7

Interaction of Ecosystem Processes and Weathering Processes

MICHAEL ANTHONY VELBEL

Department of Geological Sciences, Michigan State University, USA

7.1 INTRODUCTION

The purpose of this chapter is to explore the conceptual treatment of elemental exchange between botanical and inorganic compartments of small forested catchments, and the consequences of that treatment for geochemical mass balance of small catchments. The geochemical mass balance approach is used by geochemists (to estimate rates of inorganic processes, e.g. weathering of minerals in soils) and by ecologists (as one component of quantifying elemental additions to, losses from and internal cycling within terrestrial ecosystems). Geochemical studies commonly ignore biological effects; ecological studies commonly oversimplify the representations of inorganic geochemical processes. However, for the few ecosystems that have been studied in the requisite detail, the two approaches gave surprisingly consistent quantitative results.

How important are ecosystem processes in geochemical mass balances of catchments? Can they be neglected? Should they be treated as an input, or perhaps as a governing factor? This paper quantitatively investigates the consequences of different explicit assumptions regarding biomass behaviour for weathering rates calculated using mass balance methods. The geochemical mass balance method was modified by Velbel (1985a, 1986) and Taylor and Velbel (1991) to include botanical exchange terms, and applied to forested catchments of the southern Appalachian Mountains (USA). This chapter (a) reviews the previous work on biomass-inclusive mass balance calculations in the southern Appalachian Mountains, (b) examines the sensitivity of previous biomass-inclusive results to variations in the assumed biomass composition and (c) extends the biomass-inclusive mass balance approach to other forested catchments in the southern and central Appalachian Mountains for which biomass effects on elemental budgets have not been previously incorporated into geochemical mass balance calculations of weathering rates.

7.2 BACKGROUND

Silicate mineral weathering reactions are fundamental processes in the reaction of acid precipitation with susceptible landscapes (Cosby et al., 1985a, 1985b; Reuss et al., 1987;
Solute Modelling in Catchment Systems

Binkley et al., 1989; Turner et al., 1990; Kauffmann et al., 1991) and in the contributions of continental crustal weathering to global geochemical cycles (Berner and Berner, 1987). The rates at which weathering reactions proceed are crucial to the consumption (neutralisation) of environmental acidity and to the consumption (transfer from atmosphere to oceans) of atmospheric carbon dioxide. Geochemical mass balance (input—output budgeting) is commonly used to calculate weathering rates (Garrels and Mackenzie, 1967; Cleaves et al., 1970; Clayton, 1979; Velbel, 1985a, 1992; Taylor and Velbel, 1991, and references therein), especially in small catchments. Small catchments are hydrologically and topographically well-defined drainage basins, for which inputs, outputs and internal properties (e.g. rock type, soil type, vegetation type) can be characterized with relative ease. Small catchments are thus both easily studied in terms of hydrologic and geochemical dynamics, and are a fundamental, landscape-scale unit appropriate for studying regional (bio)geochemical processes at natural space and time-scales (as opposed to simulations of such processes in the laboratory).

Many researchers employ the “balance sheet” approach, a system of simultaneous linear equations with constant coefficients. Weathering rates are calculated by solving the system of equations that represent the steady-state input—output behaviour of the catchment (Plummer and Back, 1980, eqn 3):

\[
\phi \sum_{j=1}^{\phi} \alpha_j \beta_{c,j} = \Delta m_c, \quad c = 1, \ldots, n
\]  

(1)

where \( \phi \) is the number of (mineral) phases \( j \) whose transformations account for the change of mass of species \( c \) within the system, \( \Delta m_c \) is the total (known) change in mass of species \( c \) across the boundaries of the system (output minus input), \( \beta_{c,j} \) is the stoichiometric coefficient of species \( c \) released to solution by the weathering of phase \( j \) and \( \alpha_j \) is the weathering rate of phase \( j \). Where multiple mass balance equations are stoichiometrically linked to one another through one or more phase(s) \( j \) containing more than one species \( c \), a system of \( n \) equations results. If the number of mass balance equations \( (n) \), each for a different species \( c \) equals the number of unknowns \( (\phi, \) the number of phases \( j \) whose transformations account for changes of mass of \( c \) within the system), eqn (1) can be solved for mineral weathering rates \( (\alpha_j) \) by conventional techniques of linear algebra. The “balance sheet” method of Garrels and Mackenzie (1967), which has also been employed by numerous other workers (see Taylor and Velbel, 1991) to calculate individual mineral weathering rates, is merely a long-hand, pencil-and-paper solution to the system of mass balance equations (1). The relationship between this use of mass balance equations (1) and that Plummer and Back (1980) is discussed by Velbel (1986).

This system of linear equations represents the steady-state input—output behaviour of the modelled system. Most workers also assume that the steady-state assumption for the entire system means that botanical factors can be ignored, in other words, that there is no net elemental transfer between biomass and inorganic compartments of the system. There are certainly types of catchments (e.g. alpine catchments, above tree-line, which lack forest biomass) where element transfers involving biomass may be justifiably ignored, because there is no significant biomass (Reynolds and Johnson, 1972; Drever and Hurcomb, 1986; Giovancoli et al., 1988; Frogner, 1990; Turner et al., 1990; Stauffer, 1990; Mast et al., 1990). However, in many forested catchments, even small changes in the abundant biomass might consume or release significant amounts of elements. The assumption of steady-state input—output
behaviour of the system is not equivalent to stating that there is no net change in individual compartments (e.g. biomass; see Taylor and Velbel, 1991). The widely invoked assumption that biomass is at “steady state” (usually interpreted to mean that total biomass is constant) is both (a) mathematically a second, explicit assumption, unrelated to the assumption of overall steady state and (b) also generally erroneous. One potential consequence is systematic errors in weathering rates calculated by mass balance.

