HBFF.

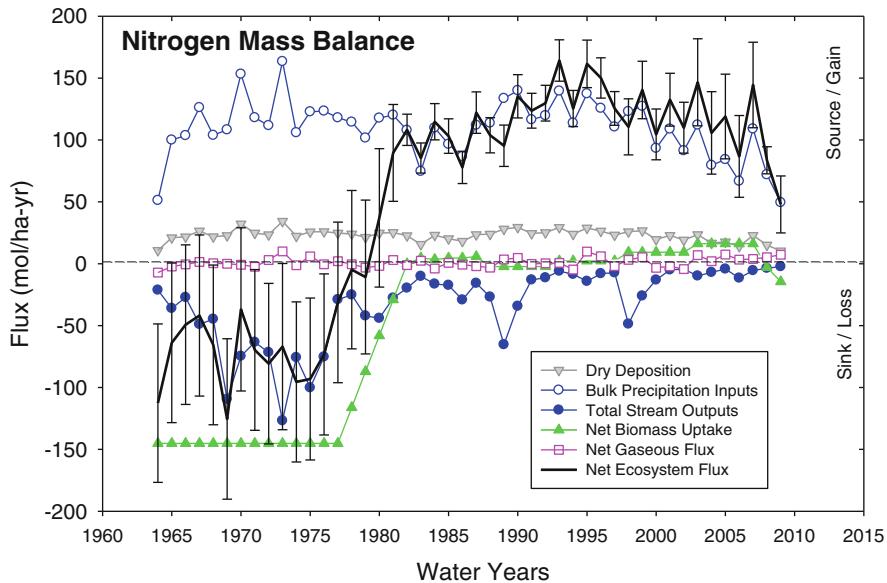


Fig. 60 Annual ecosystem mass balance for dissolved inorganic nitrogen in Watershed 6 of the Hubbard Brook Experimental Forest during 1963–2009. Open circle is bulk deposition input; filled circle is streamwater output; filled triangle is net biomass storage; inverted filled triangle is dry deposition; red square is gaseous losses based on N_2O flux estimates; and straight line is Net Ecosystem Flux obtained by difference

Potassium

This record of annual mass balance is extended some 17 years beyond that published by Likens et al. (1994). As was the situation for calcium and sodium, streamwater outputs greatly exceeded bulk precipitation inputs of potassium (Fig. 58) throughout the long-term study (1963–2009). Also, as with calcium and sodium, dry deposition inputs were included as part of bulk precipitation (Likens et al. 1994). Annual net soil release was calculated as a function of net biomass uptake and a fluctuating NHF, which in turn is a function of annual streamflow (Fig. 54). The net biomass uptake had an estimated uncertainty of ± 30 to 120 %, the NHF 7 %, giving an estimated NEF uncertainty of ~ 30 %. The uncertainty in NEF was large during 1963–1980 and much smaller thereafter because of the smaller effect of reduced net biomass storage (Fig. 58).

Mirroring the annual net storage of potassium in biomass, net soil release was large during 1963 to ~ 1982 (especially 1963 to 1977) and then fluctuated somewhat above zero thereafter. The NEF value fluctuated around zero throughout the study with periods of positive values, suggesting possible storage of potassium in the soils of the HBEF. The aggressive demand for potassium by the biomass is obvious in these mass balances (Fig. 58). Over the long term essentially balanced total NEF was slightly negative, -0.4 kmol/ha (Fig. 58; Table 32). Nevertheless, long-term

total net soil release of potassium is ~37 % that for sodium, but the NEF values are not different (Table 32; Figs. 57 and 58). The weathering sources of potassium and sodium are different in the HBEF (see Chap. 5).

Sulfur

In response to long-term values for atmospheric emissions of SO₂ (Chap. 3; Likens et al. 2001, 2002a), sulfate input in bulk precipitation peaked at HBEF in 1973. Sulfate input has been declining steadily since (Table 17). Dry deposition of sulfur is assumed to be ~21 % of bulk precipitation inputs (Mitchell et al. 2011), and net soil release is prorated and extended based on 44 mol S/ha-year in 1964–1969 and 128 mol S/ha-year in 1993–1998 (Fig. 55). Interestingly, net soil release is equal to or larger than the bulk precipitation inputs in 2008 and 2009, suggesting that desorption of stored sulfur in the ecosystem from past atmospheric inputs may be becoming increasingly important in the mass balance of sulfur. As described above, the NEF values are small and varied between +86.8 and –229.5 mol S/year (+0.3 and –0.8 kg S/ha-year) and averaged -54.3 ± 72.9 (SD) mol S/year (-0.19 ± 0.25 kg S/ha-year) during 1964–1998. The NEF is roughly balanced over the 48 years because of the tendency for declining bulk precipitation inputs to be balanced by declining streamwater outputs and increasing net soil release (Fig. 59). The long-term cumulative NEF is small, but negative, –0.3 kmol/ha (Table 32).

Likens et al. (2002a) suggested four hypotheses to account for the small and inconsistent imbalance in NEF: underestimates of (1) dry deposition, (2) sulfate desorption from soils, (3) weathering release, and (4) net mineralization of organic sulfur. In evaluating these hypotheses, they concluded that net desorption of sulfate and primarily net mineralization of soil organic sulfur were the most likely mechanisms to cause any imbalance (more likely since 1985; Fig. 59) in the NEF.

Nitrogen

Nitrogen is a very interesting, yet difficult, element to characterize quantitatively by mass balance, particularly over a long period and at the watershed scale. It is an extremely interesting element, primarily because it is fundamentally important to biota and has been thought to be limiting (*sensu* Liebig’s Law of the minimum) to productivity in the northern hardwood forest ecosystem. Since there are negligible nitrogen-bearing rocks in the HBEF, all of the nitrogen in the watershed-ecosystems of the HBEF must have been obtained from the atmosphere and accumulated by the biota in the past 14,000 years following the glacial retreat from this area. Gaseous fluxes into the ecosystem via fixation and out of the ecosystem via denitrification are very difficult to measure quantitatively at the watershed scale (e.g., Groffman and Rosi-Marshall 2013).

Table 32 Cumulative Totals of all Fluxes in Mass Balance for Watershed 6 of the Hubbard Brook Experimental Forest^a

Element	Bulk precipitation (kmol/ha)		Dry deposition (kmol/ha)		Net soil release (kmol/ha)		Stream export (kmol/ha)		Net biomass intake (kmol/ha)		Gaseous losses (kmol/ha)		NEF (kmol/ha)		Flux In/Out
	In	In	In	In	Out	Out	Out	Out	Out	Out	Net	-8.282	Loss		
Calcium	1.581	In BP	3.991		-10.586		-3.268		na						
% Total in or out	28.4		71.6		76.4		23.6								
Potassium	0.841	In BP	3.988		-2.853		-2.395		na				-0.419		Loss
% Total in or out	17.4		82.6		54.4		45.6								
Sodium	2.784	In BP	10.804		-14.085		-0.105		na				-0.602		Loss
% Total in or out	20.5		79.5		99.3		0.7								
Sulfur	14.149	2.971	4.946		-21.963		-0.437		na				-0.334		Loss
% Total in or out	64.1	13.5	22.4		98.0		2.0								
DIN	5.087	1.068	0.000		-1.570		-2.204						1.847		Gain
% Total in or out	82.6	17.4	0.0		36.4		51.2						12.4		
Chlorine	4.411	0.882	0.129		-5.431		-0.486		na				-0.495		Loss
% Total in or out	81.3	16.3	2.4		91.8		8.2								

^aCalcium, potassium and sodium for 1963–2009. Sulfur, DIN and chloride for 1964–2009. For calcium, potassium and sodium dry deposition included in bulk precipitation total. Stream export includes dissolved and particulate substances. There are no gaseous losses for calcium, potassium, sodium, sulfur and chlorine. DIN is dissolved inorganic nitrogen. NEF is Net Ecosystem Flux; values may differ slightly due to rounding errors

Here (Fig. 60), only hydrologic fluxes of dissolved inorganic nitrogen (DIN), that is, nitrate and ammonium, will be considered as dissolved organic nitrogen (DON) in bulk precipitation averaged 1.1 ± 0.6 kg N/ha-year and DON in stream water averaged 1.0 ± 0.4 N/ha-year for 1995–2012, representing small and essentially balanced fluxes.

In Fig. 60, dry deposition is assumed to be 21 % of bulk precipitation (Lovett et al. 1997), which agrees reasonably well with the CASTNET value for our site. Gaseous losses (0.27 – 1.4 kg N/ha-year) are based on N_2O estimates (Kulkarni et al. 2008; Groffman et al. 2009), and N-fixation inputs (~2 kg N/ha-year) are based on Roskoski (1980).

The long-term mass balance (NEF) for nitrogen essentially shows a sinusoidal pattern of ecosystem release during 1964–1980 and accumulation during 1980–2009 (Fig. 60). Overall, the NEF balance for DIN is positive (1.8 kmol N; Table 32). This NEF pattern is driven largely by net biomass uptake, and secondarily by bulk precipitation input, which has been declining since ~1995 and currently is lower than in 1964 (Fig. 60). This fascinating pattern begs the question of where this nitrogen is being stored in the ecosystem and whether this pattern has occurred in the past and whether it will occur in the future.

Nitrogen Retention in Forested Watershed-Ecosystems

Normally, watershed-ecosystems of the HBEF are very retentive (bulk precipitation input minus stream water output) against loss of dissolved inorganic nitrogen (DIN) in stream water (Fig. 61). This “action” against loss might be expected since nitrogen is thought to be a limiting element for biological productivity and its ultimate source in the atmosphere. Even vernal “dams” have been proposed to function as retention mechanisms at the HBEF (Muller and Bormann 1976).

The interannual pattern of retention is quite variable, however (Fig. 61), with minimal % retention in 1969 and very high % retention from 1992 to 2009. Relatively high inputs and losses of DIN in streamwater occurred during 1965–1978 and 1969–1976, respectively (Fig. 60). Decreased retention occurred during water-years of forest disturbance (frost 1969, 1988; ice storm 1998; Fig. 61).

Seasonally, the summer growing season is consistently, highly retentive of DIN, and spring and fall tend to be less retentive than summer and winter (Fig. 62). The spring season is more variable in terms of % retention of DIN than the other seasons.

