2 Hydrology

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2.1 INTRODUCTION

Water plays a key role in natural ecosystems. It is the primary transport medium for dissolved and suspended solids, and it determines the rate at which these solids are removed from the system, conventionally defined as the output flux. If one is to gain an understanding of the biological, chemical and physical processes that operate within an ecosystem, a detailed understanding of the hydrological characteristics is required.

2.2 THE CATCHMENT AS A STUDY UNIT

The catchment, or drainage basin, is the basic unit of study in hydrology, because it represents an area with an easily definable topographic boundary, which, as a first approximation, also defines the watershed boundary. Precipitation falling on the catchment, adjusted for evapotranspiration losses, generally is channelled to leave it at a single point. This scheme (Figure 1.1) makes the catchment an attractive unit of landscape to study, not only for hydrology, but also biogeochemistry, because element budgets can be readily defined, bound by mass balances for the catchment. Normally, the water divide is determined from a topographic map as the line enclosing the area collecting an imagined overland flow to the point for which the catchment is to be defined. In many areas, however, surface flow is of little importance, and the hydrologic boundary for the catchment is controlled by the groundwater divide. In areas with shallow groundwater and high relief, the two water divides normally coincide, and the actual water divide can be obtained with reasonable accuracy from the topography. On the other hand, the catchment may be difficult to define in areas of low relief and in areas underlain by permeable rock where the groundwater divide does not coincide with the topographic divide, i.e. groundwater flow occurs across the topographic divide.

Catchments of high relief are well defined by topography, but often present difficulties in obtaining a representative value for precipitation input, especially if the input is dominated by snowfall. For the majority of catchments, however, inputs can be quantified with reasonable accuracy, and estimates of losses from evapotranspiration can be quantified over long periods, based on the assumption





that there is no change in the water stored in the catchment, and subsurface seepage is negligible. This represents a fundamental characteristic of catchment hydrology in the form of the mass balance equation for a specified time interval;

$$R = P - ET + dS \tag{2.1}$$

where P is precipitation, R is runoff, ET is evapotranspiration, and dS represents the change in storage, which includes surface water (including the stream channel, ponds, lakes, surface depressions or swamps), soil moisture, groundwater and snowpack. Over short periods, typically less than a year (such as season, day or hour) groundwater storage and the spatial distribution of soil moisture content will change in response to the prevailing inputs and climate. Consequently, investigations of hydrologic processes on these time scales require detailed knowledge of the water including fluxes, changes in storage, and transfers throughout the catchment.

In general, the advantages of discretizing hydrological response into drainage systems to minimize variance in hydrologic and hydrochemical responses outweigh the problems of heterogeneity of soil, vegetation cover, geology and management practice across a drainage basin. Also, if the catchments selected for study are relatively small, it is theoretically possible to minimize this heterogeneity, although if the catchment is too small, heterogeneity is a problem. Small catchments tend to be much more responsive to small perturbations in natural external factors, such as precipitation quantity and quality or temperature, thereby improving not only the ability to detect the response, but also improving the ability to understand the mechanisms producing the system's response. The upper limit for the area of a "small catchment" is not defined, but may be regarded as being somewhere in the range of 10 to 100 km². The term "small catchment" is normally used for catchments that are small enough to be considered spatially homogeneous in some aspect and/or for which input, storage and hydrologic status can be quantified with reasonable accuracy. There is, however, a lower limit for the area of a catchment to be studied because heterogeneities among other problems may become problematic. The position of the water divide can normally be determined with an accuracy dependent on map scale, regardless of catchment area. Thus, the relative accuracy in the determination of the catchment area decreases as the area decreases. Furthermore, the relative importance of groundwater leakage may increase as the catchment area decreases due to shallow groundwater outflow in parallel with the surface water outlet and to deeper groundwater flow in a larger flow system. For these reasons, it may not be possible to establish accurate water budgets, and consequently, chemical budgets, for very small catchments in the order of hectares or less.

The response of a catchment to an influx, in terms of quantity and/or quality of water, or to a long-term change in climatic variables, will be detected through

changes in fluxes both within and outside the catchment. This is exemplified on a seasonal basis by variations in the catchment flow regime and the outflux of nutrients such as nitrate (Webb and Walling, 1985; Betton et al., 1991). Seasonality of rainfall and snowmelt inputs determines the annual flow regime, whereas, within each season, short-term variations in transport along hydrologic pathways occur during storms (Burt and Arkell, 1986). The magnitude of the hydrologic and chemical response is highly correlated with soil moisture status and rainfall intensity in the catchment. For example, water yield for a given storm size (magnitude and intensity) is greater when a catchment is wet than when it is dry. Also, from a hydrochemical standpoint, streamwater nitrate concentrations in many temperatezone catchments tend to be greatest in winter and lowest in spring and summer when the growing plants utilize most of the available nitrogen (Webb and Walling, 1985; Betton et al., 1991; Reynolds et al., 1992). During storms, however, pulses of nitrate can occur in association with high concentrations in rainfall, particularly when the soil is saturated which promotes rapid runoff with little infiltration (Murdoch and Stoddard, 1992). To enable trend detection across this range of time scales, and to determine the controlling processes, it is essential to consider a sampling design that will capture the short-term variations in hydrology and solute composition. In a small catchment, the intensity of sampling necessary to describe changes in fluxes and storages must be carefully selected. Sampling must be frequent enough to characterize variations, but, because it is cost prohibitive, usually cannot be continued with what typically turns out to be a high frequency for long periods, therefore it must be integrated with less frequent, systematic "background" observations.

Crucial to the understanding of catchment processes, and the ability to predict future changes in the ecosystem, is the identification of hydrologic pathways within the catchment, and the related transit times for water through various biological and geological surroundings. Transit times for water in a small catchment, that is the time from input to output of individual water molecules (or equivalently, the age of the water at the moment of discharge), vary markedly. They may range from minutes for channel precipitation and water reaching the stream as overland flow to hours or a few days for the most shallow groundwater recharged close to the area where groundwater is discharged to the stream. Water with the longest residence time is typically deep groundwater, which can reside in the catchment for several years. The transit times are determined by the velocity and pathways of the water particles which in turn are determined by the hydraulic conductivity and the porosity of the soil and bedrock, the rate of groundwater recharge and the topography.

Transit times also vary markedly from storm to storm. The wetter the soil and the higher the groundwater table, the larger will be the contribution of short-residence-time water to the runoff. Many studies have shown that water achieves the chemical or isotopic signature of its flowpath or storage medium (Jenkins *et al.*,

1990; Hooper et al., 1990; Robson and Neal, 1990). Water signatured by surface soils is generally rich in dissolved organic matter and has low pH. Such water usually has a short residence time, but can contribute significant amounts to the storm runoff at the basin outlet. Water draining deep soils, on the other hand, is conventionally thought to have a longer residence time, and is characterized by high concentrations of weathering products, such as base cations and silica, and high alkalinity. At the catchment outlet, the changing mix of these waters with different catchment signatures produces the observed temporal response. The situation is complicated, however, in that different signatures may be observed from all compartments in the catchment depending on the characteristics of the water that causes a hydrologic event. For example, the release of strong mineral acids during snowmelt can produce a different chemical response than an acidic rainfall, and sea-salt-rich rainfall can produce a different chemical response than sulphate-rich rainfall. Moreover, catchments with different hydrologic characteristics can show different chemical responses for the same input (Figure 2.1). For the snowmelt and rainfall cases, a key to understanding the different types of response lies, to a large extent, in differences in the catchment hydrology. Also, variations in hydrologic and chemical response within a catchment are primarily affected by variations in the antecedent wetness of the catchment and the ability of the catchment to store, cycle and release various types of chemical constituents.

