

# SCOPE 51 - Biogeochemistry of Small Catchments

## 14 Chemical Weathering in Small Catchments: Climatic and Anthropogenic Influences

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## 14.1 INTRODUCTION

Chemical denudation through weathering of soil and rock minerals is an important component of the biogeochemistry of ecosystems ([Chapter 4](#)). In virtually all environments, weathering results in the neutralization of hydrogen ion ( $H^+$ ) and the production of soluble basic cations ( $C_B$ : Ca, Mg, K and Na), aluminium and silica ( $H_4SiO_4$ ). Thus, it has been recognized that weathering plays an important role in the buffering of surface waters (e.g. Johnson, 1984; Bricker and Rice, 1989) and the supply of nutrient cations (Ca, Mg and K) to the soil (e.g. Likens *et al.*, 1977).

Chemical weathering rates are influenced by many edaphic factors. The importance of the mineralogy and geochemistry of the rock being weathered is obvious. Climate also has a major influence. Under pristine conditions, weathering rates should be highest in warm, moist climates.

Weathering is also a major sink for  $H^+$  in most natural systems (the rare exception being those underlain by sulphide-rich parent material). Thus, environments characterized by high fluxes of acidity are expected to have higher rates of chemical weathering. Since fossil fuel combustion and other human activities produce acidity, it is reasonable to hypothesize that weathering rates are greater in heavily impacted areas.

Our goals in this chapter are to summarize what is known from catchment studies about chemical weathering rates in different climatic regimes and the impacts of human activities on weathering rates.

Chemical weathering is one of several processes which contribute to the chemical denudation of catchments. However, measured rates of chemical denudation can be used to estimate chemical weathering rates if the rates of biomass accumulation and changes in soil exchangeable cation pools are either measured or assumed to be negligible ([Chapter 4](#)). Some of the catchment studies cited in this chapter included direct measurement of these changes. In many of the studies, biomass and soil changes were assumed to be negligible by the original investigators.

## 14.2 CLIMATIC INFLUENCES ON CHEMICAL WEATHERING

The presence of water is required for chemical weathering to occur. Also, rate constants for weathering reactions are temperature-dependent (e.g. Sverdrup, 1990). Thus, weathering rates are highly dependent on climatic conditions, particularly precipitation and temperature. Most recent work on the rates and significance of chemical weathering in small catchments has been done in the context of acid deposition effects. Hence, most data on chemical denudation rates in small catchments are currently available from northern temperate environments. Less is known about weathering within small catchments in tropical and subtropical environments. The following is a short survey of catchment studies producing weathering rate estimates in different climatic zones.

### 14.2.1 ALPINE AND SUBALPINE ENVIRONMENTS

The flux of dissolved solids from the alpine-subalpine Loch Vale catchment (Front Range, Colorado, USA), is primarily controlled by interactions between snowmelt and bedrock (Mast *et al.*, 1990). The annual release of  $C_B$  through weathering was estimated to be  $0.39 \text{ keq ha}^{-1} \text{ year}^{-1}$ . Mass balance calculations suggested that weathering of calcite supplied 40% of the total  $C_B$  released although it makes up less than 1% of the bedrock. The importance of calcite weathering in this catchment is probably the result of its chemical reactivity and the high rate of physical erosion in the Colorado alpine environment.

The results from Loch Vale are consistent with those reported by Drever and Hurcomb (1986) in a study of chemical weathering in an alpine catchment in the Cascade Mountains of Washington, USA. Although only trace amounts of calcite are present in the lithologies underlying the South Cascade Lake basin, the  $C_B$  concentrations in streams and lakes could only be explained by a combination of silicate and calcite weathering.

Caine and Thurman (1990) calculated the cationic denudation rates for nine landscape units within the Green Lakes Valley catchment, 40 km south of Loch Vale. Their estimates ranged between  $0.51$  and  $1.54 \text{ keq ha}^{-1} \text{ year}^{-1}$  with an average of  $1.20 \text{ keq ha}^{-1} \text{ year}^{-1}$ . Non-linear relationships were found between catchment area and solute concentrations. This spatial pattern was explained by increased contributions to stream solute concentrations from soil, groundwater and biotic activity at lower elevations. The results from Loch Vale and Green Lakes indicate that chemical weathering rates increase rapidly with decreasing elevation in the Front Range of the Rocky Mountains, due to changing moisture and thermal regimes, and an increasing influence of soils and biota on geochemical cycles.

### 14.2.2 NORTHERN TEMPERATE ENVIRONMENTS

Weathering rates in temperate zone catchments tend to be greater than those of alpine and subalpine catchments due to the temperature dependence of dissolution rate constants and generally higher soil water flow (e.g. Sverdrup, 1990). Differences between temperate zone catchments are due to differing acid loadings ([section 14.3.2](#)), bedrock types and flowpaths. Rates of weathering release of  $C_B$  and silica in seven temperate zone catchments are given in [Table 14.1](#). Acid inputs to the seven catchments are similar ([Section 14.3.2](#)), yet the rates of chemical weathering are quite different.

