SCOPE 51 - Biogeochemistry of Small Catchments

7 Hydrochemical Methods and Relationships for Study of Stream Output from Small Catchments

RAYMOND G. SEMKIN, DEAN S. JEFFRIES AND THOMAS A. CLAIR

7.1 BASIC HYDROCHEMICAL CONCEPTS

7.1.1 PURPOSE OF HYDROCHEMICAL INVESTIGATIONS

Aquatic research in small catchments has focused on the hydrological pathways and biogeochemical transformations of precipitation as it passes through the vegetative canopy, infiltrates the soil and rock mantle and is discharged as groundwater into streams or lakes. Various avenues of study are followed including the evaluation of the changes in stream chemistry with varying flow conditions (Johnson *et al.*, 1969; Hall, 1970, 1971; Lawrence and Driscoll, 1990) and determination of chemical budgets for terrestrial or aquatic systems (Likens *et al.*, 1977; Hultberg, 1985; Munson and Gherini, 1991).

Understanding the quantitative techniques used to characterize both hydrological and chemical processes in a watershed is basic to the conduct of hydrochemical investigations. Inaccurately measured stream discharge or inappropriate methods for sampling particulate and dissolved chemical species can lead to significant errors in establishing chemistry-discharge relationships or in mass balance calculations. The frequency of sample collection can also affect the accuracy of chemical budgets particularly in small catchments that typically exhibit episodic flow patterns. The objective of this chapter is to describe techniques for gathering hydrochemical information in a catchment. Emphasis is put on the operational requirements of "calibrating" a basin and includes discussions on streamwater composition and variability, stream discharge measurement and sampling protocol, and frequency. Also provided is a brief outline of various methods of editing, analysing and presenting hydrochemical data.

7.1.2 STREAMWATER CHEMISTRY

The general chemistry of runoff waters is best considered using the reviews of world average river water that have been prepared over the past few years. While presenting a global perspective on streamwater chemistry and the factors controlling it. the conclusions drawn are generally applicable, even at the small catchment scale. Hence we will make extensive use of Berner and Berner (1987) in the following discussion.

7.1.2.1 Dissolved substances

Major constituents

The major ion composition of surface waters is controlled by the interaction of precipitation with surficial geological and biological materials. As a consequence, the important factors in determining water chemistry are rainfall quantity and quality, evaporation, mineral weathering, topographic relief and the vegetative cover and biological activity in a given basin.

Table 7.1 Mean composition of river waters of the world (after Brownlow, 1979)

Constituent	mg l^{-1}	Meq l^{-1}
HCO_3^-	58.4	0.958
SO_4^{2-}-S	3.7	0.233
Cl^-	7.8	0.220
NO_3^--N	0.2	0.017

Total anions	78.4	1.428
Ca^{2+}	15.0	0.750
Mg^{2+}	4.1	0.342
Na^+	6.3	0.274
K^+	2.3	0.059
Total cations	27.7	1.425

Table 7.2 Source apportionment (percent) of major constituents in world river water (after Berner and Berner, 1987)

Constituent	Atmos. Salt	Weathering[a]			Pollution
		Carb.	Silic.	Evap.	
Ca^{2+}	0.1	65	18	8	9
HCO_3^-	<<1	61	37	0	2
Na^+	8	0	22	42	28
Cl^-	13	0	0	57	43
SO_4^{2-}	2	0	0	22	30
Mg^{2+}	2	36	54	<<1	8
K^+	1	0	87	5	7
H_4SiO_4	<<1	0	99	0	0

[a]Rock types: carb.=carbonates; silic.=silicates; evap.=evaporites.

The world average river concentration of major ions is approximately 100 mg l^{-1} (Berner and Berner, 1987), which is approximately 20 times greater than the concentration in rain. Evaporation can increase the total dissolved solids in rainfall by a factor of 2. Hence, the primary mechanism for elevating the ionic content of surface waters is mineral weathering.

Calcium and bicarbonate dominate the ionic chemistry of most natural fresh waters, accounting for about 60% of these ions on an equivalent basis (Table 7.1). Weathering of carbonate minerals, primarily in sedimentary rocks, is a major source of these ions (Table 7.2). Carbonic acid weathering of silicate rocks is also an important source of Ca^{2+} and HCO_3^- and also K^+, Mg^{2+}, Na^+ and dissolved Si. Dissolution of

evaporitic minerals such as halite and gypsum is a major source of Cl^-, Na^+ and SO_4^{2-} in average river water. Atmospherically dispersed sea salts are also a source of Cl^- and Na^+ in freshwaters, accounting for 13% and 8% of the world average river concentrations, respectively. Environmental pollution, through a combination of point-source and diffuse emissions of contaminants, can severely alter the quality of natural waters. Berner and Berner (1987) reported that 43%, 30% and 28% of the SO_4^{2-}, Cl^- and Na^+, respectively, in the world average river composition was derived from pollutive sources (Table 7.2).

Minor constituents

The discussion of minor constituents will be restricted to two of the elements required for the synthesis of living material: nitrogen and phosphorus. Nitrogen and phosphorus are involved in a complex series of biological reactions. Uptake of P and N by algae in the photic zone occurs at a ratio of approximately 1: 16. Recycling of these elements to the water column takes place in roughly the same ratio. Consequently, biological activity within the aquatic ecosystem is important in determining the concentration and distribution of N and P. Other important factors are climatological conditions, atmospheric deposition, weathering of P- bearing rocks, sediment-water interactions, and human activities including agricultural and forestry practices as well as the discharge of domestic wastewaters.

The terrestrial N cycle strongly influences N concentrations in surface water. Biological fixation, which accounts for »59% of the terrestrial N pool, is accomplished by microorganisms living symbiotically in higher plants, particularly legumes, and lichens on trees (Bemer and Bemer, 1987). Dissolved organic nitrogen, NO_3^-, and NH_4^+ in precipitation and dry deposition account for approximately 24% of the total fixed nitrogen delivered to land. Of this, 90% of the NH_4-N and 76% of the NO_3^--N can be attributed to human activities. The balance of the fixed nitrogen delivered to land is in the form of NO_3^- and NH_4^+ in fertilizers. Terrestrial chemical transformations of nitrogen include the fixation of molecular nitrogen and the conversion of dissolved NO_3^- and NH_4^+ into plant organic matter. The organic matter is eventually decomposed by bacteria yielding ammonia, some dissolving in soil water as NH_4^+ and some escaping from the soil as NH_3 gas. Although most of the NH_4^+ and NO_3^- from organic matter is recycled by plants, nitrogen can be lost from the land directly to the atmosphere (82% of the total N output from land is gaseous) or in river water (Berner and Berner, 1987).

The river output of nitrogen is predominantly in the form of organic N (85%) and inorganic NO_3^- and NH_4^+ derived from organic matter decomposition. The fact that the total river output of organic N amounts to only 8% of the nitrogen assimilated annually by land-based biota attests to the efficiency of terrestrial N recycling (Berner and Berner, 1987).

Phosphorus is released into the environment as soluble P, primarily through rock weathering, although complexation with iron, calcium or aluminum, or absorption by clay minerals tends to produce insoluble chemical species not readily available to plants. The relatively low concentration of phosphorus in freshwater ecosystems causes P to be the limiting nutrient for biota (Schindler, 1976).

Unlike nitrogen, phosphorus has no stable gaseous phases in the atmosphere; therefore, most P lost from the land is via runoff. Similarly, a smaller proportion of the P to land input is provided by precipitation. Of the total phosphorus output in river runoff (22 Tg $year^{-1}$), some 90% is particulate organic and inorganic P and approximately one-half of this is related to anthropogenic activities such as deforestation

and agriculture (Berner and Berner, 1987). About 50% of the 2 Tg year^{-1} of dissolved P discharged by rivers is inorganic phosphate, mainly orthophosphate. This form of P is bioavailable.

Trace constituents

Geochemically speaking, a trace constituent is any element that is not a significant component of a mineral, i.e. it does not occur in its formula. In general, the concentration of a trace constituent in the earth's crust is <0.1% by weight (Brownlow, 1979).

The speciation and bioavailability of trace elements are regulated by physical and chemical interactions and equilibria. Various factors, including pH, redox potential, temperature, water hardness, carbon dioxide levels, the type and concentration of available ligands and chelating agents, as well as the nature and concentration of the trace element, affect these interactions. The presence of high concentrations of trace elements, particularly heavy metals, is problematic in view of the potential toxicity and bioavailability and the chance of bioaccumulation and hazards to human health. Heavy metals do not degrade but are transferred or stored in the aquatic environment where they may become available under the appropriate conditions.