Taylor and Velbel (1991) constructed geochemical mass balances for seven small forested catchments of the US Department of Agriculture (Forest Service) Coweeta Hydrologic Laboratory in the Nantahala Mountains of the southern Blue Ridge Appalachians, North Carolina, USA. All seven catchments are “control” catchments, which have been free of any intentional anthropogenic disturbances since 1924. Four of the catchments (2, 18, 34, 36) are underlain by the Tallulah Falls Formation; the other three (14, 27, 32) are underlain by the Coweeta Group. The two lithostratigraphic units on which the soils and saprolites of the study area are developed both consist of high-grade (amphibolite facies) metasedimentary schists and gneisses. The Tallulah Falls Formation was metamorphosed from sedimentary protoliths of slightly lower compositional maturity than the Coweeta Group; consequently, the rocks of the Tallulah Falls Formation have a higher abundance of weatherable parent minerals than the rocks of the Coweeta Group. The higher “weatherability” of the Tallulah Falls Formation relative to the Coweeta Group accounts for the fact the Tallulah Falls Formation catchments have (a) higher long-term average cation fluxes (especially Na and K; see Taylor and Velbel, 1991, and Table 7.1), (b) higher calculated rates of mineral weathering (Table 7.1) and (c) higher long-term average stream water pHs and dissolved silica and cation concentrations than Coweeta Group catchments (Velbel, 1985b). The geology, hydrology, topography, climate and land-use history of the study area are described in more detail by Velbel (1985a) and Swank and Crossley (1988).

Taylor and Velbel (1991) constructed geochemical mass balances for the seven Coweeta control catchments by using a system of linear equations formalized as eqn (1). Mineralogical and petrographic (micromorphological) data determine stoichiometries of mineral weathering reaction. By evaluating and reinterpreting published hydrological and hydrogeochemical data and combining them with the known stoichiometries of the mineral weathering reactions, Velbel (1985a, 1985b; Taylor and Velbel, 1991) found that four transformations influence dissolved elemental budgets in the catchment. The four reactions are the weathering of three major weatherable rock-forming minerals:

1. Biotite mica to vermiculite:

\[
K_{0.85}Na_{0.02}(Mg_{1.2}Fe^{II}_{1.3}Al_{0.45})^{VI}(Al_{1.2}Si_{2.8})^{IV}O_{10}(OH)_2 + 0.19 O_2 + 0.078 H^+ + 0.31 H_2O \\
+ 0.016 Ca^{2+} + 0.04 Na^+ + 0.35 Al(OH)_2^{+}(aq) + 0.3 Fe(OH)_2^{+}(aq) \rightarrow \\
K_{0.25}Na_{0.06}Ca_{0.16}(Mg_{1.1}Fe^{II}_{0.5}Fe^{III}_{1.1})^{VI}(Al_{1.2}Si_{2.8})^{IV}O_{10}(OH)_2 \times 0.133 Al_6(OH)_{15} + 0.6 K^+ \\
+ 0.1 Mg^{2+}
\]

2. Almandine garnet to gibbsite, goethite and solutes:

\[
Ca_{0.2}Mg_{0.5}Mn^{III}_{0.2}Fe^{II}_{2.2}Al_{2}Si_3O_{12} + 0.625 O_2 + 2.5 H^+ + 8.35 H_2O \rightarrow \\
2FeOOH(s) + 0.1 Fe(OH)_3^{+}(aq) + Al(OH)_3(s) + Al(OH)_2^{+}(aq) \\
+ 3 H_4SiO_4(aq) + 0.5 Mg^{2+} + 0.2 Ca^{2+} + 0.2 MnO_2(s)
\]

3. Plagioclase feldspar to kaolinite, gibbsite and solutes:
TABLE 7.1 Mineral weathering rates from catchment balances of North Carolina (Coweeta) catchments with alternate biomass

<table>
<thead>
<tr>
<th>Catchment</th>
<th>Mineral</th>
<th>Without biomass</th>
<th>Coweeta</th>
<th>Hubbard Brook</th>
<th>UK deciduous</th>
<th>Walker Branch</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Plagioclase</td>
<td>535</td>
<td>567</td>
<td>553</td>
<td>545</td>
<td>540</td>
</tr>
<tr>
<td></td>
<td>Garnet</td>
<td>164</td>
<td>240</td>
<td>179</td>
<td>207</td>
<td>235</td>
</tr>
<tr>
<td></td>
<td>Biotite</td>
<td>124</td>
<td>432</td>
<td>302</td>
<td>293</td>
<td>195</td>
</tr>
<tr>
<td>14</td>
<td>Plagioclase</td>
<td>250</td>
<td>257</td>
<td>254</td>
<td>252</td>
<td>251</td>
</tr>
<tr>
<td></td>
<td>Garnet</td>
<td>176</td>
<td>195</td>
<td>180</td>
<td>187</td>
<td>194</td>
</tr>
<tr>
<td></td>
<td>Biotite</td>
<td>97</td>
<td>175</td>
<td>144</td>
<td>141</td>
<td>116</td>
</tr>
<tr>
<td>18</td>
<td>Plagioclase</td>
<td>439</td>
<td>460</td>
<td>451</td>
<td>445</td>
<td>442</td>
</tr>
<tr>
<td></td>
<td>Garnet</td>
<td>192</td>
<td>242</td>
<td>202</td>
<td>220</td>
<td>238</td>
</tr>
<tr>
<td></td>
<td>Biotite</td>
<td>126</td>
<td>325</td>
<td>241</td>
<td>235</td>
<td>172</td>
</tr>
<tr>
<td>27</td>
<td>Plagioclase</td>
<td>232</td>
<td>230</td>
<td>231</td>
<td>232</td>
<td>232</td>
</tr>
<tr>
<td></td>
<td>Garnet</td>
<td>201</td>
<td>197</td>
<td>200</td>
<td>199</td>
<td>197</td>
</tr>
<tr>
<td></td>
<td>Biotite</td>
<td>104</td>
<td>85</td>
<td>93</td>
<td>93</td>
<td>100</td>
</tr>
<tr>
<td>32</td>
<td>Plagioclase</td>
<td>351</td>
<td>353</td>
<td>352</td>
<td>352</td>
<td>351</td>
</tr>
<tr>
<td></td>
<td>Garnet</td>
<td>297</td>
<td>293</td>
<td>288</td>
<td>290</td>
<td>293</td>
</tr>
<tr>
<td></td>
<td>Biotite</td>
<td>123</td>
<td>150</td>
<td>139</td>
<td>138</td>
<td>129</td>
</tr>
<tr>
<td>34</td>
<td>Plagioclase</td>
<td>483</td>
<td>500</td>
<td>493</td>
<td>489</td>
<td>486</td>
</tr>
<tr>
<td></td>
<td>Garnet</td>
<td>263</td>
<td>304</td>
<td>271</td>
<td>286</td>
<td>301</td>
</tr>
<tr>
<td></td>
<td>Biotite</td>
<td>131</td>
<td>294</td>
<td>225</td>
<td>221</td>
<td>169</td>
</tr>
<tr>
<td>36</td>
<td>Plagioclase</td>
<td>641</td>
<td>662</td>
<td>653</td>
<td>648</td>
<td>644</td>
</tr>
<tr>
<td></td>
<td>Garnet</td>
<td>285</td>
<td>334</td>
<td>294</td>
<td>312</td>
<td>330</td>
</tr>
<tr>
<td></td>
<td>Biotite</td>
<td>141</td>
<td>338</td>
<td>255</td>
<td>250</td>
<td>187</td>
</tr>
</tbody>
</table>

