

SCOPE 51 - Biogeochemistry of Small Catchments

8 Element Budgets

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8.1 INTRODUCTION

The very definition of a catchment points to the concept of the water cycle: the catchment is a landscape unit where all outflowing water is derived from precipitation falling on the surface of the catchment. A catchment may be defined in the horizontal sense by the topographical water divide and vertically in some arbitrary way (for instance, as the zone of intensive biological and biogeochemical activity between unweathered and impermeable bedrock up to tree tops).

The object of study in small catchment research is extremely broad since any catchment consists of many subsystems interacting in quite a complex way. The study of small catchments consists mainly of tracing and quantifying the hydrological cycle, e.g. transport of the water from the atmosphere through vegetation, soil and bedrock to a groundwater reservoir or to stream runoff, and chemical changes alongside this course. Resulting chemical composition of streamwater is usually too complex to be easily explained in quantitative terms; our ability to perform this task, however, is a measure of our understanding the processes operating inside the catchment.

8.2 INPUT-OUTPUT BUDGETS

The elementary tool used for interpretation of measured data is calculation of the mass flux for any individual element, e.g. determination of the total amount of an element or compound entering or leaving the catchment.

Mass fluxes may be classified with respect to the studied system (catchment) as *inputs*, i.e. fluxes entering the system, *outputs*, i.e. fluxes removing mass from the system. Highly important for ecosystem functioning, but difficult to quantify from catchment studies are *internal* fluxes, i.e. redistribution of the mass inside the system, for instance between the soil pool and above-ground vegetation.

The most important *inputs* into the catchment are atmospheric deposition (composed of wet deposition, dry deposition and cloud deposition-see [Chapters 2](#) and [3](#)), weathering input (i.e. release of mass from the fresh bedrock-see [Chapter 4](#)) and direct anthropogenic input, such as liming or fertilizing. Less obvious are possible lateral inputs across the watershed boundary, e.g. lateral flow of groundwater.

With respect to *outputs*, most of the catchment studies are concerned with runoff output ([Chapter 7](#)), which is beyond any discussion the most important removal pathway for the majority of compounds of interest. Other outputs include groundwater seepage through fractured bedrock, gaseous emissions from the soil, harvest or timber removal.

Recently, considerable interest focused on the study of throughfall, which is an example of *internal flux*. Throughfall is the flux of precipitation below the canopy (see [Chapters 3](#) and [10](#)). The difference between open-field precipitation input and below-canopy throughfall flux is called net removal. For elements highly active in biogeochemical cycling, such as potassium, manganese or nitrogen, net removal mirrors leaching or consumption of these elements at the canopy surfaces. For other, less active elements (sulphur, sodium) it is assumed that both leaching and adsorption in canopies are negligible and net removal may serve as an estimate of dry deposition from atmosphere, e.g. net removal equals dry deposition and throughfall is considered to be an input flux (wet and dry deposition) instead of internal flux.

The input-output budget represents a balance sheet approach to the evaluation of known fluxes, comparison of measured or estimated inputs with outputs. Both fluxes are defined relatively, with respect to the definition of the catchment used. Inputs are entered with a positive sign in the equation, outputs with a negative sign.

For each element an equation can be written in the following general form:

$$\text{Inputs} - \text{Outputs} = \text{Net} \quad (8.1)$$

An expanded form of this equation is, for example, [Equation 4.1](#), where inputs are partitioned into individual terms like wet atmospheric deposition, dry deposition of solid particles, dry deposition of gases, etc.

An excess of inputs over outputs means that there is accumulation of the given element inside the catchment, the budget is therefore positive (i.e. *net gain*).

Net release occurs when output is higher than the accounted input and the net term is therefore negative.

If inputs equal outputs, the net term equals zero and the system appears to be in a *steady state*, i.e. state in which inputs outweigh outputs and the total pool of a given element inside the catchment is not changing. Unless there are signs of serious perturbation, it is often assumed that individual catchment compartments like soil or above-ground biota are in steady state. However, it may be difficult, if not

impossible, to prove experimentally the steady state assumption beyond any doubt. For Hubbard Brook it is assumed that fixation of the elements in biomass balances their release through decay of dead tissues (Likens *et al.*, 1977).

The assumption of a steady state of the individual compartments is important for simplifying the mass equation to a frequently used form:

$$\text{Atmospheric input} + \text{Weathering Input} = \text{Stream Export} \quad (8.2)$$

Quantification of element fluxes in small watersheds will produce an estimate of the weathering rate in steady-state systems. In reality, few watershed studies strictly conform to a steady-state system; so often watershed budgets are in effect controlled by chemical erosion rates rather than weathering rates. Retention of elements within the watershed in such systems therefore leads to underestimates of the weathering rates.

The atmospheric input into small catchments differs from the surface runoff output via stream because of the reactions with biota, soils and bedrock. Chloride and sulphate are believed to be an exception from this rule. Annual Cl input should equal output because Cl is not thought to accumulate within watersheds (Cleaves *et al.*, 1974) and also no important sources were found. Recent data, however, question the assumption of chloride behaviour as an inert tracer, it is probably involved in biological cycling more extensively than previously thought (Peters, 1991).

Sulphate is considered to be a mobile anion, i.e. an ion which passes through the system without forming stable secondary minerals or being used by biota. There could, however, be sources of sulphur inside catchments (sulphide minerals in bedrock), under thermodynamically favourable conditions secondary minerals like basaluminite or basanite may be formed. Sulphate adsorption is a well-established process of sulphate immobilization in soils, namely in those high in weathered sesquihydroxides (Johnson and Henderson, 1979). Finally, sulphur enters biological cycling, although in a far lower proportion than nitrogen or potassium.

Johnson *et al.* (1968) coupled their data on atmospheric input and stream export and derived the weathering rates of the bedrock just from the difference between atmospheric input and stream export. Eaton *et al.* (1978) applied the same approach for determination of sulphur dry deposition.

