HYDROCHEMISTRY OF FORESTED CATCHMENTS

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“The song of a river ordinarily means the tune that waters play on rock, root, and rapid. ...This song of the waters is audible to every ear, but there is other music in these hills, by no means audible to all. To hear even a few notes of it you must first live here for a long time, and you must know the speech of hills and rivers. Then on a still night, when the campfire is low and the Pleiades have climbed over rimrocks, sit quietly and listen for a wolf to howl, and think hard of everything you have seen and tried to understand. Then you may hear it—a vast pulsing harmony—its score inscribed on a thousand hills, its notes the lives and deaths of plants and animals, its rhythms spanning the seconds and the centuries.”

Aldo Leopold, *Song of the Gavilan* [Reprinted in part from Leopold (1940), by permission of The Wildlife Society.]

ABSTRACT
The pathways that water may take through a catchment and its reactions with organisms and soils are myriad and ever varying. A promising means to unraveling the mystery of watershed hydrochemistry is the study of “small” catchments, yet the hydrochemical function of even the smallest of catchments involves an amazingly intricate web of flowpaths and biogeochemical processes. Monitoring of catchments and comparison of their inputs to their outputs yields clues to their workings. Manipulation of catchments offers some means of “controlled” experimentation as to their nature. Modeling of catchment hydrochemical response attempts to put it all together. Every forested catchment is individual in its structure and hydrochemical response, yet a select, carefully studied few often are drafted to serve as representatives in assessments of responses to environmental influences or perturbations (e.g., acid rain). Many factors must be considered in such extrapolations. Studies of forested catchments often are driven by environmental concerns and thus fluctuate accordingly as to their location and intensity. Despite such fluctuations, the future of the field is clear and bright. Much has been

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learned as a result of recent studies, not only of what to think about catchment function but, more importantly, how to think about it.

INTRODUCTION

Many fascinating connections exist among the physical, chemical, and biological processes (Figure 1) that shape the chemical composition of water flowing from forested catchments. Where water goes in a forested catchment, how long it lingers, what materials and organisms it encounters on its journey—all interact to determine its character. All combine to present a fascinating puzzle to those who study catchment hydrochemistry. As John Muir, the American naturalist, wrote, “When we try to pick out anything by itself, we find it hitched to everything else in the universe.” This certainly seems true in the study of watershed hydrochemistry, regardless of whether we are trying to understand natural systems for our own basic curiosity or in order to better understand and to predict the response of ecosystems to large-scale stresses such as acidic deposition, non-point source pollution, or changes in climate. As we attempt to understand how substance “A” comes to be at point “B” at concentration “C,” we find ourselves at every turn meeting questions that require us to cross long-established disciplines—from hydrology to aqueous geochemistry to microbiology and more. We find ourselves everywhere needing to learn more about “what the other guy knows.” These efforts challenge us. They make us think and re-think! They keep us questioning.

HYDROLOGIC PROCESSES AND FLOW PATHS IN FORESTED CATCHMENTS

Four primary factors combine to determine the chemical and isotopic characteristics of waters draining from forested watersheds. These factors are (a) the chemical composition of incident precipitation, (b) the abiotic materials or the biota that water contacts as it moves through a watershed, (c) the abiotic reactivity of the materials or biotic activity of the organisms contacted, and (d) the length of contact with those materials or organisms. A key factor in this equation is the pathway that water follows through the catchment. The pathways that water follows determine the materials it contacts and the length of that contact, and thus they play a pivotal role in determining drainage water composition. In its travels through a forested catchment water may encounter forest canopy and understory plants, plant stems, litter and organic soil layers, mineral layers.

A catchment (or watershed) is a unit of natural landscape (i.e. including bedrock, soils, biota) delineated by a topographic divide that converges at a downstream terminus, defined by the point at which flow from the catchment is measured.
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Watershed Ecosystem Dynamics

Figure 1 Conceptualization of interconnected watershed physical, chemical, and biological processes. Reprinted from Johnson & Van Hook (1989), by permission of Springer-Verlag.

of soil, coarse tills, and bedrock as well as a host of macro- and micro-biota. All act to alter its composition.

Study of drainage water chemical and isotopic composition helps to unravel the mysteries of where water has been in a watershed and how long it has been there. We can use knowledge of past pathways and residence times under known antecedent and precipitation (or snowmelt) conditions, to better understand how watersheds “work” and perhaps to predict their future hydrochemical behavior or condition. The analysis of rainfall/runoff events (stormflow generation) is particularly useful in the study of the hydrologic behavior of forested catchments. It is under these dynamic transitory conditions that watersheds reveal their workings. Studies of stormflow generation, particularly over the last 30 years, have added much to our knowledge and appreciation of the variability and complexity of catchment hydrochemistry.
A variety of storage zones, transport processes, or flow paths may exist and operate for watersheds. In general, however, one can characterize stormflow for a catchment as originating by way of any (or any combination) of four basic paths: (a) direct interception of precipitation by the stream channel, (b) surface flow, (c) subsurface flow, or (d) groundwater flow. The relative importance of each of these pathways varies both among and within individual watersheds depending on topography, forest type, soil makeup, and geological structure. Within any particular watershed, pathways may also vary depending on antecedent conditions of wetness and intensity of rainfall (or snowmelt).

Direct interception of precipitation by the stream channel is self-explanatory as both a mechanism and a pathway. Although direct channel precipitation may contribute to small flow peaks at times, its quantitative contribution to overall stormflow is usually slight in headwater forested catchments.

The topic of surface flow in watersheds (commonly termed overland flow) has a long history in catchment hydrology. Horton (1933) proposed that overland flow resulted when rainfall rates exceeded soil infiltration rates leading, in turn, to substantial surface runoff causing rapid increases in stream flow. This type of flow, commonly termed Hortonian overland flow (sometimes sheet flow or infiltration-excess flow), can be very important in arid areas where soils may swell and greatly reduce infiltration rates or in areas where soils may be disturbed or compacted (e.g. croplands or heavily grazed areas). It may also be important in watersheds with extensive rock outcrops. Usually it is of minor importance in forested watersheds.

Other sources of overland flow may exist, however. Musgrave & Holtan (1964) used the term “return flow” to describe the situation in which subsurface flow returns to the surface as the water table (or perched water table due to shallow impervious layers) rises to the surface in response to precipitation or snowmelt. As precipitation falls on these saturated areas, it too will flow overland. Together these components comprise “saturation overland flow” (e.g. see Dunne & Leopold 1978). Such flow may occur adjacent to the stream channel or further upslope at points of flow convergences within the catchment. Hewlett & Hibbert (1967) proposed that during rainfall or snowmelt events, such areas of flow contribution immediately adjacent to the stream expand laterally from the stream as well as longitudinally upstream leading to greater expanses of directly contributing zones. As rainfall or snowmelt later dissipate, these zones shrink. Hewlett & Hibbert (1967) termed this conceptualization of flow production the “variable source area concept.” Hibbert & Troendle (1988) have provided an authoritative review of the concept and its development from earlier work (most notably at the Coweeta Hydrologic Laboratory).

Hewlett & Hibbert (1967) were careful to point out that although increases in overland flow would occur as contributing zones expanded and channel length
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Extended during storms, “most or all of the water may still be entering these channels as subsurface flow.” Building on their own observations and the observations of others, they hypothesized that in small (for them, <50 km²) temperate forest watersheds of the eastern United States, most of stormflow runoff comes as subsurface flow. In so doing they directly challenged the ruling idea of the day that overland flow was the dominant component of stormflow generation. In their classic publication, Hewlett & Hibbert (1967) posed the key question that in many ways still challenges forest hydrologists: “If we assume that subsurface flows predominate on most wildland soils, how do direct runoff and base flow get to the channel?”