Units: moles of reaction (as written in text) per hectare per year.

\[
\begin{align*}
\text{Ca}_x\text{Na}_{(1-x)}\text{Al}_{(1+2x)}\text{Si}_{(3-x)}\text{O}_8 + [4.5 - 3.5x + 2.5y(1+x)] \text{H}_2\text{O} + (1+c) \text{H}^+ &= \\
x\text{Ca}^{2+} + (1-x)\text{Na}^+ + [(2.2x) + y(1+x)] \text{H}_2\text{SiO}_4(\text{aq}) + (1+y)\text{Al(OH)}_3 + \\
0.5(1+x)(1-y)\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4
\end{align*}
\]

(where \(x\) is the mole fraction anorthite in the plagioclase; \(x = 0.25\) for rocks of the Coweeta Group and \(x = 0.32\) for rocks of the Tallulah Falls Formation (Velbel, 1985a) and \(y\) is the (unknown) fraction of Al released by feldspar weathering which goes into gibbsite).

4. Uptake of mineral nutrients by the forest biota.

The rates of these four transformations are the four unknowns in eqn (1); therefore, mass balance equations for four elements are needed in order to solve the system of equations in the desired number of unknowns. The stoichiometries of these reactions are known for minerals and can be approximated for biomass (using the data of Day and Monk, 1977; Boring et al., 1981; Taylor and Velbel, 1991; see Table 7.2), and net fluxes for Na, Mg, K and Ca are known (from Swank and Waide, 1988; Taylor and Velbel, 1991; their Table 2), so the system
Interaction of Ecosystem Processes and Weathering Processes

TABLE 7.2 Molar ratios of major rock-derived cations in temperate forest biomass (Mg = 1)

<table>
<thead>
<tr>
<th>Catchment</th>
<th>Na</th>
<th>Mg</th>
<th>K</th>
<th>Ca</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coweeta</td>
<td>0.143</td>
<td>1.0</td>
<td>2.68</td>
<td>2.57</td>
<td>Taylor and Velbel (1991)</td>
</tr>
<tr>
<td>Hubbard Brook</td>
<td>0.2</td>
<td>1.0</td>
<td>4.22</td>
<td>6.41</td>
<td>Likens et al. (1977)</td>
</tr>
<tr>
<td>UK deciduous</td>
<td>n.r.</td>
<td>1.0</td>
<td>2.63</td>
<td>4.29</td>
<td>Cole and Rapp (1981)</td>
</tr>
<tr>
<td>Walker Branch</td>
<td>n.r.</td>
<td>1.0</td>
<td>1.0</td>
<td>4.0</td>
<td>Katz (1989)</td>
</tr>
</tbody>
</table>

n.r. = not reported.

of equations can be solved. Rates of primary mineral weathering and mineral nutrient supply to the terrestrial biota were calculated by this method (Taylor and Velbel, 1991).

Taylor and Velbel (1991) demonstrated the effects on calculated weathering rates of including and ignoring botanical terms by comparing the results of two different sets of geochemical mass balance calculations of weathering rates for the Coweeta control catchments (using different sets of assumptions but identical input data). The results of the comparative mass balance calculations for seven undisturbed catchments at Coweeta (Taylor and Velbel, 1991) are included in Table 7.1. The “Coweeta biomass” column shows the results of solving a system of four equations (steady-state mass balance equations for K, Na, Ca and Mg) in four unknowns (weathering rates of almandine garnet, oligoclase-andesine plagioclase feldspar and biotite mica, and exchange with forest biomass). The “without biomass” column shows mineral weathering rates calculated without the botanical exchange term. Weathering rates calculated using the two different assumptions differ by as much as a factor of four (Taylor and Velbel, 1991). The difference is most pronounced for minerals that contain major nutrient elements and for rates calculated from mass balances of those nutrient elements. These results, although provocative, are only applicable to the specific catchments studied. In this paper, similar comparisons of calculated mass balances with and without biomass terms permit examination of the interactions between geochemical and ecological terms in other Appalachian catchments.

7.3 METHODS

The present study examines only rates from studies in which weathering rates of multiple silicate minerals were determined simultaneously. Ideally, there would be numerous solute mass balance studies of forested catchments which report weathering rates of multiple silicate minerals. However, many mass balance studies calculate only “lumped” weathering rates (e.g. total release by weathering of cations or silica, in moles or eq ha\(^{-1}\) yr\(^{-1}\)), without apportioning the fluxes among individual minerals. In other instances, there are obvious errors and/or inconsistencies in the published mass balances (e.g. negative weathering rates for rock-forming silicates, implying formation of minerals like feldspar during weathering, a physically unreasonable result), rendering suspect the previously published fluxes and/or stoichiometries. Additionally, many mass balance studies that calculate weathering rates for individual silicate minerals involve catchments with ecosystems other than forests (e.g. bog, alpine). For this study, only forested catchments in the southeastern United States were examined. There are many previous geochemical mass balance studies in this geographic region; many of these have neglected possible biomass exchange of mineral-derived elements. Forested catchments outside this region, and other ecosystem types, will be the subjects of future research.
Following Taylor and Velbel (1991), the present study examines variations in calculated weathering rates which result from different mathematical assumptions regarding biomass effects which are demonstrated by comparing the results of two different sets of geochemical mass balance calculations of weathering rates for the catchments examined. In most cases examined here, the original calculations assume both steady state for the overall system and no net exchange of elements between biomass and the rest of the system (Taylor and Velbel, 1991). Although more mathematically restrictive and less likely to represent the behaviour of natural botanical systems, the introduction of these two assumptions simplifies the mass balance calculation by eliminating the necessity of introducing botanical coefficients into the equations.

