12 Hydrochemical Studies

NILS CHRISTOPHERSEN, THOMAS A. CLAIR,
CHARLES T. DRISCOLL, DEAN S. JEFFRIES,
COLIN NEAL AND RAYMOND G. SEMKIN

12.1 INTRODUCTION

In the present chapter, we define hydrochemical catchment studies as investigations focusing on the chemical composition of the runoff and the processes in the terrestrial and aquatic environments controlling this composition. The hydrochemical response represents an integration of hydrological, chemical, physical and biological reactions within catchment ecosystems. Of specific interest are the changes in hydrochemistry caused by anthropogenic factors, such as acidic deposition, land-use changes and climatic change. Small catchments may serve as early warning systems of ecological change because they are located at the headwaters or uplands of larger drainage areas; they are physically well-defined allowing for the construction of accurate element balances and are sensitive to disturbances.

Most research on small catchments to date has been conducted in Western Europe and North America. This is particularly true for hydrochemistry, where the impact of acidic deposition has spurred many studies. During the SCOPE Workshop in Most, Czechoslovakia, in 1990 several examples of hydrochemical investigations from other areas were also presented.

In this chapter, examples of hydrochemical studies from established catchments in Canada, Norway, the United Kingdom and the USA are used. They provide case studies of how intensive hydrochemical investigations can be used to study important aspects of the interplay between the terrestrial and aquatic environments. First, data on carbon cycling and dissolved organic carbon (DOC) are presented for the Hubbard Brook Experimental Forest (HBEF) in New Hampshire, USA, and two sites in Nova Scotia, Canada. The carbon cycle is important both from the standpoint of water quality and within the larger framework of global change. Second, the issue of episodic acidification of streams is considered with examples from the Turkey Lake catchment in Canada, Birkenes and Ingabekken in Norway, and Plynlimon in mid-Wales, UK. Finally, the application of mathematical models is discussed. Models provide an important tool for integrating the various short- and long-term processes controlling streamwater chemistry.

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12.2 CARBON CYCLING AND DOC

Organic carbon forms the basis for many of the most abundant chemical components in nature. Widespread transfer of carbon from organic to inorganic pools, from fossil fuel combustion and/or changes in land-use, may result in increased production of atmospheric CO_2. Small catchments are well suited to study carbon budgets and carbon cycling. An example is provided by the Hubbard Brook Ecosystem study, in the White Mountains of New Hampshire, USA.

Of particular hydrochemical importance is dissolved organic carbon (DOC). It often plays a major role in determining the acid–base and metal complexation characteristics of soil water and streamwater. An example given in this chapter is from Nova Scotia where coloured water is abundant due to large areas of peatlands.

12.2.1 CARBON BUDGET FOR HUBBARD BROOK

A detailed carbon budget has been developed for Hubbard Brook (Figure 12.1). Data for the budget were obtained from several process-level studies (Gosz *et al.*, 1976; McDowell and Likens 1988; Lawrence *et al.*, 1986; Driscoll *et al.*, 1988; Johnson *et al.*, 1991) and are compiled here. This budget includes pools and transfers of both organic and inorganic carbon.

Carbon pools (304 000 kg C ha^{-1}) for this northern hardwood forest are virtually entirely organic in nature. These include plant biomass (146 000 kg C ha^{-1}; 48%), the forest floor (22 800 kg C ha^{-1}; 7.5%) and the mineral soil (135 000 kg C ha^{-1}; 44%). The estimated turnover time of organic carbon in these pools is quite different; ranging from 9 years for the forest floor to 23 years for forest vegetation to 675 years for mineral soil carbon.