Soluble metals can exist as simple or complex-free metal ions, ion pairs, coordination compounds or un-ionized organometallic chelates or complexes. The degree of metal speciation is a function of the pH, the stability of the hydrolysis products and the metal ion's tendency to form complexes with other organic (O and N functional groups) and inorganic (OH^-, CO_3^{2-}, SO_4^{2-}, Cl^-) ligands (Pagenkopf, 1978; Connell and Miller 1984). Because of the difficulty in measuring different metal species and the relative toxicities of the various forms, a total metal concentration is usually used when defining water quality guidelines and criteria.

Metal ions can be removed from solution by adsorption, ion exchange, complexation, precipitation and co-precipitation processes. Bottom sediments act as a sink for metals; however, various reactions both microbiological and physicochemical, can transform and redistribute the metals within the sediments and to the water column.

7.1.2.2 Suspended substances

The importance of suspended matter relates to its influence over water clarity and temperature and its interaction with both organic compounds and inorganic ions. The nature and discharge of suspended substances is determined by such factors as soil and vegetative cover, bedrock geology, relief and area of the drainage basin, climate and stream velocity. Land-use activities in a basin, including deforestation, agriculture, engineering works (reservoirs, bank stabilization, soil conservation, etc.) will also affect the concentration and distribution of suspended sediments. Major rivers have an average suspended solid concentration of 100 to 1000 mg l^{-1} with a world mean estimated to be 360 mg l^{-1} (Berner and Berner, 1987). Compared to the global chemical denudation rate of approximately 23 tonnes km^{-2} year^{-1} related to export of dissolved substances, the mechanical denudation rate of about 152 tonnes km^{-2} year^{-1} of suspended substances attests to the overall importance of the particulate load in riverine transport (Berner and Berner, 1987).

Particulate matter in natural water is generally divided into two fractions: (1) the inorganic component consisting of hydrous oxides and suspended minerals; and (2) organic macromolecules and organic colloids (Pagenkopf, 1978). The composition of inorganic suspended matter reflects chemical weathering of parent rock material, removal of more soluble elements, and perhaps reprecipitation of insoluble elements in secondary weathering products. As a consequence, river suspended matter is typically

enriched in relatively insoluble elements such as Al and Fe and depleted in the more easily weathered elements such as Na and Ca relative to the composition of the parent rock and to the dissolved load (Table 7.3).

Suspended particulate matter can have a high surface area and, depending upon its distribution and the sign and intensity of the surface electric charge, can exert control over the concentration and behaviour of solutes in water. In particular, the concentration of metal and organic compounds can be regulated by sorption processes associated with suspended matter. The adsorption of metal ions is strongly pH-dependent and favoured when the metal ion hydrolyses (Pagenkopf, 1978). The hydrophobicity of a dissolved organic compound influences the tendency for sorption to occur, i.e. the lower the compound's solubility in water, the greater the likelihood of adsorption to suspended matter. The type of functional groups and configuration of the organic molecule, its water solubility, ionization, polarity and charge distribution on cations all play an important role in characterizing the sorption phenomenon. (Water Quality Branch, 1987).

Table 7.3 Concentration of major elements in continental rocks, particulate (part.) and dissolved (diss.) matter (after Berner and Berner, 1987)

Element	Surficial rock conc. $(mg\ g^{-1})$	River part. conc. $(mg\ g^{-1})$	River diss. conc. $(mg\ g^{-1})$	Particulate load $(10^6\ t\ year^{-1})$	Dissolved load $(10^6\ t\ year^{-1})$	Park/ rock.	Part. load/ (Part. Load + Diss. load)
Al	9.3	94.0	0.05	1457	2	1.35	0.999
Ca	45.0	21.5	13.40	333	501	0.48	0.40
Fe	35.9	48.0	0.04	744	1.5	1.33	0.998
K	24.4	20.0	1.30	310	49	0.82	0.86
Mg	16.4	11.8	3.35	183	125	0.72	0.59
Na	14.2	7.1	5.15	110	193	0.50	0.36
Si	275.0	285.0	4.85	4418	181	1.04	0.96
P	0.6	1.2	0.03	818	1	1.89	0.82

Elizabeth Kay Berner/Robert A. Berner, The Global Water Cycle: Geochemistry and Environment, © 1987, pp. 188, 208. Reprinted by permission of Prentice Hall, Englewood Cliffs, New Jersey.

7.1.2.3 Composite parameters

Conductivity

Conductivity, or specific conductance, is a measure of the ionic content of a water sample and is commonly recorded potentiometrically by means of two platinized electrodes and a Wheatstone bridge. Freshly-distilled water has a conductivity of 0.5-2 μS cm^{-1}. Most natural waters fall in the range of 50-500 μS cm^{-1} range whereas highly mineralized waters have conductivity values in excess of 1000 μS cm^{-1} (Pagenkopf, 1978). An empirical relationship exists between specific conductance and total dissolved solids. Multiplying the conductivity value by a factor of 0.5 to 1.3 can provide a reasonable estimate of the TDS content (Pagenkopf, 1978). However, due to ion pairing in solutions of high ionic strength, the relationship may not be applicable in saline waters.

pH and alkalinity

The pH of water is a master variable (Stumm and Morgan, 1981) influencing virtually all physical, chemical and biological processes. It is the primary driving variable for weathering and therefore controls the concentration of most major ions in natural waters. The pH of water also affects transformation reactions and the availability of nutrients and metals. The biological processes of photosynthesis and respiration and physical actions of turbulence and aeration can influence pH by varying the CO_2 content in the water.

Hydrogen ion concentration is controlled by various buffer systems. Alkalinity is a measure of water's capacity to neutralize acidic compounds and is measured by successively titrating a water sample with strong acid to the bicarbonate and carbonic acid equivalence points. Although carbonates provide the primary buffering system in water, other species including naturally occurring organic anions, hydroxides, sulphides, silicates and phosphates may be important in regulating pH if they are present in significant concentrations.

7.1.3 STREAMWATER CHEMISTRY VARIABILITY

7.1.3.1 Temporal variability

Short-term variability

In small catchments, the stream discharge can be rather flashy with rapid flow, increases during prolonged heavy rain or snowmelt especially in small basins with steep slopes and. thin soils. Runoff generally subsides rapidly once precipitation ceases. Concomitant with these fluctuations in stream discharge, the chemical composition of streamwater can vary substantially. Common observations include a sharp decline in alkalinity and pH, Si, Ca^{2+}, Mg^{2+} and Na^+ with increasing flow. By contrast, the concentrations of dissolved organic C, K^+, Fe and Al tend to increase (Cresser and Edwards 1987; Hooper and Shoemaker, 1985; Sullivan *et al.*, 1986). These changes in streamwater chemistry during storm or snowmelt events are attributed to varying water pathways in the subsurface, involving, for example, alterations from micropore to macropore flow (Wilson *et al.*, 1990) or changing contributions from various soil horizons (Swistock *et al.*, 1989; Mulder *et al.*, 1990).

When hypothesizing variable flow paths, it is implicitly assumed that each water pathway gives rise to a characteristic solution composition related to the chemical controls afforded by different soil environments. Therefore, predicting the short-term variation in the chemical composition of streamwater requires a knowledge of the catchment's hydrological behaviour under diverse conditions as well as insight into chemical processes occurring in the relevant soil environments.

Seasonal variability

Chemical variations may occur over longer or seasonal time scales. For example, Sullivan *et al.* (1986) and McAvoy (1988) attributed increases in streamwater H^+ and Al observed during spring snowmelt and autumn rainstorms to seasonal variations in hydrology, e.g. shallow water flowpaths during wet conditions and deeper water pathways during base flow.

The autumnal increase in Cl^- in Birkenes streamwater (Christophersen *et al.*, 1990) is due partly to evaporative concentration of soil solutions during the preceding months and partly to seasonally elevated Cl^- concentrations in precipitation inputs. Christophersen *et al.* (1982) had previously attributed the contemporaneous sharp increase in streamwater SO_4^{2-} at Birkenes, observed after prolonged dry

summers, to S-mineralization processes in the catchment.

Strong seasonal declines in streamwater NO_3^-, occurring from spring snowmelt through summer, have been related to soil frost promoting nitrification (Likens *et al*., 1977), as well as to increased NO_3^- uptake during the growing season (Reid *et al., 1981)*.