In the present study, only the overall input—output behaviour of the system is assumed to be at steady state, and mathematical coefficients are introduced into the equations to allow elemental exchange with biomass (Taylor and Velbel, 1991). Data on the chemical composition of annual increments and/or net primary production (NPP) for ecosystems relevant to the study catchments in the southern and central Appalachians (northern hemisphere temperate hardwood forests) were retrieved from the ecological literature, to estimate the appropriate abundance ratios of major rock(weathering)-derived elements (K, Ca, Mg, Na) in biomass NPP in the individual study areas (Table 7.2). It is through the use of these ratios that biological effects are included in geochemical mass balance calculations (Velbel, 1985a, 1986; Taylor and Velbel, 1991).

In order to eliminate the possibility that the choice of a different stoichiometry for a mineral common to the two approaches is the cause of different results, this study uses the same stoichiometric coefficients for mineral weathering reactions as those of the original studies. In addition, to prevent different input parameters from dominating differences between previous results and the present study, the same (measured) net elemental fluxes (output minus input) are used.

### 7.4 SENSITIVITY OF CALCULATED WEATHERING RATES TO VARIATIONS IN ASSUMED BIOMASS COMPOSITION: NORTH CAROLINA REVISITED

Taylor and Velbel (1991) calculated weathering rates for seven control catchments in the Coweeta Hydrologic Laboratory, using elemental exchange ratios for biomass from a detailed study of one of the seven catchments. Because the biomass composition they used is derived from the forests of the study area itself, the rates so calculated are the best possible estimate, and inferences based on these calculations are likely to be quite reliable. However, to test how sensitive the rates would be to error or variation in the biomass composition, weathering rates for the seven Coweeta control catchments were recalculated using the three other biomass compositions compiled for this study.

The results are shown in Table 7.1. Although the numerical values of the calculated rates vary widely, two major points emerge:

1. The magnitude of the variation introduced into the estimates of weathering rates by changing the cation composition of the modelled forest biomass follows the pattern of sensitivity originally described by Taylor and Velbel, (1991). Rates of plagioclase weathering are not significantly affected by including or excluding biomass terms (Taylor and Velbel, 1991) or by varying the biomass composition used (Table 7.1), because the weathering rate of plagioclase is determined almost exclusively by the mass balance equation for Na. Sodium is
Interaction of Ecosystem Processes and Weathering Processes

not a major plant nutrient, so, even when invoked, the botanical exchange coefficient is very small and has little effect on the Na mass balance equation. Rates of garnet weathering are invariably higher in the calculations which included botanical exchange than in the commonly used method which ignores biomass (Taylor and Velbel, 1991), regardless of the specific biomass composition used (Table 7.1). Garnet weathering rates are calculated from the mass balances of Ca and Mg, both of which are important plant nutrients. Biotite mica weathering rates are also invariably higher in the calculations which included botanical exchange than in the commonly used method which ignores biomass (Taylor and Velbel, 1991), again regardless of the specific biomass composition used (Table 7.1). Furthermore, the biotite weathering rates show the largest variability with changing biomass composition (Table 7.1) — in other words, of all the minerals investigated at Coweeta, the weathering rate of biotite is the most sensitive to variability in assumed biomass composition. The biotite weathering rate is calculated primarily from the mass balance equation for K, a major plant nutrient. The sensitivity of mineral weathering rates to biomass composition is most pronounced for minerals that contain major nutrient elements and for rates calculated from mass balances of those nutrient elements (Taylor and Velbel, 1991). The one exception to the described patterns (catchment 27) is discussed in more detail below.

2. The observed patterns of change in the calculated weathering rate with varying biomass composition are the same, regardless of the specific biomass composition used. The absolute value of the calculated rate may depend upon the specific composition used to calculate it. However, the rate calculated with any specific biomass included always bears the same relationship to the rates calculated without biomass, regardless of the biomass composition used. If the biomass-included rate using one biomass is higher than the rate calculated without biomass, the use of any other biomass also yields a rate higher than the rate calculated without biomass.

7.5 CHANGES IN CALCULATED WEATHERING RATES UPON INCORPORATION OF BIOMASS TERMS IN CATCHMENTS IN MARYLAND AND VIRGINIA

7.5.1 Maryland Piedmont: Pond Branch, Maryland

The geochemical mass balance of the Pond Branch (Maryland) catchment was studied by Cleaves et al. (1970). Pond Branch is situated in the Piedmont Province, is almost entirely forested and is underlain by the Lower Pelitic Schist Member of the Wissahickon Schist. The schist consists of quartz, plagioclase, muscovite, biotite and staurolite, with minor garnet, kyanite, apatite, tourmaline, zircon and chlorite. Mass balances for three elements (Na, Mg and SiO$_2$) and certain specific assumptions regarding the relative proportions were used to solve for the rates of four weathering reactions:

1. Plagioclase to kaolinite:

\[
Ca_{0.22}Na_{0.78}Al_{1.22}Si_{2.78}O_8 + 0.61 H_2O + 1.22 H_2CO_3 = 0.22 Ca^{2+} + 0.78 Na^+ + 1.56 SiO_2(aq) + 1.22 HCO_3^- + 0.6 Al_2Si_2O_5(OH)_4
\]

2. Kaolinite to gibbsite:

\[
Al_2Si_2O_5(OH)_4 + H_2O \Rightarrow 2 Al(OH)_3 + 2 SiO_2(aq)
\]