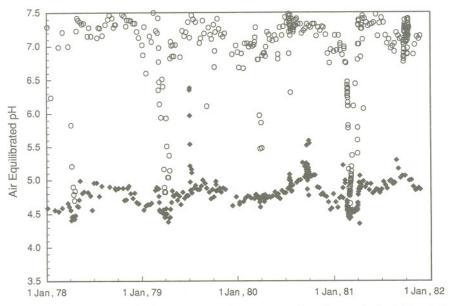


Figure 2.1 The pH variation in streamwater from two small catchments in the Adirondack Mountains, New York, from 1978 to 1981. Open circles are for samples collected at Panther Lake outlet and the solid diamonds are for Woods Lake outlet.

2.3 STREAMFLOW GENERATION MECHANISMS

2.3.1 CONCEPTUAL APPROACHES

The temporal and spatial response of streamflow to precipitation and snowmelt has traditionally been attributed to variation in the importance of different hillslope processes and pathways (Kirkby, 1978). Spatial variation occurs largely in response to differences in local topography, vegetation, soil characteristics and geology within and among catchments. Temporal variability in runoff response from a catchment may also be caused by these factors as well as by changes in the pattern of inputs, such as the timing and intensity of the rainfall, and by the influence of antecedent moisture conditions.

Several hypotheses have been advanced to describe the mechanism and pathways by which streamflow, in particular short-term response or quickflow, is generated from rainfall or snowmelt. Direct channel precipitation usually makes up a small percentage of the total streamflow during storms but for many catchments, it has been considered to be unimportant. Likewise, Hortonian overland flow (Knapp, 1970), which is direct surface runoff across saturated soils where rainfall intensity exceeds the infiltration plus depression storage, is unlikely to be an important hydrologic pathway, except in arid areas.

An alternative and more universally applicable hypothesis for overland flow generation has been termed saturation overland flow, whereby all rainfall infiltrates the soil surface before it moves downslope (Hewlett, 1961; Hewlett and Hibbert, 1967). Where the water table is close to the surface, particularly those areas adjacent to the stream, the water table rises to meet the surface, and all precipitation falling on these saturated areas runs off across the surface. As the storm or snowmelt progresses, this "contributing area" expands and, subsequently, contracts after the rainfall or snowmelt stops. This phenomenon is known as the variable source concept (Hewlett and Hibbert, 1967). Such variable source areas, however, not only occur in areas immediately adjacent to the stream or in valley bottoms, but wherever flow convergence occurs on the hillslope. This may occur: (1) in slope concavities where the convergence of hillslope water leads to subsurface flow rates that exceed the lateral hydraulic conductivity of the soil so that water will enter the hollow formed at break of slope more rapidly than it can leave downslope in the soil; (2) in slope concavities where a change in slope gradient, assuming subsurface flow rates to be proportional to hydraulic gradient, will allow water to enter at a greater rate than it can leave; (3) in areas of thinner soil where water holding and transmitting capacity is low; and (4) because the soil exhibits a decrease in hydraulic conductivity with depth causing layers of temporary saturation within the profile (Ward, 1984). These saturated areas can provide water rapidly to the stream via pipes and macropores. During a storm, water is transmitted to the stream from these disjunct saturated areas, while upslope rainfall recharges the soil moisture store and eventually contributes to stream baseflow.

The main weakness in the variable source area concept lies in the assumption that water can move rapidly to contribute to streamflow during the storm. To achieve this, the mechanism of translatory flow was hypothesized, whereby the lateral throughflow of "old" rainwater stored in the soil is released to streamflow by a process of displacement by new rain, and each new increment of rainfall infiltrates and displaces all of the preceding increments (Hewlett and Hibbert, 1967). The oldest increment is then forced into the stream from the bottom of the slope. This, however, is unlikely to occur in upland catchments where the soil cover is of variable depth, and continuous upslope saturation of the soil is unlikely. Furthermore, an input will result in an equivalent output only if the available moisture storage capacity is full. This mechanism, therefore, will be most effective after a prolonged period of rain, particularly on the lower slopes. A similar response may be produced if the pore water pressure increases with depth in the lower slopes, allowing the capillary fringe to saturate rapidly with the addition of small amounts of water from throughflow. The capillary fringe is the unsaturated zone above the water table into which water rises from the saturated zone by capillarity (Linsley et al., 1975). This capillary fringe effect facilitates a rise in the shallow groundwater table adjacent to the stream and contributes to the storm hydrograph (Ragan, 1968).

Recent studies using environmental isotopes suggest that yet another mechanism may be important, even in steep upland catchments underlain by relatively impermeable bedrock. These isotope studies indicate that the streamwater during storms is dominated by "old" or pre-event water. Clearly, capillary fringe effects and translatory flow alone could move pre-event soil water into the stream, but travel times would be limited by relatively low saturated hydraulic conductivity. Along the edge of transient discharge areas, however, the water table and its associated capillary fringe are very close to the ground surface. Soon after rain or snowmelt begins, infiltrating water rapidly converts the near-surface, tension-saturated, capillary fringe into a saturated zone or groundwater ridge (Sklash and Farvolden, 1979). This ridge increases the potential for rapid displacement of preevent water and results in an increase in size of the groundwater discharge area which is essential for producing large groundwater contributions to the stream. The groundwater table higher up on the slopes will also increase, but the groundwater there will have little effect on streamflow during the early part of a storm. But, in some cases, the upslope groundwater could contribute water to streamflow as streamflow decreases after the event, particularly in areas with moderate to high relief and a continuous saturated zone through the hillslope.

It is important to realize that all of these processes may operate on a given catchment, and that each catchment may be dominated by a particular mechanism, depending on climatology and geology. This would explain the reported differences in the pre-event water component from catchments around the world. It is also probable that different processes are dominant on a given catchment at various times as a function of storm intensity and duration, and catchment antecedent

wetness. Again, this helps to explain differences in the pre-event water component observed at individual sites. However, it is vital for biogeochemical investigations that the dominant flow generation mechanism be identified on any catchment given the close links between hydrologic pathways and stream chemistry.

2.3.2 MATHEMATICAL MODELLING

Mathematical models in hydrology are useful for accessing the conceptualization of dominant hydrologic processes operating in a catchment. A model, once calibrated and verified on a catchment, provides a multi-purpose tool for further analysis. The model can be used to test hypotheses and gain a better understanding of how the catchment behaves under different conditions in the future, that is, to make predictions. Models also represent a means of integrating measured data collected spatially and temporally from the catchment and can be used to provide estimates for missing data.

From the research standpoint of building models to gain a better understanding of the effect of watersheds on the hydrological cycle, a rigorous approach is needed to combine and solve the equations of mass, energy and momentum describing the movement of water over and through the soil and in stream channels and aquifers. However, our knowledge of catchment hydrology and ability to couple together and solve the relevant equations have significant gaps. A more empirical and theoretically less rigorous approach has, therefore, evolved. In this case, models are required to provide simulations of flow that agree closely with observed flows, achieved through some model fitting or optimization procedure.

Whichever type of model is selected for a catchment, the final structure necessarily represents a simplification of reality. Qualitatively, changes in hydrological processes and model variables may be determined at very small space and time scales. Yet, in practice, the building and application of a model usually requires bulk estimates of the behaviour of the system. As a consequence, it is likely that several models, and indeed several parameter combinations for the same model, may give similar results. This is conventionally quantified as an error term between observed and simulated data. Often, however, different models or parameters produce a better fit to different parts of the hydrograph record. For example, some models may adequately reproduce short-term hydrograph peaks but fail to simulate observed recessions, or vice versa. From the point of view of choosing an appropriate model for a given catchment, it also is worth stressing that more complex model structures do not necessarily produce better results. For hydrochemical models, hydrology is only one of many signals that must be reproduced, albeit an important signal, because it is the most readily quantifiable.