Hewlett & Hibbert (1967) perceived direct runoff (stormflow) from a rainstorm as composed partly of some of the actual rainfall (often termed “new” water), but mostly of pre-event water (“old” water) displaced by the rain from the soil column. They termed the piston-type flow produced by this displacement as “translatory flow” and noted that it should be most important in lower- to mid-watershed slopes. Such a “matrix flow,” however, seems incapable of delivering flows at rates sufficient to match observed increases in stormflow [e.g. see review discussions by Turner et al (1990), Bonell (1993), and Jenkins et al (1994)].

Sklash & Farvolden (1979) proposed an alternative mechanism of near-stream matrix flow to account for rapid stormflow generation. They combined hydrometric and isotope studies in forested and partly forested catchments in Quebec to show that groundwater (saturated matrix flow of “old” water) contributed between 60% and 80% of stormflow generation in their studies. They combined their field observations with computer simulations to build upon prior work of Ragan (1968) and to propose that “groundwater ridging” was occurring and was sufficient to account for delivery of most of the storm flow. In this process, newly infiltrating water quickly converts the capillary fringe (just above the saturated zone) to a state of saturation (groundwater ridge). This increases both the size of the near-stream discharge area and the near-stream head, thus leading to relatively rapid and substantial increases in flows of pre-event water to the stream channel. This phenomenon would of course be most important in lower valley near-stream zones [discussions by Bonell (1993) and Jenkins et al (1994)]. Although Turner et al (1990) termed this proposed process “the most widely accepted hypothesis to explain observations of rapid subsurface response in forested catchments,” Bonell (1993) noted that some subsequent studies of flow generation in forested catchments failed to demonstrate the mechanism and cautioned that “it is clear that further experimentation is necessary to verify the generality of this process.”

Water may also move in forested catchments through large pores in the soil (Beven & Germann 1982, Germann 1986, 1990). Hydrologists call such pores
macropores [though pores larger than 1 cm (e.g., see Bonell 1993) may be termed pipes]. Decaying of root channels, burrowing of animals (large and small), and cracking of clay soils are all processes that create macropores and pipes. Water may move through macropores vertically (e.g., through unsaturated soils to the saturated zone) or laterally (principally through saturated zones). In so doing, macropore or pipe flow can rapidly bypass some areas of relatively slower matrix flow only to later arrive at and substantially interact with other, perhaps newly, saturated matrices (McDonnell 1990). In some cases macropores may discharge water directly back to the surface in some convergence zones of the watershed or directly into stream channels (e.g., see McDonnell 1990). In most forested catchments in humid temperate climates, however, the most likely role for macropore flow is to transmit water primarily within the soil and regolith. Most often researchers do not (or cannot) know the extent of macropore interconnections within any particular watershed (Bonell 1993).

Regardless of the particular path or mix of paths that water takes as it flows through catchments to become surface water runoff, one thing now seems clear—in most forested catchments in most situations stormflow appears to be composed predominantly of old (pre-event) water. As reviewed by Turner et al (1990) and Bonell (1993), evidence for this conclusion has mounted consistently with the ever increasing number of isotopic (see reviews by Sklash & Farvolden 1982, Buttle 1994) and chemical tracer studies of stormflow sources in forested catchments. Despite the apparent general applicability of this conclusion, however, one must be careful not to apply it without evidence to any particular catchment at any particular time. The sources of water in stormflow and the types of pathways that water takes through catchments most certainly can and will vary between (even adjacent) catchments and within catchments depending on local topography, antecedent conditions of wetness, and rainfall or snowmelt intensity. Mulholland et al (1990), for example, have presented an interesting case study of within-watershed variation of flow generation processes for a forested catchment.

The pathways that water takes through a forested catchment play a major role in determining that water’s physical, chemical, and isotopic composition (e.g., Mulder et al 1991). Conversely, these streamwater characteristics can help to tell us where the water has been. In recent years, dramatic increases have occurred in the use of various types of tracers to study flow paths and processes in forested catchments. Tracers have included temperature (Shanley & Peters 1988), specific conductance (Pilgrim et al 1979), and a host of chemical constituents (e.g., SiO$_2$, Ca$^{2+}$, Mg$^{2+}$, Cl$^-$, Br$^-$, SO$_4^{2-}$; see Jenkins et al 1994). Use of chemical tracers both benefits from, and is complicated by, the fact that chemical modifications possibly, but do not necessarily (Hooper & Kendall 1994), occur anywhere along the flow path.
Environmental isotopes [those of water itself (e.g. $^{18}$O) or of solutes (e.g. $^{15}$N)] may provide useful information on flow paths and processes in forested catchments. In recent years there has been a tremendous growth in the use of environmental isotopes for these purposes (Sklash 1990, Buttle 1994, Kendall et al 1995). The isotopic composition of pre-event water held within the watershed commonly differs from that of rainfall (Kendall et al 1995), which itself can vary seasonally or from storm to storm (Pearce et al 1986, Kendall et al 1995). Therefore, any mixing of new water and old water is likely to change the isotopic composition of the resultant stormflow. By solving the mass balance equations (e.g. Buttle 1994) for the fluxes of water and the isotopes, one can compute the relative contributions of the new and old water sources to flow from forested catchments. One must always be careful, however, to ensure that important assumptions of the technique are met (see Buttle 1994, Kendall et al 1995).

To date, the most commonly used environmental isotopes have been the stable isotopes of water—$^{18}$O and deuterium ($^2$H) (Buttle 1994, Kendall et al 1995, Gat 1996). The use of these isotopes has two significant advantages. First, they are natural constituents of the water molecule and thus go exactly where the water goes. Second, they are readily available and “applied” (i.e. in rain and snowfall). Their use can entail some potential complications, however. For example, canopy interception of rainwater can be accompanied by significant (e.g. 20%) evaporation, resulting in fractionation (Saxena 1986, DeWalle & Swistock 1994). Other physical interactions may also lead to fractionation (Kendall et al 1995). Fractionation alters the isotopic composition of the input water and complicates the analysis.

Another component of the water molecule that researchers sometimes have used as a tracer to study flow paths and flow generation processes is tritium ($^3$H). Horton & Hawkins (1965), for example, applied tritium to the top of a saturated soil laboratory column and observed that nearly all of the early water leaving the water column was untritiated pre-event water “pushed ahead” of the tritium containing pulse. Their observations appear to have significantly influenced Hewlett & Hibbert (1967) in their proposal of the importance of translatory (piston) flow in catchments. Although the use of tritium in whole-catchment studies can be informative (especially in combination with other isotopic or geochemical tracers; Rose 1996), its use is relatively infrequent now. Its principal utility seems to have been to date groundwater in relation to precipitation enriched by atmospheric bomb testing of the midcentury (Jenkins et al 1994).

The innovative use of other tracers in catchment hydrochemical research is increasing at a rapid rate. Recently used tracers have included $^{222}$Rn (e.g. Genereux & Hemond 1990, Genereux et al 1993), $^{13}$C (e.g. Kendall et al 1994), as well as isotopes of Sr, Pb, and others of the uranium and thorium series. For example, at Sleepers River Research Watershed in northern Vermont a number
of hydrogeologic conditions exist that allow innovative site-specific analyses to be performed (Bullen et al 1994, Kendall et al 1994). At that site, (a) shallow groundwater and mineral soil water have isotopic signatures for Pb isotopes (resulting from decays through the uranium series) that differ from the signature produced from atmospherically deposited Pb; (b) shallow groundwater is enriched in radiogenic $^{87}$Sr compared with unsaturated soil water; and (c) carbonates in the upper mineral horizons (shallow flowpaths) have been largely stripped by weathering relative to bedrock (deeper flowpaths). Bullen et al (1994) and Kendall et al (1994) have used these conditions to further identify flowpaths during snowmelt and stormflow events. Other sites, no doubt, have specific conditions that would allow researchers to perform other such innovative analyses.