Units used for mass fluxes are usually $\text{kg ha}^{-1} \text{ year}^{-1}$ or $\text{g m}^{-2} \text{ year}^{-1}$. For an evaluation of acidification processes mass fluxes are often expressed as $\text{kmol ha}^{-1} \text{ year}^{-1}$ or $\text{keq ha}^{-1} \text{ year}^{-1}$.

Mass fluxes calculated in small catchments consider usually only solutes, ignoring suspended matter. This approach is acceptable in very small forested catchments with mild relief. Human activity (logging, road construction), change in land-use (conversion to fields) or increase in relief lead to increase in suspended matter export which then has to be included in input-output calculations.

Common problems involved in measuring and evaluation of input-output budgets are treated in more depth in [Sections 8.3](#) and [8.4](#). Here only some of the most obvious problems are mentioned, for which the monitoring design should be checked first if reliable budgets are to be produced.

1. Pronounced net release for elements.

- a. Check whether all forms of input are accounted for (wet deposition, dry deposition, weathering). If

the catchment lies in a mountainous area, estimate cloud deposition.

- b. Check the water budget: reported precipitation amounts are often smaller than the real water input, precipitation total increases with altitude.
- c. How is outflow of water from the catchment measured? Small relative error in high flow discharge measurements can significantly affect the annual budget.
- d. Check whether the element with positive budget can be weathered from bedrock (do not forget that a whole-rock chemical analysis may be useless for your evaluation if inhomogeneities, e.g. calcite veins, are present).
- e. Are there any signs of possible communication between the catchment and regional groundwater systems?
- f. Are there any reasons to assume that your system is in transition because of changing land-use, increasing/decreasing atmospheric inputs? Is there any documented anthropogenic disturbance, manipulation? Every catchment evolves due to changing environmental conditions (climate, human impact) towards equilibrium state. Comparison of suspicious data with other data sets is useful only for finding the order of magnitude discrepancies.

2. Pronounced accumulation of elements.

- a. What sampling scheme is used for runoff monitoring? Fixed time sampling interval oversamples baseflow conditions and undersamples high-flow, short-lasting events. If there is positive correlation of given element with flow, absence of chemical analysis during the high flow period may lead to underestimation of the output flux.
- b. What is the pattern of vegetation inside the catchment? Areas close to the stream channel or extensive areas elsewhere occupied by young forest bear strong impact on the budget as they may be responsible for elevated bioaccumulation.
- c. What is the health status of the forest? Natural forest is frequently nitrogen-limited, i.e. it is able to consume all incoming nitrogen and thus highly positive budgets for nitrogen are believed to be a sign of healthy forest ecosystems. On the other hand, net release of nitrogen belongs to the symptoms of disturbance, specifically forest dieback (Nilsson and Grennfelt, 1988).
- d. What is the depth, mineralogy and cation/anion exchange status of the soils? Old weathered soils can effectively retain sulphate and phosphate.
- e. How steep is the catchment valley? Is it possible that the watershed boundary is different from the topographic catchment boundary? What are the directions of forest roads and ditches? They may drain the catchments particularly at high flow situations, e.g. snowmelt or intensive rainfall, exceeding infiltration capacity of soils.

8.3 SELECTION OF WATERSHEDS FOR SMALL WATERSHED STUDIES AND PRACTICAL CONSIDERATIONS

Site selection and characterization is an essential prerequisite of mass balance studies. Such an approach must consider watershed uniformity in terms of climate, vegetation, land-use, soils and parent material. One of the main advantages of the small watershed approach is that homogeneous, separate

hydrochemical units can be studied. It is highly beneficial to use paired watersheds arrangement, where two or more very similar catchments differing only in one controlled parameter (e.g. manipulation, aspect, vegetation cover) are compared. Comparisons of this kind have proven to be a productive way of small catchment research (Swank and Crossley, 1988; Hornung *et al.*, 1985; Reynolds *et al.*, 1986; Paces, 1986; Wright and Henriksen, 1990).

Climatic conditions can vary enormously in upland areas because of orographic and elevational effects that make accurate quantification of inputs difficult. Such effects can be minimized by limiting the elevational range of the watershed and excluding sites in which orographic effects are important. It is also essential to consider climatic conditions in terms of the operational aspects of the study, because accessibility to the watershed may be restricted at certain times of the year.

The most important consideration in site selection is undoubtedly uniformity of parent material as this directly affects soils, vegetation and hydrochemistry. It is usually desirable to carry out a small-scale geological mapping survey of the watershed under consideration to identify possible sources of heterogeneity. Spatially insignificant features such as veins and minor igneous intrusions can have a disproportionately large effect on solute chemistry (Hornung *et al.*, 1985).

For this reason small watershed studies are conducted on uniform parent material. In many watersheds in the Northern Hemisphere bedrock is covered by thick deposits of glacial or fluvio-glacial material (the Turkey Lakes Watershed-Jeffries *et al.*, 1988; ILWAS watersheds-April and Newton, 1985). This introduces further variability as drift material is often heterogeneous and its mineralogy is different from the bedrock.

Potential errors in watershed input-output budgets may arise from unmeasured losses or gains of elements. Watersheds should be reasonably water-tight and this precondition has to be tested. A basic knowledge of the permeability and structure of bedrock gives a strong indication of possible losses by deep seepage. Evapotranspiration can be estimated by comparing annual precipitation volume with stream runoff volume. This estimate can be compared with regional values to give a good indication of the water-tightness of the watershed (Likens *et al.*, 1977; Creasey *et al.*, 1986). Potential evapotranspiration calculated from meteorological data using models like PROSPER (Huff and Swank, 1985), SOIL (Jansson, 1991) or hydrological part of ILWAS (Goldstein *et al.*, 1984) sets an upper limit for evapotranspiration loss of water.