The contrast between Panther Lake and Woods Lake watersheds, both in the Adirondack Mountain region of New York State, can be attributed to differences in the depth of base-rich glacial till and subsequent differences in flowpaths. In Panther Lake watershed, flow through the deeper, base-rich glacial till results in complete neutralization of acid inputs. At Woods Lake watershed, the shallow glacial till results in shorter groundwater residence times and incomplete neutralization of acidity. As a result, weathering release is lower and surface waters are being acidified at Woods Lake (April *et al.*, 1986).

The Fort River and Hubbard Brook catchments have similar climates, acid inputs, lithologies and forest types. Nevertheless, the weathering release rates at Hubbard Brook are about 50% greater than at Fort Smith. Yuretich and Batchelder (1988) attributed the differences in chemical weathering rates between these two catchments to differing water flowpaths, potential contributions of cation exchange and different types of secondary minerals formed within the soils.

The chemical denudation rates of the cool and wet climates of England and Scotland were fairly similar to those found in the northeastern USA ([Table 14.1](#)).

**Table 14.1** Annual output of major cations and silica ( $\text{keq ha}^{-1}\text{year}^{-1}$  or  $\text{kmol ha}^{-1}\text{year}^{-1}$  [ $\text{SiO}_2$ ]) due to chemical weathering from seven catchments

Location	Northeast USA				British Isles		
Catchment	Woods Lake <sup>a</sup> New York	Panther Lake <sup>a</sup> New York	Fort River <sup>b</sup> Mass.	Hubbard Brook NH	Narrato <sup>c</sup> England	Glendye <sup>d</sup> Scotland	Afon <sup>e</sup> Cyff Wales
Na	0.02	0.20	0.15	0.22	0.29	0.44	0.23
K	-0.02	0.03	0.05	0.15	0.08	0.06	0.03
Ca	0.17	1.16	0.62	0.97	0.57	0.86	0.94
Mg	0.03	0.29	0.25	0.27	0.19	0.43	0.61
SiO <sub>2</sub>	-	-	0.84	-	1.54	1.37	0.40
Total C <sub>B</sub>	0.20	1.68	1.07	1.61	1.13	1.79	1.81
Precip.(mm)	1270	1210	1250	1250	1904	1375	3032

<sup>a</sup>April *et al.*, 1986.

<sup>b</sup>Yuretich and Batchelder, 1988 (corrected for road-salt contribution).

<sup>c</sup>Williams *et al.*, 1986.

<sup>d</sup>Creasey *et al.*, 1986.

<sup>e</sup>Reynolds *et al.*, 1987.

### 14.2.3 THE TROPICS

Most of the work on weathering rates in the tropics has been done on large river systems (e.g. Amazon: Stallard and Edmond, 1983, 1987; Orinoco; Saunders and Lewis, 1989; Ganges/Brahmaputra: Sarin *et al.*, 1989). However, the work on the Caura River, a tributary of the Orinoco River, with a catchment area of 47 500 km<sup>2</sup>, can provide some information on smaller river systems. The rate of rock weathering,

based on discharge-weighted yield of Si, was estimated to be 18 m per million years (Lewis *et al.*, 1987). A comparison of solute transport in two river systems in South America and average values for moist tropical environments ([Table 14.2](#)) suggests that chemical erosion rates in the tropics are usually higher than those in temperate and alpine/subalpine zones. It should be noted, however, that the values in [Table 14.2](#) were obtained from published values for large river systems. Direct extrapolation to denudation rates in small catchments of the tropics is tenuous. However, data from a small catchment study in a pre-montane wet forest in Brazil indicate large year-to-year variations in accumulation and depletion of elements (Ovalle *et al.*, 1987). The weathering rate, derived from chemical composition of bedrock and the mass balance of silica, varied from 0.50 to 1.00 keq ha<sup>-1</sup> year<sup>-1</sup>, comparable to weathering rates observed in temperate climates ([Table 14.3](#)).

**Table 14.2** Annual output of major cations and silica (keq ha<sup>-1</sup> year<sup>-1</sup> or kmol ha<sup>-1</sup> year<sup>-1</sup> [SiO<sub>2</sub>]) due to chemical weathering from two river systems in South America and moist tropical values

	Caura <sup>a</sup> River	Apure <sup>b</sup> River	Moist <sup>c</sup> Tropical
Na	1.20	0.89	0.77
K	0.37	0.27	0.15
Ca	0.73	3.98	1.47
Mg	0.50	1.22	1.04
SiO <sub>2</sub>	1.52	0.93	0.68
Total C <sub>B</sub>	2.80	6.36	3.43

<sup>a</sup>Lewis *et al.*, 1987.

<sup>b</sup>Saunders and Lewis, 1989.

<sup>c</sup>Meybeck, 1983.