A relatively recent development in methods for studying catchment hydrochemical response has been the adoption of three-component flow separations. DeWalle et al (1988) used a three-component tracer model with measurements of $^{18}$O to discriminate among the relative contributions of channel precipitation, soil water, and groundwater to stormflow generation in a small watershed (Fish Run) of the Appalachian Plateau. Prior to their work, nearly all chemical or isotopic separations had been two-component models of new water vs old water, necessarily lumping soil water and groundwater together as the old water component. Now, three-component separations are becoming increasingly common in hydrochemical studies of catchments (e.g. Christophersen et al 1990, Hooper et al 1990, Genereux et al 1993, O’Brien & Hendershot 1993, Ogunkoya & Jenkins 1993, Bazemore et al 1994, Hinton et al 1994). As with two-component separations, care must be taken, of course, when applying three-component separations to make sure that all necessary assumptions are met (see Buttle 1994 and Hinton et al 1994 for discussions).

Researchers have used isotopic or chemical tracers not only in isolation but also in combination and in association with catchment hydrometric data (Kennedy et al 1986, Obradovic & Sklash 1986, Pearce et al 1986, Sklash et al 1986, Genereux et al 1993, Bazemore et al 1994, Buttle 1994, Hinton et al 1994). Such integrated use can be especially powerful in studying stormflow sources, pathways, or processes in forested catchments. Such techniques, when thoughtfully applied, hold promise to increase our understanding of the physical and chemical ways in which forested watersheds and the surface waters draining them are interconnected.

CHEMICAL AND BIOLOGICAL INTERACTIONS IN FORESTED CATCHMENTS

Equally important to the pathways of water movement in determining catchment hydrochemistry are the physical, chemical, and biological processes that
act within catchments to determine the composition of drainage waters. Among
the most important of such processes are (a) the physical processes of erosion
and gas exchange; (b) the chemical processes of weathering, chemical precip-
itation, cation exchange, and ion sorption; and (c) the biological processes of
uptake, respiration, decomposition, mineralization, and microbiologically me-
diated oxidation and reduction. Even the most cursory inclusive treatment of
these processes is outside of the scope of this review. A number of sources
provide excellent descriptions and discussions of these processes within the
context of catchment hydrochemistry (e.g. Trudgill 1986, Binkley et al 1988,

More important than a recounting here of the specifics of each process is the
realization that it is the sum total of interactions (summed in different ways on
different catchments and summed in different ways at different times within
an individual catchment) that determine the chemical composition of drainage
waters. An illustrative discussion of some of the factors that influence catchment
hydrochemical response to the input of a particular pollutant, in this case acidic
deposition, provides a useful example of such interactions.

Combustion of fossil fuels by electric utilities, factories, and motor vehicles
yields emissions of oxides of sulfur and nitrogen that react in the atmosphere
to produce acidic deposition (often called acid rain; see Bricker & Rice 1993).
The major cationic components of acid rain are hydrogen and ammonium ions.
Its major anions are sulfate and nitrate. When this chemical mixture enters a
forested catchment it becomes subject to both a host of sequential processes and
simultaneous reactions acting (and interacting) in ways that are not yet fully
understood.

For example (and in no particular sequence in space or time), hydrogen ions
in acid rain can increase the dissolution (chemical weathering) of primary or
secondary minerals in the catchment. One effect of such weathering is to in-
crease the concentration of “base” cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) as well as
of aluminum in soil solution. Aluminum concentrations also may be increased
in soil solution by the dissolution of amorphous or crystalline aluminum trihy-
droxide phases. These dissolved species as well as the H^+ (and other cations)
in the acid rain engage in cation-exchange reactions with cations held on the
soil exchange complex. In cation exchange the ions of higher valence are
placed preferentially from the soil. Thus trivalent aluminum will be dis-
placed in greater proportion than divalent or monovalent base cations or H^+
(Brady 1974). Often, forest soils that receive substantial acidic deposition al-
ready are “acidic”—they have low percentage base saturation (percentage of
soil exchange capacity occupied by base cations) and their exchange complex is
dominated by aluminum and H^+. The increased ionic strength of soil solutions
that results from acidic deposition leads to enhanced levels of cation exchange
(Reuss et al 1987, Binkley et al 1988, Turner et al 1990). In this situation substantial aluminum previously held on soil exchange sites can be mobilized to solution. Dissolved aluminum is a weak acid in solution and can decrease the pH of the soil solution (Binkley et al 1988). Taken together, this series of exchange and equilibrium reactions is referred to sometimes as “salt effect acidification” (Reuss & Johnson 1985, 1986, Binkley et al 1988). If soil base saturation (percentage of soil exchange capacity occupied by base cations) is greater than roughly 15–20%, the effect of this acidification on soil solution acid neutralizing capacity (ANC) will be minor (Reuss & Walthall 1989). At percentage base saturation lower than roughly 15% (e.g. acid forest soils) the effect is more pronounced and can be important for resulting water quality. When such affected soil solutions leach to streams and lakes the result can be surface water acidification—the lowering (sometimes dramatic) of ANC of those waters.

The effect of leaching of low pH soil solutions to surface waters can vary depending upon the ANC of the soil solutions and the effects of gas exchange. Because of the effects of root and bacterial respiration in soils, soil atmospheres invariably have concentrations of CO₂ well above ambient atmospheric concentrations (Brady 1974). When soil waters that have equilibrated with soil atmosphere drain to surface waters, CO₂ degasses from the solution. If the leaching soil solution has positive ANC, then the degassing will increase its pH (but will not affect ANC, as no net proton acceptors or donors have been added to the solution). If ANC has become negative, however, then pH increases associated with CO₂ degassing will be negligible (Reuss & Johnson 1985, 1986).

Not only can acidic deposition decrease the pH and ANC of soil solutions and surface waters, it can also cause acidification of soils—the decreasing of soil percentage base saturation. This occurs when base cations exchanged from the soil complex leach to surface waters faster than chemical weathering can serve to replace them on the complex. This effect has an important interaction in the overall process of acidification. As soil base saturation decreases, H⁺ and aluminum occupy a progressively higher fraction of the exchange complex and in the soil solution. This, in turn, will lead to more acidic soil solutions and surface waters. In addition, the aluminum leached is toxic to aquatic biota (Baker et al 1990, Baker et al 1996, Van Sickle et al 1996). (It was the ultimate toxic effects of acidic deposition on fish species that has led, via increased research funding, to many recent advances in our understanding of catchment hydrochemistry.)

The greater the loading (concentration x volume) of acidic deposition to catchment soils, the greater the loading of sulfur (mostly as sulfate) and nitrogen (mostly in the forms of ammonium and nitrate). Sulfur and nitrogen engage in a variety of reactions that significantly affect catchment hydrogeochemical response to acidic deposition (Galloway 1996).
For sulfur, the inorganic anion adsorption of sulfate onto hydrous oxides of iron and aluminum (Chao et al. 1964) is a major control on its mobility in catchment soils. The process not only acts to retain sulfur deposited to catchments (sometimes very large percentages of deposition; Rochelle et al. 1987, Rochelle & Church 1987), but it also acts as a net neutralization mechanism either through anion exchange for hydroxide ions or through creation of a cation exchange site (Rajan 1978). Sulfate adsorption is concentration dependent. Under conditions of continuing sulfur loadings, progressively smaller fractions of the inputs are adsorbed and retained, and sulfate concentrations in soil waters and receiving surface waters continue to increase (Reuss & Walthall 1989).