Hydrological models can be classified as those that consider a catchment as a spatially variable system and are termed "distributed", and those in which the catchment is described in terms of average quantities, called "lumped models". It is also possible to classify models that fall between these categories as "semi-

distributed". Such approaches utilize conceptual functional relationships for hydrological processes that are applied to a relatively small number of what are assumed to be homogeneous parts of the catchment treated as "lumped units".

Lumped models rely on simplifications of the physical and biological interactions and processes that determine the hydrological response of a catchment. The choice of what to simplify is dictated by a wide range of considerations, but most commonly it includes some spatial averaging of the system. The implication is that the catchment is represented mathematically using only depth and time dimensions, and no account is taken of variation of precipitation, vegetation, soils, geology or topography within the catchment. Clearly, such model structures are most applicable to small areas in which the physical characteristics are relatively homogeneous, but considerable success has been achieved on larger catchments. These models are often termed "conceptual" since they represent hydrological processes by different functional forms defined intuitively, and as these must represent an average behaviour over the entire catchment, the parameters often have no physical basis and cannot be measured in the field. Lumped models rely mainly on comparison between observed and simulated catchment outflows for calibration of internal model parameters, usually by invoking an appropriate optimization technique.

Distributed models in hydrology are usually physically based in that they are defined in terms of theoretically acceptable continuum equations. They do, however, involve some degree of lumping since analytical solutions to the equations cannot be found, and so approximate numerical solutions, based on a finite difference or finite element discretization of the space and time dimensions, are implemented. Such numerical solutions rely on the definition of a grid within the catchment which is frequently larger than the scale of the hydrological processes. Also, physically based models are typically based on process relationships or "laws" that are empirically derived. The most important difference between distributed and lumped conceptual models, however, is that physically based models have parameters that can, in principle, be measured in the field. Examples of models based on physical hydrology and incorporating the spatial inhomogeneity of catchments are the Institute of Hydrology Distributed Model (Calver, 1988) and the Système Hydrologique Européen (Jonch-Clausen, 1979). Incorporation of particle travel times (Calver and Binning, 1990) has helped further develop these models, but the incorporation of chemistry into distributed models will likely be much further in the future.

Lumped hydrological models may be based solely on the techniques of systems analysis in that they relate input to output without making reference to the hydrological mechanisms operating within the catchment. This approach can be based on, for example, constrained linear systems (Todini and Wallis, 1977) or on transfer functions (Box and Jenkins, 1970). The unit hydrograph approach, developed as an engineering tool by Sherman (1942), falls into this category and represents the runoff resulting from an effective rainfall input over the whole catchment in a given time period. The assumptions inherent in this approach are that streamflow

exhibits a linear response to rainfall excess and that infiltration capacity, rainfall and rainfall intensity are distributed homogeneously over the catchment. Refinements to the approach have been made by subdividing the catchment into several sub-basins and then routing available or instantaneous unit hydrographs for the different tributaries (Chow, 1964). The most encouraging development of this approach, however, is by Jakeman *et al.* (1990), whereby quick and slow flow components are identified.

Other lumped models represent the catchment as several tanks or boxes and these lend themselves more readily to simulating both flow and water quality, as water and solutes can be tracked on a mass balance basis (e.g. PULSE, Bergstrom et al., 1985 and BIRKENES, Christophersen et al., 1982). The boxes and flowpaths between them are sometimes, but not always, constructed to represent hydrological processes loosely, and different functional forms are defined intuitively for individual catchments. Parameter values are calibrated from a period of observations in a model fitting procedure.

The robustness of these lumped models is well demonstrated by their transferability between sites. This can be attributed to their relatively simple structure. This simplicity of structure, however, has its drawbacks in that the entire hydrograph record is rarely simulated accurately; either peak flows or recessions are fitted well. Further limitations have been noted when the model structures have been used to simulate streamflow and environmental isotopes, of which the latter give a very damped streamwater response to the rainfall inputs (Hooper et al., 1988). Consequently, hydrograph peaks cannot be simulated by rapid transmission of rain into the stream. These difficulties in the application of conceptual hydrologic models to catchment data, that encompass the problems of model internal structure, are extremely serious in the context of biogeochemical studies. Perpetuation of misinformation may occur particularly if these hydrochemical models are to be used to test hypotheses of catchment response that, in turn, depend heavily on appropriate identification of hydrological flow paths (Wheater et al., 1986). On the other hand, acceptable applications of lumped conceptual models applied to catchments other than where they were first developed have been achieved (Stone et al., 1990).

Semi-distributed hydrological models effectively bridge the gap between the lumped models and the fully distributed, physically based models. They utilize conceptual relationships for hydrological processes that are applied to several relatively homogeneous sub-areas of the catchment. TOPMODEL (Beven and Kirkby, 1979) is based upon the variable source area concept and generates the hydrograph through a combination of quickflow (saturation overland flow) and delayed subsurface flow. Sub-catchments, assumed to have a relatively homogeneous hydrological response, are designated on the basis of the channel network. The model has proved effective in matching simulated and observed flows at a variety of sites in different geographical and geomorphological settings (Beven *et al.*, 1984; Wollock *et al.*, 1990). The ILWAS model (Gherini *et al.*, 1985) is a further example of a semi-distributed model in which the soil profile in each defined sub-basin is described by up to five equally sloping soil layers, and the degree of saturation

within a layer determines vertical and lateral water movement. This model has been used successfully in several locations (Goldstein *et al.*, 1987; Chen *et al.*, 1991).

In conclusion, it must be stated that although models represent useful tools for integrating data, filling gaps in data, and interpreting catchment response, careful thought must be given to modelling at the outset of a basin research programme. A sampling strategy must be designed that will enable a chosen modelling strategy to be implemented. In other words, a model should be selected and applied at the onset of a project and not after a data set has been collected.

2.4 METHODOLOGY FOR COMPUTING A WATER BALANCE

The fundamental data that are central to any catchment hydrology study are those that define the terms of the catchment water balance equation, defined in Section 2.2. For annual budgets, the hydrological year is typically defined to begin at a time when the variation in storage between years is at a minimum. The change in storage between water years, however, can be a significant percentage of annual runoff, so that for data analysis, a data set covering many years is preferable. In the temperate zone of the Northern Hemisphere, the water year is conventionally assumed to start on 1 October, although site-specific discrepancies, such as snow-pack accumulation, may dictate a slightly different starting point. When calculations of the components of the water balance equation are required for periods shorter than annually, the change in storages within the catchment system must be estimated, in particular the water in unsaturated and saturated zones.

2.4.1 DATA COLLECTION

The data necessary to define the terms of the water balance equation must be measured in the field. Field measurements are problematical in that (1) techniques must be derived or chosen to quantify correctly the water flux or storage volume in question, and (2) the measurements, often taken at a specific point in the catchment, must be extrapolated to the entire catchment. The measurement sites, therefore, should be chosen to be representative of wider catchment areas. Of the components of the water balance, measurements can readily be made for the precipitation inputs and streamflow outputs of the catchment, whereas more effort and cost are associated with measurements of soil moisture and groundwater. Evapotranspiration is generally estimated by difference in the water balance equation because measurement techniques are very expensive and generally imprecise or inaccurate, particularly when scaled to the whole catchment and these techniques will not be discussed here.