The chloride budget is often used to identify additional potential losses. Large differences in the mass balance for Cl, provided dry-deposited chloride flux is accurately known, may be an indication of deep seepage in the watershed.

In most watershed studies different approaches should be used to assess the water-tightness of the watershed, although the water and Cl budgets can only be used after the study has been in progress for sufficient time. If available, various geophysical techniques such as seismic refraction can be used at an early stage to identify deep seepage and groundwater sources (Galfi and Palos, 1970).

Groundwater inputs to the watershed are another potential source of error in the balancing the input-output budgets. The catchment size significantly limits danger of major groundwater sources, as they are commonly developed as part of the larger-scale groundwater systems downstream. The presence of springs or small-scale variations in solute chemistry and temperature within a watershed at baseflow, point towards groundwater inputs. These will affect the solute balance if they originate from outside the watershed; the net result is elevated value of estimated weathering or atmospheric input. In contrast, groundwater leakage outside the catchment may be falsely interpreted as decreased weathering rate or atmospheric input.

In the absence of sufficient geological exposure, soils provide a substantial amount of information on watershed uniformity. Although soils show natural elevational changes in horizon thickness and type, the lower B and C horizons directly reflect the nature of the parent material. A reconnaissance soil survey yields valuable information on disturbances and erosion within the watershed. Soil erosion either occurs as a continuous gradual process or as a catastrophic, highly localized event. In the latter case the watershed will take considerable time to return to steady state.

Natural and man-made perturbations in watersheds (e.g. burning, clearcutting) will be reflected by long-term effects on vegetation. Land-use change, involving the chemical and physical management of upland areas in the recent past, is a feature of many areas. It is difficult to know for how long liming, for example, will modify chemical outputs from an upland area (Hornung *et al.*, 1985). Historical records and local sources of information often provide vital information on the physical and chemical equilibrium state of the experimental area. Feger *et al.* (1990) reported for two catchments significantly different patterns of nitrogen budgets because of the change in tree species composition 150-200 years ago. If this observation is confirmed, many studies on the input-output budgets may be plagued by dramatic land-use changes that took place after the industrial revolution. Specifically, in Central Europe most of the semi-natural mixed hardwoods were replaced by Norway spruce planted for commercial reasons.

Many small watershed studies are specifically set up to gauge the human impact on isolated natural systems. In these systems annual mass balances are usually highly variable and single year data cannot realistically be used to measure effect on specific processes, such as weathering rates. Even in undisturbed watersheds annual input-output budgets vary in response to natural climatic variability.

Potassium input-output budgets derived in the first two years of the Hubbard Brook study were in error by 56%, when compared with the data collected over a longer, more representative period (Likens *et al.*, 1967). A 25 year record of the chemistry of bulk precipitation and streamwater chemistry testifies for further variability, i.e. marked decline in base cation concentrations and inputs (Driscoll *et al.*, 1989). This shows the value of long-term small watershed studies in producing accurate estimates of fluxes of elements.

Long-term data sets are extremely valuable in studying environmental change on ecosystems. In southernmost Norway, at Birkenes site such records began in 1972. Steady decline in calcium and magnesium was observed throughout the 1972-87 period. This trend is the opposite to the observed gradual decline in sulphate deposition and streamwater concentrations (Christophersen *et al.*, 1990); the reason for this behaviour may be ongoing acidification of the catchment soils.

Few researchers are lucky enough to have the resources available to set up highly instrumented small watershed studies. Although sophisticated filter gauge collectors, wet-only samplers, data loggers and automatic stream-solute samplers are advantageous, reasonably accurate small watershed budgets can be obtained with simple equipment. The most important and probably the most expensive outlay will be to set up a means of accurately measuring discharge. This usually involves constructing a control structure and this, associated with well-sited precipitation collectors and a representative river-water sampling procedure, will provide the basis for a sound estimate of annual input-output budgets. In some cases, however, the value of many small watershed studies is diminished by insufficient planning and site validation. Site selection, in terms of reconnaissance ground surveys, preliminary sampling and rain collection trials, associated with information on the history of the watershed, will provide a firm basis for a successful small watershed study.

8.4 DEVELOPMENT OF WATERSHED ELEMENT BUDGETS

Measurement of inputs and outputs of dissolved, gaseous and particulate materials in small watersheds poses several technical/instrumental problems. It also requires careful consideration of sampling interval, handling/preparation of the sample, storage and analysis. Another important consideration is quality control. This has been highlighted by Hornung *et al.* (1990) as a major problem when comparing results from different areas.

8.4.1 ATMOSPHERIC DEPOSITION AND THROUGHFALL INPUTS

Precipitation inputs into watersheds occur by wet, dry or occult deposition. Methods for deposition collection have been extensively reviewed by Gregory and Walling (1973). Bulk deposition collectors, e.g. collection vessels exposed continuously over the entire period of interest, are most commonly used in small watershed studies, although these tend to undersample dry and occult inputs and lead to errors in the estimate of bulk deposition.

Snow represents a particularly difficult input to quantify. This problem is even amplified in sparsely vegetated mountainous areas with exposed upland watersheds (Creasey *et al.*, 1986). Snow can be blown over large distances into and out of the watershed and in this way the precipitation collector may lose or retain snow and under or overestimate atmospheric inputs into watersheds.

In some areas dry and occult depositions represent the major inputs into the watershed. This problem is enhanced in the vicinity of seashore, sources of industrial air pollution and at high-elevation sites, exposed to cloud deposition events. Relative error associated with determination of dry or occult deposition in the vicinity of sources may become unacceptably high. For instance, Paces (1985) reports results from a catchment located in a heavily industrialized region; this catchment is accepting $19.8 \text{ kg ha}^{-1} \text{ year}^{-1}$ in bulk sulphur deposition and input of ; another $88.6 \text{ kg ha}^{-1} \text{ year}^{-1}$ is inferred as sulphur dioxide dry deposition.