The biological processes of vegetative and microbial uptake, decomposition, mineralization, and oxidation and reduction reactions play major roles in determining nitrogen cycling in forested catchments (Aber et al. 1989). In recent years researchers have focused much more attention on the idea that forests might reach a condition where nitrogen was available in excess of the total ecosystem biotic (vegetative and microbial) demand. Aber et al. (1989) have termed such a situation nitrogen saturation. [In contrast, Ågren & Bosatta (1988) defined nitrogen saturation as the rarer condition whereby nitrogen outputs from a catchment equaled or exceeded inputs over periods (e.g. a year) sufficiently long to nullify “temporary disturbances.” This latter definition is favored by some (e.g. Christ et al. 1995, Van Sickle & Church 1995) because it is more quantitative.] Factors such as levels of atmospheric deposition of nitrogen, stand age, catchment history (e.g. timbering), and relative supplies of water and other nutrients for vegetative and microbial growth seem to play the most significant roles in determining the relative cycling within and leaching of nitrogen from forests (Aber et al. 1991). As levels of available ammonium rise in forest soils, so do levels of microbial nitrification (the biologically mediated conversion of ammonium to nitrate). Increased nitrification leads to increased levels of $H^+$ (which will then affect soil exchange reactions), as well as increased soil solution nitrate concentrations.

In the soils of forested catchments strongly affected by acid rain, the result of these various different yet highly connected processes can be (or can come to be) soil solutions dominated by the anions $SO_4^{2-}$ and (to a much less frequent degree) $NO_3^-$. Such soil solutions also would have elevated levels of the cations $H^+$ and $Al^{3+}$, leading to adverse effects on receiving waters and their biota.

As water moves downward through soil, the dominance of specific reactions and reaction products vary and shift as a function of the differing characteristics of the existing soil horizons (Brady 1974, Richter & Markewitz 1995). Thus, the paths that the deposition and resulting soil solutions take through a forested catchment can greatly affect the chemistry of drainage waters. Solutions moving through poorly buffered near surface soils may lead to drainage waters with...
poor water quality, both over long-term periods (Newton & April 1982) and over very brief periods (“episodes”) associated with snowmelt or heavy rainfall (Eshleman 1988, Wigington et al 1990, 1996a). If drainage paths are deeper within the watershed, however, neutralization by much more highly buffered groundwaters (e.g. resulting from slow weathering over much longer residence times) can eliminate much of the adverse effects (Newton & April 1982).

This example presents only a few of the ways in which individual processes can interact with substances entering a forested catchment to influence hydrochemical response. Many more are known (but cannot be addressed here); numerous interactions likely are unknown. Forested catchments function in complex ways that can be difficult to observe and extremely difficult to quantify.

APPROACHES TO STUDYING CATCHMENT HYDROCHEMISTRY

The “Small Catchment Approach”

A very powerful approach to understanding the hydrochemistry of forested catchments is through the study of “small catchments” (Moldan & Černý 1994), sometimes known as the small watershed approach (Likens et al 1977, 1995). A catchment or watershed is generally considered “small” if it is on the order of 500 ha or less (e.g. see Moldan & Černý 1994). Small catchments are often (and sometimes incorrectly) assumed to be hydrologically “closed”—that is, underlain by impermeable bedrock such that all water (excluding water vapor) leaving the catchment flows through the catchment outlet. In the absence of dramatic wind effects or of unbalanced large scale animal movements, closed catchments allow for the measurement of losses from the system in the form of chemical outputs in streamwater (Likens et al 1977, 1995). The determination of such a major component of watershed losses is a powerful tool in understanding the hydrochemical function of forested ecosystems.

Quite a number of well-integrated small catchment studies now exist, or have quite recently existed, around the world (e.g. see Andersson & Olsson 1985, Jeffries et al 1988, Hauhs 1989, Johnson & Van Hook 1989, Hornung et al 1990, Wheater et al 1990, Kirkby et al 1991, Baron 1992, Adams et al 1994, Seip et al 1995). Two of the earliest small catchment studies were the Coweeta Hydrological Laboratory (Swank & Crossley 1988b) and the Hubbard Brook Ecosystem Study (Likens et al 1977, 1995). These research sites continue to operate and to produce many important research findings.

COWEETA HYDROLOGICAL LABORATORY  The Coweeta Hydrologic Laboratory encompasses 2,185 hectares (ha) in the Nantahala Mountain Range of western North Carolina in the Blue Ridge Physiographic Province (Swank &
Crossley 1988b). The US Department of Agriculture–Forest Service (USFS) established the site in 1934 (Douglass & Hoover 1988) for the purpose of evaluating effects of forest practices on soil and water characteristics, with the major original emphasis being on stream flow and water balance. Workers at Coweeta began measuring precipitation there in 1934 and in the period 1936–1939 established six climatic stations. Stream gaging began on nine streams in 1934, and the number of streams being actively gaged has varied over the years (e.g. 28 in 1941, 16 by 1988) (Swift et al 1988). In 1968 Coweeta scientists began measuring stream chemistry, and by 1972 they had established much of the current system for long-term water chemistry measurements (Swank & Waide 1988). Monitoring of stream chemistry at Coweeta has been continuous since that time, varying on component tributaries depending on the nature of active projects. With the advent of paired water balance and chemical monitoring at Coweeta the researchers there opened the door to the first integrated hydrochemical research on southern Appalachian forest ecosystems. The hydrochemical monitoring at Coweeta, especially as performed on both reference and manipulated catchments and in concert with more detailed process-level research, has proven to be a powerful tool in observing and unraveling catchment behaviors (with particular emphasis on responses to disturbance) at the ecosystem level (Swank & Crossley 1988a,b).

HUBBARD BROOK EXPERIMENTAL FOREST In 1955 the USFS set aside a 3,037-ha watershed in the White Mountain National Forest in New Hampshire “as a major center for hydrologic research” (USDA Forest Service 1991). This site is the now well-known Hubbard Brook Experimental Forest. In the first eight years of work there, researchers developed a network of stream gages and precipitation and weather stations as well as sites for monitoring vegetation and soils on small experimental watersheds. The major emphasis in these first studies was on evaluating the effects of forest land management “on water yield and quality and flood flow” (USDA Forest Service 1991). Funding through a cooperative agreement between the USFS and Dartmouth College and from the National Science Foundation allowed the Hubbard Brook Ecosystem Study to begin in earnest in 1963 (USDA Forest Service 1991). A small staff at the site began measurements of precipitation chemistry in 1963–1964 and stream chemistry in 1964–1965 (Likens et al 1977, 1995). Thus was begun the first small watershed hydrochemical study of elemental cycling. Since this work began in the early 1960s, researchers at the Hubbard Brook have gathered a wealth of monitoring and site-intensive data (Veen et al 1994) and have published many research papers (Likens 1994) on the structure and function of this northeastern forested system. Integration of plot and site-specific intensive data with stream hydrochemical records at
Hubbard Brook continues to yield answers, offer clues, and prompt questions regarding ecosystem function (e.g. Likens et al 1996) that otherwise might elude us.