Norton (1974) studied chemical weathering in the 5000-ha Rio Tanama catchment in Puerto Rico. Extrapolation of Norton's data is tentative because the sites were only sampled once. Chemical denudation in the Rio Tanama catchment was estimated as 30 m per million years. Based on these data, removal rates of Ca, Mg, K and Na were approximately 3.6, 2.6, 0.3 and 2.2 keq ha<sup>-1</sup> year<sup>-1</sup>, respectively. Silica release was about 2.7 kmol ha<sup>-1</sup> year<sup>-1</sup>. It is difficult to estimate weathering rates because atmospheric inputs were not quantified and may be substantial due to sea spray. However, the release of silica (a good general measure of weathering) from the Rio Tanama catchment is greater than values for other tropical and temperate catchments ([Tables 14.1](#), [14.2](#), [14.3](#)).

**Table 14.3** Mass balance (kg ha<sup>-1</sup> year<sup>-1</sup>) in a tropical pre-montane wet forest, 350 ha granite basin at Tijuca National Park, Brazil (Ovalle *et al.*, 1987). Mass balance (*B*) between atmospheric inputs (*A*), weathering (*W*) and stream outputs (*S*) for years 1983 to 1985

A	W	S	B	A	W	S	B	A	W	S	B
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Na	23	9	58	-26	30	5	27	8	23	6	37	-38
K	3.5	7	11	-0.5	5.7	4	5.5	4.2	3.2	5	8.2	0
Ca	5.3	5	9.7	0.6	5.0	2	3.8	3.2	4.3	3	4.3	3
Mg	4.4	2	6.7	-0.3	4.7	1	2.4	3.3	4.2	1	5.9	-0.7
Cl	36	0	86	-50	60	0	42	18	44	0	57	-13
SiO <sub>2</sub>	0.1	59	59	0	0.1	30	30	0	0.1	39	39	0

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### 14.3 EFFECTS OF HUMAN ACTIVITIES

A number of studies have used proton budgets to show that chemical weathering is a major sink of H<sup>+</sup> (Driscoll and Likens, 1982; van Breemen *et al.*, 1983, 1984). A proton budget is a summary of the net transfers of H<sup>+</sup> occurring within an ecosystem, based on the stoichiometries of biogeochemical reactions involving ionic elements (Binkley and Richter, 1987). Proton budgets are thus a convenient means of integrating the biogeochemical cycles of various elements.

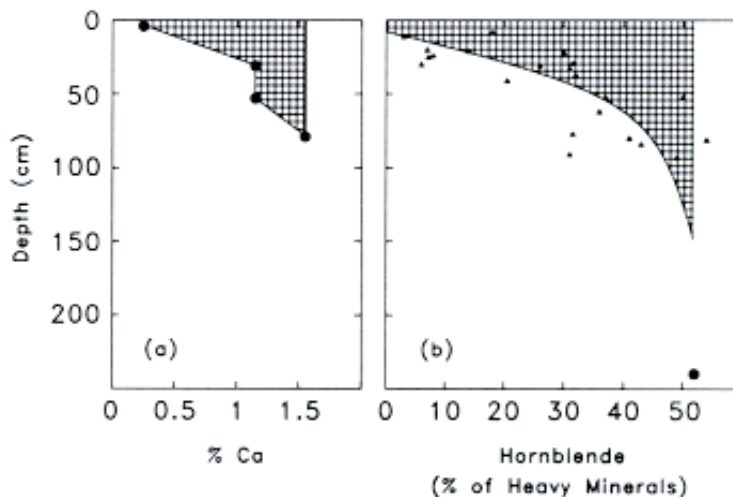
Viewing the weathering process as a major component of the proton budget is particularly useful when considering the impacts of human activities on ecosystems. Many human activities result in the net production of acidity, including combustion of fossil fuels, use of nitrogen fertilizers and timber harvesting. Since weathering is a major proton sink in most ecosystems, it is reasonable to hypothesize that the additional proton load imposed by human activities should result in increased rates of chemical weathering.

In this section, our goal is to summarize what is known about the influences of human activities on chemical weathering rates, with special emphasis on small catchment studies. We will focus our attention on temperate ecosystems for two reasons. First, due to high population density and high levels of industrialization, many of the world's most severely polluted areas lie in temperate regions. Also, a large majority of small catchment studies have taken place at temperate sites.

#### 14.3.1 ESTIMATES OF LONG-TERM CHEMICAL WEATHERING RATES

Estimates of weathering rates in the absence of anthropogenic influence must be established as a baseline in order to assess the effects of human activities. This is made difficult by the fact that air pollution caused by industrial activity impacts even remote areas. Long-term (>10 000 year) chemical weathering rates have been used for this purpose, and can be estimated from the depletion of cations or minerals in the soil (e.g. April *et al.*, 1986; Sverdrup and Warfvinge, 1988; Olsson and Melkerud, 1989).

The depletion method is particularly useful in glaciated environments, where the time of soil development is fairly well constrained. An average rate of weathering can be estimated by dividing the amount of C<sub>B</sub> or heavy minerals lost from the profile by the time since glaciation ([Figure 14.1](#)). The depletion method assumes a uniform distribution of C<sub>B</sub> or heavy minerals in the soil profile immediately after glaciation. Evidence reported by Mahaney and Halvorson (1986) indicates that hornblende abundance in neoglacial sediments is more or less evenly distributed with depth. Hornblende is considered representative of the more weatherable minerals in glacial environments (e.g. Hall and Martin, 1986; Sverdrup, 1990), and has been used as an indicator of weathering intensity in depletion studies (April *et al.*, 1986).