3. Biotite to vermiculite:
Solute Modelling in Catchment Systems

\[
3[K_2(Mg_3Fe_2)Al_2Si_6O_{20}(OH)_4] + 8 H_2O + 12 H_2CO_3 \rightarrow \\
2((Mg_3Fe_3)Al_2Si_3O_{20}(OH)_8) \times 8 H_2O + 6 K^+ + 3 Mg^{2+} + 3 Fe^{2+} \\
+ 8 SiO_{2(aq)} + 12 HCO_3^-
\]

4. Vermiculite to kaolinite:

\[
2((Mg_3Fe_3)Al_2Si_3O_{20}(OH)_8) \times 8 H_2O + 30 H_2CO_3 \rightarrow \\
3 Al_2Si_2O_5(OH)_4 + 6 Mg^{2+} + 6 Fe^{2+} + 4 SiO_{2(aq)} + 29 H_2O + 30 HCO_3^-
\]

7.5.2 Maryland Blue Ridge

Katz et al. (1985) and Katz (1989) examined geochemical mass balances in several catchments in the Catoctin Mountains of Maryland, all of which are underlain by greenstone metabasalt of the Catoctin Formation. The Catoctin Formation consists of chlorite, albite, epidote and actinolite, with minor quartz and calcite.

7.5.2.1 Hauver Branch Maryland

Katz et al. (1985) studied the Hauver Branch catchment, which hosts a mature deciduous forest cover. Mass balance for four elements (Na, Ca, Mg and SiO\(_2\)) were used to solve for the rates of weathering reactions:

1. Albite to kaolinite:

\[
NaAlSi_3O_8 + H^+ + 9/2 H_2O \rightarrow Na^+ + 1/2 Al_2Si_2O_5(OH)_4 + 2 H_4SiO_4
\]

2. Calcite dissolution:

\[
CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-
\]

3. Chlorite to kaolinite:

\[
Mg_5Al_2Si_3O_{10}(OH)_8 + 10 H^+ \rightarrow 5 Mg^{2+} + H_4SiO_4 + Al_2Si_2O_5(OH)_4 + 5 H_2O
\]

4. Actinolite dissolution:

\[
Ca_2(Mg_3Fe_2)Si_4O_{22}(OH)_2 + 14 H^+ + 8 H_2O \rightarrow 2 Ca^{2+} + 3 Mg^{2+} + 2 Fe^{2+} + 8 H_4SiO_4
\]

Fluxes were corrected for anthropogenic addition of deicing salts.

7.5.2.2 Owens Creek, Maryland

Katz (1989) examined the Owens Creek catchment, which is located several kilometres north of Hauver Branch. Bedrock geology (Catoctin Formation metabasalt and metarhyolite) and vegetation (hickory, poplar, birch and oak) in the Owens Creek catchment are similar to Hauver Branch. Mineral weathering reaction stoichiometries used to constrain the Owens Creek mass balance are identical to those listed above for Hauver Branch. In addition to correcting fluxes for deicing salts, Katz (1989) introduced a mass balance equation for K and included in the system of equations coefficients for botanical exchange of K, Ca and Mg in molar proportions derived from the forest ecosystem in Walker Branch, Tennessee, several hundred kilometres to the southwest. The biomass terms were invoked primarily to account for the abundance of K observed in the catchment efflux; note that none of the major weatherable
minerals typical of the Catoctin metabasalt releases K upon weathering. Therefore, the observed excess of K in output relative to input must be derived from some non-geological source, such as decay of biomass.

7.5.3 Virginia Blue Ridge: Mill Run, Virginia

The Mill Run catchment, located in the Blue Ridge Mountains of Virginia, was studied by Afifi and Bricker (1983). Bedrock consists of the Massanutten Sandstone (Silurian), actually a low-grade metasandstone comprising predominantly quartz, with minor albite plagioclase, orthoclase, chlorite and amphibole. Complete forest cover consists of second-growth mixed oak—hickory with scattered stands of conifers.

The original Afifi and Bricker (1983) mass balance invoked the following weathering reactions for the weatherable silicate minerals of the Massanutten Sandstone:

1. Albite to kaolinite:
   \[ \text{NaAlSi}_3\text{O}_8 + H^+ + 9/2 \text{H}_2\text{O} \rightarrow \text{Na}^+ + 1/2 \text{Al}_2\text{Si}_5\text{O}_8(\text{OH})_4 + 2 \text{H}_4\text{SiO}_4 \]

2. Orthoclase to kaolinite:
   \[ \text{KAlSi}_3\text{O}_8 + H^+ + 9/2 \text{H}_2\text{O} \rightarrow \text{K}^+ + 1/2 \text{Al}_2\text{Si}_5\text{O}_8(\text{OH})_4 + 2 \text{H}_4\text{SiO}_4 \]

3. Chlorite to kaolinite:
   \[ \text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8 + 10 H^+ \rightarrow 5 \text{Mg}^{2+} + \text{H}_2\text{SiO}_4 + \text{Al}_2\text{Si}_5\text{O}_8(\text{OH})_4 + 5 \text{H}_2\text{O} \]

4. Amphibole to kaolinite and goethite:
   \[ \text{NaCa}_2(\text{Mg}_3\text{Fe}_2)(\text{Al}_3\text{Si}_9)\text{O}_{22}(\text{OH})_2 + 11 H^+ + 3/2 \text{H}_2\text{O} \rightarrow \text{Na}^+ + 2 \text{Ca}^{2+} + 3 \text{Mg}^{2+} + 3/2 \text{Al}_2\text{Si}_5\text{O}_8(\text{OH})_4 + 2 \text{FeOOH} + 2 \text{H}_4\text{SiO}_4 \]

Each of the catchment studies listed above produced silicate weathering rates estimated from geochemical mass balance. The rates reported by the original researchers or recalculated for this study are shown in Table 7.3. Also shown in Table 7.3 are the weathering rates recalculated in this study using the original stoichiometries and fluxes, with the addition of stoichiometric coefficients for biomass.