**Catchment Monitoring**

One of the most productive means of studying hydrochemistry of forested catchments is through a carefully organized and executed program of extended catchment monitoring. Especially useful is the joint monitoring of catchment inputs and outputs (ˇCern´y et al 1994). Monitoring is an important and useful tool (Likens 1988) for several reasons. Certainly it provides the best means “to formulate meaningful, testable hypotheses” (Likens 1983) about catchment behavior. Additionally, through the use of withheld data or split data sets, it provides ways to test hypotheses (e.g. using mathematical models; Cosby et al 1996). The obvious utility of the approach has led to the creation of numerous site-specific (e.g. seeˇCern´y et al 1995) and integrated (e.g. Johnson & Lindberg 1992, Newell 1993) programs of catchment monitoring and associated research.

A number of recent interesting examples of long-term hydrochemical monitoring leading to the formulation of hypotheses on catchment hydrochemical function come from, or involve, work at Hubbard Brook. For example, as a result of controls on pollutant emissions, the deposition of base cations to forested watersheds in certain parts of the world has decreased (Hedin et al 1994). Hubbard Brook lies in one such area (Likens & Bormann 1995). Driscoll et al (1989) examined monitoring data of precipitation inputs and streamwater outputs of chemical species at Hubbard Brook and noted that during the period 1964–1987, both inputs and outputs of base cations declined significantly. Although they noted that several mechanisms might be involved in causing the declines of base cations in outputs, they favored the hypothesis that decreases in inputs played a major role in causing decreased outputs—a hypothesis further emphasized by Hedin et al (1994), Likens & Bormann (1995), and Likens et al (1996). Dillon (1989), however, pointed out that the majority of the declines in base cations in deposition at Hubbard Brook occurred during the early period of the record, whereas the decreases in the base cation concentrations of the runoff water changed predominantly in the last part of the record, a circumstance seemingly not supportive of the Driscoll et al (1989) hypothesis. In addition, Holdren & Church (1989) noted that an existing hypothesis of watershed function (i.e. leaching associated with mobile acid anions; Galloway et al 1983, Reuss & Johnson 1986) also could explain the decrease in streamwater base cations, a hypothesis strongly supported by Kirchner & Lydersen (1995) in explaining their observations of base cation decreases in runoff from acidified Norwegian catchments.
Extending their analysis of nutrient cation loss at Hubbard Brook, Likens et al (1996) compared data sets of atmospheric deposition, streamwater chemistry, soil chemistry, vegetation chemistry, and forest growth and hypothesized that the decreased growth of forests observed at the site could be related to the loss of base cations (especially calcium) seen in streamwaters there. Whatever mechanism may dominate the loss of base cations from the soil exchange complex of this watershed (and likely others in the region), the effect is real and is of considerable importance to the quality of the receiving waters as well as to the forest of the catchment.

A second example of the use of long-term monitoring of catchment hydrochemistry in unraveling catchment function comes from the study of the phenomenon of watershed nitrogen saturation. Regardless of whether one favors the Aber et al (1989) definition of nitrogen saturation or that of Ågren & Bosatta (1988), concerns about environmental consequences are the same, namely that increased leaching of nitrogen from forested catchments may lead to increased acidification of upland surface waters or to eutrophication of either coastal estuaries (Hecky & Kilham 1988) or, more rarely, of fresh waters, where nitrogen is the limiting nutrient (see discussion by Stoddard 1994).

Driscoll & Van Dreason (1993) observed that from the period 1982–1991, 9 of 15 Adirondack drainage lakes studied in a regional monitoring project showed increases in nitrate concentrations, whereas none showed decreases. Murdoch & Stoddard (1992) analyzed surface water monitoring data from the Catskill Mountain region of New York state for varying time periods and found increasing nitrate concentrations from a number of sites, especially during the period from the early 1970s to 1990. Inasmuch as both regions receive elevated inputs of nitrogen from acidic deposition, the authors all speculated that decreased biotic demand within the terrestrial portions of the systems might be leading to the increased surface water nitrate concentrations—i.e., that the catchments were moving towards or experiencing nitrogen saturation.

Subsequent catchment hydrochemical monitoring in the region, however, has shown a more complicated and interesting effect. Driscoll et al (1995) reported that since 1991 there has been a notable decline in nitrate concentrations in Adirondack lakes such that there are now no significant trends in nitrate concentrations for these waters for the period 1982–1994.

Similarly, Mitchell et al (1996) found that nitrate losses from four forested catchments distributed across the northeastern United States declined markedly in the early 1990s (Figure 2). Losses of nitrate from Hubbard Brook Watershed 6 (New Hampshire), East Bear Brook Watershed (Maine), Arbutus Watershed in the Adirondack Mountains (New York), and Biscuit Brook in the Catskill Mountains (New York) were notably high during the spring snowmelt of 1990. Following this period of high loss of nitrate from the catchments, loss rates de-
Figure 2  Streamwater concentrations (monthly average) of nitrate in four forested northeastern catchments before and after a period of unusual cold and soil freezing. Reprinted from Mitchell et al (1996), by permission of the American Chemical Society.
creased substantially, leading to a reversal of increases from the preceding years. The high losses of spring 1990 seemed to be associated with an extremely cold and dry period in the preceding winter. A severe cold period in December 1989 combined with lack of snow cover most likely led to substantial freezing of soils across the region (Mitchell et al 1996). Boutin & Robitaille (1995) showed that soil freezing induced by removal of snow from the ground in mature stands of sugar maple in Quebec induced high leaching losses of nitrogen (as nitrate). Mitchell et al (1996) hypothesize that the combination of deep freezing of soils in the four catchments they studied followed by wet conditions that facilitated loss in runoff served to remove labile nitrogen from the watersheds. They also noted that high nitrate concentrations were observed in streamwaters at Hubbard Brook following periods of soil freezing during the winters of 1969–1970 and 1973–1974 (Likens & Bormann 1995). Likens (1992) had previously noted the capacitance-like pattern of nitrogen storage and periodic loss at Hubbard Brook and had wondered whether this pattern indicated an important role in the effects of changing atmospheric inputs of nitrogen in that the trends in inputs and outputs seemed roughly to parallel each other.

The analysis and hypothesis formulations illustrated above could not have been undertaken without the critical baseline information provided by careful long-term monitoring of catchments. The resolution of the operant mechanisms and their quantification undoubtedly will be tied to continued monitoring studies.

Hydrochemical monitoring of catchments sheds light on catchment function not only over the long term (e.g., years) but also over shorter term intervals. For example, the importance or even dominance of a variety of biogeochemical functions or reactions wax and wane over the course of a year as inputs of heat, energy, and moisture vary through their annual cycles. One very interesting example is that of the annual cycling of nitrogen in forested catchments. During annual growing periods, uptake of available nitrogen by vegetation may result in very little nitrogen leaching from catchment soils to surface waters. During annual periods of vegetation dormancy, however, surface water concentrations of nitrogen (usually in the form of nitrate) often increase (Stoddard 1994), sometimes quite dramatically. Long-term changes in the status of catchment nitrogen cycling (e.g., as affected by maturation of forests or elevated inputs from atmospheric deposition) may also be reflected not only in long-term monitoring data (Kahl et al 1993, Mitchell et al 1996, Norton et al 1994) but also in observations of qualitative and quantitative changes in seasonal patterns of streamwater concentrations (Stoddard 1994) (Figure 3).