**Figure 14.1** Calcium (a) and hornblende (b) depletion curves for the Panther Lake watershed in the Adirondack Mountains, New York, USA. The amount depleted can be computed by calculating the hatched area and multiplying by the soil bulk density (using appropriate unit conversions). This value can be divided by the time of soil formation to estimate the long-term depletion rate (adapted from April *et al.*, (1986); reproduced by permission of the author and the Geological Society of America).

Estimates of average long-term base cation release from weathering range from 0.10 to 1.12 keq ha<sup>-1</sup> year<sup>-1</sup> (Table 14.4). The estimates for European sites average 0.48 keq ha<sup>-1</sup> year<sup>-1</sup>, while estimates from three sites in North America average 0.51 keq ha<sup>-1</sup> year<sup>-1</sup>. Differences in climate, till chemistry, mineralogy and post-glacial ecosystem development may contribute to regional variations in long-term cation release rates.

**Table 14.4** Long-term rates of release of basic cations (Ca<sup>2+</sup> + Mg<sup>2+</sup> + K<sup>+</sup> + Na<sup>+</sup>) from weathering in Northern Europe and the eastern North America. Data are based on element- or mineral-depletion methods

Site	Weathering rate (keq ha <sup>-1</sup> year <sup>-1</sup> )	Reference
Daseberg, FRG	1.09	Mazzarino <i>et al.</i> , 1983
Gårdsjön, Sweden	0.16 <sup>a</sup>	Sverdrup and Warfvinge, 1988
Masbybacken, Sweden	0.15	Jacks and Aberg, 1987
Norlidden, Sweden	0.10	Melkerud, 1983
Risfallet	0.25	Lundstrom, 1993
Skanes Varsjo, Sweden	0.60	Olsson and Melkerud, 1989
Spanbeck, FRG	1.12	Mazzarino <i>et al.</i> , 1983
Svartberget, Sweden	0.31	Lundstrom, 1993
Westerhof, FRG	0.58	Mazzarino <i>et al.</i> , 1983
Woods Lake, USA	0.62 ± 0.21	April <i>et al.</i> , 1986
Panther Lake, USA	0.50 ± 0.25	April <i>et al.</i> , 1986
Plastic Lake, Canada	0.42	Kirkwood and Nesbitt, 1991

<sup>a</sup>"Bottom of Profile" case.

## 14.3.2 ACID DEPOSITION AND PRESENT-DAY WEATHERING RATES

Concern over the potential effects of acidic precipitation on water quality has motivated much of the recent research in chemical weathering. Potential effects include damaged fisheries, forest decline and corruption of potable water supplies. As discussed in [Chapter 4](#), chemical weathering is the major acid neutralization process in many ecosystems. Consequently, the relationship between acid inputs and the release of dissolved cations via weathering reactions is critical to the evaluation of the potential for acidification of soils and streams. Catchment studies have played a major role in shaping our understanding of the relationship between weathering and acid deposition, as we illustrate below. The reader is directed to Johnson (1984), Wright (1988), and the special issue of the *Journal of the Geological Society*, London (1986, volume 143) for more general coverage of this topic.

**Table 14.5** Inputs of acidity ( $\text{keq ha}^{-1}\text{year}^{-1}$ ) to selected watersheds in Europe and North America. References are listed in [Table 14.6](#)

Site	Country	Dry deposition			Total
		H <sup>+</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	
X-0	Czechoslovakia	0.42	0.48	-	0.90
X-8	Czechoslovakia	0.37	0.48	-	0.85
X-14	Czechoslovakia	0.46	5.54	-	6.00
Lozere:	France				
Beech		0.44	-	-	0.44
Spruce		0.50	-	-	0.50
Vosges	France	-	-	-	1.76
Soiling:	Germany				
Beech		1.16	0.84	-	2.00
Spruce		2.03	1.87	-	3.79
Beddgelert	GB	1.31	-	-	1.31
Dartmoor	GB	-	-	-	1.05
East Twin	GB	0.81	-	-	0.81
Glendye	GB	0.80	0.16	-	0.96
Kershope	GB	0.40	-	-	0.40
Peatfold	GB	0.48	0.0	-	0.48
Plynlimon	GB	0.89	-	-	0.89
Langtjern	Norway	0.46	0.13	-	0.59
Gårdsjön	Sweden	1.02	0.18	0.02	1.22
Cristallina	Switzerland	0.19	-	-	0.19
Zota	Switzerland	0.19	-	-	0.19
Coweeta	USA	0.39	0.02	0.004	0.41
Fort River	USA	0.99	-	-	0.99
Hubbard Brook	USA	0.87	0.42	-	1.29

Idaho Batholith	USA		-	-	-
Loch Vale	USA	0.14	-	-	0.14
N. Cascades	USA		-	-	-
Panther Lake	USA	0.80	-	-	0.80
Woods Lake	USA	0.80	-	-	0.80