2.4.1.1 Precipitation

Water is transported to the catchment by precipitation (e.g. rain, snow and sleet), riming (removal of moisture by freezing on vegetation) and the impaction of clouds. The relative importance of these processes will depend on a variety of fac-

tors that are both large scale (climate) and small scale (local topography) in nature. Precipitation volumes collected at different sites within a relatively small area can vary dramatically in response to local surface topography, vegetation cover, precipitation type and storm type, and extreme care should be taken in the extrapolation of volumes over larger areas. Further uncertainties in precipitation estimates to small catchments are due to deficiencies in the physical collection of the precipitation. Collection efficiency is the most problematic for solid precipitation, that is snow and sleet (Goodison *et al.*, 1989). Generally, gauges tend to underestimate the actual amount of precipitation falling to the ground as a result of wind effects above the rim of the gauge, wetting of the gauge, evaporation, rain splash and blowing of snow (Table 2.1).

Table 2.1 Major uncertainties and estimated magnitudes of errors associated with the collection of precipitation (adapted from Sevruk, 1982)

Error	Magnitude	Meteorological factors
Wind deformation above the gauge	2-10%(rain) 10-50%(snow)	Wind speed and precipitation structure
Wetting of the walls of the gauge	2-10%	Frequency and type of precipitation
Splash (out and in)	1-2%	Precipitation intensity and wind speed
Blowing and drifting of snow	?	Wind speed and condition of the snow cover

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Fog can be considered as clouds that are in contact with the surface. Fog may be an important deposition mechanism in upland catchments but rarely important in the lowlands. It is in these high altitude catchments that forests are abundant and the trees coupled with high elevation greatly enhance cloud water interception (Lovett *et al.*, 1982). The effect results from increased wind speeds at higher altitudes and the relatively high needle surface area of the conifers, which are common at high elevations, coupled with significant periods of cloud immersion (Unsworth and Fowler, 1988). The frequency of cloud immersion at a site is a function of elevation, aspect and local climate. These factors can combine to create marked seasonal trends in water input (Lindberg and Johnson, 1989). Several methods have been employed to ascertain the amount of water deposited by clouds to alpine systems. These include direct collection of cloudwater (Falconer and Falconer, 1980), measurement of throughfall and stemflow during fog episodes (Lovett *et al.*, 1982) and modelling of cloud droplet impaction to vegetation (Lovett, 1984).

2.4.1.2 Streamflow

Discharge or streamflow, typically expressed as m³ s⁻¹ or l s⁻¹, is the only phase of the hydrologic cycle for which reasonably accurate measurements of volume can

be made. The term "runoff" refers to an areal volume and is expressed as a depth (cm or mm). Streamflow data are generally derived from continuous or frequent records of water level or stage and periodic determinations of discharge. The frequency of stage measurement in small streams should be consistent with the rate of change in the hydrograph in response to water input caused by storms or snowmelt. The frequency typically used on catchments of 1 to 10 km² in area is 15 minutes, but more frequent measurements are typically needed for better accuracy on smaller catchments or streams that have a rapid response. Given the relatively high frequency (<15 minutes) typically needed for measuring stage in small catchments, stage can be measured and recorded automatically by several devices including pressure transducers, float and counter weight assemblies, and manometers, all of which can be connected to a variety of mechanical or electronic recorders (Rantz, 1982a). The stage height is converted to discharge through a rating curve or equation that relates the stream stage for particular time intervals to the instantaneous discharge. The ratings are typically determined from repeated field calibrations in natural channels and from theoretical or laboratory calibrations for artificial controls (Rantz, 1982b).

A station for gauging discharge in a natural stream section should be located where there is a strong and constant relation between stage and discharge. The best natural control sections are found where the velocity of the water increases from subcritical to supercritical, as occurs upstream of a rapid. In small watercourses, however, an artificial hydrologic control is preferred, such as a flume or weir, to increase accuracy and precision of the computed discharge (World Meteorological Organization, 1971). In all cases, discharge measurements are needed to periodically check or verify the stage—discharge relationship, because bed geometry within a natural section or above a weir or flume may change affecting channel hydraulics. Instantaneous flow measurements are conventionally carried out using velocity—area or dilution gauging techniques (Rantz, 1982a). The former involves the integration of a grid of velocities measured perpendicular to the flow direction using a current meter. Methods of dilution gauging may be employed including instantaneous (slug) injection or constant injection of tracers such as dye, salt or iodide (Rantz, 1982a).

2.4.1.3 Soil moisture

Soil wetness is measured to estimate soil water storage, and several measurement techniques exist (Stafford, 1988). One basic method is to auger out a soil sample for weighing, drying and re-weighing to give the mass wetness (Gardner, 1986). If the volume of the sample and the dry bulk density of the soil is known, the volumetric wetness may be calculated. Such a destructive sampling technique is often inappropriate for application in small catchments where the soil disturbance may affect the behaviour of other aspects of the system. Other techniques to estimate soil wetness have been developed including neutron scattering (Bell, 1969),

nuclear magnetic resonance (Paetzold et al., 1985) and dielectric measurements (Cihlar and Ulaby, 1974).

The energy state of soil water is essential information when interactions with vegetation or soil water flow are of interest. The moisture status in the soils and other aguifer materials can be determined by recording the pressure head or tension relative to a fixed moisture potential. A basic instrument for measuring the potential pressure of a soil matrix is the tensiometer. A typical tensiometer consists of a pressure gauge, which measures the pressure (when saturated) or tension (when unsaturated) that the soil moisture exerts on a column of water, a porous cup, which is in contact with the soil water at the measuring level, and a water body, typically a PVC pipe. Tensiometers can be readily automated by replacing the gauge with a pressure transducer that can be connected to a field computer or other electronic recording device. Other techniques exist, such as gypsum blocks (Strangeways, 1983), but these are less accurate than tensiometers and tend to decay rapidly in acidic soils. If the functional relationship between volumetric water content and matrix potential pressure, called the characteristic soil-moisture curve, can be defined, tensiometer readings can be translated into soil water content or wetness. Since soil water content will vary considerably, both vertically and horizontally, across the hillslope, careful consideration needs to be given to the design of the tensiometer network. For example, groundwater recharge through vertical water movement dominates at the top of hillslopes, whereas groundwater discharge and lateral water movement dominate at the base of slopes and near channel areas.

A relatively new technique that lends itself to automation and yields an integrated moisture content over a larger area then the aforementioned techniques is Time Domain Reflectometry, TDR (Topp *et al.*, 1980). The method uses the properties of electromagnetic waves which are affected by the dielectric properties and moisture content of an aquifer material. The transit time of a wave along a pair of parallel rods in the material is measured using a cable tester and the time is translated into a soil moisture value through a standard algorithm adjusted for the site-specific soil dielectric property. The moisture content between the rods can be estimated with an accuracy better than 1%. The method has proven useful in tracking wetting fronts in a soil matrix (Ledieu *et al.*, 1986).

2.4.1.4 Groundwater

Groundwater is often the largest storage component in the catchment. Also, large fluctuations in groundwater storage can occur seasonally or even in shorter periods during storms or snowmelt. In order to adequately estimate changes in the groundwater storage, it is necessary to determine the extent of the groundwater, including the thickness and spatial distribution of the saturated zone, and physical characteristics, such as porosity and dimensional hydraulic conductivity, of the aquifer(s) in the catchment. The distribution and characteristics of the aquifer generally can be

estimated from a combination of geophysical techniques (Zohdy *et al.*, 1984), such as seismic refraction, ground-penetrating radar (GPR), electromagnetic methods (Keller and Frischknecht, 1982), and sampling of aquifer materials during the installation of wells.