It seems that most of the seasonal variations in streamwater chemistry are driven by climatic (e.g. evaporation, precipitation quantity and quality, temperature) and biotic factors (e.g. nutrient assimilation, mineralization, nitrification, production of organic acids, transpiration). Therefore, similar to the short-term variations, seasonal variations are largely governed by processes taking place in the terrestrial part of the catchment.

Long-term variability

Changes occurring over several years, decades or even centuries may be related to changes in soil chemical, biological or physical properties, or changes in forest status. Long-term monitoring programmes of chemical parameters in streamwater are required to directly detect such changes and to date, only few such data sets (up to 25 years) exist. Data records have been collected in forested ecosystems in northeastern North America and northwestern Europe that are affected by acidic deposition. These multi-year data series show a general decline in the concentration of base cations in the runoff waters (Hubbard Brook, Driscoll *et al*., 1989; Ontario Lakes, Dillon *et al*., 1987; Birkenes, Christophersen *et at*., 1990). It is hypothesized that this decline results from a decrease in base saturation due to prolonged leaching of base cations; these catchments are characterized by already base-poor soils.

Also observed at these sites is a downward trend in streamwater SO_4^{2-} during the last decade that coincides with a decrease in the atmospheric deposition of SO_4^{2-}. The contemporaneous decrease in base cations and input acidity suggests that the rates of mineral weathering in these catchments are still too low to replenish the stores of exchangeable base cations. A decrease in a soil's base saturation is expected to be associated with a decline in soil pH and an increased solubility of soil-bound trace elements and Al.

The above discussion of temporal variability shows that the chemical evolution of surface waters occurs largely in the terrestrial environment. However, some variability may be related to processes occurring within the aquatic environment. For example, CO_2 degassing (e.g. Reuss and Johnson, 1985, 1986) and cation exchange with streambed material (e.g. Henriksen *et al*., 1988) can significantly alter the ionic composition on at least an episodic time scale. In-lake alkalinity generation (Schindler, 1986) is a process that may also cause temporal variability on a seasonal scale.

7.1.3.2 Spatial variability

Spatial variation in streamwater chemistry is reported in various catchment studies. At the Hubbard Brook Experimental Forest, Lawrence and Driscoll (1990) related chemical variations to changing flow that depended on elevation of the sampling site. At higher elevations, both H^+ and Al concentrations decreased hyperbolically with increases in stream discharge, whereas at lower elevations, they increased asymptotically with flow. The differing chemical responses were attributed to changes in subsurface flow paths at higher locations and the effects of variable source area at middle- or low-elevation sites. Chemical fluxes also varied downstream in the watershed. For example, the H^+ flux decreased from high to low elevation. The H^+ loading was greatest in coniferous, high-level areas where soils enriched in organic matter showed limited mineral dissolution. At mid-elevations, where deciduous forest

predominates, H^+ was effectively neutralized through dissolution of labile soil Al, and at still lower elevations, a thicker soil profile allowed for neutralization and a reduction of the H^+ flux via silicate weathering.

At the Turkey Lakes Watershed (TLW) in Ontario (Jeffries *et al*., 1988), stream waters in the headwater reaches of the basin are characterized as Ca^{2+}-SO_4^{2-} waters with alkalinity values about 50 μeq l^{-1}. At low elevation, Ca^{2+} levels double and HCO_3^- replaces SO_4^{2-} as the dominant anion with alkalinity values about 180 μeq l^{-1}. The increasing ion concentrations and shifts in dominance recorded in a downstream direction at the TLW can be attributed to a $CaCO_3$ enrichment and increased mineral weathering in low elevation soils coupled with longer subsurface flow paths in the deeper tills of the low elevation areas. More alkaline groundwater also contributes a greater fraction of total flow at low elevations.

7.1.4 STREAM OUTPUT FROM CATCHMENTS

7.1.4.1 Sampling frequency

A goal of data collection in catchment research is to reflect accurately natural variability. Success in achieving this goal is generally a function of sampling frequency; however, the sampling frequency used in many catchment studies is defined by subjective judgement and/or cost constraints. Other more objective methods for establishing sampling protocols have been proposed.

Pomeroy and Orlob (1976) related sampling frequency to basin area and the ratio of maximum to minimum flow. They suggested that large catchments (>2600 km^2) should be sampled at least monthly, while a small basin (26 km^2 required sampling twice a week. Weekly sampling is justified for streams exhibiting maximum to minimum flow ratios >100. This is probably typical of most small catchments.

Sampling frequency is often evaluated to estimate a mean chemical level that has a specified statistical confidence, particularly when the intent is to assess the potential of exceeding some water quality standard. Assuming that the data are independent (i.e. not serially correlated) and normally distributed having a variance $= s^2$, the number of samples *(n)* required each year to estimate future annual means within a specified 95% confidence interval *(x)* may be calculated as follows (Sanders *et al*., 1983):

$$n = [2(1.96)/x]^2 \text{ x } s^2 \tag{7.1}$$

Unfortunately, both of the statistical conditions are commonly violated (i.e. serial correlation is likely and many water concentration and flow data are log- normally rather than normally distributed). The most important point is that sampling frequency varies directly with parameter variance. It is for this reason that streamflow, which typically varies over a 2-3 order-of-magnitude range or greater (particularly in small catchment settings), is often inferred from continuous measurement of water level at a location of "controlled" flow (i.e. weir, flume, or natural stream section of known cross-section), the inference being made from a stage-discharge relationship derived from less frequent measurements.

Sampling schedules for chemical variables are rarely specified on a parameter- by-parameter basis, but rather, a compromise frequency is adopted for monetary and logistical reasons. Within a research framework that emphasizes elucidation of important catchment processes as is the case in many small catchment studies, it is typically the mass flux (i.e. concentration x flow) rather than chemical

concentration that is of primary concern. Hence, when specifying the sampling frequency for runoff waters, one must consider the accuracy required of the mass fluxes that are eventually calculated.
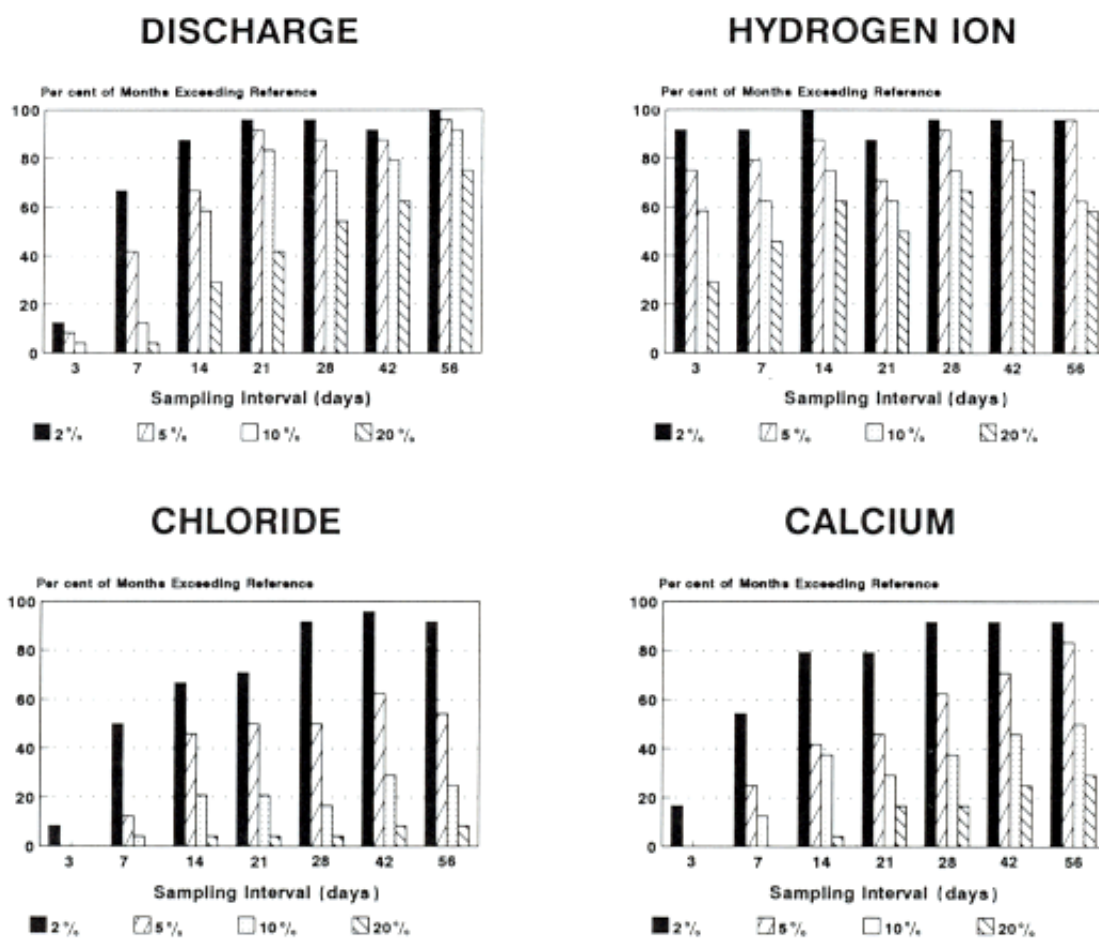
Figure7.1 Acceptable monthly discharge and ion fluxes calculated for varying sampling frequency.