**Table 14.6** Chemical weathering release of basic cations ( $C_B$ ) and aluminium ( $\text{keq ha}^{-1} \text{ year}^{-1}$ ) in selected catchments in Europe and the USA

Site	Ca	Mg	K	Na	Al	$C_B$	$C_B+Al$	Reference	
X-0	0.51	0.26	0.11	0.27	-	1.15	-	1	
X-8	0.28	0.18	0.08	0.28	0.41	0.82	1.23	2	
X-14	0.54	0.71	0.15	0.89	1.13	2.29	3.42	2	
Lozere:									
Beech	0.14	0.20	0.09	0.17	-	0.60	-	3	
Spruce	0.56	0.45	0.17	0.22	-	1.40	-	3	
Vosges	0.32	0.17	0.25	0	1.64	0.74	2.38	4	
Solling:									
Beech	0.02	0.27	0.00	0.00	-	0.29	-	5	
Spruce	0.00	0.36	0.08	0.00	-	0.44	-	5	
Beddgelert	0.46	0.04	0	0	1.98	0.50	2.48	6	
Dartmoor	0.57	0.19	0.08	0.29	-	1.13	-	7	
EastTwin	0.37	0.85	0.14	0.25	-	1.61	-	8	
Glendye	0.86	0.43	0.06	0.44	-	1.79	-	9,10	
Kershope	1.04	0.22	0	0	1.23	1.26	2.49	6	
Peatfold	1.01	0.49	0.03	0.10	0.09	1.63	1.72	9,11	
Plynlimon	0.96	0.60	0.03	0	0.00	1.59	1.59	6	
Langtjem 01	0.26	0.08	-0.01	0.05	0.15	0.38	0.53	12	
Gårdsjön									
1	F-	0.34	0.44	0.07	0.01	-	0.86	-	13
	F-2	0.31	0.24	0.04	0.02	-	0.61	-	13
	F-3	0.32	0.22	0.04	0.02	-	0.60	-	13
Cristallina	-	-	-	-	-	0.19	-	14	
Zota	-	-	-	-	-	0.16	-	14	



Coweeta WS-2	-	-	-	-	-	-	0.37	15,16
WS-18	-	-	-	-	-	-	0.70	15,16
WS-27	-	-	-	-	-	-	0.28	15,16
Fort River	0.62	0.25	0.05	0.15	0	1.07	1.07	17
Hubbard Brook	0.97	0.27	0.15	0.22	0.11	1.61	1.72	
Idaho Batholith	0.68	0.12	0.04	0.53	-	1.37	-	18
Loch Vale	0.24	0.07	0.02	0.06	-	0.39	-	19
N Cascades	-	-	-	-	-	0.93	-	20
Panther Lake	1.15	0.29	0.03	0.20	-	1.68	-	21,22
Woods Lake	0.17	0.03	-0.02	0.02	-	0.20	-	21,22

1 Paces,1985.	2 Paces,1986.	3 Lelong <i>et al.</i> , 1990.
4 Probst <i>et al.</i> , 1990.	5 Matzner,1989.	6 Hornung <i>et al.</i> ,1986.
7 Williarns <i>et al.</i> ,1986.	8 Waylen,1979.	9 Creasey <i>et al.</i> ,1986.
10 Reid <i>et al.</i> , 1981.	11 UKRGAR, 1990.	12 Wright, 1983.
13 Hultberg, 1985.	14 Giovanoli <i>et al.</i> ,1988.	15 Velbel, 1985.
16 Swank and Waide, 1988.	17 Yuretich and Batchelder. 1988.	18 Clayton and Megahan, 1986.
19 Mast <i>et al.</i> , 1990.	20 Reynolds and Johnson, 1972.	21 April <i>et al.</i> , 1986.
22 Goldstein <i>et al.</i> , 1984.		

**Table 14.7** Inputs of acidity and weathering release of basic cations ( $\text{keq ha}^{-1} \text{ year}^{-1}$ ) from selected catchments underlain by mafic or calcareous bedrock

Site	Bedrock	H <sup>+</sup> Inputs	C <sub>B</sub> Release	Reference
Trent Basin, GB	Shale/Sandstone/ Limestone	0.18	6.59	Foster, 1987
Karpenissi, Greece	Siltstone/Shale/ Marl	0.003	5.44	Nakos and Vouzaras, 1988
Hauver Branch, USA	Metabasalt	1.03	2.20	Katz <i>et al.</i> 1985
Soldier's Delight, USA	Serpentinite	0.94	1.40	Cleaves <i>et al.</i> 1974

Data from 32 catchments in the USA and Europe show a wide range of acid inputs and weathering release of C<sub>B</sub> (Tables 14.5 and 14.6). The sites referenced in Tables 14.5 and 14.6 all lie on felsic bedrock, which is believed to be most sensitive to acid deposition (Bricker and Rice, 1989). Data from sites on mafic and carbonate bedrock are less abundant, but generally show higher weathering release rates (Table 14.7).