To characterize the energy state of groundwater as a basis for estimating groundwater discharges, three concepts have to be distinguished: the pressure head (or pressure potential), the total head and the groundwater table. The pressure head is the water level at a point relative to the atmospheric pressure and is measured by a tube with intake only at the point under consideration, i.e. a piezometer, and recorded as the water level at the point. The total head is the sum of the pressure head and the elevation of the point above a reference level (often sea level). The groundwater table is the level in the ground where the pressure head is zero and is conventionally measured using a tube with intakes or screening continuously below the water table. The groundwater flow is proportional to the total head gradient, i.e. the pressure head difference between two points along the direction of flow. Its direction can be determined by piezometers installed at different depths and different positions on the hillslope. In recharge areas, the head gradient is directed downward, and in discharge areas, it is directed upward. Along most of the slope, however, the flow is more or less lateral and downslope.

To calculate groundwater flow at a section of a slope, the head gradient estimated from the differences in groundwater level in at least two wells is needed along the gradient (direction of flow) and the transmissivity (depth and average hydraulic conductivity) of the aquifer. If flow is to be determined at a specified depth interval, the hydraulic conductivity of that layer must also be known. To study the mechanisms and process of groundwater discharge to a stream (streamflow generation), a dense network of spatially and vertically distributed wells close to the stream is required, and a network covering the whole slope length is needed for storage calculations. A shallow groundwater table may rise rapidly with water input, and frequent measurements, preferably utilizing recording instruments, are needed to monitor these changes. The potential problem of groundwater transfer between adjacent catchments, and the consequent inaccuracy in the water balance equation because of inaccurate delineation of the true hydrologic divide, require that some measurements of the water table be made across the catchment/topographic divide.

2.4.2 TRACER HYDROLOGY

The most direct way to obtain information about flowpaths and transit times for water in a catchment is by the use of tracers. By using some solute dissolved in or transported by the water, characteristic of the water molecule such as the radioactive or stable isotopes of hydrogen and oxygen, or physical characteristic of the water such as temperature, it sometimes is possible to determine the timing, mixing and movement of different water types in a catchment. When differentiating

water types the utility of tracers comes from the differences in tracer content or behaviour among source waters. The most attractive tracers for use in hydrology, therefore, are those that interact least with their surroundings. Tracers in hydrology can be divided into two groups, artificial and environmental, depending on whether the tracer is added intentionally to the system or is added by natural processes.

2.4.2.1 Stable isotopes of oxygen and hydrogen

The isotopes of oxygen and hydrogen are attractive as hydrologic tracers, because they are part of the water molecule. About 0.2% of the molecules of natural water contain the stable isotope ¹⁸O and about 0.3% deuterium (²H). The stable isotope content of a sample is usually expressed as the relative deviation of the isotopic ratio ¹⁸O/¹⁶O (or ²H/¹H) in the sample relative to that in Standard Mean Ocean Water (SMOW). The values are usually expressed as per mil (‰), and the analytical accuracy of the measurement is about 0.1 and 1.0 ‰ for ¹⁸O and ²H, respectively (Hoefs, 1988).

Both ¹⁸O and ²H are normally regarded as conservative in water travelling through a catchment. Any change in the isotopic ratio is assumed to result from the mixing of water with different isotope content. However, situations occur in which isotopic composition changes have to be considered. Water in contact with the atmosphere tends to become enriched in heavy isotopes due to fractionation occurring during evaporation and molecular exchange with atmospheric vapour. In precipitation, the contents of ¹⁸O and ²H are highly correlated, and a linear regression of ¹⁸O and ²H for a given area define a consistent relation, called the meteoric water line (Craig, 1961);

$$\delta^2 H = 8 \times \delta^{18} O + 10 \, (\%o) \tag{2.2}$$

As long as the precipitated water has not been subject to enrichment by evaporation, the ¹⁸O and ²H of a sample will fall on this line. This is usually the case for groundwater, stream and lake water samples.

2.4.2.2 Tritium

The short-lived radioactive isotope of hydrogen (³H), tritium, is produced naturally in the atmosphere by the interaction of ¹⁴N and cosmic-ray neutrons. The half-life of tritium is 12.26 years. Tritium also is produced by the explosion of nuclear devices in the atmosphere, and by the operation of nuclear reactors and particle accelerators. Tritium is rapidly incorporated into water molecules and is removed from the atmosphere by precipitation. The residence time of tritium in the lower stratosphere is 1 to 10 years, but once it reaches the lower troposphere tritiated precipitation rains out in 5 to 20 days (Gat, 1980).

Tritium and its decay product, ³He, have been used primarily for dating ground-water. In particular, high concentrations of tritium generated from nuclear bomb testing in the late 1950s and early 1960s provided an excellent time marker for precipitation and its subsequent recharge to groundwater systems. Unless there is a recent influx of tritium from a specific application or an accident, tritium has limited utility in catchment studies, because the residence time of water in small catchments is typically quite short.

2.4.2.3 Chemical tracers

A wide range of chemically conservative solutes can be measured in all of the stores and transfers of water (recharge and discharge zones) within the catchment system. Solutes, such as chloride, sulphate, silica or bromide, have been used for hydrograph separation (Pinder and Jones, 1969; Hooper and Shoemaker, 1986; Kobayashi et al., 1990; Robson and Neal, 1990) and as tracers within catchments to infer water pathways and response times (Kennedy et al., 1984; Jardine et al., 1989; Espeby, 1990; Roberge and Jones, 1991). The basic premise for applicability of chemical tracers to evaluating hydrologic processes is that the tracers, that are either applied artificially or occur naturally, also signature source waters as do the isotopes. The interpretation of such chemical data requires care in that the catchment is a major source of some constituents, such as base cations and silica, and the atmosphere is a major source of others, such as sulphate and chloride, but each may change within the catchment. For example, sulphate budgets may balance in heavily acidified catchments, whereas chloride budgets may not balance in the short term due to interactions with vegetation (Harriman et al., 1990; Peters, 1991).

2.4.2.4 Temperature

The physical characteristics of water within the catchment system have also been utilized to understand hydrologic processes. In particular, temperature has proved useful in investigations of streamflow generation (Kobayashi, 1985; Pangburn, 1987; Shanley and Peters, 1988). The basic construct is that the temperature of a source water such as precipitation or snowmelt is considerably different from that of other source waters such as soil water or groundwater. For example, if a stream is composed primarily of groundwater (cold) prior to a rainstorm, a relatively hot rain deposited on the catchment should warm the stream provided it contributes to streamflow. However, if at the onset of the rainstorm the streamwater temperature decreases, the initial contribution to streamflow must necessarily be groundwater discharge (Shanley and Peters, 1988). This technique may be especially useful in areas where the melting of a permanent or transient snow/ice cover contributes to streamflow.

2.5 DATA ANALYSIS TECHNIQUES

Once established, a small catchment that has been instrumented to collect the fundamental data outlined in Section 2.4, will generate large amounts of data. These data may be analysed and evaluated in several ways to derive hydrological information necessary for integrating with other biogeochemical data collected from the catchment study regarding such issues as the hillslope hydrological response, including the dominant pathways, rates of water movement, storage times and contributions to stream discharge.