Although particulates and droplets can be directly collected using specialized filter collectors, other indirect methods are more widely used to estimate dry/occult deposition in small watersheds. Throughfall can be monitored in carefully placed bulk collectors and used as a measure of total atmospheric inputs, if it is assumed that wet deposition washes off dry and occult-deposited particles from vegetation surfaces (Grennfelt *et al.*, 1985). However, it must be assumed that no ion exchange reactions occur in the canopy and this is clearly not always the case (e.g. Nihlgård, 1970; Mayer and Ulrich, 1974).

Chloride has also been used to estimate dry and occult deposition. Dry-deposited chloride is estimated from the difference between the wet-deposited chloride flux (wet-only or bulk samples) and streamwater output. The dry-deposited amounts of other marine-derived elements, such as Mg and Na, can then be estimated from the cation/chloride ratio (Edwards *et al.*, 1984). Grennfelt *et al.* (1985) used this approach for adjustment of deposition values for the Gårdsjön Lake area.

Both these methods for estimating dry and occult deposition are based on several underlying assumptions, which may be more accurately met in some areas than others. Particulate inputs into watersheds are invariably the most difficult to measure accurately and errors may be large in certain regions. Ideally more than one method should be employed to estimate dry and occult inputs in small watershed studies.

Small catchments have been widely used for calculation of sulphur dry deposition. This task has been successfully undertaken especially in catchments located in previously glaciated areas with thin soils (such as HBEF, TLW, Birkenes, Gårdsjön), but failed in areas with deeper soils. Presence of Fe and Al hydroxy oxides in these soils promotes elevated sulphate adsorption resulting in net gain of sulphur in these catchments (Rochelle *et al.*, 1987).

8.4.2 SOIL AND BIOMASS POOLS AND TRANSFERS

Soil is chemically, biologically and hydrologically dynamic, with changes occurring over all time scales from minutes to tens of thousands of years. In the present context, changes over less than a decade or so are most relevant.

For upland watersheds it is often assumed that soil organic matter contents and distribution are at or near equilibrium. If this is not the case, it is necessary to be able to estimate the effects of organic matter accumulation or degradation upon element fluxes. This is especially important for soil organic matter constituent elements. For example, large amounts of N may be retained in thickening organic horizons, even in mature forests (Billett *et al.*, 1990).

The solubility of soil organic matter is also an important control on the removal of elements from watersheds. This includes not only the constituent elements, but also organically complexed metallic ions.

Secondary minerals are an important sink for a number of elements (Al, Si, K, Mg) produced by the weathering of primary minerals. Interactions between solutes in soil water and secondary minerals will modify ionic inputs from soil drainage water by fixation, ion exchange and sorption reactions. Estimates of weathering rates for elements such as Ca and Na, which remain largely in solution, are likely to be most accurate (Paces, 1986).

Apart from its influence upon deposition fluxes, vegetation modifies element budgets via uptake from the soil solution and incorporation into biomass. Elements such as Al and Si are commonly considered to be conservative in nature and in dynamic equilibrium with the biomass (Cleaves *et al.*, 1970). Few studies have, however, verified this and there is some evidence that Si accumulates in ecosystems, either in biomass or in secondary minerals (Bartoli, 1983; Waylen, 1979). Biomass accumulation will clearly lead to short-term removal of elements such as Ca, Mg and N, P and K. For maturing trees quantification of this flux is difficult although strategically placed tension lysimeters can be used to provide an estimate of root uptake. Ideally, matched catchments, with different vegetation communities can also be used, although in practice it may be difficult to relate differences in element fluxes to vegetation effects (e.g. Feger *et al.*, 1990).

Incorporation of elements into microbial biomass is not normally regarded as a separate problem to be resolved, as it is generally assumed that this component too is at or near equilibrium. This is not necessarily true, particularly at times when there is major watershed disturbance like clearfelling.

At Coweeta all control catchments show large apparent accumulations of sulphate ranging from 6 to 11 kg ha⁻¹ year⁻¹, the lowest retention occurs at high elevations. Sulphur is being retained through sulphate adsorption and, mainly, through transformation of mobile sulphate anion into immobilized organic sulphur pool (Swank *et al.*, 1985).

Fuller *et al.* (1987) tested through the Hubbard Brook clearcut experiment at watershed W5 seven hypotheses on processes regulating the pattern of streamwater chemistry following deforestation. Deforestation led to apparent increase in nitrate concentrations and export. At the same time, stream was acidified but streamwater sulphate concentrations decreased. Fuller *et al.* (1987) explain this pattern as a consequence of enhanced sulphate adsorption in mineral soil. This marked increase in retention capacity resulted from the temporary soil acidification by nitric acid formed through breakdown of organic matter. Mitchell *et al.* (1989) verified this scheme through direct measurements of soil-adsorbed sulphate increase that explains 88% of the streamwater sulphate decline.

8.4.3 STREAM EXPORT OF ELEMENTS

The main losses of dissolved and particulate materials derived from weathering and erosion in watersheds occur by transport in rivers. Although watershed studies that measure both particulate and dissolved fluxes are relatively scarce, several studies have shown that particulate losses may be significant (Likens *et al.*, 1977; Reynolds, 1986).