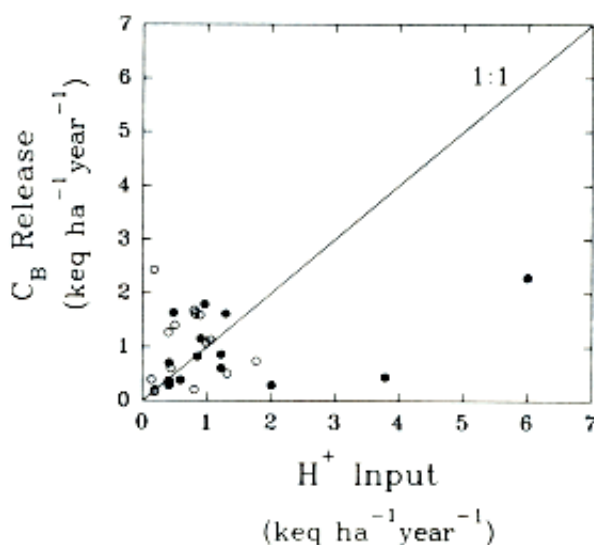
For comparison, the catchments in Tables 14.5 and 14.6 have been arbitrarily divided into two groups based on acid inputs. For cases where both precipitation H<sup>+</sup> and dry SO<sub>2</sub> deposition were estimated, sites with total acid inputs less than  $0.5 \text{ keq ha}^{-1} \text{ year}^{-1}$  were considered "relatively undisturbed". Sites with

total acid inputs greater than  $0.5 \text{ keq ha}^{-1} \text{ year}^{-1}$  were considered "acid-impacted". An acid input of  $0.5 \text{ keq ha}^{-1} \text{ year}^{-1}$  corresponds to about  $1500 \text{ mm year}^{-1}$  of rainfall with a pH of 4.5. The cutoff value of  $0.5 \text{ keq ha}^{-1} \text{ year}^{-1}$  is also consistent with the average long-term weathering rates for European and North American catchments ([Section 14.3.1](#)). For cases where dry  $\text{SO}_4^{2-}$  deposition was not estimated, the cutoff value was  $0.4 \text{ keq ha}^{-1} \text{ year}^{-1}$ .

The average atmospheric input of acidity in the relatively undisturbed catchments was  $0.23 \text{ keq ha}^{-1} \text{ year}^{-1}$ . Average weathering release of  $\text{C}_B$  at these sites was  $0.55 \text{ keq ha}^{-1} \text{ year}^{-1}$ .

For the acid-impacted catchments, acid inputs and  $\text{C}_B$  release from weathering were  $1.33$  and  $1.05 \text{ keq ha}^{-1} \text{ year}^{-1}$ , respectively. In four catchments where Al was monitored, the release of  $\text{C}_B + \text{Al}$  was  $1.86 \text{ keq ha}^{-1} \text{ year}^{-1}$ . At these four sites, Al accounted for an average of 34% of the cation charge released in weathering reactions.

Because of the differences in the various catchment studies included in [Tables 14.5](#) and [14.6](#), as well as the inherently large variability in mass balance estimates of weathering rates (e.g. Paces, 1983), we can only make tentative conclusions from these data. First, the average  $\text{C}_B$  release of  $0.55 \text{ keq ha}^{-1} \text{ year}^{-1}$  in relatively undisturbed catchments indicates that present-day weathering rates in remote areas generally do not exceed long-term rates. However, several of the relatively undisturbed catchments are in alpine environments, which typically have low weathering rates ([Section 14.2.1](#)).



**Figure 14.2** Weathering release of basic cations ( $\text{C}_B$ ) vs. total hydrogen ion inputs for the watersheds listed in [Tables 14.5](#) and [14.6](#). Dry deposition of  $\text{SO}_4^{2-}$  was included in the  $\text{H}^+$  inputs at sites represented by closed circles.

Second, the average weathering release of  $\text{C}_B$  in acid-impacted catchments was only  $0.5 \text{ keq ha}^{-1} \text{ year}^{-1}$  greater than  $\text{C}_B$  release from relatively undisturbed catchments, even though the average acid input was  $1.11 \text{ keq ha}^{-1} \text{ year}^{-1}$  greater. If added acidity is only partially neutralized by weathering release of  $\text{C}_B$ , the remaining  $\text{H}^+$  must pass through the ecosystem or be neutralized by Al release or soil exchange. All of these processes result in soil or stream acidification or both (van Breemen *et al.*, 1983).

This point is illustrated in [Figure 14.2](#). The point for a catchment would lie on the 1:1 line if all  $H^+$  inputs were neutralized by weathering release of basic cations in a 1:1 stoichiometric ratio. Incomplete neutralization of  $H^+$  would place a site below the line, indicating soil or surface water acidification. Sites falling above the 1:1 line must have some unmeasured or internal source of  $H^+$ , or a stoichiometric ratio greater than 1.