2.5.1 HYDROGRAPH ANALYSIS

The time series record of flow at the catchment outlet provides the most basic hydrological data and may be utilized in simple analyses for comparing the hydrology of catchments, inferring dominant flowpaths, and determining the rates of streamflow response to precipitation and snowmelt. Conventionally, this analysis has centred on the calculation of lag times and time to peak discharge as a measure of the rate of runoff response to storms and snowmelt. Summaries of the flow

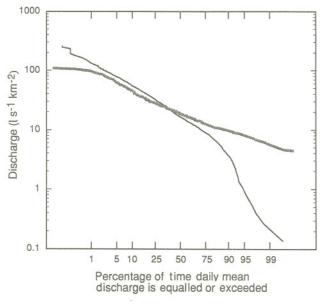


Figure 2.2 Flow duration curves for the outlets of two small lake watersheds in the Adirondack Mountains, New York. The thick grey line is for 1978–81 at Panther Lake and the thin solid line is for 1978–89 at Woods Lake. The hydrology at Panther Lake is dominated by groundwater and that at Woods Lake is dominated by surface runoff.

data in the form of flow duration curves are a means of comparing the hydrologic response among catchments (Searcy, 1959) and of evaluating factors controlling differences in the hydrologic response (Dingman, 1978). A flow duration curve is a distribution of the percentage of time a given flow is equalled or exceeded for a given time period. The slope of such curves allows inference to be drawn on the relative contributions of groundwater to streamflow (Figure 2.2), especially because this is strongly determined by the nature of the bedrock and soil (Peters and Driscoll, 1987).

2.5.2 GRAPHICAL HYDROGRAPH SEPARATION

Several approaches have been taken to subdivide hydrographs into components of flow. For example, the recession curve, which represents the depletion of water from storage in the catchment, can be derived by plotting the discharge at some time against the discharge at some fixed time later (Barnes, 1939). The slope of the resulting curve is the recession constant. However, the data for any particular stream do not usually yield a straight line. According to Barnes (1940), if the recession is plotted on semi-logarithmic axes, the recession can be divided into three straight lines, each of which represents different types of storage including stream channels, surface soil and groundwater. Rather than labelling the individual sources, it may be sufficient to identify components of different rates of water yield. For example, Hewlett and Hibbert (1967) recognized that each catchment has a characteristic hydrologic response in the long term. And, if a non-arbitrary response factor could be defined, the factor would be useful for comparative basin hydrologic analysis. Hewlett and Hibbert (1967) presented two simple response factors: one is the quick flow fraction of rainfall or snowmelt that moves rapidly to the stream during an event; and the other is the total water yield for the event. Each factor typically is easy to derive from discharge and precipitation data, and can be applied to individual hydrologic events. Although these factors do not identify contributions of specific water sources in the catchment, when they are used with other measures of the basin physiography, including channel slope and area, and hydrologic characteristics, including time to peak discharge and recession rates, the factors bound the magnitude and rates of response of the catchment. In addition, they provide qualitative information on the relative importance of hydrologic processes.

2.5.3 HYDROGRAPH SEPARATION USING TRACERS

The general technique for applying environmental isotopes or chemical tracers to streamflow generation mechanisms is to solve a mass balance for the constituents of interest. The prerequisite for the successful application of this technique is that all source waters are identified, have differing but constant isotopic composition,

and mix conservatively. For example, a two-component mixing model for assessing streamwater sources consists of two equations one for the mass of water and the other for the isotopic content or mass of solute which also must include the mass components for water (Dinçer *et al.*, 1970):

$$X = (C_s - C_1)/(C_2 - C_1)$$
(2.3)

where *X* is the fraction of pre-event water, subscript s represents the stream, 1 and 2 represent the two respective components, and *C* is the tracer concentration. The sources chosen for the two components are typically precipitation and groundwater for rain storms, and snowpack and groundwater for snowmelt. Two-component mixing models assume that both the "event" and "pre-event" water are isotopically uniform, although their isotopic compositions often show large spatial and temporal variability (Kennedy *et al.*, 1986).

Almost all hydrograph separations have been made using only two sources of water, ignoring the possibility that soil (vadose) waters may be significant sources of water and that these soil waters may show major spatial and temporal variations in chemical and isotopic content (Kennedy et al., 1986; DeWalle et al., 1987). However, streamflow during storms (or snowmelt) can be composed of at least four components (Fritz et al., 1976): (1) direct rainfall on the stream channel or on contributing wetlands; (2) overland flow; (3) groundwater discharge into the stream or wetlands; and (4) subsurface stormflow (interflow, or mobile unsaturated zone water) into the channel bank. The first component is entirely event or "new" water; the other three may contain various amounts of "new" and "old" water. The composition of the latter three components is actually a mixture, because they represent hydrologic pathways instead of unique single water sources. Consequently, for each of these four components, one might expect spatial and temporal variability. The two-component separation is still valid, provided that the components are simply mixtures of "new" and "old" water and are not characterized by water from a different source and with a different tracer identity.

The mixing models are oversimplified and beset with several limitations. First, tracers that are assumed to be conservative may not be. Many solutes have been treated as conservative when, in fact, they may not have been (Pilgrim *et al.*, 1979). The water isotopes (T, D, ¹⁸O) are part of the water molecule and, hence, are more "conservative" than solutes, but can still be affected (fractionated) by phase changes such as liquid to gas during evaporation (Fritz *et al.*, 1976). At the Panola Mountain Research Watershed, a small forested catchment in the southeastern US, a three-component mixing model was developed using soil solution end members for the six solutes which mix conservatively (Hooper *et al.*, 1990). The model could explain from 82 to 97% of the variation of individual solute concentrations in streamwater, and it could be used to solve for contributions of source waters, that is hydrologic pathways, using only solute concentrations.

2.6 SUMMARY

The small catchment is the most basic landscape unit for studying hydrologic processes, because its homogeneity with respect to hydrologic and watershed characteristics minimizes the need for inferential methods and maximizes the use of direct, and generally more accurate, hydrologic measurements. The primary elements that need attention to begin a study are the collection and interpretation of precipitation input and streamflow output because all hydrologic processes in a catchment are bound by the basic water balance. Subsequent investigations of the relative importance of various internal processes provide the knowledge of how the catchment cycles the water it receives and can provide indications of how the various storages will respond under a variety of conditions.

2.7 SUGGESTED READING

Some excellent references are available for the various aspects of the hydrologic cycle. Some of these were cited previously in this chapter. A general treatment of the hydrologic cycle can be found in any number of engineering textbooks on hydrology, such as Linsley *et al.* (1975) or Chow (1964). For information on the collection and analysis of precipitation, see Corbett (1967), and an annotated bibliography on instrumentation by Rodda (1973). For methods of streamflow monitoring, see Rantz (1982a, b), and for a discussion of artificial hydrologic controls see World Meteorological Organization (1971). General principles and concepts of groundwater monitoring are presented by Freeze and Cherry (1979) or Todd (1980); well installation, operation and monitoring are described in Driscoll (1986); and a general overview including data collection techniques, geophysical investigations and methods for determining aquifer characteristics are described in a technical publication of the US Department of Interior, Bureau of Reclamation (1977).

2.8 REFERENCES

Barnes, B.S. (1939) The structure of discharge-recession curves. Amer. Geophys. Union Trans., Part IV: 721-725.

Barnes, B.S. (1940) Discussion of the analysis of runoff characteristics. *Trans. Am. Soc. Civ. Eng.* **105**: 106.

Bell, J.P. (1969) A new design principle for neutron soil moisture gauges; "The Wallingford" neutron probe. Soil Sci. 108(3): 160.

Bergstrom, S., Carlsson, B., Sandberg, G. and Maxe, L. (1985) Integrated modelling of runoff alkalinity and pH on a daily basis. *Nordic Hydrology* 16: 89–104.

Betton, C., Webb, B.W. and Walling, D.E. (1991) Recent trends in NO₃⁻-N concentration and loads in British Rivers. *IAHS Publ.* **203**: 169–180.

Beven, K.J. and Kirkby, M.J. (1979) A physically based variable contributing area model of basin hydrology. *Hydrol. Sci. Bull.* 24(1): 43.