Gaseous fluxes of CO_2 are particularly important, including fixation of CO_2 by plant biomass (7180 kg C ha^{-1} $year^{-1}$) and release of CO_2 by soil organic matter and root respiration (6000 kmol C ha^{-1} $year^{-1}$). Note that this latter flux is highly uncertain due to limited measurements and high variability (Yavitt 1991, unpubl. data, Dept. of Natural Resources, Cornell University, Ithaca, NY, USA). The major transfers of organic carbon include accumulation of biomass (3600 kg C ha^{-1} $year^{-1}$), accumulation of soil organic matter (200 kg C ha^{-1} $year^{-1}$, discussed below), root litter (960 kg C ha^{-1} $year^{-1}$ and litterfall (2570 kg C ha^{-1} $year^{-1}$). The distribution of litterfall includes perennial tissue (38%), deciduous tissue (60%) as well as shrub and herbaceous material (2%) (Gosz *et al.*, 1972). The forest floor appears to be at steady state with respect to organic carbon.

Water fluxes of carbon occur largely as organic carbon. Concentrations of dissolved organic carbon (DOC) and inorganic carbon (DIC) are low in precipitation. It is interesting to note that the input of DOC to the ecosystem is essentially equal to the output, despite large pools and transfers of carbon within the ecosystem (Figure 12.1). Patterns of DOC in soil water are intriguing at the HBEF. A large drainage flux of DOC is evidently originating from the forest floor (217 kg C ha^{-1} $year^{-1}$).

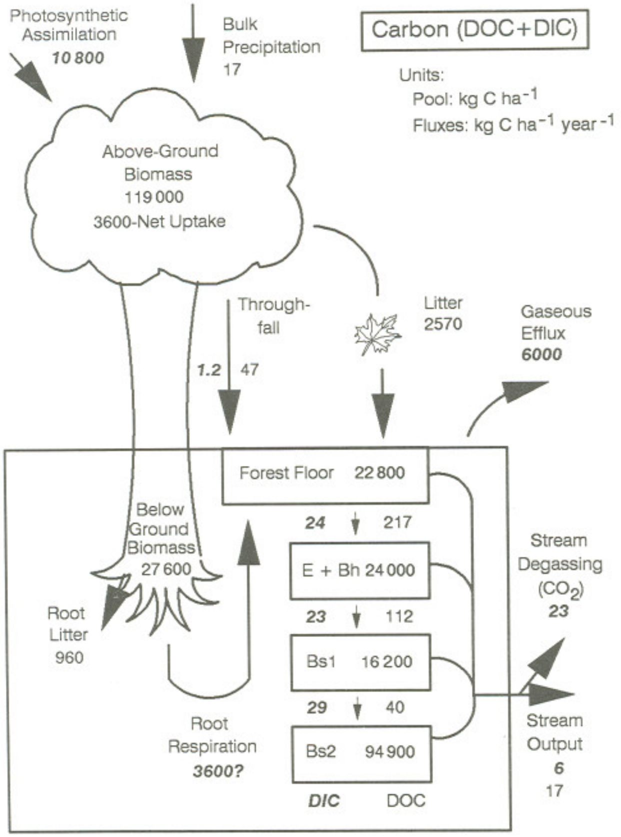

Figure 12.1 Detailed carbon budget for the biogeochemical reference watershed (W 6) at the Hubbard Brook Experimental Forest, NH. Only organic carbon pools are significant. Fluxes of organic and inorganic (in italic) carbon are shown. This budget was developed from individual studies done over different periods, but generally for 1984–88).

This carbon flux diminishes through the mineral soil and glacial till. The fate of this carbon is uncertain.