At even shorter time scales, relatively abrupt changes (i.e., hours to days) in watershed leaching and consequent stream chemistry may be caused by the effects of snowmelts or heavy rainstorms (Wigington et al 1990, 1996a). Patterns
Figure 3  Top panels are schematic representations of nitrogen cycle in watershed at progressive stages of watershed nitrogen loss. Sizes of arrows indicate the magnitude of process or transformation. Differences between winter-spring and summer-fall seasons are shown on opposite sides. (a) STAGE 0 of watershed nitrogen loss. (Top panel) At Stage 0, nitrogen transformations are dominated by plant and microbial assimilation (uptake), with little or no NO$_3^-$ leakage from the watershed during the growing season. (Bottom panel) Small amounts of NO$_3^-$ may run off during snowmelt, producing the typical Stage 0 seasonal NO$_3^-$ pattern. Data in lower panel are from Black Pond, Adirondack Mountains. Reprinted from Stoddard (1994), by permission of the American Chemical Society.
Figure 3  (b) STAGE 1 of watershed nitrogen loss. (Top panel) As in Stage 0, uptake dominates the nitrogen cycle during the growing season at Stage 1 and little or no NO$_3^-$ leaks from the watershed during the summer and fall. The primary difference between Stage 0 and Stage 1 is the delay in the onset of N limitation during the spring season. (Bottom panel) Large runoff events (e.g. snowmelt or rainstorms) during the dormant season can produce episodic pulses of high NO$_3^-$ concentrations, as shown in the typical Stage 1 seasonal NO$_3^-$ cycle. Data in bottom panel are from Constable Pond in the Adirondack Mountains. Reprinted from Stoddard (1994), by permission of the American Chemical Society.
Figure 3  (c) STAGE 2 of watershed nitrogen loss. (Top panel) Uptake of nitrogen by forest plants and microbes is much reduced at Stage 2, resulting in loss of NO$_3^-$ to streams during winter and spring and to groundwater during the growing season. Loss of gaseous forms of nitrogen through denitrification may also be elevated at Stage 2 if conditions necessary for denitrification are present. Although episodes of higher NO$_3^-$ concentrations continue to occur during high-flow events such as spring snowmelt, the primary difference between Stage 1 and Stage 2 is the presence of elevated NO$_3^-$ concentrations in groundwater. (Bottom panel) The typical seasonal NO$_3^-$ pattern at Stage 2 includes both high episodic concentrations and high base-flow concentrations. Data in bottom panel are from Fernow Experimental Forest, Control Watershed No. 4, West Virginia. Reprinted from Stoddard (1994), by permission of the American Chemical Society.
Figure 3  (d) STAGE 3 of watershed nitrogen loss. (Top panel) At Stage 3, no sinks for nitrogen exist in the watershed and all inputs, as well as mineralized nitrogen, are lost from the system either through denitrification or in runoff water. Because mineralization supplies nitrogen in excess of deposition, concentrations of NO$_3^-$ in runoff may exceed those in deposition. (Bottom panel) Typical seasonal NO$_3^-$ pattern at Stage 3 includes concentrations at all seasons in excess of concentrations attributable to deposition and evapotranspiration. Data are from Dicke Bramke in Germany and revised from Stoddard (1994) (JL Stoddard, personal communication). Reprinted from Stoddard (1994), by permission of the American Chemical Society.
in the ionic chemistry during such hydrologically driven episodes also can shed light on both processes and flow paths that control catchment hydrochemical function and response (Wigington et al 1996b).

Monitoring across a variety of time scales undoubtedly will continue to provide critical information for both the qualitative and quantitative understanding of how forested catchments operate.

**Catchment Manipulations**

Researchers in the earth sciences often link effect to cause first through observation. Direct experimental manipulation is, of course, the most direct route to hypothesis formation and testing. The more complicated the system under investigation, the more difficult it is to reach correct interpretations. Forested catchments (no matter how small) are still large, complex natural systems. Although manipulation of such systems is difficult physically and interpretation of results challenging intellectually, such efforts can be very rewarding.

The earliest hydrochemical studies of catchment manipulations were those of the effects of tree removal (e.g. Likens et al 1977, Swank & Crossley 1988a). More recently, researchers have experimented with chemical manipulations to forested catchments (Adams et al 1993, Rasmussen & Farrell 1994, Wright & Tietema 1995) with interesting and important results. As an example, an interesting paired-catchment manipulation has occurred as part of the Bear Brook Watershed Manipulation (BBWM) Project in Maine (Thornton & Wigington 1990).

The purpose of this project has been to investigate, using chemical manipulations, the response of whole terrestrial ecosystems to increased loading of acidic or acidifying substances. The project has included a wide range of activities. Process research there (laboratory and plot studies) has focused on better understanding the biogeochemistry of aluminum, sulfur, nitrogen, and dissolved organic carbon. Investigators there also have studied controls on cation supply by the mechanisms of chemical weathering and cation exchange.

The focus of the work, however, has been the manipulation of one of a pair of contiguous small (~10 ha) catchments with the second of the pair serving as a reference site (Kahl et al 1993, Norton et al 1994). The paired catchments for the BBWM are East Bear Brook (reference) and West Bear Brook (experimental). These catchments have flows and hydrologic behaviors that are highly similar. Researchers began monitoring of the catchments in early 1987 and began chemical manipulation of West Bear Brook in November 1989. Before manipulation, the chemical compositions of the two streams were remarkably close across all stages of flow. Consequently, chemical budgets for the two watersheds were very similar.
Manipulations of the West Bear Brook catchment have consisted of additions of dry ammonium sulfate (with distinct isotopic signatures for both sulfur and nitrogen) applied bimonthly at a rate of 1,800 equivalents per ha per year. The additions have tripled the annual catchment loading of sulfur and have quadrupled the annual loading of nitrogen. In response, stream concentrations and watershed fluxes of hydrogen ions, calcium, magnesium, sodium, potassium, sulfate, nitrate, and aluminum have increased relative to the control (Figure 4), while acid neutralizing capacity has declined and chloride has remained nearly unchanged. After six years of manipulation, average annual sulfate concentration of West Bear Brook increased from about 100 microequivalents per liter to about 190 microequivalents per liter (expected steady state sulfate is about 300 microequivalents per liter). Concentrations of nitrate have also increased markedly. Total nitrogen output from West Bear Brook more than doubled, due mainly to large increases in the flux of nitrate. Stream nitrate concentrations in West Bear Brook have increased markedly not only during fall and winter when vegetation is dormant but also during the summer growing season. This indicates that leaching of nitrogen to deeper soil horizons and to flow paths that dominate summer base flow may be occurring (Kahl et al 1993, Norton et al 1994).

The responses of West Bear Brook explicitly demonstrate that increases in atmospheric inputs can have dramatic (and rapid) effects on stream chemical response. Furthermore, they provide corroborative evidence that such changes are occurring in a manner consistent with prevalent theory (e.g. Turner et al 1990) and with simulations from models based on such theory (Cosby et al 1996). This work puts us in a better observational and theoretical position both to understand the ways in which acidic deposition affects catchment hydrochemistry and to develop predictive models to postulate potential future effects.

**Modeling Catchment Hydrochemical Response**

Modeling the response of any system to variations in its environment is an excellent way to learn more about it or, more often, more about our lack of understanding of the way it operates. The more complex the system, the more difficult the modeling. At any given moment, there exist myriad pathways that water can follow within a forested catchment and an astonishing variety of biogeochemical interactions that can influence that composition of that water. When one considers that the pathways and biogeochemical influences can change at time scales as short as minutes to hours (e.g. during rainstorm events), the task becomes even more daunting. Add to this the desire of resource managers to use models to predict the influence of external pollutants (e.g. acidic deposition) at times often years to decades in the future, and challenges become formidable. In the last decade, however, more and more researchers...
CHURCH

- West Bear Brook
- East Bear Brook

Nitrate (μeq/l)

- West Bear Brook
- East Bear Brook

Sulfate (μeq/l)

- West Bear Brook
- East Bear Brook

Calcium (μeq/l)

- West Bear Brook
- East Bear Brook

Aluminum (μmol/l)

Date

manipulation begins November, 1989
and modelers have accepted the various challenges of modeling catchment hydrochemistry.