There are three likely explanations for sites which lie above the 1:1 line in [Figure 14.2](#). For many sites (e.g. Panther Lake), unmeasured dry deposition of  $SO_4^{2-}$  may be a major unmeasured  $H^+$  input. At some sites (e.g. Loch Vale and Plynlimon), minor amounts of calcite or dolomite in the bedrock may alter the stoichiometric ratio of  $C_B$  release to  $H^+$  input (Mast *et al.*, 1990; Hornung *et al.*, 1987). At other sites (for example, Glendye and Peatfold, where dry deposition of  $SO_4^{2-}$  was estimated), the importance of plant uptake as a source of  $H^+$  may be underestimated. In any catchment study, the assumption that plant growth is at steady state must be carefully assessed. Through the mid-1970s at the Hubbard Brook Experimental Forest, in the northeastern USA, plant uptake accounted for an average of 26% of the total  $H^+$  sources in the ecosystem (Driscoll and Likens, 1982). A 1% annual increase in the current (1987) forest biomass at Hubbard Brook would produce approximately  $0.27 \text{ keq ha}^{-1} \text{ year}^{-1}$  of acidity. This amount is similar in magnitude to the total atmospheric  $H^+$  input at some sites ([Table 14.5](#)).

Inputs of acidity exceed basic cation weathering in at least 14 of the sites considered ([Table 14.2](#), [Tables 14.5](#) and [14.6](#)). The number is likely to be larger considering the number of sites at which dry deposition of sulphur was not estimated.

Finally, these catchment studies do not yield a clear picture of the extent to which increased acid inputs may stimulate weathering rates. A linear regression analysis of the data in [Figure 14.2](#) did not show a significant relationship between acid inputs and weathering release. More data are needed from catchments with  $H^+$  inputs between 2 and  $6 \text{ keq ha}^{-1} \text{ year}^{-1}$ . When the data are grouped into relatively undisturbed and acid-impacted sites, the within-group averages indicate that additional acid inputs may be only partially neutralized by weathering release of  $C_B$ , as discussed above.

### 14.3.3 MANAGED FOREST CATCHMENTS

One of the most common reasons for setting up small catchment studies is to investigate the effect of afforestation and forest management practices on discharge and discharge chemistry (Hornung *et al.*, 1990). Vegetation changes will have significant effects on the cycling of  $H^+$  and major plant nutrients, such as Ca and K, and cause major changes in catchment hydrology, soil moisture regime, evapotranspiration and nutrient inputs. The literature on the subject is extensive and has reflected, particularly in the UK, the debate on the effects of afforestation on water quality and dissolved/particulate fluxes from catchments (e.g. Adamson *et al.*, 1987; Nisbet, 1990). Several studies have suggested that higher weathering rates occur in forest watersheds as compared to heath or meadow-covered catchments (Hultberg 1985; Williams *et al.*, 1987). This effect has been attributed to greater anion inputs associated with enhanced soil leaching in forests. Increased weathering rates have also been attributed to specific tree species (Nys *et al.*, 1990). This is not surprising because it is well known that coniferous trees will cause enhanced soil acidification, base cation leaching and, by inference, increased weathering rates, partly as a result of the production of acidic litter (Page, 1968; Hornung, 1985).

Two of the most extensive small catchment studies, based at Coweeta (North Carolina, USA) and Hubbard Brook (New Hampshire, USA), have involved studies of the long-term effects of forest management, in particular clear cutting practices, on solute budgets (e.g. Swank, 1986; Likens *et al.*,

1970). [Table 14.8](#) shows how solute fluxes of Ca and K increased in the first four years after the logging of a 59-ha watershed at Coweeta. Data for a whole-tree harvest at Hubbard Brook are presented in [Chapter 17](#) ([Figure 17.8](#)). In both cases, pre-logging solute levels were attained about five years after logging. A catchment deforestation experiment at Hubbard Brook, which was followed by herbicide treatment to stop revegetation, also showed increases in solute fluxes compared to undisturbed forest catchments (Likens *et al.*, 1970). Leaching of  $\text{NO}_3^-$  and  $\text{C}_B$  was greater in the herbicided clearcut than in the clearcut described in [Chapter 17](#), indicating that regrowing vegetation is an important factor in the retention of nutrients following logging.

**Table 14.8** Changes in solute fluxes ( $\text{kg ha}^{-1}$ ) after logging at Watershed WS7 at Coweeta (after Swank, 1986) Increase in solute flux

Year after logging	Increase in solute flux		
	$\text{NO}_3^- \text{N}$	K	Ca
1	0.03	0.84	1.85
2	0.26	1.98	2.60
3	1.12	1.97	2.53
4	1.27	2.41	3.17
5	0.25	0.88	1.66

The study of clearcutting effects on W5 at Hubbard Brook ([Chapter 17](#)) included measurement of some element pools rarely considered in deforestation studies. In particular, changes in soil exchangeable and root biomass pools were measured. This comprehensive nutrient accounting gives us the unique opportunity to estimate changes in weathering rates induced by logging. The estimated rates of weathering release of Ca and K increased by 90% and 29%, respectively, in three years following clearcutting. ([Figure 17.9](#)). The primary source of acidity responsible for accelerated weathering is probably nitrification, as evidenced by the simultaneous release of nitrate and calcium in streamwaters ([Figure 17.8](#)).