Beven, K.J, Kirkby, M.J., Scofield, N. and Tagg, A.F. (1984) Testing a physically based flood forecasting model (TOPMODEL) for three UK catchments. *J. Hydrol.* **69**: 119–143.

- Box, G.P. and Jenkins, G.M. (1970) Time Series Analysis, Forecasting and Control. Holden-Day, San Francisco.
- Burt, T.P. and Arkell, B.P. (1986) Variable source areas of stream discharge and their relationship to point and non-point sources in nitrate pollution. IAHS Publ. 157: 155–164.
- Calver, A. (1988) Calibration, sensitivity and validation of a physically-based rainfall-runoff model. J. Hydrol. 103: 103–115.
- Calver, A. and Binning, P. (1990) On modelling hillslope water flow paths and travel times. *J. Hydrol.* **121**: 335–344.
- Chen, C.W., Gomez, L.E. and Lund, L.J. (1991) Acidification potential of snowpack in Sierra Nevada. *J. Environ. Eng.* 117(4): 472–486.
- Chow, V.T. (1964) Handbook of Applied Hydrology. McGraw-Hill, New York.
- Christophersen, N., Seip, H.M. and Wright, R.F. (1982) A model for streamwater chemistry at Birkenes, Norway. *Water Resour. Res.* 18: 977–996.
- Cihlar, J. and Ulaby, F.T. (1974) Dielectric Properties of Soils as a Function of Moisture Content. RSL Technical Report 177-47, Univ. of Kansas Centre for Research, Lawrence, Kansas, USA.
- Corbett, E.S. (1967) Measurement and estimation of precipitation on experimental watersheds. In Sopper, W.E. and Lull, H.W. (Eds): *Forest Hydrology*. Proc. Int. Symp. on Forest Hydrol., Penn. State Univ., University Park, Pa, pp. 107-127.
- Craig, H. (1961) Isotopic variations in meteoric waters. Science 133: 1702-1703.
- DeWalle, D.R., Swistock, B.R. and Sharpe, W.E. (1987) Three-component tracer model for stormflow on a small Appalachian forested catchment. *J. Hydrol.* **104**: 301–310.
- Dinçer, T., Payne, B.R., Florkowski, T., Martinec, J. and Tongiorti, E. (1970) Snowmelt runoff form measurements of tritium and oxygen-18. *Water Resour. Res.* 6: 110–129.
- Dingman, S.L. (1978) Synthesis of flow-duration curves for unregulated streams in New Hampshire. *Water Resour. Res.* 14: 1481–1502.
- Driscoll, F.G. (1986) Groundwater and Wells, 2nd edition. Johnson Division, St Paul, Minnesota.
- Espeby, B. (1990) Tracing the origin of natural waters in a glacial till slope during snowmelt. *J. Hydrol.* **118**: 107–127.
- Falconer, R.E. and Falconer, P.D. (1980) Determination of cloud water acidity at a mountain observatory in the Adirondack Mountains of New York State. *J. Geophys. Res.* 85: 7465–7470.
- Freeze, R.A. and Cherry, J.A. (1979) *Groundwater*. Prentice-Hall, Englewood Cliffs, New Jersev.
- Fritz, P., Cherry, J.A., Weyer, K.V. and Sklash, M.G. (1976) Runoff analysis using environmental isotope and major ions. In *Interpretation of Environmental Isotope and Hydrochemical Data in Groundwater Hydrology*. IAEA, Vienna. pp. 111–130.
- Gardner, W.H. (1986) Water content. In Klute, A. (Ed.): Methods of Soil Analysis. Part 1. Physical and Mineralogical Methods. Agronomy Series, Vol. 9. Am. Soc. Agronomy, 2nd Edition, pp. 493–544.
- Gat, J.R. (1980) The isotopes of hydrogen and oxygen in precipitation. In Fritz, P. and Fontes, J. Ch. (Eds): Handbook of Environmental Isotope Geochemistry, Vol. 1A. Elsevier, Amsterdam, pp. 21–47.
- Gherini, S.A., Mok, L., Hudson, R.J.M., Davis, G.F., Chen, C.W. and Goldstein, R.A. (1985) The ILWAS model: Formulation and application. Wat. Air Soil Poll. 26: 425–459.
- Goldstein, R.A., Gherini, S.A., Driscoll, C.T., April, R., Schofield, C.L. and Chen, C.W. (1987) Lake watershed acidification in the North Branch of the Moose River: Introduction. *Biogeochemistry* 3: 5-20.

- Goodison, B.E., Sevruk, B. and Klemm, S. (1989) WMO solid precipitation measurement intercomparison: objectives, methodology, analysis. *IAHS Publ.* **179**: 57–64.
- Harriman, R., Ferrier, R.C., Jenkins, A. and Miller, J.D. (1990) Long and short-term hydrochemical budgets in Scottish catchments. In Mason, B.J. (Ed.): *The Surface Waters Acidification Programme*. Cambridge University Press, Cambridge, pp. 31–45.
- Hewlett, J.D. (1961) Soil moisture as a source of baseflow from steep mountain watersheds. USDA, SE Forest Experimental Station Paper No. 132, 10 pp.
- Hewlett, J.D. and Hibbert, A.R. (1967) Factors affecting the response of small watersheds to precipitation in humid areas. In Sopper, W.E. and Lull, H.W. (Eds): Forest Hydrology. Proc. Int. Symp. on Forest Hydrol., Penn. State Univ., University Park, Pennsylvania, pp. 275–290.
- Hoefs, J. (1988) Stable Isotope Geochemistry. 3rd edition, Springer-Verlag, New York.
- Hooper, R.P. and Shoemaker, C.A. (1986) A comparison of chemical and isotopic hydrograph separation. Water Resour. Res. 22: 1444–1454.
- Hooper, R.P., Christophersen, N. and Peters, N.E. (1990) Modelling streamwater chemistry as a mixture of soil water end-members—An application to the Panola experimental catchment, Georgia, USA. *J. Hydrol.* 116: 321–343.
- Hooper, R.P., Stone, A., Christophersen, N., de Grosbois, E. and Seip, H. M. (1988) Assessing the Birkenes model of stream acidification using a multi-signal calibration methodology. *Water Resour. Res.* 24: 1308–1316.
- Jakeman, A.J., Littlewood, I.G. and Whitehead, P.G. (1990) Computation of the instantaneous unit hydrograph and identifiable component flows with application to two small upland catchments. J. Hydrol. 117: 275–300.
- Jardine, P.M., Wilson, G.V., Luxmore, R.J. and McCarthy, J.F. (1989) Transport of inorganic and natural organic tracers through an isolated pedon in a forested watershed. Soil Sci. Soc. Am. J. 53: 317-323.
- Jenkins, A., Harriman, R. and Tuck, S.J. (1990) Integrated hydrochemical responses on the catchment scale. In Mason, B.J. (Ed.): The Surface Waters Acidification Programme. Cambridge University Press, Cambridge, pp. 47–55.
- Jonch-Clausen, T. (1979) Systeme Hydrologique Europeen: A short description. Danish Hydraulic Institute.
- Keller, G.V. and Frischknecht, F.C. (1982) Electrical Methods in Geophysical Prospecting. International Series in Electromagnetic Waves, Vol. 10. Pergamon Press, Oxford, UK.
- Kennedy, V.C., Jackman, A.P., Zand, S.M., Zellweger, G.W. and Avanzino, R.J. (1984) Transport and concentration controls for chloride, strontium, potassium, and lead in Uvas Creek, a small cobble-bed stream in Santa Clara County, California, Part. 1, Conceptual model. J. Hydrol. 75: 67–110.
- Kennedy, V.C., Kendall, C., Zellweger, G.W., Wynman, T.A. and Avanzino, R.J. (1986) Determination of the components of stormflow using water chemistry and environmental isotopes, Mattole River basin, California. J. Hydrol. 84: 107–140.
- Kirkby, M.J. (1978) Hillslope Hydrology. John Wiley & Sons, New York.
- Knapp, B.J. (1970) A note on throughflow and overland flow on steep mountain watersheds. Read. Geograph. 1: 40–43.
- Kobayashi, D. (1985) Separation of the snowmelt hydrograph by stream temperatures (Sapporo, Japan). *J. Hydrol.* 76: 155–162.
- Kobayashi, D., Suzuki, K. and Nomura, M. (1990) Diurnal fluctuations in stream flow and in specific electric conductance during drought periods. *J. Hydrol.* 115: 105–114.
- Ledieu, J., De Ridder, P., De Clerck, P. and Dautrebande, S. (1986) A method of measuring soil moisture by time-domain reflectometry. *J. Hydrol.* **88**: 319–328.
- Lindberg, S.E. and Johnson, D.W. (Eds) (1989) 1988 Annual Report of the Integrated Forest Study. ORNL/TM 11121, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Linsley, R.K., Jr, Kohler, M.A. and Paulhus, J.L.H. (1975) Hydrology for Engineers. McGraw-Hill, New York.