As with catchment studies themselves, modeling of catchment function began with hydrological topics, e.g. flow generation. With the influx of large amounts of research funding dedicated to the tasks of understanding and predicting effects of acidic deposition, the conflation of models of flow with soil profile geochemical models began in earnest. The result has been a generation of models of whole-catchment hydrochemical response (see review by Ball & Trudgill 1995). A cursory comparison of review coverage of the topic of solute modeling by Trudgill (1986, 1995) ably demonstrates the explosion of catchment hydrochemical modeling that has occurred over the past decade. Often these models have built upon recent or co-developing catchment flow generation models (e.g. TOPMODEL; Beven & Kirkby 1979, Hornberger et al 1985).

Of the numerous catchment hydrochemical models that have come into being in the last 10–15 years, several deserve mention either because of their seminal importance in the field or because of their continuing application or evolution. These models include the Birkenes model (Christophersen et al 1982), the Integrated Lake/Watershed Acidification (ILWAS) model (Chen et al 1983, Gherini et al 1985), the Trickle-Down (Schnoor et al 1984) and Extended Trickle-Down models (Nikolaidis et al 1991), and the Model of Acidification of Groundwater in Catchments (MAGIC) (Cosby et al 1985a,b).

Early models focus on watershed acidification mediated by sulfur deposition (e.g. Cosby et al 1985a). More recent model development efforts are working to incorporate nitrogen cycling into process representations (Liu et al 1992, Postek et al 1995; JD Aber, BJ Cosby, personal communications). The complexity of the biologically dominated nitrogen cycle greatly complicates this task.

Linking and applying hydrologic and biogeochemical models at catchment scales requires ingenuity. An interesting and useful aid in such modeling has been a technique called end-member mixing analysis (EMMA) (Neal & Christophersen 1989, Christophersen et al 1990, Hooper et al 1990). Instead of applying hydrologic models with knowledge of catchment chemical and biological properties to infer resulting stream chemistry, EMMA approaches the task of understanding catchment hydrochemical response in an apparent inverse,
yet more intuitive, manner. With EMMA one uses the observed chemistry of runoff to help determine prior flow paths of the water. This can be accomplished because different soil horizons often have very different chemical properties. Thus water flowing from upper horizons can be very different in chemical composition than water flowing from lower horizons. If one has concurrent measurements of chemical species in streamwater as well as from soil waters of several potentially contributing horizons, one may then use least-squares procedures to solve for the relative contributions from each of the sources—the end members. Principal necessary assumptions are that the composition of end members is constant in space and time over the applicable time period of the applied analysis, that the chemical species mix conservatively (i.e. in a nonreactive manner), and that sufficient differences exist in the composition of end members to make the analysis feasible. Hooper & Christophersen (1992) have used EMMA to provide flow routing for the application of MAGIC to the prediction of both average annual stream chemistry and episodic chemistry for a well-studied catchment in the southeastern United States.

One of the most difficult conceptual and practical problems facing modelers of catchment hydrochemical response is that of scaling. That is, how does one reconcile the huge variety and variability (in space and time) of fine-scale measures of catchment properties to the relatively gross lumping required for realistic application of physically based simulation models? Hydrologic modelers have faced this problem for some time (Beven 1989, Grayson et al 1992, Hornberger & Boyer 1995). The advent of catchment hydrochemical modeling and the attendant desire to reconcile measures of catchment chemical and biological properties (sometimes at many points in space and time) with possible flow paths and stream hydrochemical response have made the problem even more vexing (Christophersen et al 1993, Wheater et al 1993, Ball & Trudgill 1995). If one feels overwhelmed by the variability in natural systems or has difficulty reconciling current measures (e.g. soil water chemistry) within a catchment to observed stream composition, how can one ever hope to model future catchment response to changes in inputs accurately?

On the analytical front there is the possibility that empirical approaches may offer real hope for predictive uses in some carefully defined instances amid an abundance of environmental noise (e.g. see Christophersen et al 1993, Gauch 1993, Kirchner et al 1993a,b). More philosophically, a resolution perhaps lies in the realization that every tool has its appropriate uses and its limitations. The use of physically based watershed simulation models as heuristic tools to understand how catchments function thrives on the availability of data for testing for model invalidation. Such efforts should proceed at every opportunity. On the other hand, there is often a need for application of models for
predictive purposes within a management context, especially at regional scales (e.g. Church et al 1989, 1992, Thornton et al 1990, Van Sickle & Church 1995). Such applications require data aggregation at a variety of scales, and thus introduce substantial additional uncertainty into a task already replete with uncertainty. An appropriate use of models in this context is to serve in the role of “scenario testers,” e.g. “if all other factors (climate, land use, etc) remained unchanged (a condition a priori known to be unrealistic), what might be the relative effects of an increase or decrease in levels of acidic deposition on surface water quality in 50 years?” Such applications require that modelers convey to resource managers the uncertainties (quantifiably large, qualitatively huge) associated with such scenario tests and the caution that the projections, although they may seem consistent with other lines of evidence (latest conceptual theory, trends analyses, etc), cannot be validated as “truth” (Oreskes et al 1994). Currently they must remain hypotheses at best.

Modeling of the hydrochemical response of forested catchments is a field of inquiry confronted by numerous interesting and difficult questions. It will benefit from continued and iterative efforts at model development, model application, and model testing (e.g. against whole catchment manipulations; Cosby et al 1996). Continued efforts spanning spatial scales from plots to regions are needed to move the endeavor forward. Much exciting work remains to be done.

EXTRAPOLATION OF WATERSHED HYDROCHEMICAL RESPONSE

Site Representativeness

Often the intent of studying the hydrochemistry of an individual catchment is to learn about not only its function or response to a perturbation (e.g. acidic deposition), but also about the behavior of other similar catchments under the same or changing conditions. A key question that investigators often ask themselves is, “Although my catchment appears similar to others that have been studied (or to which I would like to extrapolate my findings), how similar are they really?” That is, how representative is it of others around it or perhaps, far removed (either in space or time) (Berkowitz et al 1988)? This can be a difficult thing to know. Researchers must consider a variety of factors including bedrock and surficial geology, soil development, vegetation type and age, climate, and other effects. Site history, for example, can be important. Watersheds that are now forested may previously have been burned, timbered, or farmed. Such activities can have lasting effects, for example, on catchment hydrochemical response regarding nitrogen cycling (JD Aber, JE Compton, unpublished data) as well as on other functions (Likens et al 1977, 1995, Swank & Crossley 1988a).
Statistical Sampling

Extrapolation of observations made at fine scales to coarser scales is a very challenging task (Rastetter et al 1992). One quantitative approach to the problem is to use a specified statistical approach to select catchments for study (or sampling) such that each is quantitatively representative of a larger target population of interest. Such an approach has been used in a few large research and assessment programs (e.g. Linthurst et al 1986, Kaufmann et al 1988, Church et al 1992, Stevens 1994) as well as in modeling studies based on sampling within such programs (Van Sickle & Church 1995). Such sampling and analysis programs are large, time consuming, expensive activities. Catchment sampling, and thus process-level understanding, in such programs can never be at the level attained in longer-term fully integrated studies (e.g. Hubbard Brook), but that often is not the intent of the larger sampling efforts. The coarser-scale sampling often is a key component of assessment activities focused on regional-scale adverse environmental effects (e.g. acidic deposition effects) on forested catchments. Its spatial nature is required to attack regional-scale questions, and its quantitative nature is useful in the arena of public policy where effects of real (or alleged) individual site bias may be of concern. Regional statistical sampling can be a very useful complement to finer-scale catchment studies in understanding and predicting catchment hydrochemical response.