Daily data for stream chemistry and hydrology were collected from July 1980 to June 1982 in the Mersey River catchment in southern Nova Scotia (Clair and Freedman, 1986; Freedman and Clair, 1987). These data will be used to illustrate an evaluation of sampling frequency for mass flux detemnation. Monthly and annual (water-year) yields were calculated for artificial sampling frequencies of 1, 3, 7, 14, 21, 28,42 and 56 days using the optimal procedure of Scheider *et al*. (1979). Twenty four monthly and two annual yields determined for the one-day sampling frequency (i.e. using all possible data) were taken as the reference, and the effectiveness of other sampling frequencies in reproducing this reference was assessed by direct comparison.

For brevity, only the results for stream discharge, H^+, Cl^- and Ca^{2+} are presented here. The ability of the seven sampling frequencies to determine monthly catchment yields within four accuracy classes (i.e. ±2%, ±5%, ±10% and ±20% of the reference) was assessed (Figure 7.1). For example, the first solid black bar in the discharge component of Figure 7.1 indicates that approximately 12% (i.e. 3 of a possible 24 months) failed to be within ±2% of the reference discharge when a three-day sampling frequency was used.

The Mersey River example demonstrates the trade-off between the accuracy of calculated yield and sampling frequency that must be considered when specifying the sampling routine for small catchment studies. Clearly, a small sampling frequency tends to result in better reproduction of the reference (i.e.

daily) yield values, but such a choice has significant cost and logistical implications. In the Mersey catchment, if a researcher is willing to accept a 20% failure rate to reproduce monthly yields within ±10% of the reference levels, then a sampling frequency of 7-14 days will be acceptable for discharge and many chemical variables (e.g. Cl^- and Ca^{2+} in [Figure 7.1](#)). On the other hand, extremely variable chemical parameters (e.g. H^+) require a short sampling frequency even less than three days to achieve reasonably accurate monthly yield estimates.

If relationships between water chemistry and flow are known, one can use this information to increase the accuracy of yield estimates by adopting a variable sampling frequency, i.e. collecting relatively fewer samples during periods when flow and water chemistry are fairly constant and relatively more samples during periods of change.

7.1.4.2 Mass balance/loading calculations

Determination of input and output budgets for a catchment or a lake is an accepted research tool in environmental studies (Dillon *et al*., 1982). They provide some insight into the various geochemical and biological processes operative in a lake system or stream catchment (Jeffries *et al*., 1988). Mass balance studies have been extensively used to assess the relative importance of a specific pollutant input to a lake or watershed in support of the development of an abatement strategy, e.g. the association of high phosphorus inputs with the eutrophication of a water body (Vollenweider, 1968; Dillon and Rigler, 1975; Schindler *et al*., 1978). Material balances have provided important information leading to formulation of mathematical models for predicting the chemical concentration and resultant effects of a particular substance under various input-output conditions. For example, dynamic watershed acidification models are now widely used to predict the response of surface water chemistry to changes in atmospheric deposition (ILWAS, Chen *et al*., 1983; MAGIC, Cosby *et al*., 1985).

The most accurate estimate of the mass output from a catchment is calculated from continuous concentration and discharge measurements. Daily determinations of streamflow are readily obtained with automatic stage recorders; however, the greater cost of water sampling plus analytical testing generally restricts the number of chemical samples that can be collected. Numerous methods have been reported for combining continuous flow information with periodic chemical information to estimate dissolved and particulate export from small basins (Dann *et al*., 1986).

The simplest method for calculating an annual basin export is to use an unweighted average for concentration times the total annual water volume (Paces, 1982; Yuretich and Batchelder, 1988). Where frequent chemical samples are collected over a wide flow spectrum, export results based on this procedure are, in effect, weighted with respect to flow frequency and may be comparable to other methods. However, the tendency is to have more samples from periods of low flow so that the export values tend to be biased towards baseflow conditions (Dann *et al*., 1986).

Regression methods relate instantaneous chemical concentrations to daily stream discharge thereby estimating daily concentrations. Values of daily mass loadings are then summed over a specified time period, e.g. monthly or annually. This technique has been used where the solute concentration is flow-dependent and where the frequency of chemical samples may not be uniform. Estimates of SO_4^{2-} export from a forested watershed in Pennsylvania when calculated by regression equations using monthly discharge values were relatively high compared to those calculated by other methods (Dann *et al*., 1986). Even regression equations derived from subsets of samples grouped by flow quartiles and in proportion to flow duration gave relatively high SO_4^{2-} loadings. Dann *et al*. (1986) attributed the export surplus to the fact that regression methods are biased towards higher flows which contribute more to ion export but are generally sampled less frequently than low flows. Furthermore, the regression analysis assumes that

the data are independent and normally distributed, whereas discharge and concentration data are generally time-dependent and positively skewed (Dann *et al*., 1986).

In a method based on discharge-weighting, the stream discharge is divided into flow classes per unit area. The product of proportion of total discharge for each division and its average chemical concentration gives a discharge-weighted average concentration. The mean concentrations for each grouping are then summed to yield a total annual concentration which is multiplied by the annual volume to give total export (Dann *et al*., 1986). Because the concentrations are weighted according to the distribution of flow throughout the year and baseflows make up a larger proportion of total discharge, the mass exports calculated by this technique tend to be biased towards the baseflow quality conditions. Where flow patterns vary significantly over time and where the concentrations within a flow division are highly correlated, the discharge-weighting method can provide more accurate export estimates (Dann *et al*., 1986).

A fourth method of calculating annual loadings utilizes period-weighting in which flow integrated over a time interval is multiplied by the arithmetic mean concentration at the beginning and end of the specified interval (Likens *et al*., 1977; Paces, 1985). Dann *et al*. (1986) considered this technique to be the most accurate, requiring the least sampling, giving reasonable reproducible results and placing the least conditions on the data set.

There are slight variations on this period-weighting method. For example, Scheider *et al*. (1979) reported that the best estimate of phosphorus loadings in streams tributary to Harp Lake, central Ontario, could be obtained from the product of integrated discharge vs. time and the P concentration at the mid-point of the time interval. This method was also used at the Turkey Lakes Watershed in Ontario to estimate stream and lake export of major ions and nutrients (Jeffries *et al*., 1988), and in the Mersey River study of sampling frequency discussed above.

7.2 METHODS FOR QUANTITATIVE OBSERVATION

7.2.1 STREAM DISCHARGE

Discharge or streamflow, typically expressed as m^3 s^{-1} or 1 s^{-1}, integrates all meteorological and hydrological factors operative in a drainage basin and is the only phase of the hydrologic cycle for which reasonably accurate measurements of volumes can be made (Bruce and Clark, 1969).

Streamflow data are generally derived by inference from continuous or frequent (i.e. daily) records of water level (stage) and periodic determinations of discharge using an established interrelationship, or stage-discharge rating curve. Stage is measured relative to a known elevation either manually or with a water level recorder. Estimates of discharge involve a measurement of stream velocity using a current meter at approximately equally spaced intervals (£20) across a perpendicular transect of the stream channel, followed by multiplication by the cross-sectional area of each interval to yield the discharge of that packet of water. Packet values are summed to provide the total discharge.