Laboratory experiments and soil analysis suggest that it is largely retained in the mineral soil by sorption reaction with sesquioxides (McDowell and Wood 1984; Driscoll *et al.*, 1985; Nodvin *et al.*, 1986). It is not clear how much carbon is oxidized and lost as CO_2. As an upper limit calculation, if all the DOC removed from soil water is retained as organic carbon in the mineral soil, the rate of carbon accumulation would be 630 kg C ha^{-1} year^{-1}. If this value compares to the rate of organic carbon accumulation since glaciation (135 000 kg C ha^{-1} year^{-1}/14 000 years = 9 kg C ha^{-1} year^{-1}), clearly the current rate of organic carbon accumulation exceeds the historical rate. This pattern suggests that either more than 95% of the organic carbon removed from soil water is oxidized or the current rate of carbon accumulation is greater than the historical rate, or both. Schlesinger (1990) summarized rates of organic carbon accumulation for mineral soil and concluded that the mineral soil was at steady state with respect to organic carbon and therefore not a significant sink within the global carbon budget. It is interesting that the historical rate of carbon accumulation for Hubbard Brook is somewhat lower than the world average (2417 kg C ha^{-1} $year^{-1}$). However, the current rate (630 kg C ha^{-1} $year^{-1}$) is much greater than any values reported. Clearly there is considerable uncertainty in terrestrial carbon budgets and more information is needed on a range of ecosystems to represent accurately the global budget.

12.2.2 DISSOLVED ORGANIC CARBON AT TWO SITES IN NOVA SCOTIA

In many hydrochemistry studies, discrepancies in ion balance are used to estimate concentrations of organic anions in water and to assess indirectly DOC reactivity in solution. Direct estimate of DOC fractions now permits a better understanding of DOC chemistry. These techniques allow for more detailed characterization of acid–base and metal complexation reactions of DOC, and also allow for understanding of the overall watershed processes important in carbon cycling.

Two Nova Scotia streams, the Mersey River (basin area 297 km^2) and Moose Pit Brook (16.7 km^2) were studied; both sites are poorly drained, and over one-quarter of the Moose Pit Brook surface area is covered by *Sphagnum* bogs. The most detailed DOC studies were performed on 250 l samples collected in mid-January, mid-March, late April, mid-June and mid-November 1989. These samples were concentrated using reverse osmosis (RO) with a 200 molecular weight cut-off (Clair *et al.*, 1991). Sampling times were representative of specific flow conditions known to occur in the region. Quality control showed that more than 96% of all carbon was retained by the membrane, and that the fraction lost in the filtrate was composed mostly of small molecules, containing carboxylic acid and neutral functional groups.

The RO concentrate was freeze-dried to produce a powder, which was analysed using cross polarization/magic angle spin ^{13}C nuclear magnetic resonance (CP/MAS ^{13}C nmr). This analysis produces a spectrum giving the relative proportions of carbon in different types of structures in the organic carbon molecule (Wershaw, 1985). Carbon was then apportioned into unsubstituted and substituted aliphatic, aromatic, phenolic carboxylic, and carbonyl fractions.

The 1989 water export from the basins was typical for the sites, with high water discharge occurring in the winter and spring and low values in the summer, increasing again in the late autumn. The results show that the per cent composition of the less labile aromatic fraction of the DOC over a typical one-year period ranged from 13.7 to 21% in the Mersey River, and between 15.8 and 24.2% in Moose Pit Brook. This means that freshwater DOC is more labile and therefore more reactive than is usually thought (Schnitzer and Khan, 1972; Stevenson, 1985). The data also show that DOC becomes less labile over the course of the year, with the unsubstituted aliphatic fraction decreasing from the winter into the summer, while the structurally more complex substituted aliphatic and aromatic carbons increase over this period. This pattern was consistent at both stream sites, as well as in bog waters and in a lake which was sampled, too.

Assuming that the DOC originating in the terrestrial environment is more aromatic than in stream-generated DOC, we hypothesize that aromatic fractions resulting from decomposition of plant matter are retained by the soil matrix which allows more of the aliphatic fraction to be transported through the soil profile. It is the aliphatic fraction, containing carboxylic acids, which provides acidity, acid buffering and metal complexation sites which complicate the interpretation of freshwater chemistry data.