7.6 DISCUSSION

Cleaves et al. (1970) were among the first to address the impact of biomass on mass balance calculations of mineral weathering rates. They observed that, when mass balance for Na, Mg and silica was achieved, the weathering reactions produced more K and Ca than was observed in the catchment output. From this they concluded that K and Ca were taken up by an unmeasured sink within the catchment and that the unmeasured sink was the forest. Likens et al. (1977) showed that failure to account for botanical uptake of elements resulted in estimated weathering rates which underestimated the actual rates by a factor of two. Despite these demonstrations, only a relatively small number of mass balance studies (Paces 1983; Schnoor and Stumm, 1985; Velbel, 1985a, 1992; Clayton, 1988; Sverdrup, 1988; Sverdrup and Warfvinge, 1988; Katz, 1989; Taylor and Velbel, 1991; Probst et al. 1992) have incorporated botanical uptake and/or release terms into their mass balance equations. However, most mass
### MINERAL WEATHERING RATES

<table>
<thead>
<tr>
<th>Catchment</th>
<th>Mineral</th>
<th>Original published rate</th>
<th>Biomass Coweeta</th>
<th>Biomass Hubbard Brook</th>
<th>Biomass UK deciduous</th>
<th>Biomass Walker Branch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pond, Branch, Maryland</td>
<td>Plagioclase</td>
<td>148</td>
<td>148</td>
<td>147</td>
<td>146</td>
<td>146</td>
</tr>
<tr>
<td></td>
<td>Biotite</td>
<td>32</td>
<td>8</td>
<td>7</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Vermiculite</td>
<td>12</td>
<td>6</td>
<td>5</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Kaolinite</td>
<td>30</td>
<td>37</td>
<td>44</td>
<td>45</td>
<td>50</td>
</tr>
<tr>
<td>Hauver Branch, Maryland</td>
<td>Albite</td>
<td>316</td>
<td>315</td>
<td>315</td>
<td>316</td>
<td>316</td>
</tr>
<tr>
<td></td>
<td>Calcite</td>
<td>249</td>
<td>235</td>
<td>227</td>
<td>226</td>
<td>192</td>
</tr>
<tr>
<td></td>
<td>Chlorite</td>
<td>115</td>
<td>113</td>
<td>114</td>
<td>113</td>
<td>112</td>
</tr>
<tr>
<td></td>
<td>ActiSholite</td>
<td>23</td>
<td>24</td>
<td>24</td>
<td>23</td>
<td>24</td>
</tr>
<tr>
<td>Owen and Hunting Creek, Maryland</td>
<td>Albite</td>
<td>45</td>
<td>44</td>
<td>44</td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>Calcite</td>
<td>479</td>
<td>511</td>
<td>504</td>
<td>502</td>
<td>469</td>
</tr>
<tr>
<td></td>
<td>Chlorite</td>
<td>11</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>ActiSholite</td>
<td>22</td>
<td>26</td>
<td>26</td>
<td>26</td>
<td>26</td>
</tr>
<tr>
<td>Mill Run, Virginia</td>
<td>Albite</td>
<td>73</td>
<td>66</td>
<td>60</td>
<td>58</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>Orthoclase</td>
<td>121</td>
<td>137</td>
<td>139</td>
<td>140</td>
<td>151</td>
</tr>
<tr>
<td></td>
<td>Chlorite</td>
<td>40</td>
<td>37</td>
<td>33</td>
<td>32</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Amphibole</td>
<td>17</td>
<td>25</td>
<td>31</td>
<td>33</td>
<td>77</td>
</tr>
</tbody>
</table>

Units: moles of reaction (as written in text) per hectare per year.

* Original rate calculated from mass balance including biomass terms. For all others, the original published rate was determined from mass balances that excluded consideration of botanical factors.

* Original rate in micromoles litre\(^{-1}\) converted using measured discharge.

Balance studies in forested catchments, and some stream acidification models, leave out botanical exchange terms entirely.

The widespread neglect of botanical factors in geochemical estimates of weathering and soil formation rates stems from misunderstanding of the nature of “steady state” as it applies to the biological compartment of terrestrial biogeochemical cycles (Taylor and Velbel, 1991). At the landscape scale, “steady state” in forest biomass exists in the form of the “shifting-mosaic steady state” of Bormann and Likens (1981), in which a steady-state landscape consists of a geographic patchwork of different ecosystems, each at a different stage of succession and nutrient demand. The landscape-scale distribution of these successionaly diverse patches reaches a steady-state distribution if the landscape as a whole is free from large-scale regional perturbations. On geologic time-scales and global spatial-scales, the local and temporary fluctuations in elemental storage and cycling by the shifting mosaic of ecosystem stages average out spatially and temporally. However, on the time-scales (months to decades) and the spatial-scales (small forested catchments) of interest in the present discussion, ignoring botanical exchange effects can cause large errors in weathering and soil-formation rates calculated from elemental budgets (Taylor and Velbel, 1991).

Taylor and Velbel (1991) proposed that the ratios of weathering rates calculated with and without including expressions for botanical exchange are related to the state of the catchment forest ecosystems. Table 7.1 illustrated this. For most Coweeta control catchments, mineral
weathering rates are greater when calculated with biomass terms in the mass balance than when calculated without such terms (the ratio of "biotic/abiotic" rates exceeds unity). If the botanical compartment is actively taking up nutrients, the measured net cation (e.g. K, Ca, Mg) efflux (by streams) is not the only output term; biomass is also an output from the mineral compartment (Sollins et al., 1980). Because both rates are calculated using the same net solute fluxes, this behaviour implies that (a) more weathering must take place to produce the observed flux when biomass is included than when biomass is excluded and (b) there must be an intra-catchment sink to account for the excess solutes that are released by the greater amount of weathering but that do not show up in the solute effluxes. The most likely sink is the catchment forest biomass itself.

The role of net uptake (aggradation) of forest biomass is discussed in detail by Taylor and Velbel (1991). Not all of the mineral nutrient elements in the growing biomass come directly from the mineral compartments. A given year’s net primary production includes a large proportion of mineral nutrients recycled from decay of the previous year’s litter. Much of the nutrient content of “new” tissue (e.g. leaves, sapwood) consists of nutrients translocated from other parts of the tree (Whittaker et al., 1979; Tanner, 1985; Mahendrappa et al., 1986; Monk and Day, 1988). again indicating that the nutrients in new tissue are only partly derived from the minerals in the soil. Taken together, these observations indicate that some 50—90% of the annual uptake from the soil litter pool is recycled; only the remaining 10—50% are “new” additions, and these can be added by both atmospheric input (Swank and Henderson, 1976) and weathering (Taylor and Velbel, 1991). It is the weathering portion of this “new” input that is estimated by the mass balance calculations. The biomass “uptake” calculated by geochemical mass balance represents only the annual increment of nutrient “withdrawal” from the mineral compartment, and is therefore considerably less than the actual net primary production measured by the forest ecologists.