The stage-discharge rating curve is influenced by the stream control, i.e. the physical characteristics of the downstream channel. When the downstream control changes due to channel erosion or deposition, a new rating curve must be determined. This may happen infrequently at some sites, while at other stations, several rating curves may be needed annually. Problems arising from an unstable stream control are generally solved by construction of artificial flow control structures such as weirs, constricted-section devices and flumes.

7.2.2 SUSPENDED SEDIMENT SAMPLING

Suspended sediment samplers are selected on the basis of both sampling programme objectives and the depth and velocity of the stream. Three types of samplers are generally utilized. Instantaneous samplers consist of flow-through cylinders with end valves that close to confine a water-sediment mixture. These devices provide only an instantaneous concentration and should not be used for calculations of sediment loading. Pump samplers, which extract a mixture of the sediment suspension only at a fixed point in the water column, can collect a sample integrated over time.

Apart from the fact that both of the above devices sample at a fixed point only, their main disadvantage is that they do not sample the sediment-water mixture isokinetically, i.e. the "transport" environment around the sampler intake differs from that of the ambient streamflow. To overcome this problem, samplers were designed in which a variable-size intake nozzle allowed the water-sediment mixture to enter a sample bottle at the same velocity as the surrounding stream (United States Geological Survey, 1978; Guy and Norman, 1970). In addition to being time-integrating, these samplers function in either a point-integration (PI) or depth-integration (DI) mode. In the former, a water-sediment mixture representative of the mean concentration at a given point in the stream is collected over a short-time interval. Depth-integrating samplers accumulate the suspension as the device is lowered at a uniform rate to the streambed and then pulled back to the surface. Since each sample volume is proportional to the stream velocity at that depth, the sample is considered to be discharge-weighted. One disadvantage is that these samplers can only come to within 9 to 15 cm of the streambed which necessitates the use of other equipment for collecting bed load. Furthermore, both PI and DI samplers are restricted by limitations imposed by nozzle size and sample bottle capacity making their use in small catchment studies problematic. For large, deep rivers, Meade and Stevens (1990) describe a collapsible-bag sampler that isokinetically collects suspended sediments to depths as great as 80 m.

Suspended sediment concentrations can be heterogeneous along a stream cross-section, particularly at high flow conditions. Factors such as solid size and source, channel form and stream velocity all influence the distribution of suspended particles. In small, well-mixed streams, a single sampling "vertical" can be used at the mid-point of the cross-section or, preferably, at the deepest point of the channel. Where the stream is larger but limited information exists on the stream velocity and distribution of suspended solids, four or more sampling verticals should be located at the mid-points of section panels of equal width (equal-width-increment method; Tassone and Lapointe, 1989). If stream velocities have been measured, then sampling verticals (at least five) should be located at the centroid of section panels of equal discharge (equal-discharge-increment method; Tassone and Lapointe, 1989).

The sampling site should be at or near the stream gauging station where the stream section is morphologically stable, i.e. the slope and width of the upstream and downstream channels should be constant and the channel banks stable. The station should be distant from the confluence of two streams to avoid backwater problems upstream and excessive heterogeneity of suspended solid concentrations downstream of the junction. If sampling is conducted from or near a bridge or other artificial structure influencing the stream section, spurious concentrations may arise from sediment debris accumulating on the upstream side of the supporting piers or from increased stream scouring as the velocity increases through any pier constrictions.

Once the sample is collected, various treatments exist to effectively dewater the sediment-water mixture. Gravimetric testing involves passing the mixture through a pre-weighed filter paper, oven-drying and reweighing the solids/filter paper. If detailed chemical analyses are to be performed on the solids, Horowitz (1988) recommended batch centrifugation and particle settling followed by centrifugation as alternative methods to in-line filtration, which can be laborious and expensive for a large-scale sampling programme.

7.2.3 DISSOLVED SUBSTANCES SAMPLING

Sampling methods for surface waters are determined by the parameters of interest and their required accuracy and precision, by the characteristics of the watershed, i.e. flow regime, climatic conditions, biota and by various logistical considerations.

The simplest sampling method is a grab sample in which water is collected at a predetermined location, depth and time. For small streams, a grab sample taken at the centroid of flow is usually adequate. For larger streams, a depth-integrated sample is collected over a vertical section or over the entire depth of the water column at a selected location and time. Composite samples, on the other hand, are obtained by mixing several discrete samples of equal or weighted volumes in one bottle. Such samples are either sequentially (time) or flow-proportionally composited. Grab samples may be collected manually or by means of a sampling rod, a Van Dorn or Kemmerer bottle, or a pump-type sampler. Composite samples can be made from several grab samples or obtained with special composite samplers.

Sampling should be carried out at the station prior to conducting other associated activities such as stream discharge measurements to preclude sample contamination. Provided that climatic conditions are favourable, *in situ* measurements of pH, specific conductance, dissolved oxygen and temperature are recommended. Field filtration of water samples through the use of in-line filter packs or pressure chambers will further ensure the integrity of the dissolved chemical species prior to analysis. Sub-sampling in the field followed by various preservation techniques for heavy metals and total nutrients can also be carried out provided that extreme care is taken to avoid contamination, although problems associated with transporting the preserving chemicals and working in inclement weather often necessitate that this activity be conducted in a laboratory. Field notes should document any physical or biological changes in the stream channel or in the surrounding basin as well as meteorological conditions that might influence the hydrology and/or chemistry of the surface water.

Table 7.4 Recommended containers, method of preservation and storage time for water quality samples (after Department of Environment, 1979)

Parameter	Container	Preservative	Storage time
pH Spec. cond. Alkalinity Acidity TIC, TOC	Polyethylene	None	6 h
NH_4^+ NO_3^-, NO_2^- TKN^a Major ions Phosphorus	Polyethylene	Cool, 4 °C	24 h except 7 days for major ions
dissolved inorganic	Glass	Filter 0.45 μm	24 h on site
ortho $total^a$	Glass	cool, 4 °C	24 h
Heavy metals	Polyethylene	2 ml conc. $HNO_3 \, l^{-1}$ sample	6 months

TIC, Total inorganic carbon; TOC. Total organic carbon; TP, Total phosphorus; TKN, Total kjeldahl nitrogen. [a]Samples for TKN, TP may be preserved with 2 ml conc. H_2SO_4 l^{-1}.

The proper choice of sample containers and preservation techniques are important steps in ensuring the stability of the chemical species from the time of sample collection to analysis (Table 7.4). If storage is required before chemical measurements are initiated. it is usually in a darkened cold room and only for a pre-defined time period (Table 7.4).

Quality control measures are an important component of any sampling and analysis programme. Blank and duplicate samples can test the purity of chemical preservatives. assess contamination from sample containers. filter papers. filtering equipment. etc.. or detect other systematic and random errors generated from the time of sampling to analysis. Replicate samples serve to check the reproducibility of the sampling. Spiked samples containing a range of known concentrations for a given constituent can also be used to document systematic errors or bias in the analytical methodology (Water Quality Branch. 1983).

7.3 INTERPRETATION OF HYDROCHEMICAL DATA

The first step in analysing any hydrochemical data is to ascertain the validity of the chemical measurements. For dissolved substances, a charge balance between cation and anion equivalents is calculated. A second procedure is to compare measured specific conductance with that calculated from the laboratory results. If cations and anions fail to balance within ±10%, the chemical data should be considered suspect. Where the sample solutions are very dilute (e.g. precipitation), more tolerance in achieving an electrochemical balance may be acceptable. Most stream samples are analysed for pH, Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2-}, Cl^- and alkalinity and the nutrients NO_3^- and NH_4^+. In areas of organic-rich soils, organic anions may be a significant component of surface and soil water chemistry. If these compounds are not measured, then an anion deficit may be recorded. Organic anion concentrations may be estimated from TOC/DOC and pH data (Oliver *et al*., 1983). In certain environments, extended reactions involving mineral weathering, ion exchange, chemical reduction, etc., may result in the release of metallic cations that can also contribute substantially to the ionic composition of waters.