Chlorine

Chloride deposition prior to about 1980 was presumably higher than currently because of coal burning, which releases HCl into the atmosphere (Graedel and Keene 1996; Lovett et al. 2005). Since about 1980 chloride input in bulk

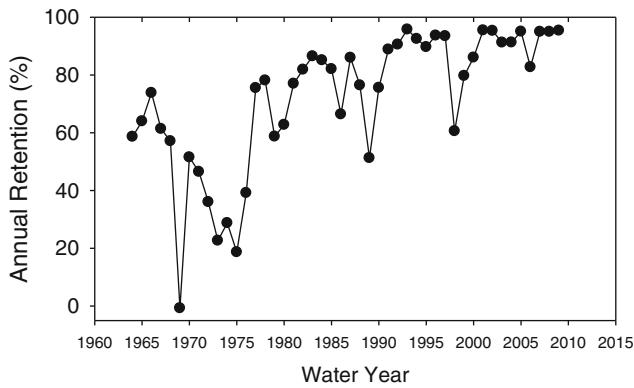


Fig. 61 Annual retention of dissolved inorganic nitrogen (bulk precipitation input minus streamwater export for Watershed 6 of the Hubbard Brook Experimental Forest during 1964–2009)

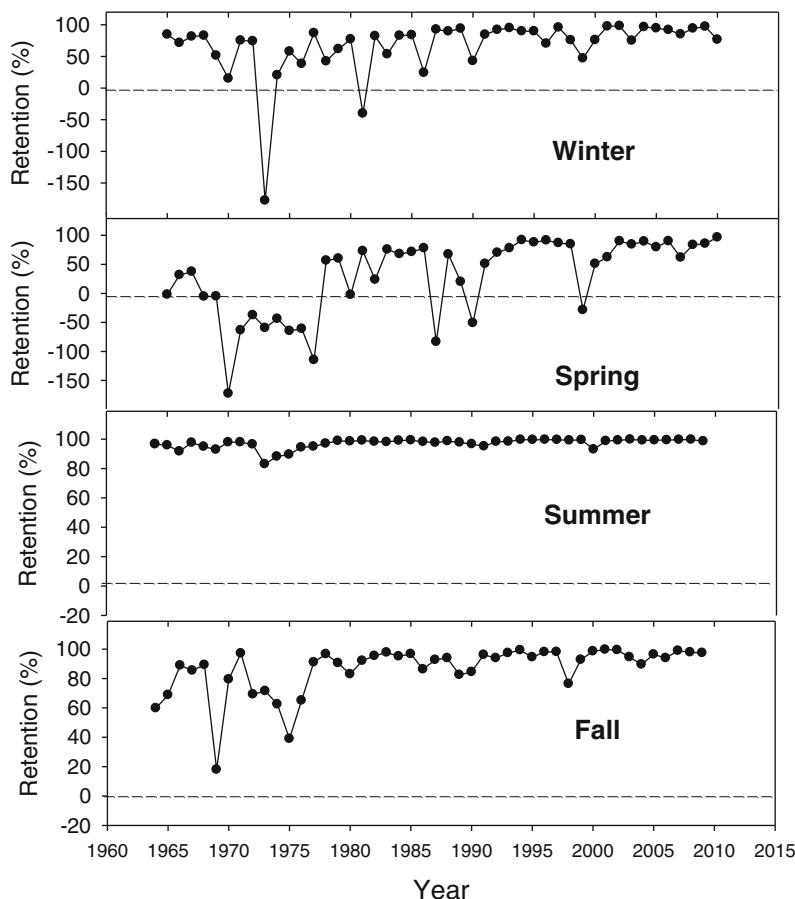


Fig. 62 Average seasonal retention of dissolved inorganic nitrogen (bulk precipitation input minus streamwater output for Watershed 6 of the Hubbard Brook Experimental Forest during 1964–2009). Winter=December, January, February; Spring=March, April, May; Summer=June, July, August, September; Fall=October, November

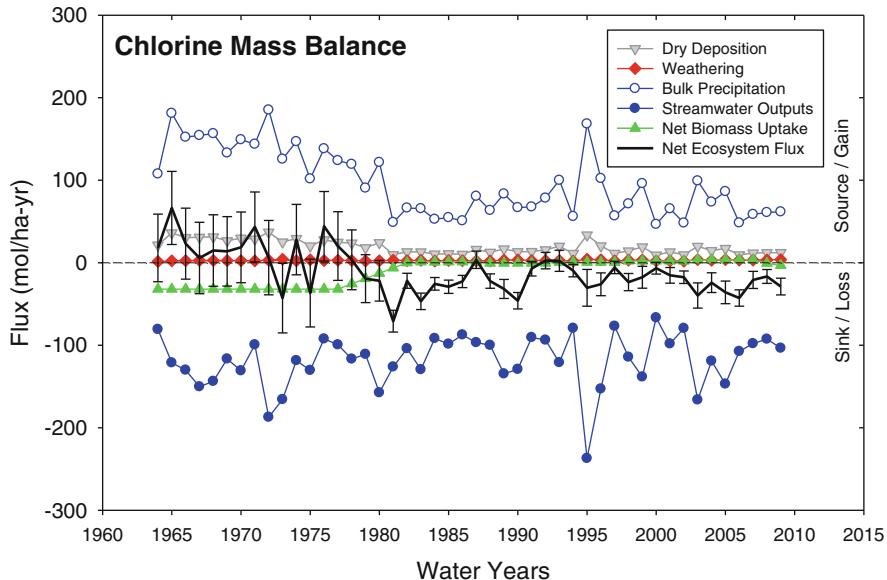


Fig. 63 Annual ecosystem mass balances for chloride in Watershed 6 of the Hubbard Brook Experimental Forest during 1964–2009. Open circle is bulk deposition inputs; inverted filled triangle is dry deposition inputs (estimated as 20 % of bulk deposition). Dry deposition in winter assumed negligible; filled diamond is weathering (estimated at 1.7 mol ha/year); filled triangle is net biomass uptake; filled circle is streamflow output; and straight line is Net Ecosystem Flux obtained by difference [modified and extended from Lovett et al. (2005)]

precipitation has been lower and variable, but averaged ~60 mol/ha-year (1.7 kg Cl/ha-year) (Fig. 63). Wet years in 1973 and particularly 1995 produced high inputs in bulk precipitation. Dry deposition of chloride is assumed at 20 % of bulk precipitation values (Lovett et al. 2005). Rather than using net soil release, which could be large, highly variable, and difficult to estimate (Svensson et al. 2012), we used chloride weathering, which is very small (1.7–3.4 mol/ha-year) (Lovett et al. 2005). Annual values are calculated as a function of streamflow. Relatively large amounts of chloride are lost in streamwater and wet years (1973 and 1995) predominate in this regard (Fig. 63). There is a strong correlation between inputs of chloride in precipitation and streamwater outputs (Fig. 63). The average streamwater output from 1964 to 2009 is ~125 mol/ha-year (3.5 kg Cl/ha-year). Small amounts of chloride (~30 mol Cl/ha-year) are accreted in biomass in an aggrading forest, but this storage is assumed to be minimal after ~1982 (Lovett et al. 2005). The result of this approach is that NEF becomes a “proxy” for net soil release. Net soil release, primarily from soil organic matter, has been relatively large, but may have decreased with time at the HBEF (Lovett et al. 2005). Thus, the NEF is

variable but mostly negative after 1978, averaging -0.5 kmol Cl for the period 1964–2009 (Table 32; Fig. 63). Despite the decline in atmospheric inputs, the coincidental decline in the net biomass sink allowed for continued streamwater export of chloride (Fig. 63).

Figures 53, 54, and 55. Ecosystem Diagrams: Further Explanations

General. The boxes within the ecosystem diagrams represent ecosystem standing stocks or pools of elements. The values within these boxes are the size of the elemental pool in mol/ha. The arrows between the various pools represent annual ecosystem fluxes in mol/ha-year. All values are given for Watershed 6 of the Hubbard Brook Experimental Forest.

The last cutting of the forest at Hubbard Brook took place between 1909 and 1917. Indications are that the majority of the cutting took place closer to 1917 than to 1909. Therefore, we made the assumption that major forest regrowth was initiated around 1915.

Pools. Aboveground Living Biomass: Living biomass was measured by Whittaker et al. (1974). At the same time representative samples were taken and analyzed by Likens and Bormann (1970) for various elemental constituents. Whittaker et al. (1974) also measured the productivity of the forest for two pentads (1956–1960 and 1961–1965). The biomass accretion values in the diagrams for 1964–1969 represent a mean of these two pentads and are multiplied by the elemental concentrations of Likens and Bormann (1970). This approach assumes that tissue concentrations have not changed since 1970. Biomass and chemical data in later pentads come from Likens et al. (1994) (potassium), (1998) (calcium), and (2002a) (sulfur).

Belowground Living Biomass: Belowground biomass was measured, and elemental composition was determined in the same manner as the aboveground living biomass.

Forest Floor: For the early pentad (1964–1969), the biomass and the elemental composition of the upper organic layers of the soil (to an average depth of 8.9 cm) were measured by Gosz et al. (1976) and Dominski (1971). The biomass of larger litter (e.g., limbs and boles of trees) on the forest floor was measured by Covington (1976), and its elemental composition was determined from Gosz et al. (1972). The rate of forest floor accretion was estimated by Covington (1976) by measuring the biomass of a successional sequence of northern hardwood stands ranging in age from 3 to 200 years. Elemental composition is from Gosz et al. (1976).

Biomass accretion and elemental composition in the forest floor in later pentads come from Likens et al. (1994) (potassium), (1998) (calcium), and (2002a) (sulfur).

Mineral Soil and Rock: Estimates of the amount of organic and inorganic matter in the mineral soil and of rock in the soil profile to a depth of 45 cm for 1964–1969 were measured by Dominski (1971), and the elemental composition of mineral soil is from Gosz et al. (1976), Lunt (1932), and Johnson et al. (1968); the elemental composition of rock is from Johnson et al. (1968) assuming 50 % unweathered Kinsman quartz monzonite and 50 % unweathered Littleton gneiss. Although an arbitrary soil depth of 45 cm was used, we assume the majority of the active soil processes (biogeochemical) occur within the upper 45 cm of soil.

Available Soil Nutrients: Estimated from soil depth, bulk density, and elemental analyses (Lunt 1932).

Estimates for later pentads are as above.

Elemental Fluxes. Bulk Precipitation: Chemical inputs in rain and snow to the ecosystem have been measured since 1963 (Buso et al. 2000). Numbers used here are weighted mean annual inputs (see Table 11).

Litterfall: The fall of litter from forest vegetation to the forest floor was measured, and its elemental composition was determined by Gosz et al. (1972).

Translocation: The movement of chemicals back into woody tissues at the time of autumn senescence for leaves is calculated as translocation = (production + bud litter + root exudates + throughfall and stemflow) – (uptake – shrub and herb litter).

Throughfall and Stemflow: The washing and leaching of chemicals from the forest canopy by precipitation was determined by Eaton et al. (1973).

Root Exudation: The loss of chemicals from roots by root exudates was measured by Smith (1976).

Root Litter: The biomass of root litter was estimated by Whittaker et al. (1974). Elemental composition of roots was taken from Likens and Bormann (1970). Estimates for later pentads are as above.

Net Soil Release: As described in Chap. 5.

Uptake: Uptake by forest vegetation was calculated as uptake = litterfall + net throughfall and stemflow + root exudates + root litter + living biomass accumulation.

Hydrologic Export: Export of dissolved chemicals represents means for 1964–1969 and 1987–1992 (Ca, K) and 1993–1998 (S). Particulate losses represent means for 4 years (Tables 19, 27).

Mass Balances (NEF)—Further Explanations: P=bulk precipitation input, D=dry deposition, NSR=net soil release, S=streamwater output, W=weathering, B=net biomass uptake, G=net gaseous exchange, NHF=Net Hydrologic Flux.