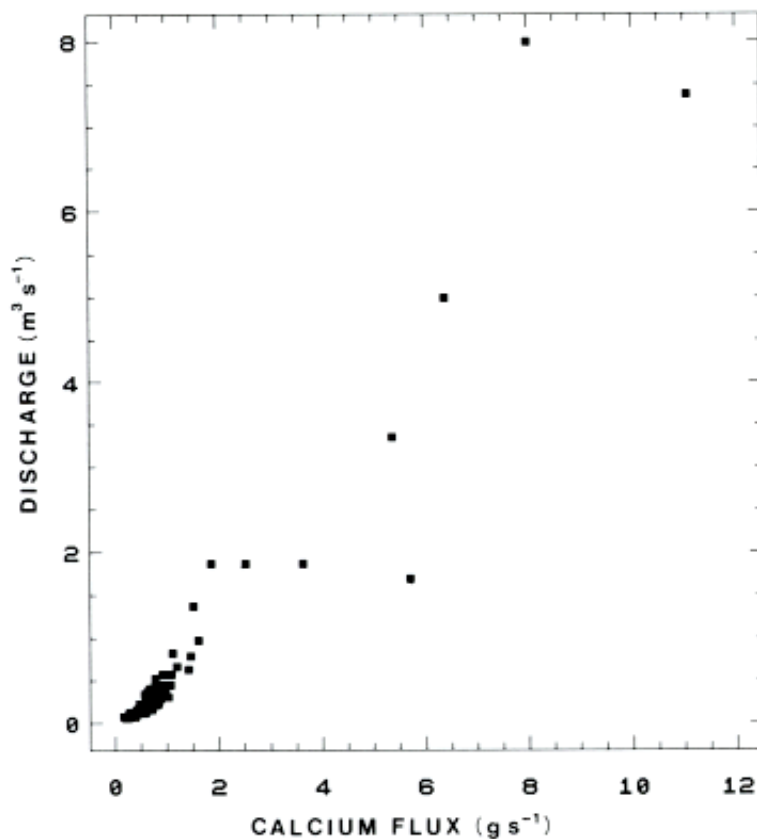


Figure 8.1 The relationship between discharge and Ca flux in the Allt Darrarie watershed, NE Scotland.

An adequate sampling frequency is essential in terms of monitoring dissolved and particulate (suspended load and bed load) fluxes from watersheds (Edwards *et al.*, 1984; Walling and Webb, 1986). Solute concentrations of ionic species involved in weathering reactions tend to exhibit an inverse relationship with discharge. It is, however, important to sample high discharge events when fluxes of solutes may be large.

For example, [Figure 8.1](#), Shows the relationship between discharge and Ca flux in the Allt Darrarie watershed in NE Scotland for weekly samples over a two-year period. Calcium fluxes vary from 0.21 g s^{-1} at low flow to 11.07 g s^{-1} at high flow. Although concentrations of elements like Ca decrease with increasing discharge during storms, fluxes clearly increase. It is therefore essential to use a sampling strategy which adequately allows for episodic events, including both storms and snowmelt. This is particularly important when sampling the suspended load in rivers. A cumulative duration curve of the dissolved and suspended load of the River Creedy in the United Kingdom Shows that 90% of the suspended and dissolved loads leave the watershed on 22 and 204 days of the year, respectively ([Figure 8.2](#)). Suspended material is predominantly moved during periods of high flow and representative sampling during this part of the hydrograph is crucial.

Quantification of elemental fluxes from small watersheds requires the measurement of the concentrations

of elements as solutes and particulate materials, and of discharge. Accurate measurement of discharge is important because annual fluxes of elements from watersheds relate directly to discharge (Johnson *et al.*, 1968). In watersheds with long runs of data, cation outputs can be predicted from annual discharge (Likens *et al.*, 1977).

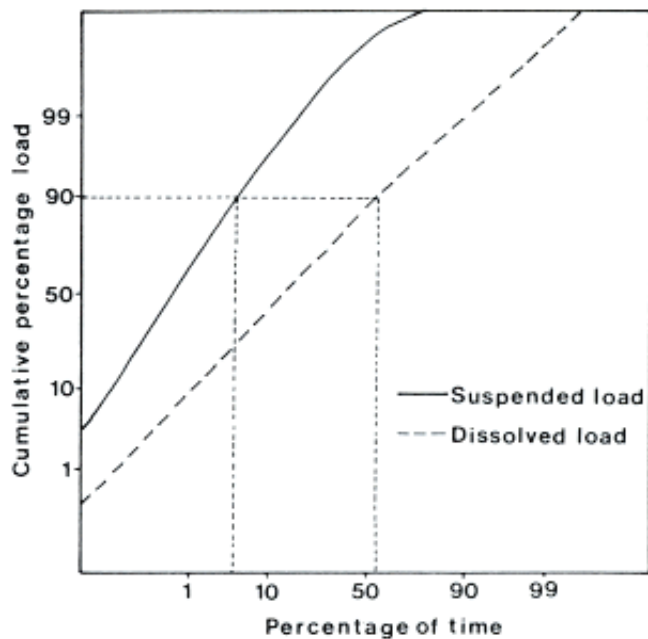


Figure 8.2 Duration curve of dissolved and suspended load of the Creedy, United Kingdom (after Walling and Webb, 1986; reprinted by permission of John Wiley & Sons Ltd).

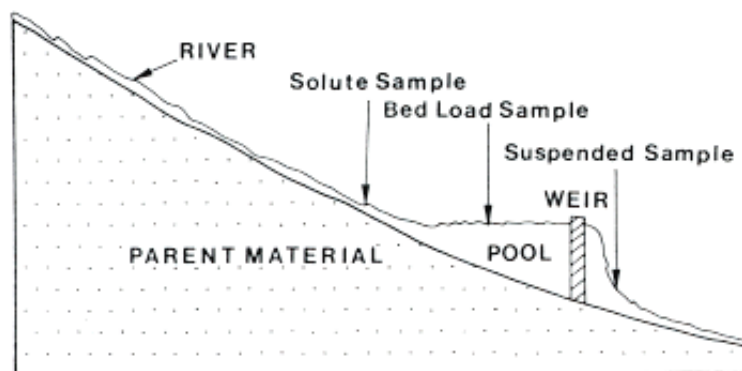


Figure 8.3 A sampling procedure for the measurement of dissolved and particulate fluxes (modified from Likens *et al.*, 1977; reproduced by permission of SpringerVerlag).