Mineral components of the forest soil are included in the calculations, through the stoichiometric coefficients of the mineral weathering reactions. Organically mediated non-biologic soil materials such as calcium oxalate accumulations can be regarded as internal components of the biological nutrient cycle, which do not act as sinks for soil-derived nutrients, but as “regulators” of botanically recycled nutrients. Graustein et al. (1977) and Cromack et al. (1979) observed that fungal hyphae in contact with mineral fragments are devoid of calcium oxalate crystals, and concluded that the oxalate has been removed from the weathering site by forming soluble complexes with Fe and Al derived from the weathering of the mineral fragments. Any Ca released by the weathering of the mineral fragment was similarly mobilized, because there is no free; uncomplexed oxalate with which it may precipitate. In contrast, fungal hyphae in the spaces between soil grains possess calcium oxalate crystals. The Ca in these crystals is probably not the same Ca that was released by weathering of nearby mineral fragments: it is more likely to be Ca “stripped” from the ambient soil solution percolating through the intergranular pore spaces.

The “ambient” Ca may be partially derived from mineral weathering, but must also include significant proportions of atmospherically derived Ca and/or recycled Ca released by the decay of plant litter on the forest floor. If the botanical cycle of Ca is similar to that of chemically analogous Sr, the forest biota, litter and soil may be dominated by externally (atmospherically) derived Ca, either primary or recycled. Graustein (Graustein, 1981, 1989; Graustein and Armstrong, 1983) showed that Sr in forest biomass was derived largely from atmospheric input and that plant Sr is largely botanically recycled Sr of atmospheric origin. Furthermore,
Graustein found that groundwaters and streamwaters of his study area bore no imprint of atmospherically derived Sr, implying that the atmospherically derived nutrient is effectively stripped from incoming solutions and recycled botanically. Leakage of Sr from the botanical cycle is minimal, relative to the release of bedrock Sr to groundwaters below the soil. In other words, the contribution to the groundwaters by weathering of bedrock minerals must be much larger than the contribution to the groundwater by leakage of atmospherically derived nutrients from the botanical cycle. If the botanical cycle of Ca is as tight as that of Sr, this may imply that the ecological function of forest floor oxalate may be more to regulate the botanical recycling ("tightness") of recycled Ca, rather than to extract Ca from soil minerals. Externally derived and recycled Ca are stored in fungal mats of calcium oxalate; the mineral-derived Ca, like the Sr with "bedrock" isotopic signature (Graustein, 1981, 1989; Graustein and Armstrong, 1983), is released from soils minerals, and much or most of it passes out of the soil and into the groundwaters and streamwaters.

Fungally regulated Ca is most likely either primary or recycled atmospheric Ca. If it is atmospheric (Swank and Henderson, 1976), it is implicitly included in the $\Delta m_t$ term of eqn (1); if recycled, it is merely storage, derived from the decay of the plant tissue with known composition. Growth of this plant tissue by removal of nutrients from the dissolved compartment is explicitly incorporated into the mass balance equations. Botanical recycling is an internal component of the biomass term in the dissolved mineral-nutrient budget and need not be considered separately. Non-biological forest soil components (e.g. forest floor mats of fungal calcium oxalate, etc.) are a regulatory device in the botanical nutrient cycles, and are not sinks or reservoirs of elements derived from mineral weathering.

Degradation of biomass can add elements to the efflux (thereby returning more elements to the solutions than are taken up into new growth; see Whittaker et al., 1979; Sollins et al., 1980: Jordan, 1982), which would be an internal source (Katz, 1989). In such cases, mineral weathering rates are slower when calculated with biomass terms in the mass balance than when calculated without such terms (the ratio of "biotic/abiotic" rates is less than unity). This implies that (a) less weathering must take place to produce the observed flux when biomass is included than when biomass is excluded and (b) there must be an intra-catchment source to supply the additional solutes that must be added to the amount supplied by weathering to produce the solute effluxes. The most likely source is the catchment forest biomass itself. This behaviour is known from managed landscapes (Katz, 1989) and from a few undisturbed forested catchments (Taylor and Velbel, 1991).

Interpreted in this light, the ratio of "biotic/abiotic" weathering rates can distinguish catchments in which forest biomass was aggrading over the period of solute sampling from those with declining biomass (Taylor and Velbel, 1991). This hypothesis is borne out by the known state of the forest ecosystems in the seven Coweeta control catchments. Most Coweeta control catchments exhibit increases in calculated weathering rates when biomass exchange coefficients are introduced (indicating net uptake by biomass; see Taylor and Velbel, 1991). However, one catchment (catchment 27) exhibits slight decreases, suggesting net loss of biomass, adding nutrients of biological origin to the stream efflux (Taylor and Velbel, 1991). Catchment 27 is the only control catchment on Coweeta Group rocks which was partially defoliated by fall cankerworm during the 1970s (Swank and Douglass, 1977; Swank and Crossley, 1988). Taylor and Velbel (1991) conclude that the "anomalous" ratios for mineral weathering rates in catchment 27 calculated with and without biomass exchange terms are due to decay of defoliation products. Catchment 36 (on rocks of the Tallulah Falls Formation) also
experienced fall cankerworm infestation over part of the same period, but the infestation on
catchment 36 may not have been extensive enough to cause extensive biomass decay or
otherwise detectably perturb major element budgets. The possibility that the effects of fall
cankerworm infestation were significant on catchment 27, and present but less significant on
catchment 36, is supported by two observations; infestation was of shorter duration on
catchment 36 than on catchment 27, and perturbations of budgets of solutes which are
extremely sensitive to biomass disturbance (e.g. nitrate nitrogen) were significantly smaller on
catchment 36 than on catchment 27 (Swank and Waide, 1988, Tables 4.6 and 4.11). Thus, the
results of Taylor and Velbel’s (1991) mass balance calculations with biomass terms included
are consistent with what is known about the actual state of the forest ecosystems in the modelled
catchments.