Calcium

- P Measured, $\pm 5\%$ uncertainty
- D Included in P
- NSR 37 % of Na NHF based on possible reactants; $\pm 35\%$ uncertainty
- S Measured $\pm 5\%$ plus particulate matter loss based on average annual streamflow (increases uncertainty to 6 %)
- B Maximum value from Fig. 53 = -202 mol/ha-year ; ± 30 to 120 % uncertainty
- G No gas flux

Potassium

- P Measured, $\pm 5\%$ uncertainty
- D Included in P
- NSR Used 1964–1969 average (179) until 1982 and = to NHF for 1982–2009; $\pm 50\%$ uncertainty
- S Measured $\pm 5\%$ plus particulate losses based on average annual streamflow (increases uncertainty to 6 %)
- B Maximum value from Fig. 54 = -148 mol/ha-year ; ± 30 to 120 % uncertainty
- G No gas flux

Sodium

- P Measured, $\pm 5\%$ uncertainty
- D included in P
- NSR = NHF, but modified as average NHF value per mm annual streamflow; $\pm 10\%$ uncertainty
- S Measured, $\pm 5\%$ plus particulate matter losses based on average annual streamflow (increases uncertainty to 6 %)
- B Maximum value from -6.5 mol/ha-year from Bormann and Likens 1979; $\pm 100\%$ uncertainty
- G No gas flux

Sulfur

- P Measured, $\pm 5\%$ uncertainty
- D Used mean of Mitchell et al. (2011) estimate = 21 % of P; $\pm 50\%$ uncertainty based on span of estimate
- NSR Used gradually increasing linear extension of 44 mol/ha 1964–1969 through 128 mol/ha 1993–1998 from Fig. 55 to 2008–2009; $\pm 50\%$ uncertainty
- S Measured, $\pm 5\%$ uncertainty, plus particulate matter losses based on average annual streamflow (increases uncertainty to 6 %)
- B Maximum value from HBES model = -27 mol/ha ; ± 50 to 120 % error
- G No gas flux

DIN

- P Measured, $\pm 5\%$ uncertainty
- D 21 % of P; $\pm 50\%$ uncertainty based on span of estimate
- NSR No weathering; NSR might be = NEF
- S Measured, $\pm 5\%$ uncertainty plus particulate matter losses based on average annual streamflow (increases uncertainty to 7 %)
- B Maximum value based on Bormann and Likens 1979 = 145 mol/ha (9 kg N) ± 30 to 120 % uncertainty

(continued)

G NET gas flux based on N₂O release (4 to 23 mol/ha; Kulkarni et al. 2008) and fixation (0 to 32 mol/ha; Roskoski 1980); both fluxes regressed against wetness (streamwater range); mostly cancel each other; ±100 % uncertainty on Net value

Chloride

P Measured, ±5 % uncertainty

D Estimated at 20 % based on similar D for S and DIN; ±50 % uncertainty

NSR =W used average weathering inputs in a ratio with Average annual streamflow ±30 % uncertainty

S Measured, ±5 % uncertainty; no estimate for particulate matter losses available

B Estimated at 32 mol/ha-year max ±~100 % uncertainty

G No gas flux

Chapter 7

The Northern Hardwood Ecosystem in the Hubbard Brook Valley in Relation to Other Forest Ecosystems

Forests and woodlands cover some $57 \times 10^6 \text{ km}^2$, which is about 38 % of the total continental area or 11 % of the Earth's surface. Despite this relatively small area, 92 % of the Earth's plant biomass and 46 % of its annual net primary production come from forest (Table 33). The ~80 billion metric tons of dry plant matter produced (net) each year by forests exceeds the total net primary production of the oceans, even though the oceans are more than six times larger in area. The animal biomass in these forests represents some 68 % of the total found on continental land masses [Whittaker and Likens 1973; but see Cole (2013, pp. 113–114)].

The structure and well-being of forest ecosystems to a large extent reflect the chemical balance that is extant for the ecosystem. Previous editions of this book compared biogeochemical data from the HBEF with data from other studies done at various places throughout the world. In 1977 (First Edition) the Internet did not exist to host large amounts of publically available biogeochemical data. Thus, the attempt to capture data on streamwater chemistry from the literature for sites around the world was interesting and informative. Now, however, massive amounts of data from the U.S. Geological Survey (<http://www.usgs.gov> or <http://water.usgs.gov/data/>), the U.S. Environmental Protection Agency (<http://www.epa.gov>), the U.S. Forest Service Experimental Forests and Ranges, the U.S. National Science Foundation LTREB and LTER sites, state and local municipalities, and private groups in the USA are available on the Internet. Likewise, biogeochemical data are available on the Internet from similar international groups worldwide. Thus, the original table may be of some historical interest, but is neither representative nor comprehensive given the available information today. It is possible, however, that this little book, first published in 1977, did help to promote this proliferation of long-term biogeochemical data and its availability.

Data in Table 34 have been revised and focused on a few long-term temperate, forested watersheds in eastern North America for comparison with data from W6 of the HBEF. While we emphasize in this book that long-term data are critical for analyzing the biogeochemistry of complicated watershed-ecosystems, these “snapshots” focused on one or a few annual inputs, outputs, and net hydrologic fluxes for selected watersheds and solutes allow for concise, but useful, comparisons.

Table 33 Estimates of area, biomass, and productivity circa 1975 for major components of the biosphere^a

	Area, 10^6 km^2	Plant biomass, 10^9 dry tons	Net plant productivity, 10^9 dry tons/year	Animal biomass, 10^6 dry tons	Animal productivity, 10^6 dry tons/year
Forest and woodlands	57	1,700	79.9	680	442
Total continental area	149	1,837	117.5	1,015	827
Total ocean	361	4	55.0	998	3,057
Total biosphere	510	1,841	172.5	2,013	3,884

^aIt is assumed that dry matter $\times 0.45 =$ carbon. Modified from Whittaker and Likens (1973, 1975)

In general, the findings from these studies (Table 34) show many common patterns. Several conclusions emerge:

1. Chemicals in precipitation and in dry deposition are significant additions quantitatively to the budgets for most of these forest ecosystems.
2. These atmospheric additions are biogeochemically and ecologically important (see previous chapters).
3. Precipitation inputs of inorganic nitrogen exceed losses in streamwater by ~ 2 to >10 times for these forest ecosystems. The net retention of dissolved inorganic nitrogen in the Cone Pond watershed is the highest and almost complete. Phosphorus inputs in precipitation probably exceed streamwater outputs as well, but the values are small and difficult to quantify. The Taughannock Creek watershed, which includes drainage from agricultural land, shows small net losses of phosphorus. In this case, human activities or production of animal wastes probably has overwhelmed the capacity of the natural ecosystem to conserve phosphorus within this watershed (e.g., Likens 1974a, b; Likens and Bormann 1974b).
4. With the exception of potassium in Cone Pond Inlet, there are consistent net losses of calcium, magnesium, sodium, and potassium from forest ecosystems that must be made up from weathering. The small net gain of potassium in Cone Pond Inlet probably reflects reduced amounts of readily weatherable minerals and strong biotic retention in this depleted ecosystem.
5. Geologic substrates play a major role in determining the amount and composition of chemicals lost in streamwater. Watersheds on relatively soluble bedrock (Sleepers River, VT; Taughannock Creek, NY; Walker Branch, TN) lose large quantities of the major cations via streamflow.
6. Forest ecosystems in coastal locations or otherwise dominated by maritime air masses have relatively large inputs of sea salts, e.g., sodium and chloride in precipitation (e.g., Art 1976; Svensson et al. 2012), whereas interior sites are more dominated by inputs of calcium and magnesium salts.
7. With the exception of the Turkey Lakes Watershed, which is approximately balanced, all of the net hydrologic flux values for chloride in these diverse watershed-ecosystems are negative, suggesting an unmeasured input, but more likely an internal source of chloride.

Table 34 Nutrient budgets for various temperate zone terrestrial ecosystems in Eastern North America (kg/hay/year)

Location ^a	Atmospheric deposition	Streamwater output	Net gain or loss	Annual precipitation (cm)	Dominant vegetation ^b	Geology ^c
<i>Calcium</i>						
Coweta, NC (1)	4.4	5.3	-0.9	215	Q, C, Ac	Mg, Msh
HBEF, NH (2)	1.0 ^d	6.6	-5.6	165	Ac, F, B, Pic, Ab, Ts	Ig, Msh
Cone Pond Inlet, NH (3)	1.2 ^d	2.5	-1.3	145	Ts, Pic, Ab	Ig
Long Island, NY (3)	3.3	9.6 ^e	-6.3	124	Q, Pin	Ss
E. Bear Brook, ME (4)	0.4 ^f	10.1	-9.7	159	F, Ac, B, Pic, Ab, Ts	Ig, Msh
S.E. U.S. (5)	6	19	-13	127	Q, Pin	Ss, Ssh, Mg, Msh
Fernow, WV (6)	2.2 ^d	8.6	-6.4	125	Q, L, Ac, B, F	Ss, Ssh, Ms, Msh
Taughannock Creek, NY (7)	11.2 ^d (0.8 ^g)	182	-171	96 (111 ^g)	Ac, Ti, Ts	Ssh, Sc
Sleepers River, VT (8)	1.3 ^d	226	-225	149	Ac, B, Fr, F	Mc
Walker Branch, TN (9)	1.3 ^f	147	-146	118	Q, C	Sc
Biscuit Brook, NY (10)	1.2 ^h	16.5	-15.3	165 ⁱ	Ab, Ac, B, F, Pic, Ts	Ss
Turkey Lakes Watershed, ON (Canada) (11)	2.7 ^h	20.8	-18.1	107	Ac, B, Pic, Ts	Ig
<i>Magnesium</i>						
Coweta, NC	1.0	3.1	-2.1	215	Q, C, Ac	Mg, Msh
HBEF, NH	0.3 ^d	2.2	-1.9	165	Ac, F, B, Pic, Ab, Ts	Ig, Msh
Cone Pond Inlet, NH	0.3 ^d	0.8	-0.5	145	Ts, Pic, Ab	Ig
Long Island, NY	2.1	7.3 ^e	-5.2	124	Q, Pin	Ss
E. Bear Brook, ME	0.4 ^f	2.5	-2.1	159	F, Ac, B, Pic, Ab, Ts	Ig, Msh
S.E. U.S.	2	6	-4	127	Q, Pin	Ss, Ssh, Mg, Msh
Fernow, WV	0.3 ^d	3.3	-3.0	125	Q, L, Ac, B, F	Ss, Ssh, Ms, Msh
Taughannock Creek, NY	1.6 ^d (0.1 ^g)	34.8	-33.2	96 (111 ^g)	Ac, Ti, Ts	Ssh, Sc
Sleepers River, VT	0.2 ^d	9.5	-9.3	149	Ac, B, Fr, F	Mc
Walker Branch, TN	0.2 ^f	77	-77	118	Q, C	Sc

(continued)

Table 34 (continued)

Location ^a	Atmospheric deposition	Streamwater output	Net gain or loss	Annual precipitation (cm)	Dominant vegetation ^b	Geology ^c
Biscuit Brook, NY	0.3 ^h	3.5	-3.2	165 ⁱ	Ab, Ac, B, F, Pic, Ts	S _s
Turkey Lakes Watershed, ON (Canada)	0.5 ^h	1.5	-1.0	107	Ac, B, Pic, Ts	I _g
<i>Sodium</i>						
Coweeta, NC	3.6	8.2	-4.6	215	Q, C, Ac	Mg, M _{sh}
HBEF, NH	1.1 ^d	7.2	-6.0	165	Ac, F, B, Pic, Ab, Ts	I _g , M _{sh}
Cone Pond Inlet, NH	1.0 ^d	4.6	-3.6	145	Ts, Pic, Ab	I _g
Long Island, NY	17	23 ^e	-6	124	Q, Pin	S _s
E. Bear Brook, ME	5.2 ^f	15.6	-10.4	159	F, Ac, B, Pic, Ab, Ts	I _g , M _{sh}
S.E. U.S.	5	26	-21	127	Q, Pin	S _s , S _{sh} , Mg, M _{sh}
Taughannock Creek, NY	1.4 ^d (0.3 ^g)	18.9	-17.5	96 (111 ^g)	Ac, Ti, Ts	S _{sh} , Sc
Sleepers River, VT	0.8 ^d	6.5	-5.7	149	Ac, B, Fr, F	Mc
Walker Branch, TN	1.0 ^f	2.7	-1.7	118	Q, C	Sc
Biscuit Brook, NY	1.2	2.2	-1.0	165 ⁱ	Ab, Ac, B, F, Pic, Ts	S _s
Turkey Lakes Watershed, ON (Canada)	0.7 ^h	2.1	-1.4	107	Ac, B, Pic, Ts	I _g
<i>Potassium</i>						
Coweeta, NC	4.1	5.0	-0.9	215	Q, C, Ac	Mg, M _{sh}
HBEF, NH	0.6 ^d	1.4	-0.8	165	Ac, F, B, Pic, Ab, Ts	I _g , M _{sh}
Cone Pond Inlet, NH	0.4	0.3	+0.1	145	Ts, Pic, Ab	I _g
Long Island, NY	2.4	3.9 ^e	-1.5	124	Q, Pin	S _s
E. Bear Brook, ME	0.5 ^f	1.8	-1.3	159	F, Ac, B, Pic, Ab, Ts	I _g , M _{sh}
S.E. U.S.	1	6	-5	127	Q, Pin	S _s , S _{sh} , Mg, M _{sh}
Fernow, WV	1.1 ^d	3.6	-2.5	125	Q, L, Ac, B, F	S _s , S _{sh} , Ms, M _{sh}
Taughannock Creek, NY	1.1 ^d (0.2 ^g)	5.6	-4.5	96 (111 ^g)	Ac, Ti, Ts	S _{sh} , Sc