A sampling procedure for the measurement of solute and particulate fluxes is illustrated in [Figure 8.3](#). River-water solute ion concentrations can either be monitored continuously using ion selective electrodes or by composite sampling which gives a single representative sample over a given period. However, the most popular method of sampling involves taking single spot samples at fixed intervals. The choice of method depends not only upon logistical and financial considerations but also upon the hydrochemical behaviour of the watershed.

Suspended load and bed load can be measured using a number of techniques (Reynolds *et al.*, 1990).

These vary from taking large spot samples (followed by filtration) to the use of turbidity meters for quantification of suspended load. Bed load is commonly measured using sediment traps, either associated with permanent structures (such as flumes or reservoirs) or by using portable bed load samplers. Alternatively, river-bed tracing methods can be used. In steep "flashy" watersheds particulate loads are difficult to measure accurately, because particulate concentrations are very low at baseflow and peak rapidly after a specific flow velocity has been exceeded. The importance of accurate measurement of particulates is illustrated in [Table 8.1](#), which shows that for some weathering-derived elements, in particular Fe, Al and P, particulate losses can make up a significant percentage of the overall output from small watersheds (Likens *et al.*, 1977).

Table 8.1 Annual outputs of dissolved and particulate constituents from watershed W6 at Hubbard Brook (after Likens *et al.*, 1977)

| Element | Particulate and dissolved (kg ha ⁻¹) | Particulate (% of total) | Dissolved (% of total) |
|---------|--|--------------------------|------------------------|
| Al | 3.37 | 40.9 | 59.1 |
| Ca | 13.93 | 1.7 | 98.3 |
| Cl | 4.58 | 0 | 100 |
| Fe | 0.64 | 100 | 0 |
| Mg | 3.34 | 5.7 | 94.3 |
| N | 4.01 | 2.7 | 97.3 |
| P | 0.02 | 63.2 | 36.8 |
| K | 2.40 | 21.7 | 78.3 |
| Si | 23.8 | 26.0 | 74.0 |
| Na | 7.48 | 3.3 | 96.7 |
| S | 17.63 | 0.2 | 99.8 |
| | 12.3 | 32.4 | 67.5 |

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Discharge measurement involves one of a large number of methods which have been summarized in detail by Gregory and Walling (1973). The choice of method largely depends upon the nature of the watershed and the characteristics of the channel flow. Techniques range from dilution and volumetric gauging to the use of permanent control structures such as weirs and flumes. One of the most popular structures in small watershed studies is the V-notch sharp crested weir ([Figure 8.4](#)). Flow velocity is computed from the relationship between the shape of the control structure and the height of water in the

control structure. For obtaining accurate results it is crucial to maintain the measuring structure free of bed load.

Outputs from small watersheds are calculated by multiplying discharge by concentration for a given sampling frequency. To a certain degree, the larger the amount of concentration/discharge data, the more accurate the budget. This relatively simple calculation can be refined by using regression equations relating concentration to discharge (Clayton, 1986), although this method produces lower fluxes, particularly in "flashy" upland watersheds (Edwards *et al.*, 1984).

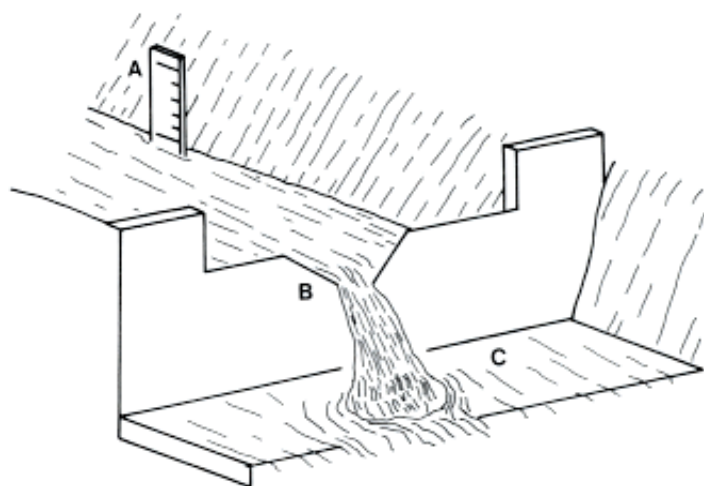


Figure 8.4 A typical control structure for the measurement of discharge in small watershed research (after Gregory and Walling, 1973; reprinted by permission of the authors and publishers, Edward Arnold): A, gauge board or staff gauge; B, 90° V-notch; C, concrete platform.

8.4.4 OTHER FLUXES

Unlike those of the metallic elements and P, the C, N and S cycles all have significant gaseous components. For precise budget assessments these components must be quantified, or ignoring them justified. Species to be considered include carbon dioxide and methane, sulphur dioxide and hydrogen sulphide, ammonia, oxides of nitrogen, vapour-phase nitric acid and gaseous nitrogen. Both deposition and evolution fluxes should be monitored, unless a particular flux is known to be negligible at the catchment of interest. Field-based knowledge of denitrification fluxes, especially when nitrogen gas is evolved, is still very limited. Andreae and Schimel (1989) have recently edited a comprehensive text on gas exchange between terrestrial ecosystems and the atmosphere.

Element budgets can also be influenced by additional inputs and outputs of wind-blown material. Aeolian fluxes are most likely to be important in watersheds in industrial, semi-arid/arid or glacial regions or in areas in which there are largescale erosion problems (e.g. Paces, 1986).

8.5 SUMMARY

The difference between solute inputs and outputs in small watersheds (sometimes called the watershed balance sheet approach), is a commonly used method for measuring mineral weathering rates (e.g. Verstraten, 1977; Waylen, 1979; Creasey *et al.*, 1986; Likens *et al.*, 1977).

The use of the watershed mass balance approach to calculate weathering rates has a number of important underlying assumptions. These are: (i) all inputs and outputs of water originate from precipitation alone;

(ii) the watershed is in a steady state with respect to biomass accumulation and soil chemistry/mineralogy; and (iii) water storage within the watershed does not change over a long period of time. Although the rationale and validity behind these assumptions have already been discussed, the concept of steady state in watersheds is in reality difficult both to define and to measure.