The analysis of hydrochemical data utilizes a variety of techniques from relatively simple descriptive statistics to more complicated methods including the calculation of saturation indices and mass balances, regression analyses and the development of solution equilibrium models. The effort expended in data evaluation is in part determined by the objectives of the programme and the type of data available, be it regional survey information or an intensive, process-oriented catchment study. In this section, no attempt is made at addressing all the hydrochemical assessment procedures available to the analyst. Only a brief outline of some commonly used methods is provided to document both the variety and range of complexity existent in various data treatments.
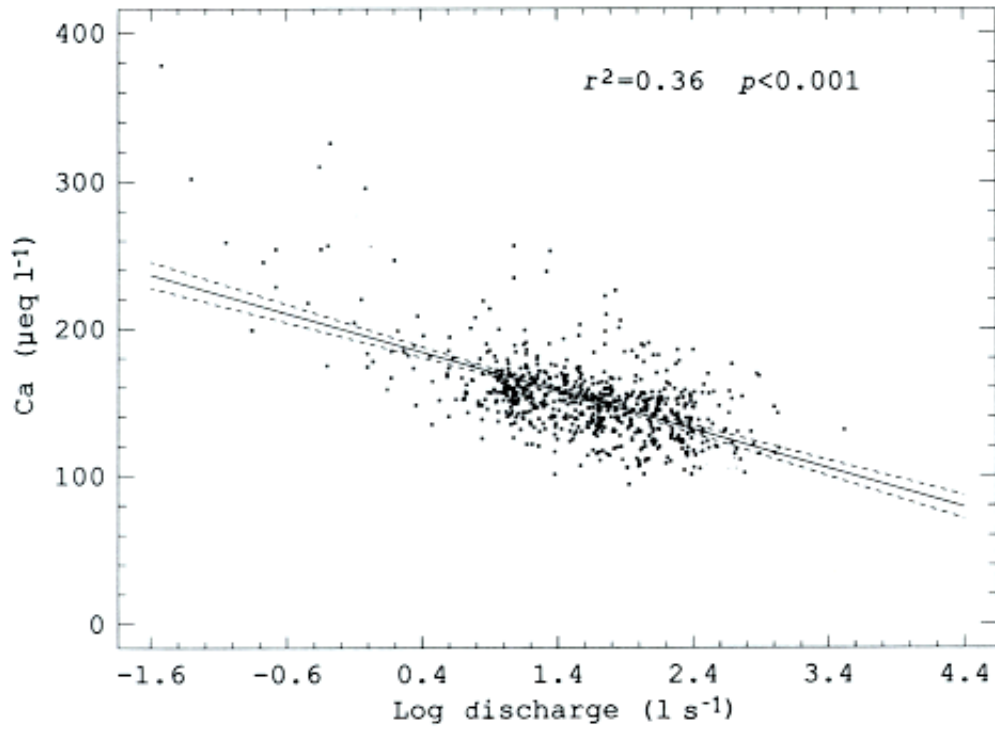
Figure 7.2 Decrease in calcium concentrations with increasing discharge at the Turkey Lake Watershed (TLW).
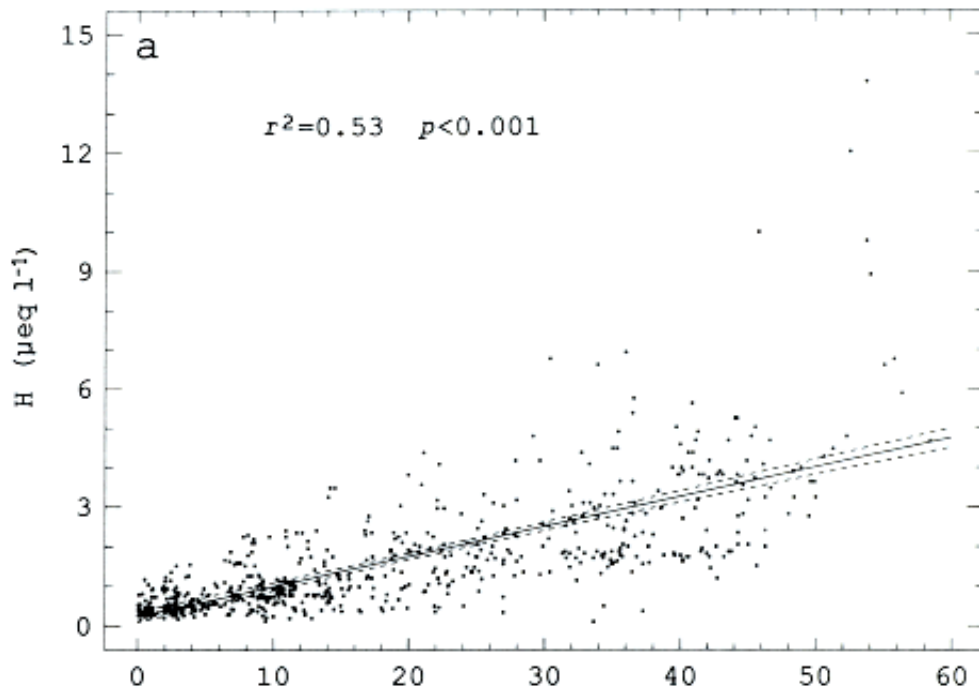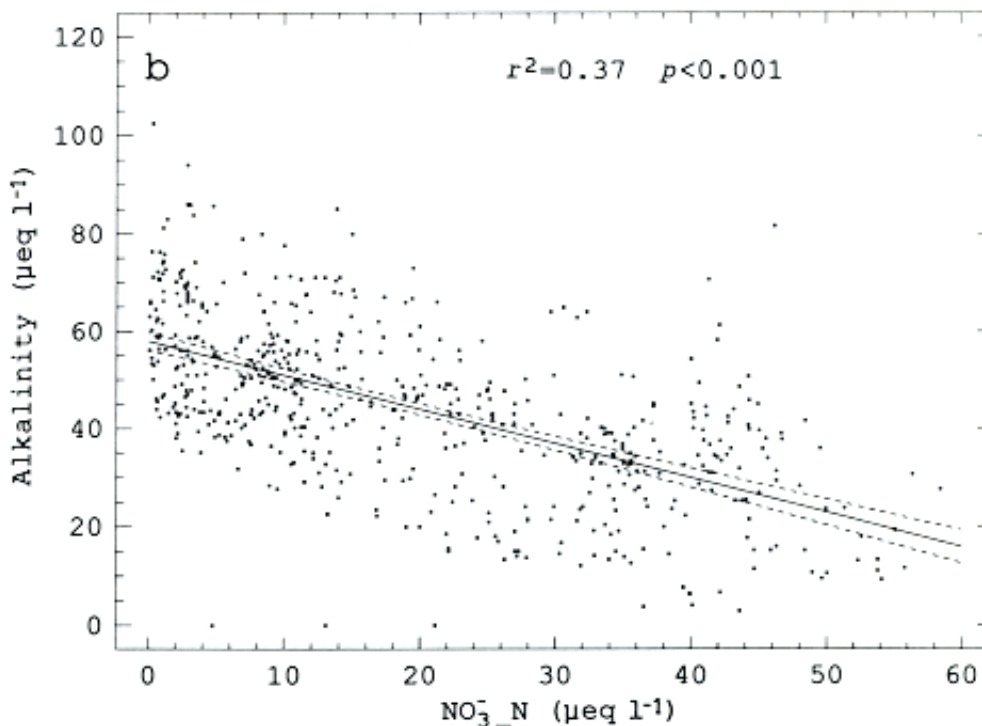
Figure 7.3 Inter-ion relationships at the Turkey Lakes Watershed (a) H^+ vs. NO_3^-; (b) alkalinity Vs. NO_3^-

Concentrations of dissolved and suspended matter will vary with the hydrologic conditions prevalent at the time of sampling. Information regarding the source and routing of subsurface waters to the stream channel can be extracted from recording the behaviour of stream constituents under varying flow regimes. For example, increased H^+, Al, NO_3^- and K^+ concentrations with elevated stream discharge and a concomitant decrease in base cations and SO_4^{2-} have been observed at Hubbard Brook (Johnson *et al*., 1969; Lawrence and Driscoll, 1990) and Turkey Lake ([Figure 7.2](#)). Baseflow is characterized by higher pH and base cation values.

Inter-ion relationships also provide information on the various chemical and biological processes operative in a watershed. Plots of H^+ vs. NO_3^-, and of alkalinity vs. NO_3^- ([Figure 7.3](#)) illustrate the noisy but significant interdependence of the concentrations of these ions in streamwaters at the Turkey Lakes Watershed.