Development of a Catchment Taxonomy

There may be other ways to attack the problems of determining site representativeness and the appropriate extrapolation of site-specific data. One of the principal conclusions to come from the American Geophysical Union Chapman Conference on Hydrogeochemical Responses of Forested Catchments (Church et al 1990) convened in the Fall of 1989 was that integrated watershed research, indeed, is hampered by a lack of a structured and efficient means of communication of results among studies. Researchers at one watershed, for example, may know quite a lot about how water moves through their system and how it interacts geochemically with their particular rocks and soils. Researchers at another watershed also may have the same kind of knowledge on their local scale. These researchers have difficulty, however, communicating their results accurately and efficiently with one another within an organized relevant context. This is because there is lack of a general uniform scheme or organizational structure for the portrayal of results of watershed studies and experiments.

Something that would be a great aid to watershed researchers would be the development of a taxonomic scheme for watersheds based upon not just catchment characteristics (e.g. aspect or percentage of conifer coverage), but also on catchment hydrochemical function (e.g. whether the system exhibits nitrogen
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saturation; Stoddard 1994). Such a catchment taxonomy would aid researchers by organizing site-specific knowledge on catchment hydrochemistry into a uniform structure related to a general paradigm designed to address watershed function.

With such a taxonomy and with a compendium of catchments placed within it, researchers for a particular watershed could investigate where their watershed might be classified within the scheme and they could relate results of their specific experiments to experiments performed by researchers at other (perhaps quite distant) sites. If the researchers at different sites had similar types of watersheds (based on the taxonomy) and observed similar results from similar experiments, then this would serve to corroborate their conclusions. If the researchers had drawn different conclusions from the similar results, the use of the taxonomy could lead to profitable discussions as to why. Similarly, if researchers observed different responses in watersheds presumed to be similar within the taxonomy, this would also call for reevaluation.

In addition to assisting in analyzing existing data, such a taxonomy also could aid in organizing experiments yet to be performed. Researchers could benefit by knowing what watersheds are similar or dissimilar (in structure and function) to theirs and thus could contact other researchers directly to discuss more efficiently the pros and cons of potential experiments. Results of observations and experiments past and present would lead to constant evaluation of the experiments, the watersheds, and the taxonomy. Such an open perspective would lead to iterative improvement in both the taxonomy and, more importantly, in the understanding of catchment hydrochemical function.

RECENT TRENDS AND FUTURE OF WATERSHED HYDROCHEMICAL RESEARCH

Attacking the complex environmental problem of effects of acidic deposition on soils and surface waters has called for investigation of forest watershed systems in an integrated fashion. Over the past 15 or so years, the intense (and highly funded) study of the environmental effects of acidic deposition has led hydrologists, geochemists, and biologists to work together better to integrate their studies and to think of catchments as integrated units (e.g. Church et al 1990, Neal & Hornung 1990). Consequently, a generation of watershed scientists has come to appreciate the value of working as part of a multidisciplinary team.

Although major questions related to the effects of atmospheric deposition of nitrogen remain, the heavily funded days of acid rain research are over, and funding of fully integrated studies of catchment hydrochemistry has decreased dramatically. This comes at a time when many studies had established
a strong groundwork of specific site knowledge, research capabilities, and, just as important, project infrastructure to tackle additional challenges regarding the workings of forested catchments. Thus, numerous studies have been disrupted or dismembered. Baseline monitoring programs eventually will indicate the need to better understand catchment processes and their interconnections (Likens 1983). When funding returns for whole-watershed hydrochemical studies there will be a great inefficiency in reestablishing work at prior research sites. Hopefully, key site data and institutional memory will not be lost. More effective than such an oscillation of research driven by legislative or programmatic priorities would be a more stable long-term combination of monitoring and site-specific research. The current structure of agencies that fund such research and of the laws that govern the mechanisms by which such research can be funded, however, present a formidable barrier to achieving that goal.

What specifically the near-term future holds for integrated research in forested catchments is unclear. The long-term future, however, is bright and exciting. Regardless of whether it comes through “fits and starts” or whether through a more smoothly functioning continuation of established research sites and teams, research on the hydrochemistry of forested catchments will continue to be a fascinating field. Recent advances, combined with a new and keener perspective of catchments as integrated wholes, promise to make future work more productive and stimulating than ever.

CLOSING THOUGHT

“There are men charged with the duty of examining the construction of the plants, animals, and soils which are the instruments of the great orchestra. These men are called professors. Each selects one instrument and spends his life taking it apart and describing its strings and sounding boards. This process of dismemberment is called research. The place for dismemberment is called a university.

A professor may pluck the strings of his own instrument, but never that of another, and if he listens for music he must never admit it to his fellows or to his students. For all are restrained by an ironbound taboo which decrees that the construction of instruments is the domain of science, while the detection of harmony is the domain of poets.” Aldo Leopold, Song of the Gavilan [Reprinted in part from Leopold (1940), by permission of The Wildlife Society.]

Aldo Leopold wryly yet eloquently argues the case for holistic approaches in the natural sciences. Multidisciplinary studies promise to help us better to understand and comprehend catchment hydrochemical function. Such approaches will yield answers to our questions of today and will provide us with more (and ever more challenging) questions for tomorrow. Day by day we detect more of the harmony of the “great orchestra.” There is much to anticipate.
SUGGESTED READING/SOURCES OF INFORMATION

There exist a number of excellent sources of information on hydrochemistry of forested catchments.

The following journals routinely carry research and review articles in the topical area and sometimes devote entire volumes to the topic.

*Biogeochemistry* (Kluwer Academic)

*Ecological Applications* (Ecological Society of America)

*Global Biogeochemical Cycles* (American Geophysical Union)

*Hydrological Processes* (John Wiley & Sons)

*Journal of Environmental Quality* (American Society of Agronomy, Crop Science Society of America)

*Journal of Hydrology* (Elsevier Science), e.g. see Special Issue “Transfer of Elements Through the Hydrological Cycle.” 1990. vol. 116

*The Science of the Total Environment* (Elsevier Science)

*Water, Air & Soil Pollution* (Kluwer Academic), e.g. see special issue devoted to the conference “Acid Reign ’95” 1996. vol. 85 nos. 1&2


*Water Resources Research* (American Geophysical Union), e.g. see special section “Catchment Hydrochemistry.” 1990. vol. 26:2947–3100

A number of professional societies and organizations hold annual meetings or special conferences that either contain special symposia on or are in some cases devoted entirely to, hydrochemical studies. The Fall and Spring Annual Meetings of the American Geophysical Union (AGU), for example, often contain special sessions dealing with topics in hydrochemistry. The AGU also sponsors special Chapman conferences in the field (e.g. *Hydrogeochemical Responses of Forested Catchments* held September 1989 and *Nitrogen Cycling in Forested Watersheds* held September 1996). Since July 1991 the Gordon Research Conferences also have sponsored a week-long Gordon Conference *Hydrological-Geochemical-Biological Processes in Forested Catchments* every other year.

Information relevant to hydrochemistry of forested catchments is becoming available on the World Wide Web. The following addresses may be particularly useful to students of the topic.

American Geophysical Union—http://earth.agu.org/kosmos/homepage.html

Coweeta Hydrological Laboratory—http://oikos.ecology.uga.edu/


Hubbard Brook Ecosystem Study—http://www.yale.edu/edex/index2.html

National Science Foundation Long-Term Ecological Research—

http://lternet.edu/
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