Sleepers River, VT	0.7 ^d	11.2	-10.5	149	Ac, B, Fr, F
Biscuit Brook, NY	0.2 ^b	2.7	-2.5	165 ⁱ	Ab, Ac, B, F, Pic, Ts
Turkey Lakes Watershed, ON (Canada)	0.3 ^b	0.6	-0.3	107	Ac, B, Pic, Ts
<i>Dissolved inorganic nitrogen (NH₄-N + NO₃-N)</i>					
Coweeta, NC	6.2	0.66	+5.5	215	Q, C, Ac
HBEF, NH	5.3 ^j	0.23	+5.1	165	Ac, F, B, Pic, Ab, Ts
Cone Pond Inlet, NH	3.5 ^{i,k}	<0.1	+3.5	145	Ts, Pic, Ab
E. Bear Brook, ME	1.7 ^f	0.3	+1.4	159	F, Ac, B, Pic, Ab, Ts
S.E. U.S.	2 ^k	1 ^k	+1 ^k	127	Q, Pin
Fernow, WV	7.4 ^b	4.4	+3.0	125	Q, L, Ac, B, F
Taughannock Creek, NY	10.3 ^j (5.4 ^g)	5.6	+4.7	96 (111 ^g)	Ac, Ti, Ts
Sleepers River, VT	4.7 ^d	1.9	+2.8	149	Ac, B, Fr, F
Walker Branch, TN	1.7 ^f	0.03	+1.7	118	Q, C
Biscuit Brook, NY	8.2 ^b	3.3	+4.9	165 ⁱ	Ab, Ac, B, F, Pic, Ts
Turkey Lakes Watershed, ON (Canada)	25.6 ^b	2.1	+23.5	107	Ac, B, Pic, Ts
<i>Phosphorus</i>					
Coweeta, NC	0.04	<0.01	+0.04	215	Q, C, Ac
HBEF, NH	0.02 ^d	0.01	+0.01	165	Ac, F, B, Pic, Ab, Ts
Taughannock Creek, NY (0.03 ^g)	0.186 ^d (0.03 ^g)	0.197	-0.011	96 (111 ^g)	Ac, Ti, Ts
Sleepers River, VT	0.15 ^d	0.13	+0.02	149	Ac, B, Fr, F
Walker Branch, TN	—	0.03	—	118	Q, C
Biscuit Brook, NY	—	<0.001	—	165 ⁱ	Ab, Ac, B, F, Pic, Ts
Turkey Lakes Watershed, ON (Canada)	—	0.01	—	107	Ac, B, Pic, Ts

(continued)

Table 34 (continued)

Location ^a	Aerospheric deposition	Streamwater output	Net gain or loss	Annual precipitation (cm)	Dominant vegetation ^b	Geology ^c
<i>Sulfate-Sulfur</i>						
Coweta, NC	7.5	6.4	+1.1	215	Q, C, Ac	Mg, M _{sh}
HBEEF, NH	6.7 ^j	12.6	-5.9	165	Ac, F, B, Pic, Ab, Ts	Ig, M _{sh}
Cone Pond Inlet, NH	6.7 ^d	9.7	-3.0	145	Ts, Pic, Ab	Ig
E. Bear Brook, ME	3.7 ^f	13.2	-9.5	159	F, Ac, B, Pic, Ab, Ts	Ig, M _{sh}
S.E. U.S.	8	7	+1	127	Q, Pin	S _s , S _{sh} , Mg, M _{sh}
Fernow, WV	11.6 ^b	8.1	+3.5	125	Q, L, Ac, B, F	S _s , S _{sh} , Ms, M _{sh}
Taughannock Creek, NY	18.1 ^d (4.4 ^g)	38	-19.9	96 (111 ^g)	Ac, Ti, Ts	S _{sh} , Sc
Sleepers River, VT	3.8 ^d	17.6	+	149	Ac, B, Fr, F	Mc
Walker Branch, TN	5.5 ^f	5.4	+0.1	118	Q, C	Sc
Biscuit Brook, NY	8.2 ^b	9.9	-1.7	165 ⁱ	Ab, Ac, B, F, Pic, Ts	S _s
Turkey Lakes Watershed, ON (Canada)	6.1 ^h	5.5	+0.6	107	Ac, B, Pic, Ts	Ig
<i>Chloride</i>						
Coweta, NC	6.2	9.1	-2.9	215	Q, C, Ac	Mg, M _{sh}
HBEEF, NH	2.6 ^j	3.3	-0.7	165	Ac, F, B, Pic, Ab, Ts	Ig, M _{sh}
Cone Pond Inlet, NH	1.9 ^d	3.4	-1.5	145	Ts, Pic, Ab	Ig
E. Bear Brook, ME	8.3 ^f	18.0	-9.7	159	F, Ac, B, Pic, Ab, Ts	Ig, M _{sh}
Taughannock Creek, NY	11.5 ^d (0.7 ^e)	41.7	-30.2	96 (111 ^g)	Ac, Ti, Ts	S _{sh} , Sc
Sleepers River, VT	1.7 ^d	2.4	-0.7	149	Ac, B, Fr, F	Mc
Walker Branch, TN	2.2 ^f	6.5	-4.3	118	Q, C	Sc
Biscuit Brook, NY	2.5 ^b	3.7	-1.2	165 ⁱ	Ab, Ac, B, F, Pic, Ts	S _s
Turkey Lakes Watershed, ON (Canada)	0.9 ^h	0.6	+0.3	107	Ac, B, Pic, Ts	Ig

^a(1) S. Laester, personal communication for precipitation and streamwater chemistry in Watershed 27 (2008). (2) Present study; average for 2008 water-year. (3) S. Bailey, unpublished averages for water-year 2007–2008 (4) Woodwell and Whittaker (1967). (5) L. Rustad, I. Fernandez for 2008 water-year. (6) Gambell and Fisher (1966). (7) M.B. Adams for 2005 calendar year for Watershed 4 (Adams et al. 2006). (8) Likens (1974a, b) for 1970–1971. (9) S. Bailey and J. Shanley, unpublished averages for water-year 2008 and 2009, Watershed 9, personal communication. (10) Lutz et al. (2012); 2008 water-year. (11) D. Burns, personal communication, calendar-year, volume-weighted average for 2008. (12) I. Creed, personal communication, average for 2006 water-year catchment #32

^bVegetation footnotes: Ab, Abies; Ac, Acer; B, Betula; C, Cary; F, Fagus; Fr, Fraxinus; L, Liriodendron; Pin, Pinus; Ps, Pseudotsuga; Q, Quercus; Ti, Tilia; Ts, Tsuga

^cGeology footnotes: Ig, igneous; granitic; Sc, sedimentary, carbonate; Ssh, sedimentary, shale; Ss, sedimentary, sandstone; Ma, Metamorphic (x refers to subscripts used above)

^dBulk precipitation

^eTo water table

^fWet only

^gWet plus dry data for 2010 from nearby Connecticut Hill CASTNET site (T.J. Butler)

^hWet plus dry deposition

ⁱMean 2007–2009

^jBulk precipitation plus dry deposition (see Table 17 for bulk precipitation)

^kNO₃-N only

8. A close correlation between the amount of precipitation and the loss of nutrients may apply to individual watersheds, such as the HBEF, but as a general principle, there is no close correlation between the amount of precipitation and loss of nutrients in forest ecosystems with different climates.
9. Net loss or gain values for sulfur budgets are significantly affected by anthropogenic contributions to wet and dry deposition. Contaminated air masses over all of these sites in eastern North America produce relatively high levels of sulfur and nitrogen in local precipitation, but these concentrations are declining in recent decades because of reductions in emissions. Interestingly and importantly, the biogeochemical control over sulfate export in stream water in forested watershed-ecosystems in eastern North America appears to be shifting from atmospheric S deposition to climate factors through effects on soil moisture as SO₂ emissions are declining and soils are becoming wetter due to climate change (Mitchell and Likens 2011; Kerr et al. 2012).
10. These forest ecosystems have conservative losses of major nutrients, such as nitrogen and phosphorus, relative to inputs or amounts cycled internally.
11. Streamwater losses may be very significantly changed by disturbance of the ecosystem, such as forest cutting, ice storms, agricultural activity, or various other land management practices, e.g., Taughannock Creek watershed. The array of biogeochemical responses to clear-cutting and recovery of the northern hardwood ecosystem at HBEF is discussed in Likens et al. (1970); Bormann and Likens (1979); Likens and Bormann (1974b); Hornbeck et al. (1986, 1987, 1990); Martin et al. (1986); Likens (2004).

Adjustments for net gaseous input and dry deposition of aerosols were not incorporated systematically in Table 34, but much more information is available than 35 years ago. Nevertheless, considerable effort should be devoted to the problem of measuring dry deposition and gaseous exchange in forested ecosystems in the future in order to reflect quantitatively these important fluxes in biogeochemical cycling and fluxes. Recently, Mitchell and colleagues (2011) used a new approach to predict SO₂ concentrations as a function of SO₂ emissions, latitude and longitude, and then estimated dry deposition from relations between concentrations and deposition flux from the U.S. CASTNET and Canadian CAPMoN networks at 15 sites in northeastern USA and southeastern Canada. Although dry deposition estimates are still relatively uncertain within the mass balance for these systems, this approach seems promising and allowed the prediction of dry deposition values for the HBEF of 0.5 to 2.5 kg S/ha-year.

Chapter 8

Summary Discussion and Conclusions

This book summarizes current understanding of the biogeochemistry of a northern hardwood forest ecosystem at the HBEF in the White Mountains of New Hampshire. It emphasizes the usefulness of the small watershed technique for biogeochemical measurement in shedding light on ecosystem function and change. The characteristics of the HBEF watersheds revolve around the forest that covers these hillslopes and the water that passes through this thin veneer of biological organisms.

Trees are long-lived and over time accumulate large amounts of biomass as wood and nutrients in that wood; it is therefore not surprising that trees dominate the forest landscape and are used to name the ecosystem types (plant associations or biomes). Humans have long looked to forest ecosystems for firewood and timber, as well as for clean water, wildlife, and recreation, but their demands often have been at variance with the structure of the forest ecosystem, and large areas have been (and are being) cleared of forest vegetation. This clearing is currently proceeding at an unprecedented rate in many forest ecosystems worldwide for human purposes, such as agriculture, housing, and reservoirs above dams (e.g., Croat 1972; Gómez-Pompa et al. 1972; Ågren and Andersson 2012, p. 280; Lindenmayer et al. 2013).

Water in some form is also a conspicuous feature of the humid forested landscape. Rain and snow not only supply the water that replenishes groundwater reserves and fills stream and river channels, ponds, lakes, and wetlands but also provide the water to facilitate weathering and the moisture and many of the nutrients for forest growth. Chemicals, particularly those without a prominent gaseous phase, such as calcium, magnesium, or potassium, are transported largely into and out of ecosystems by moving water.