Small watersheds are an excellent means of measuring environmental effects on processes such as weathering rates in the field, because they restrict spatial variability and enable accurate monitoring of inputs and outputs. In reality, however, few watershed studies are specifically set up to measure effects on specific processes and in many cases this makes interpretation of input-output budgets difficult.

8.6 SUGGESTED READING

Interested readers may find much practical information in the classical work of Likens *et al.* (1977) summarizing the first 15 years of research at Hubbard Brook, NH, USA. Swank and Crossley (1988) edited an extensive volume of information about Coweeta Hydrologic Laboratory, North Carolina, USA. Andersson and Olsson (1985) described the biogeochemistry of an acid forest lake at Swedish west coast. Concepts of the runoff generation and ties between soils and stream are explored in work of Trudgill (1986). Derivation of weathering rates is explained and discussed in depth in Colman and Dethier (1986).

8.7 REFERENCES

- Andersson, F. and Olsson, B. (Eds) (1985) Lake Gårdsjön-An Acid Forest Lake and its Catchment. *Ecol. Bull. (Stockholm)* **37**, 336 pp.
- Andreae, M.O. and Schimel, D.S. (1989) *Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere*. Dahlem Workshop Reports, Life Sciences Research Report 47, Wiley-Interscience, Chichester, 349 pp.
- April, R.H. and Newton, R.M. (1985) Influence of geology on lake acidification in the ILWAS watersheds. *Wat. Air Soil Poll.* **26**: 373-386.
- Bartoli, F. (1983) The biogeochemical cycle of silicon in two temperate forest ecosystems. In Hallberg R. (Ed.): *Environmental Biogeochemistry*. *Ecol. Bull.* **35**: 469-476.
- Billett, M.F., FitzPatrick, E.A. and Cresser, M.S. (1990) Changes in the carbon and nitrogen status of forest soil organic horizons between 1949/50 and 1987. *Environmental Pollution* **66**(1): 67-79.
- Christophersen, N., Robson, A., Neal, C., Whitehead, P.G., Vigerust, B. and Henriksen, A (1990) Evidence for a long-term deterioration of streamwater chemistry and soil acidification at the Birkenes catchment, southern Norway. *J. Hydrol.* **116**: 63-76.
- Clayton, J .L. (1986) An estimate of plagioclase weathering rate in the Idaho batholith based upon geochemical transport rates. In Colman, S.M. and Dethier, D.P. (Eds): *Rates of Chemical Weathering of Rocks and Minerals*. Academic Press, Orlando, Florida, pp. 453-466.
- Cleaves, E. T., Godfrey, A.E. and Bricker, O.P. (1970) Geochemical balance of a small watershed and its geomorphic implications. *Geol. Soc. Am. Bull.* **81**: 3015-3032.
- Cleaves, E.T., Fisher, D.W. and Bricker, O.P. (1974) Chemical weathering of serpentinite in the eastern Piedmont of Maryland. *Geol. Soc. Am. Bull.* **85**: 437-444.

- Colman, S.M. and Dethier, D.P. (Eds) (1986) *Rates of Chemical Weathering of Rocks and Minerals*. Academic Press, Orlando, Florida.
- Creasey, J., Edwards, A.C., Reid, J.M., MacLeod, D.A. and Cresser, M.S. (1986) The use of catchment studies for assessing chemical weathering rates in two contrasting upland areas in northeastern Scotland. In Colman, S.M. and Dethier, D.P. (Eds): *Rates of Chemical Weathering of Rocks and Minerals*. Academic Press, Orlando, Florida, pp. 467-502.
- Driscoll, C.T., Likens, G.E., Hedin, L.O., Eaton, J.S. and Bormann, F.H. (1989) Changes in the chemistry of surface waters: 25-years results at the Hubbard Brook Experimental Forest, N.H. *Environ. Sci. Technol.* **23**: 137-143.
- Eaton, J.S., Likens, G.E. and Bormann, F.H. (1978) The input of gaseous and particulate S to a forest ecosystem. *J. Ecol.* **54**: 87-98.
- Edwards, A.C., Creasey, J. and Cresser, M.S. (1984) The conditions and frequency of sampling for elucidation of transport mechanisms and element budgets in upland drainage basins. Proceedings of the International Symposium on Hydrochemical Balances of Freshwater Systems. Uppsala, Sweden, pp. 187-202.
- Feger, K.H., Brahmmer, G. and Zöttl, H.W. (1990) Element budgets of two contrasting catchments in the Black Forest, Federal Republic of Germany. *J. Hydrol.* **116**(1-4): 85-99.
- Fuller, R.D., Driscoll, C.T., Lawrence, G.B. and Nodvin, S.C. (1987) Processes regulating sulphate flux after whole-tree harvesting. *Nature* **325**: 707-709.
- Galfi, J. and Palos, M. (1970) The use of seismic refraction measurements for groundwater *prospecting*. *Internat. Assoc. Sci. Hydrol.* **15**: 41-46.
- Goldstein, R.A., Chen, C. W. and Gherini, S.A. (1984) *The Integrated Lake-Watershed Acidification Study 4: Summary of Major Results (EA-3221)*. Electric Power Research Institute, Palo Alto, California.
- Gregory, K.J. and Walling, D.E. (1973) *Drainage Basin Form and Process*. Edward Arnold, London, 458 pp.
- Grennfelt, P., Larsson, S., Leyton, P. and Olsson, B. (1985) Atmospheric deposition in the Lake Gårdsjön area, SW Sweden. *Ecol. Bull. (Stockholm)* **37**: 101-108.
- Homung, M., Reynolds, R. and Hat ton, A.A. (1985) Land management, geological and soil effects on streamwater chemistry in upland Wales. *Appl. Geog.* **5**: 71-80.
- Hornung, M., Rodá, F. and Langan, S.J. (Eds) (1990) A review of small catchment studies in western Europe producing hydrochemical budgets. Air Pollution Research Report 28, Commission of the European Communities, 186 pp.
- Huff, D.D. and Swank, W.T. (1985) Modelling changes in forest evapotranspiration. In Anderson, M.G. and Burt, T.P. (Eds): *Hydrological Forecasting*. John Wiley & Sons, Chichester, England, pp. 125-151.
- Jansson, P.-E. (1991) Simulation Model for Soil Water and Heat Conditions. Description of the SOIL model. Report 165. Swedish University of Agricultural Sciences. Dept. of Soil Sciences. Division of Agricultural Hydrotechnics. Uppsala, 72 pp.