12.3 EPISODIC CHANGES IN STREAMWATER CHEMISTRY

12.3.1 CASE STUDIES

Episodic changes in streamwater chemistry are often pronounced with the high H^+ and high concentrations of toxic Al occurring at high flow in acidified streams. Examples drawn from the Birkenes and Ingabekken catchments in Norway

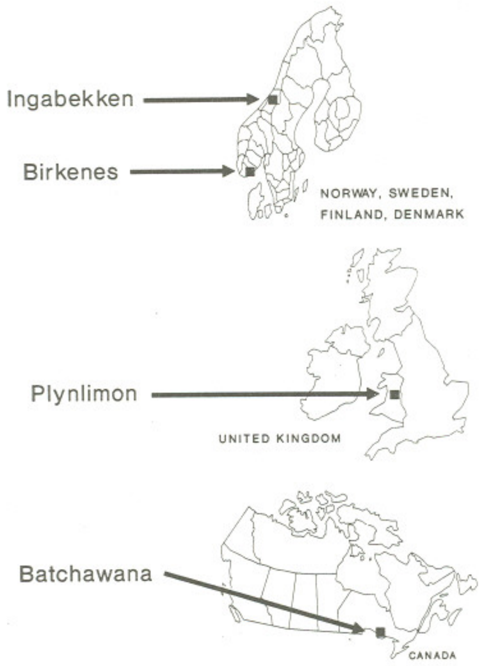

Figure 12.2 Map showing the locations of the sites for which episodic changes in streamwater chemistry are given.

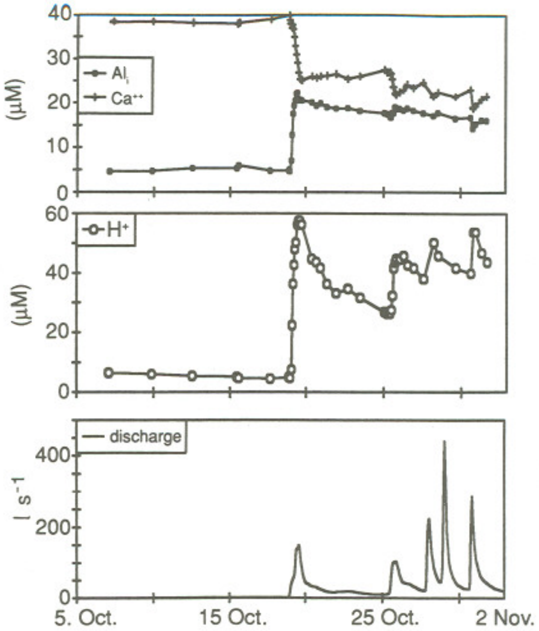

Figure 12.3 Episodic changes in streamwater chemistry at the Birkenes catchment, autumn 1986 (Christophersen *et al.*, 1990; reproduced by permission of Cambridge University Press).

(Christophersen *et al.*, 1990a,b), Plynlimon in Wales (Neal *et al.*, 1989, 1990a,b), and Batchawana Lake in the Turkey Lakes Watershed in Canada (Jeffries *et al.*, 1988) will be used as illustrations (Figure 12.2). These studies represent diverse environments and together illustrate the behaviour found in temperate areas over a range of acidic deposition.

The Birkenes catchment is a forested site (41 ha) on granitic bedrock located in southern Norway. Atmospheric inputs of SO_4 are about 6 g m^{-2} year^{-1}. Temporal variations in streamwater chemistry occur with changes in discharge (Figure 12.3). During the example event, sharp increases in H^+ and inorganic Al concentrations as well as a decrease in Ca^{2+} were evident with increases in flow following a dry period in mid-October. These patterns at Birkenes are related to the changes in hydrologic pathways with discharge; baseflow chemistry is controlled by deeper deposits along the main brook while the more acidic and Al-rich upper soil horizons contribute most of the highflow runoff.