In forested landscapes much of the water that falls to the land's surface as precipitation is first intercepted by the leaves and branches of the trees and herbaceous layer and then by litter on the ground. Therefore, the kinetic energy and chemical composition of the water may be appreciably altered before the water comes into contact with the mineral soil. The diminishment of kinetic energy both minimizes erosion and regulates nutrient flow. This ostensibly simple and obvious interaction between falling precipitation and vegetation structure emphasizes that the

regulation of ecosystem processes, such as biogeochemical flux, depends upon the structural and functional integrity of the whole ecosystem.

Water that has fallen to the surface may run off overland (minimal in most forests except during extreme events), infiltrate into the soil, or evaporate. Again, the biotic portion of the forest ecosystem may alter both the distribution of potential and kinetic energy and the chemistry of water circulating within, as well as moving through, an ecosystem.

There are several ways, then, in which water may affect the biogeochemistry of a forest ecosystem. It is helpful for quantitative studies to select ecosystems that (1) are watersheds, (2) have a relatively watertight bedrock or other substrate, and (3) have a relative uniform biogeochemical environment (Bormann and Likens 1967; Likens and Bormann 1972).

The flux of water and nutrients across an ecosystem's boundaries, as well as internal cycling, are vital for the maintenance of a natural ecosystem. Environmental stress, such as pollution, deforestation, or road building, will alter these conditions of nutrient flux and cycling and thereby disrupt the function of the ecosystem. Too little is known about the long-term legacy effects of such alterations or about the ability of an ecosystem to respond, recover, or improvise following disturbance (Franklin et al. 2000; Likens and Franklin 2009; Likens and Buso 2012).

The yield of liquid water in streamflow is an important consideration to watershed managers. For example, Douglass and Swank (1972) state that "Because the difference between precipitation input and vapor loss represents the quantity of water available for man's use, the watershed manager seeks to reduce the total vapor loss from the forest vegetation in order to increase the flow of streams" (p. 1). However, because liquid water that flows out of an ecosystem contains nutrients (whether at a constant concentration or not), it may be argued that transpiration is a nutrient conservation mechanism for the ecosystem. Moreover, as precipitation comes in contact with the vegetation, its chemistry is altered significantly. The kinetic energy of the falling raindrop is largely absorbed by the vegetation canopy, and the potential for erosion is reduced. Litter and roots in the forest soil also reduce erosion. The change of liquid water to vapor by the ecosystem also may have great impact in reducing the potential for erosion from liquid water. Therefore, the biotic structure of these forest ecosystems may alter both the potential energy and the chemistry of water as it passes through the ecosystem. Inadequate consideration has been given to the interplay of such changes in the hydrologic cycle on nutrient flux for forest ecosystems. This interplay is of particular concern when the basic structure of the forest ecosystem is altered by vegetation disturbance or removal or by climate change (e.g., Likens et al. 1970; Houlton et al. 2003; Groffman et al. 2012).

There is currently considerable effort being made to quantify biogeochemical relationships for various kinds of terrestrial ecosystems. Based on long-term studies in the HBEF, it can be emphasized that:

1. Considerable thought be given (a) to selection of the ecosystem, including boundaries, for study—millions of dollars and thousands of hours of time may be wasted by a poor initial choice; (b) to methodology, such as frequency and

- location of sampling, criteria for acceptance or rejection of particular samples, and types and reliability of chemical analyses; (c) to measures of uncertainty; and (d) to the development of a conceptual framework or model for the ecosystem. This methodology is important because small analytical mistakes can easily be blown out of proportion in the multiplication procedures that are inevitable in the construction of ecosystem budgets.
2. Ecosystems are open. Water and nutrients continually flux across the boundaries and cycle internally between the various components of the ecosystem. Studies at HBEF have demonstrated the importance of the abiotic factors and quantitative mass-balance studies for understanding the structure, function, and temporal change of forest ecosystems.
 3. Long-term records are important in identifying patterns of nutrient flux through ecosystems. Flux is greatly influenced by hydrology and, during 49-year precipitation, has ranged from 95 to 186 cm/year in W6 at the HBEF. Measurements only in these extreme years would have given poor estimates of average conditions. Over the initial 10-year period of the HBES, moreover, annual nitrate and hydrogen ion inputs in precipitation increased 2.3 and 1.4 times, respectively. The output of NO_3 in streamwater also increased during this period and seemed to be strongly influenced by soil freezing during two of the 11 winters. Subsequently, however, the pattern changed dramatically. Since 1980, average annual bulk precipitation concentrations of hydrogen ion, sulfate, and nitrate have decreased by ~60, ~40, and ~65 %, respectively. Streamwater concentrations and output of nitrate since ~1990 are consistently the lowest on record; higher values occur only following major disturbances.
 4. Although the chemistry of bulk precipitation is highly variable and dependent on complex emission patterns and meteorologic conditions, meteorologic input is an important source of chemicals for the ecosystem. For sulfur, calcium, and potassium, meteorologic input supplies about 104 times (during 1993–1998), 54 % (during 1987–1992), and 55 % (during 1987–1992), respectively, of the annual net uptake of these nutrients by green plant biomass.
 5. Meteorologic input may be strongly influenced by advertent and inadvertent manipulation by humans. Acid precipitation is a good example: most acidity in the rain and snow at HBEF is traceable to sulfur pollution emanating primarily from fossil fuel burning by electrical utilities in the midwestern USA (Likens et al. 1972; Likens and Bormann 1974a; Likens 2010), but increasingly with time and because of federal regulation of SO_2 emissions, the input of acid precipitation became increasingly related to NO_x emissions resulting from internal combustion engines.
 6. Acid rain was discovered in North America from samples of rain first collected at the HBEF in 1963 (Likens et al. 1972; Likens 2010). Long-term research and monitoring at the HBEF and elsewhere built an evidence-based framework needed for developing policy and federal and state regulation required to reduce this form of air pollution and mitigate environmental impacts (e.g., Likens et al. 1996, 1998, 2001, 2002a, 2005; Likens and Lambert 1998; Butler et al. 2001; Driscoll et al. 2001; Likens 2004; Siccamo et al. 2007; Likens and Franklin

2009; Likens and Buso 2010a). Several findings from the long-term HBES were important to the understanding, policy development, and management of this major environmental problem, including:

- Changes in emissions of sulfur and nitrogen dioxides, SO_2 and NO_x (major precursors to acid rain), as a result of federal legislation, are strongly correlated with changes in sulfate and nitrate concentrations in precipitation and stream and lake water at HBEF (Likens et al. 2001, 2002a, 2005; Butler et al. 2001; Likens and Buso 2010a).
 - Nitric acid is increasing in importance in precipitation at HBEF and is predicted to be the dominant acid in precipitation in the future without further controls on emissions of SO_2 and NO_x (Likens and Lambert 1998; Likens and Buso 2010a).
 - Calcium and other base cations have been markedly depleted in the soils of the HBEF as a result of acid rain inputs (Likens et al. 1996, 1998).
 - As much as one-half of the pool of exchangeable calcium in the soil has been depleted during the past 50 years by acid rain (Likens et al. 1998).
 - As a result of losses in soil buffering, the forest ecosystem is currently more sensitive to acid rain impacts than previously thought (Likens et al. 1996, 1998; Likens 2010).
 - Enigmatically, rapid forest biomass accumulation has ceased since ~1982 at HBEF due to increased tree mortality, related in part to the effects of acid rain (Likens et al. 1998, 2002a; Siccamo et al. 2007). This important finding is the subject of intense, ongoing investigation (Likens and Franklin 2009; Likens 2010).
7. The ecosystem acts as a “filter” for atmospheric contaminants, such as hydrogen ion, nitrogen, sulfur, phosphorus, and certain heavy metals, such as lead, which accumulate within the ecosystem. The forest ecosystem, therefore, has been acting as a pollution buffer for society; the ultimate cost of this activity is unknown, but if continued has the obvious potential for long-term ecosystem degradation.
8. As a general rule, annual evapotranspiration (mostly transpiration from vegetation) at HBEF is essentially constant over a wide range of precipitation and environmental conditions. Water converted to vapor by evapotranspiration cannot erode the system or transport dissolved substances out of the ecosystem. Thus, evapotranspiration not only serves as a regulator for the hydrologic cycle, but also affects nutrient flux as well. Moreover, the forest ecosystem exercises a strong regulatory function over the chemistry of liquid water passing through it. This regulation is achieved because the structure of the ecosystem causes all precipitation to come into intimate contact with, first, the mantle of living and dead biomass of the ecosystem and then the organic matter and minerals in the soil profile. Rapid exchange reactions in each of these compartments govern the chemical composition of liquid water leaving the ecosystem.

9. Evapotranspiration reduces the volume of liquid water in the ecosystem. Streamwater concentrations in W6 at the HBEF could be increased by 1.5 times in this way. If evapotranspiration were the only operational factor, the average streamwater output (average concentration \times amount of water) would equal the average input. Instead, the ecosystem is much more complex. Nutrients are released internally by weathering and net soil release, accumulated and stored by vegetation, and returned to the soil in throughfall, stemflow, root exudates, and litter. The result at HBEF is that on average (1963–2009) the ionic strength of streamwater (147 $\mu\text{Eq/L}$) is twice that of bulk precipitation (73.5 $\mu\text{Eq/L}$) and the average streamwater output is $2.6 \times 10^3 \text{ Eq/ha-year}$, whereas the average bulk precipitation input is $2.1 \times 10^3 \text{ Eq/ha-year}$. In addition, the proportions of dissolved species change from precipitation to streamflow, further illustrating the importance of biologic and chemical reactions occurring within the ecosystem. Nitrate input in bulk precipitation is about 2:1 on an equivalent basis with ammonium, but in streamwater output, the proportion increases to 15:1. For most of the five decades of study, hydrogen ion and sulfate have dominated precipitation ($\text{pH } \sim 4$ to 4.5), whereas calcium and sulfate dominated streamwater ($\text{pH } \sim 5$ to 5.5) chemistry.
10. Streamwater chemistry of the forest ecosystem is highly predictable. Concentrations of sodium and dissolved silica are predictably diluted as streamflow rates increase, whereas aluminum, nitrate, hydrogen ion, and dissolved organic carbon increase as streamflow increases (Johnson et al. 1969). However, changes in concentrations are relatively small (two to fourfold) in relation to the great range in flow rates (up to five orders of magnitude, annually). It is well known that some fixed time series for sampling may seriously underestimate or overestimate a highly variable parameter (e.g., Claridge 1970); however, most of the dissolved chemicals in stream water at the HBEF have such constant concentrations that serious errors are not produced by weekly sampling in most cases (Johnson et al. 1969; Likens et al. 1967). Concentrations of both nitrate and potassium in streamwater are highly dependent on seasonal biologic activity within the ecosystem. The biogeochemical reaction rates within these ecosystems are rapid; therefore, streamwater chemistry quickly and clearly reflects environmental conditions within the forest ecosystem.
11. As a consequence of generally weak solute, concentration–flow rate relations in streams in the HBEF, the output of most individual nutrients, and the total export of dissolved substances can be closely predicted from the annual output of streamwater alone.
12. The aggrading northern hardwood forest ecosystem is very resistant to particulate matter erosion. This resistance occurs because of its geology (stony till), high infiltration capacity, and highly efficient mechanisms of controlling water flow associated with living and dead biomass. In contrast to dissolved substance removal, which is essentially independent of flow rate, particulate matter erosion and export are highly dependent on flow rate. Occasional, individual storms with high discharges do most of the erosion and transport of particulate