Table 7.1 of this study shows that, although the magnitude of the weathering rates calculated
when biomass is included can vary widely, the ratio of biomass-inclusive/biomass-exclusive
rates exhibits the same behaviour described by Taylor and Velbel (1991) using only local
biomass composition. For all catchments except catchment 27, rates calculated including
biomass are greater than rates calculated without biomass, implying that the forest biomass is a
net internal sink for major rock-derived cations. Only for the catchment with degrading biomass
(catchment 27) does the incorporation of botanical terms decrease the calculated weathering
rate, implying that the biomass is acting as an additional source of major cations to the solute
effluxes. This conclusion is robust in the face of any possible uncertainty regarding the biomass
composition; the same relationships hold regardless of the specific biomass composition used to
make the calculation.

The results from catchments in the North Carolina Blue Ridge suggest that catchment mass
balances can distinguish catchments in which forest biomass was aggrading over the period of
solute samples (Coweeta catchments 2, 14, 18, 34 and 36) from those with declining biomass
(Coweeta catchment 27). By this reasoning, Pond Branch and Hauver Branch, Maryland, were
catchment systems with declining forest biomass (Table 7.3), at least during their respective
periods of study. Biomass in the Owen Creek, Maryland, catchment was also declining; the
original mass balance of Katz (1989) invokes biomass decay to achieve potassium balance, and
the mass balance is insensitive to varying biomass composition (Table 7.3). Thus, in contrast to
the pattern of aggrading biomass in the North Carolina catchments, geochemical mass balances
suggest a pattern of general loss of forest biomass in all catchments previously studied in the
state of Maryland. In order to explain observed solute fluxes, weathering rates for orthoclase
(potassium feldspar) in the Mill Run, Virginia, catchment must be higher when biomass is
accounted for (Table 7.3). This suggests that the forest in the Mill Run catchment was most
likely an aggrading ecosystem; this is consistent with its obvious second-growth character.

7.7 SUMMARY AND CONCLUSIONS

Ecosystem processes are important in geochemical mass balances of catchments. The uptake or
release of common rock-derived elements (K, Ca, Mg) during aggradation or degradation of
forest biomass can have noticeable effects on catchment solute mass balances, and on
weathering rates derived from these mass balances. The magnitude of “error” introduced into
the calculated weathering rates by omitting biomass from the mass balance depends largely on
the botanical significance of each specific element. Weathering rates vary the least for minerals
whose rate is calculated from the mass balance for botanically unimportant elements (e.g. sodic
plagioclase feldspar, whose weathering rate is determined from the catchment mass balance for Na; see Tables 7.1 and 7.3). The most variable and uncertain weathering rates are those for minerals that supply botanically important elements. Weathering rates for biotite mica (whose weathering rate is determined from the catchment mass balance for K) vary by a factor of six or more, depending on whether biomass is accounted for in the mass balance or not (Tables 7.1 and 7.3), and can vary by more than a factor of two with different choices of biomass composition (Table 7.1). Thus, the determination of weathering rates of individual minerals in catchment ecosystems can be very sensitive to the precise manner in which botanical factors are accounted for in constructing the mass balance.

The choice of how to treat ecosystems (as an input, or perhaps as a governing factor) depends in part on the purpose of the specific study, in part on how much is already known about a specific system and in part on the resources available. Where known in great detail (from ecological nutrient cycle studies; e.g. Coweeta, Hubbard Brook), ecosystem processes might be treated as a known set of inputs to catchment solute models. However, where site-specific information is lacking, it may be informative to use reasonable estimates of biomass composition (as was done in this study) and to treat the magnitude of elemental cycling as an unknown, to be freely solved for along with the weathering rates. Sensitivity of the calculated rates to variation in the selected botanical compositions can be done with selected specific examples (as in this study) or more rigorously (statistically, by, for instance, creating biomass compositions from random numbers between specified limits).

Ecosystem processes cannot be neglected in catchment solute mass balances. Catchment mass balance studies can be undertaken for a variety of reasons. The goal of a particular study may be to estimate the rate of replenishment of soil nutrient pools by primary-mineral weathering (a common ecological application of catchment mass balances), the rate of supply of “base” cations in soil cation exchange complexes and/or soil and surface waters (a common need in studies of environmental acidification) or the rate of denudation of the landscape (a common geological application). All such studies commonly (although not invariably) invoke a “lumped-parameter” modelling approach, in which key parameters (in this case, bulk “weathering” rates at which specific cations are supplied to the rest of the system by “weathering”) are assigned a single value intended to represent the behaviour of the entire catchment. However, such approaches are of limited predictive value. Rates of elemental release from different mineral sources (e.g. Ca release by weathering of calcite versus calcic silicates) have very different functional dependences on various environmental parameters (solution pH, soil temperature, hydraulic flow rates; see Drever and Hurcomb, 1986). It is therefore not enough to know the “bulk” rate of, for instance, Ca release from the rocks and soils of a catchment. One must apportion the weathering contribution of Ca among the various contributing mineral species, as is done by solving systems of simultaneous linear equations for the weathering rates of individual minerals. Furthermore, quantifying the contributions of individual mineral species cannot be accomplished in the absence of botanical information. The weathering rate of biotite in Coweeta catchment 2 is nearly four times higher when biomass is accounted for than the rate estimated from solute fluxes alone. Thus, biotite weathering is four times as effective at releasing K than might otherwise be thought. Factor-of-four variations like this may not be trivial when estimating sustainable silvicultural harvest intervals.

In order to predict how solute budgets will respond to environmental stress (removal of forest products, acid deposition, global warming), one must know what mineral species (individually or in combination) are responsible for the “bulk” release rates. Regardless of the potential
application, physically meaningful apportionment of elements among realistic suites of sources and sinks is essential to a proper understanding of the system. Both biotic and abiotic compartments of the catchment ecosystem must be included.

ACKNOWLEDGEMENTS


REFERENCES