Ingabekken (Figure 12.2) lies in mid-Norway in a pristine area receiving only about 0.2 g SO_4-S m^{-2} year^{-1}. The largely alpine catchment (18.7 ha) is underlain by granitic bedrock but deeper gley deposits contain darker amphibolitic minerals. A similar decrease in pH (from about 7 at baseflow) occurred with increased flow at

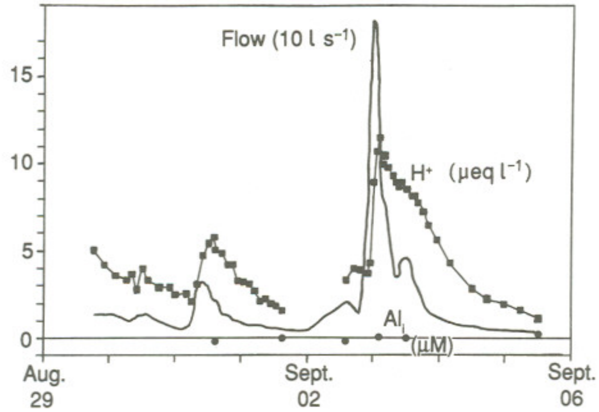

Figure 12.4 Episodic changes in streamwater chemistry at the Ingabekken catchment.

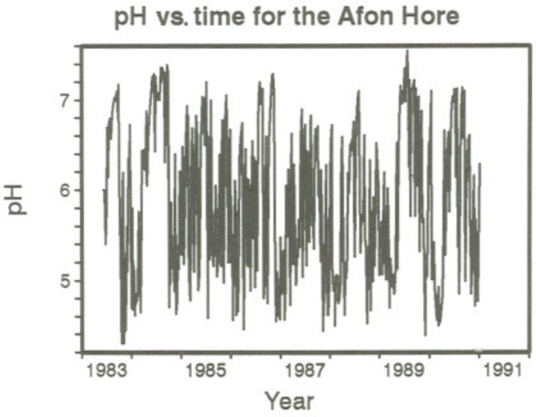

Figure 12.5 Episodic changes in streamwater chemistry at the Plynlimon catchment (Afon Hafren).

this site although pH values were always above 4.8 (Figure 12.4). Note that concentrations of inorganic monomeric Al was less than 30 µg l^{-1} under all flow conditions.

The Plynlimon study area is located at the headwaters of the River Severn in mid-Wales, United Kingdom (Figure 12.2). Bedrock geology consists of lower Palaeozoic sedimentary rocks (mudstones, greywackes, sandstones and grits). The predominant soil is a stagnopodzol but peat, brown earth and stagno-gley soils also occur. Annual sulphate deposition is about 2–2.5 g SO_4-S m^{-2} year^{-1}. At Plynlimon, baseflow waters and stormflow waters show the largest variations in chemistry with pH decreasing from 7.5 to 4.2 as flow increases (Figure 12.5). These differences reflect the large chemical gradients within the catchment. The soil zones, being organic and Al-oxide/hydroxide rich, produce acidic and Al-rich soil water solutions. The bedrock, consisting of weatherable and acid-soluble minerals such as calcite and layer lattice silicates (chlorite and illite), has the capacity to neutralize these acid waters, which, after CO_2 degassing, are of the type observed under baseflow conditions.

Batchawana Lake is at the headwaters of the Turkey Lakes Watershed, located some 50 km north of Sault Ste Marie, Ontario (Figure 12.2). The southern half of the lake (drainage area 85.6 ha) has a metamorphosed basalt bedrock overlain by a thin, often discontinuous till mantle. Soils are typically ferro-humic and humo-ferric podzols. Annual total SO_4-S deposition is about 1.2 g m^{-2} $year^{-1}$. The most pronounced chemical changes in the lake outflow take place during snowmelt (Figure 12.6). As stream discharge increased, acid neutralization capacity (ANC) declined in response to both the elevated H^+ concentrations in meltwater and a general dilution via snow melt. Calcium and SO_4^{2-} concentrations also decreased from mixing with the dilute meltwaters although the SO_4^{2-} decline was more moderate suggesting that catchment sources of SO_4^{2-} are better able to "buffer" the concentration of this ion during rapid changes in water flux than they are for other ionic constituents.