- matter. In contrast to all of the other nutrients, the bulk of iron and phosphorus is lost from watershed-ecosystems at HBEF in the particulate form. The stream-water output for these two elements therefore may reflect more closely the rate of stream discharge than the amount of annual streamflow. Samples of stream-water obtained according to a standard time series therefore may be less accurate in estimating streamwater concentrations of iron and phosphorus than for substances occurring primarily in the dissolved form. Because discharge affects the concentration of dissolved substances and particulate matter differently, any management of water quality or total export of these materials requires different approaches at different levels of discharge.
- 13. In particulate matter removal, bed load accounts for slightly more than 50 % of the material removed. Many studies can only measure suspended matter and hence tend to underestimate the total output of particulate matter from an ecosystem.
 - 14. Long-term dissolved substance losses (1963–2009) from the ecosystem (80 kg of ionic substances, 17 kg of dissolved silica, and 23 kg of dissolved organic matter per hectare-year) are about four times greater than particulate matter losses (11 kg of organic matter plus 22 kg of inorganic particles). Total losses of dissolved substances and particulate matter (198 kg/ha-year) in stream water, circa 1970, are about 1.5 times greater than total inputs in bulk precipitation (134 kg/ha-year) in that same period.
 - 15. The long-term lowering of the landscape in the HBEF, which is dominated by forests, is primarily caused by solution losses and, to a lesser extent, by particulate matter losses. Slow mass movements, such as soil creep, may deliver materials to stream beds, where they are removed. At higher elevations and with steeper slopes, debris avalanches also may play a major role in lowering the landscape. Another factor that may be of considerable importance is disturbances that temporarily destroy the forest canopy and make the ecosystem more vulnerable to both solution and particulate matter losses (e.g., Likens et al. 1970; Bormann and Likens 1979; Houlton et al. 2003).
 - 16. In establishing input–output budgets for individual nutrients, both direction of change, i.e., whether there is a net loss or gain, and magnitude of change are important. Budgets have been done in two ways in our studies, by NHF (stream-water output minus bulk precipitation input) and by NEF where all of the major ecosystem components are measured or estimated. For some ions, the NHF budget parameters may be established with one or a few years of data, for example, direction: Ca^{2+} (−), Mg^{2+} (−), Na^+ (−), Al^{3+} (−), NH_4^+ (+), H^+ (+), SO_4^{2-} (−), PO_4^{3-} (+), dissolved silica(−), HCO_3^- (−). For other ions, K^+ , NO_3^- , and Cl^- , one or a few years gave unreliable results for direction and magnitude. For some budgets, therefore, longer term studies are necessary to obtain valid budgetary data.
 - 17. Not only must net losses of ions from the ecosystem be included in an estimate of weathering flux, but those elements built into any net accumulation of biomass must also be included. At HBEF failure to include annual biomass accretion of nutrients results in an ecosystem weathering estimate that is 50 % too low.

18. Three input–output patterns emerge when small watershed data are examined on a monthly basis: output exceeds input in every month for magnesium, calcium, sodium, aluminum, and dissolved silica; output is less than input for ammonium, hydrogen ion, and phosphate; and crossover patterns, where for a time output exceeds input and then output is less than input, occur for potassium, sulfate, chloride, dissolved organic carbon, and nitrate. These patterns are distributed among elements with both sedimentary and atmospheric cycles and reflect a complex interaction involving such factors as bulk precipitation input, biologic activity, and climatic variations.
19. Chemical weathering of minerals within the ecosystem is driven by water and by protons derived from hydrogen ions in precipitation and those generated internally within the system by biogeochemical reactions involving carbon, nitrogen, and sulfur. About 50 % of the hydrogen ions generated during the weathering reaction is derived from external sources, i.e., acid precipitation, and 50 % is from internal biogeochemical sources. However, this estimate is based on the assumption that all hydrogen ions, external plus internal, are consumed in exchange reactions.
20. Complete mass balances (NEF) for the ecosystems at HBEF reveal certain fundamental features of nutrient flux and cycling not otherwise apparent. These are the following: (a) wet and dry deposition are major ecosystem sources of nutrients, particularly for sulfur, nitrogen, chloride, and phosphorus; (b) weathering/net soil release is a major source for calcium, magnesium, potassium, and sodium; (c) biologic activity and photosynthesis play significant roles in the input and storage of carbon and nitrogen and are important (impaction surfaces plus gaseous uptake) for sulfur; (d) the northern hardwood forest shows absolute gains for hydrogen ion, dissolved inorganic nitrogen, potassium, and phosphorus and losses for dissolved silica, calcium, sodium, sulfur, aluminum, magnesium, chlorine, and iron. The losses of dissolved silica, calcium, sodium, magnesium, potassium, and iron are made up by weathering of primary minerals within the ecosystem. Available weathering substrate may be decreasing with time, particularly for elements like calcium.
21. Calcium, an example of a sedimentary cycle, tends to be held within the system, with net losses in 1987–1992 being but a small proportion (2.7 %) of the calcium in the available pool (Fig. 53; Likens et al. 1998). However, net losses are 3.4 larger than annual net uptake by green plants. Although sulfur has a gaseous cycle, some 95 % of the sulfur in the ecosystem is found in the soil (Fig. 55; Likens et al. 2002a). Net gaseous uptake and aerosol deposition of sulfur accounted for about 18 % of the total meteorologic input for the system during 1993–1998. Meteorologic inputs dominate, in general, and release by weathering is small, but increasing in relative importance as meteorologic inputs decrease (Likens et al. 2002a).
22. Because the HBEF has negligible amounts of nitrogen-bearing rocks, aggrading forest ecosystems have accumulated significant amounts of nitrogen from atmospheric inputs during the past 14,000 years since glacial retreat.

23. Many of the important biogeochemical relationships and transformations within the forest ecosystem are regulated by microorganisms, such as nitrogen fixation, nitrification, and denitrification or sulfur oxidation and reduction, at HBEF (e.g., Zhang et al. 1999; Findlay 2013; Groffman and Rosi-Marshall 2013).
24. Streamwater chemistry collected and measured at high density in all tributaries throughout the Hubbard Brook Valley during spring (May–July) and fall (October–December) of 2001 gave a remarkable new landscape view of streamwater chemistry in the valley (Likens and Buso 2006). Stream water chemistry varied throughout the valley in relation to changes in elevation, distance from origin of streamflow, drainage area, and type of drainage. Concentrations of hydrogen ion, aluminum, and dissolved organic carbon varied by two to tenfold in relation to these factors, but other elements, e.g., chloride and dissolved silica, changed relatively little throughout the valley. The main Hubbard Brook, a fifth-order river, changed concentration very little throughout its 13-km length despite inputs from some 20 major tributaries.
25. Based on pH as a critical diagnostic variable in the Hubbard Brook Valley, the gauging stations in the experimental watersheds were sited near the pH inflection points of the longitudinal distance of these headwater streams. Thus, these locations are nearly optimal for measuring change in acid–base chemistry of stream water.
26. Stream water was acidified from atmospheric inputs of H_2SO_4 and HNO_3 during 1963 to 1969 and then is recovering from this acidification ($r^2=0.96$) from 1970 to the present (Likens et al. 1996; Likens and Buso 2012). The projected preindustrial revolution/post-acidic deposition value is 39 $\mu\text{eq/L}$ for the sum of base cations and 11 $\mu\text{eq/L}$ for the sum of acid anions (sulfate plus nitrate) (Likens and Buso 2012).
27. Long-term data show a dramatic and relentless dilution of both precipitation and streamwater concentrations at various watershed scales of the HBEF (Likens and Buso 2012). Concentrations project to approximately demineralized water in the near future. Since demineralized water would be unrealistic for surface waters, theoretical baselines of 3 and 5 $\mu\text{S/cm}$ (electrical conductivity), 7 and 39 $\mu\text{eq/L}$ (sum of base cations), <1 and 14 $\mu\text{eq/L}$ (acid-neutralizing capacity), and 5.5 (pH) are estimated for precipitation and stream water, respectively (Likens and Buso 2012).
28. Input–output budgets for a diverse series of relatively undisturbed vegetated watersheds throughout eastern North America have many patterns in common with HBEF. Although the magnitude of precipitation, geologic substrate, vegetation type, and proximity to marine or anthropogenic emissions varies for these diverse watersheds, the constant pattern that emerges from these data is remarkable. Inputs of phosphorus and nitrogen in bulk precipitation are generally greater than losses in drainage waters on an annual basis. Conversely, outputs of calcium, magnesium, sodium, and potassium are generally greater than precipitation inputs. Net losses of potassium are small compared to inputs. The magnitude and direction for sulfate budgets are variable and depend largely on geologic substrate and intensity of air pollution.

29. Ecosystem studies are now at the stage to provide quantitative answers for important ecological questions and management interventions. The small watershed technique is powerful in providing an experimental framework for these studies, which must consider geologic and meteorologic aspects as well as biologic features. Such questions include: (a) How do ecosystems change with time? Do they become more or less efficient in cycling and storing nutrients? (b) What are the long-term effects of disturbance on the biogeochemical flux for ecosystems (see, e.g., Bernal et al. 2012)? (c) How do the biogeochemical dynamics of individual elements interact (e.g., Likens 1981; Schlesinger et al. 2011; Schlesinger and Bernhardt 2013)? (d) How would weathering rates change in relation to changes in rates of biologic activity and/or meteorologic input? Are there conditions under which weathering does not occur? (e) Of critical importance is the finding that some of the ions produced by weathering do not move downhill (*sensu* Aldo Leopold), but are instead accumulated in the growing vegetation. If the forest were to reach some kind of steady state or rapid decline of growth, what would happen to the biogeochemistry of a complex ecosystem? This latter question is of utmost importance and urgency at the HBEF (e.g., Likens and Franklin 2009; Lindenmayer and Likens 2010, p. 123).
30. There are many major unanswered questions emanating from the long-term research of the HBES:
- how can biogeochemical results from small plot scales be extrapolated quantitatively to the watershed scale (e.g., denitrification, soil acidity, primary and secondary weathering, soil frost, hydro-pedology) when the watershed-ecosystem approach is not applicable or difficult?
 - is biological control becoming more important in the biogeochemistry of the Hubbard Brook Valley as the input of acid rain decreases? Will organic acids play an increasing role in chemical reactions in the future?
 - how, or at what rate, are soils recovering from the impact of decades of acid rain? How will base cations be replenished in the rooting zone? How long will it take to deplete stored sulfur? Will nitrogen ‘saturation’ occur before recovery is complete?
 - what will be the ecological and biogeochemical effects of relentless dilution of precipitation and stream water in the Hubbard Brook Valley?
 - how can important ecosystem relationships be predicted with reliability in a changing future, based on past relationships under very different conditions?
 - how can the small watershed approach be applied productively in attempts to integrate even more diverse and more complicated information generated in the future?
31. Because so much has changed biogeochemically at the HBEF during the past 50 years, several of the fundamental analyses and syntheses need to be extended, redone, or revised, e.g., long-term hydrological and chemical records (Chaps. 2, 3 and 4), role of hydrogen ion in weathering (Chap. 5), nutrient budget relationships (Chap. 6), quantitative elucidation of the nitrogen cycle, quantitative

impact of climate change on hydrology, and mass balances (Chaps. 2 and 6). Indeed, as in all good research, there is no lack of important research questions, even after five decades of intensive effort of the HBES.

Epilog

Aldo Leopold was a very wise and perceptive observer of nature. Some might have called him a conservationist; others might have called him an ecologist or a biogeo-chemist. Actually he was a brilliant, yet humble, student of nature in the purest sense. Much of what this little book has described in quantitative terms Aldo Leopold outlined in general terms >60 year ago in his essay *Odyssey*. *Odyssey* of Atom X captures the complicated theory of nutrient flux and cycling clearly and efficiently. Resources (nutrients) “enter” an ecosystem via atmospheric deposition and weathering release (chemical, physical, and biological); do “work” within the ecosystem by supporting productivity, food webs, decomposition, etc.; and then are lost from the ecosystem via drainage water or volatile or particulate loss to the atmosphere across the ecosystem’s boundary and by biotic uptake and long-term storage. Leopold has said this more effectively and beautifully in the *Odyssey* of Atom X than anyone!