- Lovett, G.M. (1984) Rates and mechanisms of cloud water deposition to a subalpine balsam fir forest. *Atmospheric Environment* 18: 361–371.
- Lovett, G.M., Reiners, W.A. and Olson, R.K. (1982) Cloud droplet deposition in subalpine balsam fir forests: hydrologic and chemical inputs. *Science* **218**: 1303–1304.
- Murdoch, P.S. and Stoddard, J.L. (1992) The role of nitrate in the acidification of streams in the Catskill Mountains of New York. *Water Resour. Res.* 28(10): 2707–2720.
- Paetzold, R.F., Matzkonin, G.A. and De la Santos, A. (1985) Surface soil water content measurement using pulsed nuclear magnetic resonance techniques. Soil Sci. Soc. Am. J. 49(3): 537–540.
- Pangburn, T. (1987) Forecasting of snowmelt runoff using temperature data. In Proc. 44th Annual Eastern Snow Conference, pp. 108–113.
- Peters, N.E. (1991) Chloride cycling in two forested lake watersheds in the west-central Adirondack Mountains, New York, U.S.A. Wat. Air Soil Poll. 59: 201–215.
- Peters, N.E. and Driscoll, C.T. (1987) Hydrogeologic controls of surface-water chemistry in the Adirondack Region of New York State. *Biogeochemistry* 3: 163–180.
- Pilgrim, D.H., Huff, D.D. and Steele, T.D. (1979) Use of specific conductance and contact time relations for separating flow components in storm runoff. Water Resour. Res. 15: 329–339.
- Pinder, G.F. and Jones, J.F. (1969) Determination of the ground-water component of peak discharge from the chemistry of total runoff. Water Resour. Res. 5: 438–445.
- Ragan, R.M. (1968) Laboratory evaluation of a numerical flood routing technique for channels subject to lateral inflows. *Water Resour. Res.* 2(1): 111–121.
- Rantz, S.E. (1982a) Measurement and computation of streamflow: Volume 1. Measurement of stage and discharge. US Geological Survey Water-Supply Paper 2175.
- Rantz, S.E. (1982b) Measurement and computation of streamflow: Volume 2. Computation of discharge. US Geological Survey Water-Supply Paper 2175.
- Reynolds, B., Emmett, B.A. and Woods, C. (1992) Variations in streamwater nitrate concentrations and nitrate budgets over 10 years in a headwater catchment in mid-Wales. *J. Hydrol.* **136**: 155–175.
- Roberge, J. and Jones, H.G. (1991) Subice layering and origin of acidic waters in a small boreal lake during the spring runoff. *Water Resour. Res.* 27(4): 479–492.
- Robson, A. and Neal, C. (1990) Hydrograph separation using chemical techniques: an application to catchments in Mid-Wales. J. Hydrol. 116: 345–363.
- Rodda, J.C. (1973) Annotated bibliography on precipitation measurement instruments. WMO-No. 343, Report No. 17, Geneva, Switzerland.
- Searcy, J.K. (1959) Flow duration curves—Manual of hydrology, Part 2. Low flow techniques. US Geological Survey Water Supply Paper 1542-A.
- Sevruk, B. (1982) Methods of correction for systematic error in point precipitation for operational use. World Meteorological Organization, Operational Hydrology 21, Geneva, Switzerland.
- Shanley, J.B. and Peters, N.E. (1988) Preliminary observations of streamflow generation during storms in a forested Piedmont watershed using temperature as a tracer. *J. Contam. Hydrol.* 3: 349–365.
- Sherman, L.K. (1942) Streamflow from rainfall by the unit graph method. Eng. News Rec. 108: 501–505.
- Sklash, M.G. and Farvolden, R.N. (1979) The role of groundwater in storm runoff. J. Hydrol. 43: 45-65.
- Stafford, J.V. (1988) Remote, non-contact and in situ measurement of soil moisture content: a review. J. Agric. Engng. Res. 41: 151–172.
- Stone, A., Seip, H.M., Tuck, S.J., Jenkins, A., Ferrier, R.C. and Harriman, R. (1990)

- Simulation of hydrochemistry in a highland Scottish catchment using the Birkenes model. Wat. Air Soil Poll. 51: 239-259.
- Strangeways, I.C. (1983) Interfacing soil moisture gypsum blocks with a modern data-logging system using a simple, low cost, DC method. *Soil Sci.* **136**(5): 322–324.
- Todd, D.K. (1980) Groundwater Hydrology, 2nd edition. John Wiley & Sons, New York.
- Todini, E. and Wallis, J. (1977) Using the CLS for daily or longer period rainfall-runoff modelling. In Ciriani, T.A., Maione, U. and Wallis, J.R. (Eds): Mathematical Models for Surface Water Hydrology. Wiley & Sons, London.
- Topp, G.C., Davis, J.L. and Annan, A.P. (1980) Electromagnetic determinations of soil water content: measurements in coaxial transmission lines. Water Resour. Res. 16: 574–582.
- US Department of Interior, Bureau of Reclamation (1977) Ground Water Manual: A Water Resources Technical Publication. US Government Printing Office, Washington, DC, USA.
- Unsworth, M. and Fowler, D. (Eds) (1988) *Processes of Acidic Deposition in Mountainous Terrain*. Kluwer Academic Publishers, London, 670pp.
- Ward, R.C. (1984) On the response to precipitation of headwater streams in humid areas. *J. Hydrol.* **74**: 171–189.
- Webb, B.W. and Walling, D.E. (1985) Nitrate behaviour in streamflow from a grassland catchment in Devon, UK. *Water Res.* 19: 1005–1016.
- Wheater, H.S., Bishop, K.H. and Beck, M.B. (1986) The identification of conceptual hydrological models for surface water acidification. *Hydrol. Proc.* 1: 89–109.
- Wollock, D.M., Hornberger, G.M. and Musgrove, T.J. (1990) Topographic effects on flow path and surface water chemistry of the Llyn Brianne catchments in Wales. J. Hydrol. 115: 243–261.
- World Meteorological Organization (1971) Use of weirs and flumes in stream gaging. WMO-No. 280 Technical Note 117, Geneva, Switzerland.
- Zohdy, A.A.R., Eaton, G.P. and Mabey, D.R. (1984) Applications of surface geophysics to ground-water investigations. US Geol. Survey Water Resource Investigations, Chapter D1, Book 2.