Equivalent or molar ratios of ions are used to illustrate independent or compensatory changes in parameter concentrations and infer an explanatory process. Quite often, the denominator in the ratio is selected as a conservative ion such as Cl^-. For example, Munson and Gherini (1991) proposed the use of SO_4^{2-}/Cl^- ratios in surface water and atmospheric deposition as a means of detecting SO_4^{2-} losses in a basin caused by SO_4^{2-} adsorption or reduction processes. Ion ratios have also been used for analysis of regional data sets. In acidification assessments, two commonly used ratios are ANC/C_B and SO_4^{2-}/C_B (where ANC = acid neutralizing capacity and C_B = sum of base cations) to qualitatively evaluate chemical change (Jeffries, 1991; Driscoll *et al*., 1991).

Time series plots and analyses can be an effective tool for quantifying changes in stream water chemistry occurring in response to varying patterns of atmospheric deposition or to physical changes in a

catchment (e.g. deforestation). The most useful time series evaluations are dependent upon a long-term data base (>10 years) since seasonal variation in stream water chemistry can be as great or greater than interannual variation. An example of a study site satisfying these needs is the Hubbard Brook Experimental Forest where a record of precipitation and stream water chemistry has been continuously maintained for over 25 years (Likens *et al*., 1977; Driscoll *et al*., 1989).

The rationale for and methods of computing mass balances have been described in Section 7.1.4.2. One use of input-output studies is to compare the chemical input from atmospheric deposition to export as a means of inferring biogeochemical processes active in a particular basin. General observations from diverse catchments in North America and Europe (Table 7.5) include a strong retention of input H^+ and NH_4^+ in the terrestrial basin, variable rates of NO_3^- export relative to input, and SO_4^{2-} outputs being comparable to or greater than deposition input.

Table 7.5 Comparision of atmospheric deposition and gross terrestrial export of selected ions for forested location in northeast North America and Scandinavia (after Jeffries *et al*., 1988)

Site state	TLW C	Nelson C	Harp C	Kejimkujik C	Hubbard Brook USA	Hunting Creek C	Birkenes N	Gårdsjön S
Atmospheric deposition (meq m^{-2} year^{-1})								
H^+	63.7	60.2	68.7	40	96.9	95.3	114	-
Ca^{2+}	14.2	22.9	30.1	12	10.8	12.1	15	31.4
NH_4^+	26.8	23.3	32.1	4.4	16.1	-	-	69.9
ANC	<0	<0	<0	<0	<0	<0	<0	<0
SO_4^{2-}	70.0	68.4	70.9	39.0	79.9	56.2	142	175
NO_3^-	41.4	35.9	37.0	13	31.7	25.8	84	69.3
Gross terrestrial export (meq m^{-2} year^{-1})								
H^+	1.1	7.2	1.4	9	10.3	0.05	36	45
Ca^{2+}	135	131	85.3	43	68.4	168	72	43.9
NH_4^+	0.67	1.7	1.6	-	1.9	-	-	0.16
ANC	62.5	12.1	31.5	-	12.5	169	-	-

Reproduced by permission of the Minister of Supply and Services, Canada

7.4 SUMMARY

Study of the physical and biogeochemical processes operating in small catchments and calculation of the stream output component of mass budgets require application of a broad range of hydrochemical methods. This chapter initially provides a brief discussion of streamwater chemistry including some of the factors that introduce temporal and spatial variability. This information is intended to provide some background on what may be expected when determining catchment mass export. Of primary importance in such studies is the selection of representative sampling sites and appropriate sampling frequencies. Spatial variability within a catchment can be addressed by sampling in areas of differing elevation, soil

and bedrock geology, vegetation and land-use. Variability in streamwater chemistry related to fluctuations in flow should be elucidated by sampling across a range of hydrologic conditions, from baseflow to maximum discharge events during snowmelt or heavy rainfall. Determination of the appropriate sampling frequency is inevitably a trade-off between scientific requirements and financial/logistical considerations. Highly variable parameters require short sampling intervals. Various methods of mathematically combining flow and chemistry data to determine stream output are reviewed also.

Commonly used methods for determining stream discharge and for collecting samples of dissolved and particulate constituents are presented. Quality assurance of the data is extremely important requiring due consideration of the proper sampling method, bottle type, storage and/or preservation procedure, etc., prior to appropriately quality controlled laboratory analysis. Techniques for post-analysis evaluation of data quality (e.g. charge balancing, comparison to existing information) are also discussed.

7.5 SUGGESTED READING

Global aspects of the water cycle are covered in monographs by Berner and Berner (1987); Rodda (1985) and SchJesinger (1991), chemical aspects of water are treated in a textbook by Pagenkopf (1978). Implications of sampling schemes and interrelations between the stream and the ecosystem surrounding it are discussed in Likens *et at*. (1977) and Johnson and Van Hook (1989). Reuss and Johnson (1986) discuss acid deposition and its impact on water and soil chemistry and element cycling.

7.6 REFERENCES

Andersson, F. and Olsson, B. (Eds) (1985) Lake Gårdsjön-an acid forest lake and its catchment. *Ecol. Bull. (Stockholm)* **37**, 336 pp.

Berner, K.B. and Berner, R.A. (1987) *The Global Water Cycle: Geochemistry and Environment*. Prentice-Hall, New Jersey, 397 pp.

Brownlow, A.J. (1979) *Geochemistry*. Prentice-Hall, New Jersey, 498 pp.

Bruce, J.P. and Clark, R.J. (1969) *Introduction to Hydrometeorology*. Pergamon Press, 319 pp.

Chen, C.W., Gherini, S.A., Hudson, R.J.M. and Dean, J.D. (1983) *The Integrated LakeWatershed Acidification Study. Volume I: Model Principles and Application Procedures*. Final report EA-3221, Electric Power Research Institute, Palo Alto, CA.

Christophersen, N., Seip, H.M. and Wright, R.F. (1982) A model for streamwater chemistry at Birkenes, Norway. *Water Res*. **18**: 977-996.

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.

Clair, T.A. and Freedman, B. (1986) Patterns and importance of DOC in four acidic groundwater streams in Nova Scotia, Canada. *Wat. Air Soil Poll*. **31**: 139-147.

Colman, S. and Dethier, D.P. (Eds) (1986) *Rates of Chemical Weathering of Rocks and Minerals*. Academic Press, Orlando, Florida.

Connell, D.W. and Miller, G.J. (1984) *Chemistry and Ecotoxicology of Pollution*. John Wiley and Sons, New York, 444 pp.

Cosby, B.J., Wright, R.F., Hornberger, G.M. and Galloway, J.N. (1985) Modeling the effects of acid deposition: Estimation of long-term water quality responses in a small forested catchment. *Water Resour: Res.* **21**: 1591-1601.

Cresser, M.S. and Edwards, A.C. (1987) *Acidification of Freshwaters*. Cambridge University Press, Cambridge.

Dann, M.S., Lynch, J.A. and Corbett, E.S. (1986) Comparison of methods for estimating sulphate export from a forested watershed. *J. Environ. Qual.* **15**: 140-145.

Department of the Environment (1979) *Analytical Methods Manual*. Inland Waters Directorate, Water Quality Branch, Ottawa, Canada.

Dillon, P.J. and Rigler, F.H. (1975) A simple method for predicting the capacity of a lake for development based on lake trophic status. *J. Fish Res. Board Can.* **32**: 1519-1531.

Dillon, P.J., Jeffries, D.S. and Scheider, W.A. (1982) The use of calibrated lakes and watersheds for estimating atmospheric deposition near a large point source. *Wat. Air Soil Poll.* **18**: 241-258.

Dillon, P.J., Reid, R.A. and de Grosbois, E. (1987) The rate of acidification of aquatic ecosystems in Ontario, Canada. *Nature* **329**: 45-48.

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.

Driscoll, C. T., Newton, R.M., Gubala, C.P., Baker, J.P. and Christensen, S. W. (1991) Adirondack Mountains. In Charles, D.F. (Ed.): *Acidic Deposition and Aquatic Ecosystems: Regional Case Studies*. Springer-Verlag, New York, pp. 132-202.

Freedman, B. and Clair, T.A. (1987) Ion mass balances and seasonal fluxes from four acidic brownwater streams in Nova Scotia. *Can. J. Fish. Aquat. Sci.* **44**: 538-548.

Guy, H.P. and Norman, V. W. (1970) *Field Methods for Measurement of Fluvial Sediment*. United States Geological Survey, Techniques of Water Resources Investigations. Book 3, Chapter C2, 59pp.

Hall, F.R. (1970) Dissolved solids-discharge relationships: 1. Mixing models. *Water Resour: Res.* **6**(3): 845-850.