His insight and prose have been an inspiration to me for a long time. Therefore, it seems appropriate for Aldo Leopold to have the last word in this book and so, from *A Sand County Almanac* (pp. 104–108) (1949), the following:

Odyssey

X had marked time in the limestone ledge since the Paleozoic seas covered the land. Time, to an atom locked in a rock, does not pass.

The break came when a bur-oak root nosed down a crack and began prying and sucking. In the flush of a century the rock decayed, and X was pulled out and up into the world of living things. He helped build a flower, which became an acorn, which fattened a deer, which fed an Indian, all in a single year.

From his berth in the Indian’s bones, X joined again in chase and flight, feast and famine, hope and fear. He felt these things as changes in the little chemical pushes and pulls that tug timelessly at every atom. When the Indian took his leave of the prairie, X moldered briefly underground, only to embark on a second trip through the bloodstream of the land.

This time it was a rootlet of bluestem that sucked him up and lodged him in a leaf that rode the green billows of the prairie June, sharing the common task of hoarding sunlight. To this leaf also fell an uncommon task: flicking shadows across a plover’s eggs. The ecstatic plover, hovering overhead, poured praises on something perfect: perhaps the eggs, perhaps the shadows, or perhaps the haze of pink phlox that lay on the prairie.

When the departing plovers set wing for the Argentine, all the bluestems waved farewell with tall new tassels. When the first geese came out of the north and all the bluestems glowed wine-red, a forehanded deermouse cut the leaf in which X lay, and buried it in an underground nest, as if to hide a bit of Indian summer from the thieving frosts. But a fox detained the mouse, molds and fungi took the nest apart, and X lay in the soil again, foot-loose and fancy-free.

Next he entered a tuft of side-oats grama, a buffalo, a buffalo chip, and again the soil. Next a spiderwort, a rabbit, and an owl. Thence a tuft of sporobolus.

All routines come to an end. This one ended with a prairie fire, which reduced the prairie plants to smoke, gas, and ashes. Phosphorus and potash atoms stayed in the ash, but the nitrogen atoms were gone with the wind. A spectator might, at this point, have predicted an early end of the biotic drama, for with fires exhausting the nitrogen, the soil might well have lost its plants and blown away.

But the prairie had two strings to its bow. Fires thinned its grasses, but they thickened its stand of leguminous herbs; prairie clover, bush clover, wild bean, vetch, lead-plant, trefoil, and Baptisia, each carrying its own bacteria housed in nodules on its rootlets. Each nodule pumped nitrogen out of the air into the plant, and then ultimately into the soil. Thus the prairie savings bank took in more nitrogen from its legumes than it paid out to its fires. That the prairie is rich is known to the humblest deermouse; why the prairie is rich is a question seldom asked in all the still lapse of ages.

Between each of his excursions through the biota, X lay in the soil and was carried by the rains, inch by inch, downhill. Living plants retarded the wash by impounding atoms; dead plants by locking them to their decayed tissues. Animals ate the plants and carried them briefly uphill or downhill, depending on whether they died or defecated higher or lower than they fed. No animal was aware that the altitude of his death was more important than his manner of dying. Thus a fox caught a gopher in a meadow, carrying X uphill to his bed on the brow of a ledge, where an eagle laid him low. The dying fox sensed the end of his chapter in foxdom, but not the new beginning in the odyssey of an atom.

An Indian eventually inherited the eagle's plumes, and with them propitiated the Fates, whom he assumed had a special interest in Indians. It did not occur to him that they might be busy casting dice against gravity; that mice and men, soils and songs, might be merely ways to retard the march of atoms to the sea.

One year, while X lay in a cottonwood by the river, he was eaten by a beaver, an animal that always feeds higher than he dies. The beaver starved when his pond dried up during a bitter frost. X rode the carcass down the spring freshet, losing more altitude each hour than heretofore in a century. He ended up in the silt of a backwater bayou, where he fed a crayfish, a coon, and then an Indian, who laid him down to his last sleep in a mound on the riverbank. One spring an oxbow caved the bank, and after one short week of freshet X lay again in his ancient prison, the sea.

An atom at large in the biota is too free to know freedom; an atom back in the sea has forgotten it. For every atom lost to the sea, the prairie pulls another out of the decaying rocks. The only certain truth is that its creatures must suck hard, live fast, and die often, lest its losses exceed its gains.

It is the nature of roots to nose into cracks. When Y was thus released from the parent ledge, a new animal had arrived and begun redding up the prairie to fit his own notions of law and order. An oxteam turned the prairie sod, and Y began a succession of dizzy annual trips through a new grass called wheat.

The old prairie lived by the diversity of its plants and animals, all of which were useful because the sum total of their co-operations and competitions achieved continuity. But the wheat farmer was a builder of categories; to him only wheat and oxen were useful. He saw the useless pigeons settle in clouds upon his wheat, and shortly cleared the skies of them. He saw the chinch bugs take over the stealing job, and fumed because here was a useless thing too small to kill. He failed to see the downward wash of over-wheated loam, laid bare in spring against the pelting rains. When soil-wash and chinch bugs finally put an end to wheat farming, Y and his like had already traveled far down the watershed.

When the empire of wheat collapsed, the settler took a leaf from the old prairie book: he impounded his fertility in livestock, he augmented it with nitrogen-pumping alfalfa, and he tapped the lower layers of the loam with deep-rooted corn.

But he used his alfalfa, and every other new weapon against wash, not only to hold his old plowings, but also to exploit new ones which, in turn, needed holding.

So, despite alfalfa, the black loam grew gradually thinner. Erosion engineers built dams and terraces to hold it. Army engineers built levees and wing-dams to flush it from the rivers. The rivers would not flush, but raised their beds instead, thus choking navigation. So the engineers built pools like gigantic beaver ponds, and Y landed in one of these, his trip from rock to river completed in one short century.

On first reaching the pool, Y made several trips through water plants, fish, and waterfowl. But engineers build sewers as well as dams, and down them comes the loot of all the far hills and the sea. The atoms that once grew pasque-flowers to greet the returning plovers now lie inert, confused, imprisoned in oily sludge.

Roots still nose among the rocks. Rains still pelt the fields. Deermice still hide their souvenirs of Indian summer. Old men who helped destroy the pigeons still recount the glory of the fluttering hosts. Black and white buffalo pass in and out of red barns, offering free rides to itinerant atoms ("Odyssey" was first published in the May-June 1942 issue of Audubon).

ERRATUM

Biogeochemistry of a Forested Ecosystem

Gene E. Likens

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The publisher regrets that the online and print versions of this book were published with some errors on the below pages of this book. The correct datas are listed below:

On page xx, in the “Contents” a new entry “Trace Metals” has been added before “Throughfall and Stemflow”. The revised contents is given below:

Elevational Effects	43
Acid Precipitation	44
Trace Metals.....	64
Throughfall and Stemflow	66
Streamwater Chemistry.....	68

On page 14, Photograph 3 has been replaced and the new photograph is given below:



Photograph 3 Hubbard Brook at an elevation of about 215 m. The characteristic boulder substrate and “stair-step” nature of this fifth-order stream are evident

On page 104, Photograph 8 has been replaced and the new photograph is given below:



Photograph 8 Collecting a streamwater sample from Watershed 4 at the Hubbard Brook Experimental Forest (Photo by D.C. Buso)

On page 111, the term “HBEF” in the caption of Table 25 has been expanded to “Hubbard Brook Experimental Forest”.

Table 25 Seasonal average streamwater exports for Watershed 6 of the Hubbard Brook Experimental Forest for two decades (1964–1973 and 2000–2009)

Table 34 on page 165 has been modified and the new version is given below:

Table 34 Nutrient budgets for various temperate zone terrestrial ecosystems in Eastern North America (kg/ha-year)

Location ^a	Atmospheric deposition	Streamwater output	Net gain or loss	Annual precipitation (cm)	Dominant vegetation ^b	Geology ^c
<i>Calcium</i>						
Coweeta, NC (1)	4.4	5.3	-0.9	215	Q, C, Ac	Mg, Msh
HBEF, NH (2)	1.0 ^d	6.6	-5.6	165	Ac, F, B, Pic, Ab, Ts	Ig, Msh
Cone Pond Inlet, NH (3)	1.2 ^d	2.5	-1.3	145	Ts, Pic, Ab	Ig
Long Island, NY (4)	3.3	9.6 ^e	-6.3	124	Q, Pin	Ss
E. Bear Brook, ME (5)	0.4 ^f	10.1	-9.7	159	F, Ac, B, Pic, Ab, Ts	Ig, Msh
SE. U.S. (6)	6	19	-13	127	Q, Pin	Ss, Ssh, Mg, Msh
Fernow, WV (7)	2.2 ^d	8.6	-6.4	125	Q, L, Ac, B, F	Ss, Ssh, Ms, Msh
Taughannock Creek, NY (8)	11.2 ^d (0.8 ^g)	182	-171	96 (111 ^g)	Ac, Ti, Ts	Ssh, Sc
Sleepers River, VT (9)	1.3 ^d	226	-225	149	Ac, B, Fr, F	Mc
Walker Branch, TN (10)	1.3 ^f	147	-146	118	Q, C	Sc
Biscuit Brook, NY (11)	1.2 ^h	16.5	-15.3	165 ⁱ	Ab, Ac, B, F, Pic, Ts	Ss
Turkey Lakes Watershed, ON (Canada) (12)	2.7 ^h	20.8	-18.1	107	Ac, B, Pic, Ts	Ig
<i>Magnesium</i>						
Coweeta, NC	1.0	3.1	-2.1	215	Q, C, Ac	Mg, Msh
HBEF, NH	0.3 ^d	2.2	-1.9	165	Ac, F, B, Pic, Ab, Ts	Ig, Msh
Cone Pond Inlet, NH	0.3 ^d	0.8	-0.5	145	Ts, Pic, Ab	Ig
Long Island, NY	2.1	7.3 ^e	-5.2	124	Q, Pin	Ss
E. Bear Brook, ME	0.4 ^f	2.5	-2.1	159	F, Ac, B, Pic, Ab, Ts	Ig, Msh
SE. U.S.	2	6	-4	127	Q, Pin	Ss, Ssh, Mg, Msh
Fernow, WV	0.3 ^d	3.3	-3.0	125	Q, L, Ac, B, F	Ss, Ssh, Ms, Msh
Taughannock Creek, NY	1.6 ^d (0.1 ^g)	34.8	-33.2	96 (111 ^g)	Ac, Ti, Ts	Ssh, Sc
Sleepers River, VT	0.2 ^d	9.5	-9.3	149	Ac, B, Fr, F	Mc
Walker Branch, TN	0.2 ^f	77	-77	118	Q, C	Sc
Biscuit Brook, NY	0.3 ^b	3.5	-3.2	165 ⁱ	Ab, Ac, B, F, Pic, Ts	Ss
Turkey Lakes Watershed, ON (Canada)	0.5 ^b	1.5	-1.0	107	Ac, B, Pic, Ts	Ig