- Jeffries, D.S., Kelso, J.R.M. and Morrison, I.K. (1988) Physical, chemical, and biological characteristics of the Turkey Lakes Watershed, Central Ontario, Canada. *Can. Spec. Publ. Fish. Aquat. Sci.* **45** (Suppl): 3-13.
- Johnson, D.W. and Henderson, G.S. (1979) Sulfate adsorption and sulfur fractions in a highly weathered soil under a mixed deciduous forest. *Soil Science*, **128**: 34-40.
- Johnson, N.M., Likens, G.E., Bormann, F.H. and Pierce, R.S. (1968) Rate of chemical weathering of silicate minerals in New Hampshire. *Geochim. Cosmochim. Acta* **32**: 531-545.
- Likens, G.E., Bormann, F.H., Eaton, J.S., Pierce, R.S. and Johnson, N.M. (1967) The calcium, magnesium, potassium, and sodium budgets for a small forested ecosystem. *Ecology* **48**: 772-785.
- Likens, G.E., Bormann, F.H., Pierce, R.S., Eaton, J.S. and Johnson, N.M. (1977) *Biogeochemistry of a Forested Ecosystem*. Springer-Verlag, New York, 146 pp.
- Mayer, R. and Ulrich, B. (1974) Conclusions on the filtering action of forests from ecosystem analyses. *Oecol. Plant.* **9**: 157-168.
- Mitchell, M.J., Driscoll, C.T., Fuller, R.D., David, M.B. and Likens, G.E. (1989) Effect of whole tree harvesting on the sulfur dynamics of a forest soil. *Soil Sci. Soc. Am.J.* **53**: 933-940.
- Nihlgård, B. (1970) Precipitation, its chemical composition and effects on soil water in a beech and a spruce forest in south Sweden. *Oikos* **21**: 208-217.
- Nilsson, J. and Grennfelt, P. (Eds) (1988) *Critical Loads for Sulphur and Nitrogen*. *NORD 1988:15* Nordic Council of Ministers, Copenhagen, Miljörapport 15, 418 pp.
- Paces, T. (1985) Sources of acidification in Central Europe estimated from elemental budgets in small basins. *Nature* **315**: 31-36.
- Paces, T. (1986) Rates of weathering and erosion derived from mass balance in small drainage basins. In Colman, S.M. and Dethier, D.P. (Eds): *Rates of Chemical Weathering of Rocks and Minerals*. Academic Press, Orlando, Florida, pp. 531-550.
- Peters, N.E. (1991) Chloride cycling in two forested lake watersheds in the west-central Adirondack Mountains, New York, USA. *Wat. Air Soil Poll.* **59**: 201-215.
- Reynolds, B. (1986) A comparison of element outputs in solution, suspended sediments and bedload for a small upland catchment. *Earth Surf. Proc. Landforms* **11**: 217-221.
- Reynolds, B., Neal, C., Hornung, M. and Stevens, P.A. (1986) Baseflow buffering of streamwater acidity in five mid-Wales catchments. *J. Hydrol.* **87**: 167-185.
- Reynolds, B., Hudson, J.A. and Leeks, G. (1990) Field methods for estimating solute and sediment losses in small upland streams. In Harrison, A.F., Ineson, P. and Heal, O. W. (Eds): *Nutrient Cycling In Terrestrial Ecosystems*. Elsevier, pp. 103-129.
- Rochelle, B.P., Church, M.R. and David, M.B. (1987) Sulfur retention at intensively studied sites in the U.S. and Canada. *Wat. Air Soil Poll.* **33**: 73-83.
- Swank, W.T. and Crossley, D.A. Jr (Eds) (1988) *Forest Hydrology and Ecology at Coweeta*. Ecological

Studies, Vol. 66. Springer- Verlag, New York, 469 pp.

Swank, W. T., Fitzgerald, J .W. and Strickland, T.C. (1985) Transformation of sulfur in forest floor and soil of a forest ecosystem. In johansson, I. (Ed.): *Hydrological and Hydrogeochemical Mechanisms and Model Approaches to the Acidification of Ecological Systems*. International Hydrological Programme NHP-Report 10; Uppsala, Sweden; Oslo, Norway, pp. 137-145.

Trudgill, S. T. (Ed.) (1986) *Solute Processes*. Wiley-Interscience, 512 pp.

Verstraten, J .M. (1977) Chemical erosion in a forested watershed in the Oesling, Luxembourg. *Earth Surf. Proc. Landforms* **2**: 175-184.

Walling, D.E. and Webb, B. W. (1986) Solutes in river systems. In Trudgill, S. T. (Ed.): *Solute Processes*. Wiley-Interscience, pp. 251-327.

Waylen, M.J. (1979) Chemical weathering in a drainage basin underlain by Old Red Sandstone. *Earth Surf. Proc. Landforms* **4**: 167-178.

Wright, R.F. and Henriksen, A. (1990) The RAIN project-an overview. In Mason, B.J. (Ed.): *The Surface Waters Acidification Programme*. University Cambridge Press, Cambridge, pp. 161-166.

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