Hall, F.R. (1971) Dissolved solids-discharge relationships: 2. Applications to field data. *Water Resour. Res.* **7**(3): 591-601.

Hem, J.D. (1985) *Study and interpretation of the chemical characteristics of natural waters*. U.S. Geological Survey Water Supply Paper 2254, 263 pp.

Henriksen, A., Wathna, B.M., Roeberg, E.J.S., Norton, S.A. and Brakke, D.F. (1988) The role of stream substrate in aluminum mobility and acid neutralization. *Water Res.* **22**: 1069-1073.

Hooper, R.P. and Shoemaker, C. (1985) Aluminum mobilization in an acidic headwater stream: temporal

variation and mineral dissolution disequilibria. *Science* **229**: 463-465.

Horowitz, A.J. (1988) An examination of methods for the concentration of suspended sediment for direct metal analysis. Chemical and biological characterization of sludges, sediments, dredge spoils, and drilling muds. In Lichtenberg, J.J., Winter, J.A., Weber, C.I. and Fradkin, L. (Eds): *ASTM STP* 976. American Society for Testing and Materials, Philadelphia, pp. 102-113.

Hultberg, H. (1985) Budgets of base cations, chloride, nitrogen, and sulphur in the acid Lake Gårdsjön, catchment, SW Sweden. In Andersson F. and Olsson, B. (Eds) Lake Gårdsjön -*An Acid Forest lake and its catchment*. Ecol. Bull. (Stockholm) **37**: 133-157.

Jeffries, D.S. (1991) Southeastern Canada: An overview of the effect of acidic deposition on aquatic resources. In Charles, D.R. (Ed.): *Acidic Deposition and Aquatic Ecosystems: Regional Case Studies*. Springer-Verlag, New York, pp. 273-290.

Jeffries, D.S., Semkin, R.G., Neureuther, R. and Seymour, M. (1988) Ion mass budgets for lakes in the Turkey Lakes Watershed, June 1981-May 1983. *Can. J. Fish. Aquat. Sci.* **45**: (Suppl. 1): 47-58.

Johnson, D.W. and Hook, R.I. van (Eds) (1989) *Analysis of Biogeochemical Cycling Processes in Walker Branch Watershed*. Springer-Verlag, New York, 401 pp.

Johnson, N.M., Likens, G.E., Bormann, F.H., Fisher, D.W. and Pierce, R.S. (1969) A working model for the variation in streamwater chemistry at the Hubbard Brook Experimental Forest, New Hampshire. *Water Resour: Res.* **5**: 1353-1363.

Lawrence, G.B. and Driscoll, C. T. (1990) Longitudinal patterns of concentration-discharge relationships in stream water draining the HBEF, N.H. *J. Hydrol.* **116**: 147-165.

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.

McAvoy, D.C. (1988) Seasonal trends of Al chemistry in a second-order Massachusetts stream. *J. Environ. Qual.* **17**: 528-534.

Meade, R.J. and Stevens, Jr., H.H. (1990) Strategies and equipment for sampling suspended sediment and associated toxic chemicals in large rivers-with emphasis on the Mississippi River. *Sci. Total Environ.* **97/98**: 125-135.

Mulder, J., Christophersen, N., Hauhs, M., Vogt, R.D., Andersen, S. and Andersen, D.O. (1990) Water flow paths and hydrochemical controls in the Birkenes catchment as inferred from a rainstorm high in seasalts. *Water Resour. Res.* **26**: 611-622.

Munson, R.K. and Gherini, S.A. (1991) Hydrochemical assessment methods for analyzing the effects of acidic deposition on surface waters. In Charles, D.F. (Ed.): *Acidic Deposition and Aquatic Ecosystems: Regional Case Studies*. Springer-Verlag, New York, pp. 35-64.

Oliver, B.G., Thurman, E.M. and Malcolm, R.L. (1983) The contribution of humic substances to the acidity of colored natural waters. *Geochim. Cosmochim. Acta* **47**: 2031-2035.

Paces, T. (1982) Natural and anthropogenic flux of major elements from Central Europe. *Ambio* **11**: 206-208.

Paces, T. (1985) Sources of acidification in Central Europe estimated from elemental budgets in small basins. *Nature* **315**: 31-36.

Pagenkopf, G.K. (1978) *Introduction to Natural Water Chemistry*. Marcel Dekker, New York. 272pp.

Pomeroy, R.D. and Orlob, G.T. (1976) *Problems of setting standards and of surveillance for water quality control*. California State Water Control Commission, Publ. No.36, Sacramento, CA.

Reid, J.M., MacLeod, D.A. and Cresser, M.S. (1981) Factors affecting the chemistry of precipitation and river water in an upland catchment. *J. Hydrol*. **50**: 129-145.

Reuss, J.O. and Johnson, D. W. (1985) Effects of soil processes on the acidification of water by acid deposition. *J. Environ. Qual*. **14**: 26-31.

Reuss, J.O. and Johnson, D.W. (1986) *Acid Deposition and the Acidification of Soils and Waters*. Ecological Studies, Vol. 59, Springer- Verlag, New York, 119 pp.

Rodda, J.C. (1985) *Facets of Hydrology II*. John Wiley & Sons, New York, 447 pp.

Sanders, T.G., Warden, R.C., Loftis, J.C., Steele, T.D., Adrein, D.D. and Yeojevich, V. (1983) *Design of Networks for Monitoring Water Quality*. Water Resources Publications, Littleton, Colorando, 328 pp.

Scheider, W.A., Moss, J .J .and Dillon, P.J. (1979) Measurement and uses of hydraulic and nutrient budgets. US EPA 440/5-79-001, Washington, DC.

Schindler, D.W. (1976) Biogeochemical evolution of phosphorus limitation in nutrientenriched lakes of the Precambrian Shield. In Nriagu, J.O. (Ed.): *Environmental Biochemistry*. Ann Arbor Science Publishers, Ann Arbor, Mich., pp. 647-664.

Schindler, D.W. (1986) The significance of in-lake production of alkalinity. *Wat. Air Soil Poll*. **30**: 931-944.

Schindler, D. W., Fee, E.J. and Ruszczynski, T. (1978) Phosphorus input and its consequences for phytoplankton standing crop and production in the Experimental Lakes Area and in similar lakes. *J. Fish Res. Board Can*. **35**: 190-196.

Schlesinger, W.J. (1991) *Biogeochemistry: An Analysis of Global Change*. Academic Press, New York, 443 pp.

Stumm, W. and Morgan, J.J. (1981) *Aquatic Chemistry*, 2nd edition. John Wiley & Sons, New York, 780 pp.

Sullivan, T.J., Christophersen, N., Muniz, I.P. Seip, H.M. and Sullivan, P.D. (1986) Aqueous aluminum chemistry response to episodic increases in discharge. *Nature* **323**: 324-327.

Swistock, B.R., DeWalle, D.R. and Sharpe, W.E. (1989) Sources of acidic storm flow in an Appalachian headwater stream. *Water Resour: Res*. **25**(10): 2139-2147.

Tassone, B.L. and Lapointe, F. (1989) *Suspended Sediment Sampling, Lesson Package No*. 27. Water Resources Branch. Environment Canada, Ottawa. 139 pp.

United States Geological Survey (1978) Sediment. Chapter 3 in *National Handbook of , Recommended*

Methods for Water Data Acquisition. Office of Water Data Coordination, Reston, VA. 100 pp.

Vollenweider, R.A. (1968) The scientific basis of lake and stream eutrophication, with particular reference to phosphorus and nitrogen as eutrophication factors. *Tech. Rep. OECD. Paris DAS/CSI/68.* **27**: 1-83.

Water Quality Branch (1983) *Sampling for Water Quality*. Inland Waters Directorate. Environment Canada. Ottawa, Canada.

Water Quality Branch (1987) *Canadian Water Quality Guidelines*. Inland Waters Directorate, Environment Canada. Ottawa, Canada.

Wilson, G.V., Jardine, P.M., Luxmoore, R.J. and Jones, J.R. (1990) Hydrology of a forested hill slope during storm events. *Geoderma* **46**: 119-138.

Yuretich, R.F. and Batchelder, G.L. (1988) Hydrogeochemical cycling and chemical denudation in the Fort River watershed, central Massachusetts: an appraisal of mass-balance studies. *Water Resour. Res.* **24**(1): 105-114.

[Back to Table of Contents](#)

The electronic version of this publication has been prepared at
the *M S Swaminathan Research Foundation, Chennai, India.*