<i>Sodium</i>							
Coweeta, NC	3.6	8.2	-4.6	215	Mg, Msh		
HBEF, NH	1.1 ^d	7.2	-6.0	165	Ig, Msh		
Cone Pond Inlet, NH	1.0 ^d	4.6	-3.6	145	Ig		
Long Island, NY	17	23 ^e	-6	124	Ss		
E. Bear Brook, ME	5.2 ^f	15.6	-10.4	159	Ig, Msh		
S.E. U.S.	5	26	-21	127	Ss, Ssh, Mg, Msh		
Taughannock Creek, NY	1.4 ^a (0.3 ^g)	18.9	-17.5	96 (111 ^g)	Ssh, Sc		
Sleepers River, VT	0.8 ^d	6.5	-5.7	149	Ac, Ti, Ts		
Walker Branch, TN	1.0 ^f	2.7	-1.7	118	Ac, Fr, F		
Biscuit Brook, NY	1.2	2.2	-1.0	165 ⁱ	Q, C		
Turkey Lakes Watershed, ON (Canada)	0.7 ^h	2.1	-1.4	107	Ab, Ac, B, F, Pic, Ts		
<i>Potassium</i>					Ac, B, Pic, Ts		
Coweeta, NC	4.1	5.0	-0.9	215	Ig, Msh		
HBEF, NH	0.6 ^d	1.4	-0.8	165	Ac, F, B, Pic, Ab, Ts		
Cone Pond Inlet, NH	0.4	0.3	+0.1	145	Ts, Pic, Ab		
Long Island, NY	2.4	3.9 ^e	-1.5	124	Q, Pin		
E. Bear Brook, ME	0.5 ^f	1.8	-1.3	159	F, Ac, B, Pic, Ab, Ts		
S.E. U.S.	1	6	-5	127	Q, Pin		
Fernow, WV	1.1 ^d	3.6	-2.5	125	Q, L, Ac, B, F		
Taughannock Creek, NY	1.1 ^d (0.2 ^g)	5.6	-4.5	96 (111 ^g)	Ac, Ti, Ts		
Sleepers River, VT	0.7 ^d	11.2	-10.5	149	Ac, B, Fr, F		
Biscuit Brook, NY	0.2 ^h	2.7	-2.5	165 ⁱ	Ab, Ac, B, F, Pic, Ts		
Turkey Lakes Watershed, ON (Canada)	0.3 ^b	0.6	-0.3	107	Ac, B, Pic, Ts		
<i>Dissolved inorganic nitrogen (NH₄-N + NO₃-N)</i>					Ig		
Coweeta, NC	6.2	0.66	+5.5	215	Q, C, Ac		
HBEF, NH	5.3 ^j	0.23	+5.1	165	Ac, F, B, Pic, Ab, Ts		
Cone Pond Inlet, NH	3.5 ^k	<0.1	+3.5	145	Ts, Pic, Ab		
E. Bear Brook, ME	1.7 ^f	0.3	+1.4	159	F, Ac, B, Pic, Ab, Ts		

(continued)

Table 34 (continued)

Location ^a	Atmospheric deposition	Streamwater output	Net gain or loss	Annual precipitation (cm)	Dominant vegetation ^b	Geology ^c
S.E. U.S.	2 ^k	1 ^k	+1 ^k	127	Q, Pin	Ss, Ssh, Mg, Msh
Fernow, WV	7.4 ^h	4.4	+3.0	125	Q, L, Ac, B, F	Ss, Ssh, Ms, Msh
Taughannock Creek, NY	10.3 ⁱ (5.4 ^g)	5.6	+4.7	96 (111 ^g)	Ac, Ti, Ts	Ssh, Sc
Sleepers River, VT	4.7 ^e	1.9	+2.8	149	Ac, B, Fr, F	Mc
Walker Branch, TN	1.7 ^f	0.03	+1.7	118	Q, C	Sc
Biscuit Brook, NY	8.2 ^h	3.3	+4.9	165 ⁱ	Ab, Ac, B, F, Pic, Ts	Ss
Turkey Lakes Watershed, ON (Canada)	25.6 ^h	2.1	+23.5	107	Ac, B, Pic, Ts	I _g
<i>Phosphorus</i>						
Coweeta, NC	0.04	<0.01	+0.04	215	Q, C, Ac	Mg, Msh
HBEF, NH	0.02 ^d	0.01	+0.01	165	Ac, F, B, Pic, Ab, Ts	I _g , Ms _h
Taughannock Creek, NY	0.186 ^d (0.03 ^g)	0.197	-0.011	96 (111 ^g)	Ac, Ti, Ts	Ssh, Sc
Sleepers River, VT	0.15 ^d	0.13	+0.02	149	Ac, B, Fr, F	Mc
Walker Branch, TN	—	0.03	—	118	Q, C	Sc
Biscuit Brook, NY	—	<0.001	—	165 ⁱ	Ab, Ac, B, F, Pic, Ts	Ss
Turkey Lakes Watershed, ON (Canada)	—	0.01	—	107	Ac, B, Pic, Ts	I _g
<i>Sulfate-Sulfur</i>						
Coweeta, NC	7.5	6.4	+1.1	215	Q, C, Ac	Mg, Msh
HBEF, NH	6.7 ^j	12.6	-5.9	165	Ac, F, B, Pic, Ab, Ts	I _g , Ms _h
Cone Pond Inlet, NH	6.7 ^e	9.7	-3.0	145	Ts, Pic, Ab	I _g
E. Bear Brook, ME	3.7 ^f	13.2	-9.5	159	F, Ac, B, Pic, Ab, Ts	I _g , Ms _h
S.E. U.S.	8	7	+1	127	Q, Pin	Ss, Ssh, Mg, Msh
Fernow, WV	11.6 ^h	8.1	+3.5	125	Q, L, Ac, B, F	Ss, Ssh, Ms, Msh
Taughannock Creek, NY	18.1 ^d (4.4 ^g)	38	-19.9	96 (111 ^g)	Ac, Ti, Ts	Ssh, Sc
Sleepers River, VT	3.8 ^g	17.6	+	149	Ac, B, Fr, F	Mc
Walker Branch, TN	5.5 ^f	5.4	+0.1	118	Q, C	Sc
Biscuit Brook, NY	8.2 ^h	9.9	-1.7	165 ⁱ	Ab, Ac, B, F, Pic, Ts	Ss
Turkey Lakes Watershed, ON (Canada)	6.1 ^h	5.5	+0.6	107	Ac, B, Pic, Ts	I _g

<i>Chloride</i>						
Coweeta, NC	6.2	9.1	-2.9	215	Q, C, Ac	Mg, Msh
HBEF, NH	2.6 ^j	3.3	-0.7	165	Ac, F, B, Pic, Ab, Ts	Ig, Msh
Cone Pond Inlet, NH	1.9 ^d	3.4	-1.5	145	Ts, Pic, Ab	Ig
E. Bear Brook, ME	8.3 ^f	18.0	-9.7	159	F, Ac, B, Pic, Ab, Ts	Ig, Msh
Taughannock Creek, NY	11.5 ^a (0.7 ^g)	41.7	-30.2	96 (111 ^g)	Ac, Ti, Ts	Ssh, Sc
Sleepers River, VT	1.7 ^g	2.4	-0.7	149	Ac, B, Fr, F	Mc
Walker Branch, TN	2.2 ^f	6.5	-4.3	118	Q, C	Sc
Biscuit Brook, NY	2.5 ^b	3.7	-1.2	165 ⁱ	Ab, Ac, B, F, Pic, Ts	Ss
Turkey Lakes Watershed, ON (Canada)	0.9 ^h	0.6	+0.3	107	Ac, B, Pic, Ts	Ig

^a(1) S. Laester, personal communication for precipitation and streamwater chemistry in Watershed 27 (2008). (2) Present study; average for 2008 water-year. (3) S. Bailey, unpublished averages for water-year 2007–2008 (4) Woodwell and Whittaker (1967). (5) L. Rustad, I. Fernandez for 2008 water-year. (6) Gambrell and Fisher (1966). (7) M.B. Adams for 2005 calendar year for Watershed 4 (Adams et al. 2006). (8) Likens (1974a, b) for 1970–1971. (9) S. Bailey and J. Shanley, unpublished averages for water-year 2008 and 2009, Watershed 9, personal communication. (10) Lutz et al. (2012); 2008 water-year. (11) D. Burns, personal communication, calendar-year, volume-weighted average for 2008. (12) I. Creed, personal communication, average for 2006 water-year catchment #32.

^bVegetation footnotes: Ab, Abies; Ac, Acer; B, Betula; C, Caryta; F, Fagus; Fr, Fraxinus; L, Liriodendron; Pin, Pinus; Pic, Picea; Pr, Prunus; Ps, Pseudotsuga; Q, Quercus; Ti, Tilia; Ts, Tsuga

^cGeology footnotes: Ig, igneous, granitic; Sc, sedimentary, carbonate; Ssh, sedimentary, shale; Ss, sedimentary, sandstone; Mr, Metamorphic (x refers to substrates used above

^dBulk precipitation

^eTo water table

^fWet only

^gWet plus dry data for 2010 from nearby Connecticut Hill CASTNET site (T.J. Butler)

^hWet plus dry deposition

ⁱMean 2007–2009

^jBulk precipitation plus dry deposition (see Table 17 for bulk precipitation)
kNO₃-N only

On page 170, in the paragraph beginning “Adjustments for net gaseous input....” the sentence “Nevertheless, considerable effort...” has been moved to the end of the paragraph. The revised page is listed below:

Adjustments for net gaseous input and dry deposition of aerosols were not incorporated systematically in Table 34, but much more information is available than 35 years ago. Recently, Mitchell and colleagues (2011) used a new approach to predict SO₂ concentrations as a function of SO₂ emissions, latitude and longitude, and then estimated dry deposition from relations between concentrations and deposition flux from the U.S. CASTNET and Canadian CAPMoN networks at 15 sites in northeastern USA and southeastern Canada. Although dry deposition estimates are still relatively uncertain within the mass balance for these systems, this approach seems promising and allowed the prediction of dry deposition values for the HBEF of 0.5 to 2.5 kg S/ha-year. Nevertheless, considerable effort should be devoted to the problem of measuring dry deposition and gaseous exchange in forested ecosystems in the future in order to reflect quantitatively these important fluxes in biogeochemical cycling and fluxes.

On page 173, in the list entry 3, the sentence beginning “Flux is greatly influenced...” has been revised and the corrected sentence is given below:

Flux is greatly influenced by hydrology and, during 49 years, precipitation has ranged from 95 to 186 cm/year in W6 at the HBEF.

On page 174, a reference citation “van Doorn et al. 2011” has been added after “Likens 2010” at the end of list entry 6, in the paragraph beginning “Enigmatically, rapid forest...”.

Enigmatically, rapid forest biomass accumulation has ceased since ~1982 at HBEF due to increased tree mortality, related in part to the effects of acid rain (Likens et al. 1998, 2002a; Siccama et al. 2007). This important finding is the subject of intense, ongoing investigation (Likens and Franklin 2009; Likens 2010; van Doorn et al. 2011).

On page 178, in list entry 23, the comma after “reduction” has been removed and the corrected entry is given below:

23. Many of the important biogeochemical relationships and transformations within the forest ecosystem are regulated by microorganisms, such as nitrogen fixation, nitrification, and denitrification or sulfur oxidation and reduction at HBEF (e.g., Zhang et al. 1999; Findlay 2013; Groffman and Rosi-Marshall 2013).

On page 178, in list entry 24, the word “Stream water” has been closed up to read “Streamwater” in the sentence “Streamwater chemistry varied....”.

24. Streamwater chemistry collected and measured at high density in all tributaries throughout the Hubbard Brook Valley during spring (May–July) and fall (October–December) of 2001 gave a remarkable new landscape view of streamwater chemistry in the valley (Likens and Buso 2006). Streamwater chemistry varied throughout the valley in relation to changes in elevation, distance from origin of streamflow, drainage area, and type of drainage. Concentrations of hydrogen ion, aluminum, and dissolved organic carbon varied by two to tenfold in relation to these factors, but other elements, e.g., chloride and dissolved silica, changed relatively little throughout the valley. The main Hubbard Brook, a fifth-order river, changed concentration very little throughout its 13-km length despite inputs from some 20 major tributaries.

In References, on page 193, the references “Likens GE, Bormann FH (1970); Likens GE, Bormann FH (1985); Likens GE, Bormann FH (1995)” have been rearranged and the revised order is given below:

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