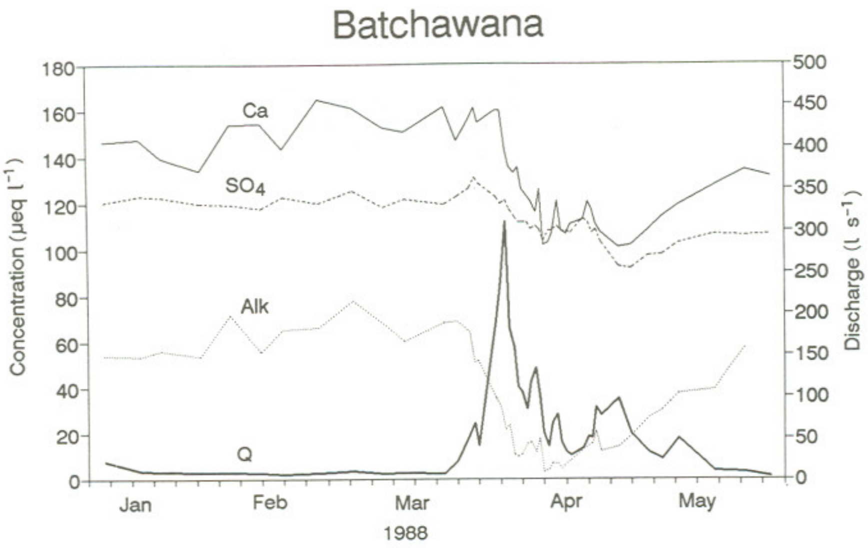

Figure 12.6 Episodic changes in streamwater chemistry at the Batchawana Lake outlet.

12.3.2 THE IMPORTANCE OF FLOW PATHS

The examples given here all show similar features in that pH and ANC decline with increasing discharge. Note that the reason for this pattern is not that rainfall or meltwater pass directly through the catchment to provide the major volume of water in the stream during the hydrograph response. Hydrograph separation using ^{18}O in the Turkey Lakes Watershed (Bottomley *et al.*, 1986) and Birkenes (Christophersen *et al.*, 1985) shows that most of the streamwater during high flows induced by snowmelt or heavy rainfall is, in fact, pre-event water. Similarly, concentrations of both ^{18}O and the chemically unreactive species Cl^- exhibit minor variations at Plynlimon compared to the high variability in precipitation inputs (Neal *et al.*, 1988; Neal and Rosier, 1990). Therefore, the large variations in stream chemistry observed at most sites relate to the hydrologic flowpath through the terrestrial catchment prior to emergence at the surface.

The best integrated evaluation of flowpath-related processes that regulate stream chemistry is given in terms of the so-called End-Member Mixing Analysis (EMMA). (See Neal *et al.*, 1990a; Robson and Neal, 1990; Christophersen *et al.*, 1990c; Hooper *et al.*, 1990 for the general basis of the approach.) This method is based on the hypothesis that streamwater chemistry can be explained by mixing variable amounts of water (depending on hydrologic conditions) from different soil compartments, each compartment having a specific "fingerprint" composition. This approach is not without problems since several chemical components, which exhibit response to flow, are chemically reactive and hence cannot be used in conservative mixing formulations. However, the ANC—suitably defined—is conservative with respect to many common reactions. When applicable, EMMA allows basic inferences to be made, which provide insight into the nature of the hydrological processes operating.

12.4 MATHEMATICAL MODELS

Over the last decade, a wide range of models have been developed that simulate surface runoff hydrology and chemistry. Most focus on prediction of chemical responses to changes in acidic deposition, and are often used as a tool for evaluating various emission management options. They also present a convenient mechanism for information synthesis and suggest research directions through identification of knowledge gaps and/or weaknesses. Substantive reviews of acidification models already exist (Reuss *et al.*, 1986; Turner *et al.*, 1990).