#### 14.3.4 AGRICULTURAL SYSTEMS

Catchment budgets in agricultural systems are significantly influenced by major additional inputs of agrochemicals, which aim to produce and maintain an optimum environment for plant growth. Chemical applications are necessary in most agricultural systems, because natural weathering rates and nutrient pools are insufficient to maintain plant growth at the levels required in modern agriculture. In unfertilized/unlimed areas weathering rates would be expected to increase in response to cropping.

Relatively few catchment studies have been set up to investigate the effects of agricultural practices on element budgets. In a rare study Correll *et al.* (1984) found that ionic outputs were lower for a forested site than in a catchment in which cereals were grown. This supports a number of studies which suggest that significant nutrient losses can occur from intensive agricultural systems which receive high nutrient inputs.

Paces (1983) compared chemical weathering rates in an agricultural catchment (X-9) in Czechoslovakia with a nearby forested catchment (X-0). Based on a sodium mass balance, he determined that the rate of oligoclase weathering in the gneissic bedrock was about 5 times greater in the agricultural catchment

than in the forested catchment ([Table 14.9](#)). It should be noted that both catchments experienced relatively high acid deposition inputs due to regional influences.

The accelerated rate of chemical weathering in the agricultural watershed studied by Paces (1983) can be attributed to the addition of fertilizers. In the forested watershed (X-0), inputs of acidity were roughly equal to weathering release of  $C_B$ . However, in another agricultural catchment (X-7),  $C_B$  release nearly doubled the atmospheric acidity input ([Table 14.9](#)) suggesting an additional source of  $H^+$ . Paces (1985) reported that  $57.6 \text{ kg ha}^{-1} \text{ year}^{-1}$  of  $NH_4^+-N$  and  $36.2 \text{ kg ha}^{-1} \text{ year}^{-1}$  of  $H_2PO_4^- -P$  were added to catchment X-7 in fertilizers. These inputs could potentially have generated  $10.6 \text{ keq ha}^{-1} \text{ year}^{-1}$  of  $H^+$ , more than enough to account for the difference between weathering release and acid inputs ( $2.50 - 1.29 = 1.21 \text{ keq ha}^{-1} \text{ year}^{-1}$ ).

**Table 14.9** Contrasting weathering rates between forested and agricultural catchments in Czechoslovakia (Paces 1983, 1985)

Catchment	Land-use	Total $H^+$ Input ( $\text{keq ha}^{-1} \text{ year}^{-1}$ )	$C_B$ release	Rate of plagioclase weathering ( $\text{mol m}^{-2}$ $\text{S}^{-1}$ )
X-0	Forest	0.90	1.15	$3.6 \times 10^{-14}$
X-7	Agriculture	1.29	2.50	-
X-9	Agriculture	-	-	$6.8 \times 10^{-13}$

#### 14.4 NEED FOR FUTURE RESEARCH

One of the most pressing needs in small catchment research is the establishment of a programme for long-term continuing measurements at representative sites on a global scale. This is particularly important in industrialized and developing regions where changes in the chemistry of atmospheric deposition may be expected. It is also important from a global perspective, because such a programme should provide significant data relative to the effects of global climate change on weathering and erosion as well as on potential degradation of soils. Weathering release rates of trace elements which may have toxic effects on biota should also be studied.

The coupling between weathering rates and erosion rates under different geomorphic and climatic conditions is not well understood. Weathering and erosion in terrestrial environments have profound effects on the physical and chemical conditions of the aquatic systems associated with them. For example, weathering reactions influence the chemistry of streams and lakes, and erosion affects the turbidity of the waters. The rate at which material is eroded from the terrestrial environment and transported through streams to lakes and reservoirs determines the life span of these water bodies. The linkages between terrestrial and aquatic systems need to be more clearly defined.

Better understanding of the effects of biological systems on weathering and erosion is needed. Little information is currently available about the effects of organisms on the mechanisms, rates, or products of weathering reactions. Although much research has been done in the past decade on the mineral reaction mechanisms and reaction rates that affect natural water chemistry, many questions remain unanswered, especially with respect to the relationship of laboratory and field kinetic studies. The list of minerals for which there are trusted reaction rate data is short, and the range of conditions covered by those data is

small. Realistic modelling of catchment geochemistry and prediction of changes related to anthropogenic stresses (e.g. acid deposition) or climatic effects (e.g. global warming) require rate data for mineral weathering reactions over the range of conditions of interest.

A research approach consisting of four elements will go a long way towards increasing our understanding of how catchments function:

1. First and foremost is the need for long-term continuing measurements in calibrated catchments located around the globe in regions representative of different natural environments and anthropogenic stresses.
2. Artificial manipulations of a subset of catchments to provide information in a short time frame on responses to perturbations that would require many years or decades to observe under ambient conditions.
3. Laboratory experiments to elucidate mineral reaction mechanisms and rates of reaction over the range of conditions observed in catchments.
4. Continuing evolution of catchment models incorporating new information on flow paths, weathering rates and biological effects as they become available through field catchment research.

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