The models vary widely in the temporal scope of their predictions. The simplest models determine a steady-state response to a given deposition (Henriksen, 1984; Thompson, 1982) and assume that water ANC is at steady state with respect to the sulphur loading. These models are not process-oriented, but extrapolation of small catchment information to a wider region may depend on application of steady-state models, since regional data bases rarely contain all the input information necessary to run the more complex time-dependent models. These latter models attempt to simulate (with varying degrees of complexity) the processes controlling water chemistry and predict not only equilibrium concentrations but also the response time.

Many time-dependent models have been devised to predict short-term event responses; they include, among others, the Birkenes model (Christophersen *et al.*,

1982) or derivations of it (e.g. the Turkey–Mersey Model, Lam *et al.*, 1986), the ILWAS model (Gherini *et al.*, 1985), and the ETD model (Nikolaidis *et al.*, 1988). In contrast, the MAGIC model (Cosby *et al.*, 1985) was designed to predict responses over annual, decade and century time scales. The Birkenes (and derivations) and MAGIC models are of simple to intermediate complexity, have received widespread application, and therefore provide a useful framework for the discussion that follows.

Most catchment simulation models operate as a series of linked hydrological and hydrogeochemical sub-models. The hydrological sub-models often reproduce the hydrograph quite well; it is well known in hydrology that different, even conflicting, model formulations regarding internal flow mechanisms may result in comparable simulations of total discharge (e.g. Booty *et al.*, 1992).

In hydrochemical applications, adequate simulation of flow through catchment sub-compartments (e.g. soil layers) is vital. The overall picture emerging at this stage is that the original Birkenes model captured an essential feature, namely the change in gross water flowpaths in the catchment depending on the hydrological conditions. It is, however, difficult to test quantitatively model results in this regard. Yet, there are some encouraging signs. For example, the Turkey–Mersey Model provides a groundwater flow simulation at a site just downstream of the Batchawana catchment that conforms well with estimates obtained with ^{18}O (relative mean square error = 15%; Lam *et al.*, 1986).

Booty *et al.* (1992) have used observations from the Batchawana catchment (1981–84) to compare the pH and ANC simulation provided by four acidification models (Turkey–Mersey, ILWAS, ETD and RAINS). The Turkey–Mersey model provided the best pH simulation and was second to the ETD model in simulating observed ANC. The performance of ETD for ANC is particularly surprising since it was the least effective of the four models in simulating flow. Clearly, additional effort is required to fully test and validate the models, and more importantly, to understand which key processes or differences in model structure are responsible for the different levels of performance shown by the models.

In our view, all acidification models should be tested more against observations and be developed iteratively. However, very limited testing of internal model mechanisms can be performed using only runoff data (cf. Hooper *et al.*, 1988; Beck *et al.*, 1990). The EMMA approach offers promise in this regard. This approach attempts to identify the key soil environments controlling streamwater chemistry, which naturally can be associated with model compartments. A model developed on this basis must not only reproduce discharge and runoff chemistry, but each compartment can also be checked against field observations (Neal *et al.*, 1989, 1990 a,b; Hooper and Christophersen, 1992). In this way, internal catchment observations can be brought to bear on model development. A challenge to further modelling work lies in obtaining a balance between relatively simple representations and incorporating the important processes operative. A challenge to the catchment researcher is to provide information on the dominant reactions occurring, to help achieve this balance, while presenting data of direct use for modelling purposes (Neal *et al.*, 1992).

12.5 CONCLUSIONS

Hydrochemistry is a useful integrator of major biological, chemical and physical processes in small catchments. It is the output that couples hydrology to terrestrial processes, including plant decomposition, soil cation exchange, chemical weathering, biological uptake and mineralization. Because small catchments are sensitive indicators of changes in ecosystems due to human activities, they should be used as early warning systems of ecological change. Reliable assessment of environmental effects for sensitive areas is difficult to achieve since there is incomplete information on the complex and interactive hydrological, chemical and biological processes operating. A basic need is the maintenance of field studies to monitor the long-term changes in streamwater quality following changes in climate, land-use and/or atmospheric pollutant inputs. On this basis, studies such as those described here are of strategic importance.

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