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# Tracking the Fate of Plagioclase Weathering Products: Pedogenic and Human Influences

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## ABSTRACT

Catchment mass balance demonstrates the role of hydrologic, pedogenic, and human influences on cycling of Ca, Al, Na, and Si, derived from plagioclase dissolution. As Na is little taken up by vegetation, does not accumulate in secondary soil pools, and is primarily in plagioclase, net Na output is a measure of plagioclase dissolution. Net Na flux is proportional to streamflow, illustrating hydrologic control of weathering. Rates of Ca, Al, and Si release from mineral dissolution are more difficult to evaluate as they are variably taken up by vegetation or stored in secondary soil pools. However, plagioclase stoichiometry provides a benchmark by which the net storage or release of these elements may be gauged. Net export of Ca relative to Na shows that Ca export was enhanced in the 1960s, peaking in the 1970s, taken as an indication of acid deposition effects on the soil exchange pool, which were further exacerbated by harvesting treatments. Net export of Si and Al relative to Na suggest dynamic biotic Si pools and provide a measure of the podzolization soil development process. Net catchment export ratios provide a tool for comparing biogeochemical processes across catchments and a basis for investigating processes controlling pool accumulation.


## 7.1. INTRODUCTION

Element mass balance is a well-known experimental technique that has been used to elucidate the cycling of elements at the catchment scale in both undisturbed, reference catchments, as well as in response to various disturbances in both natural settings and in experimentally treated or manipulated catchments. Catchment element cycling studies began at the Hubbard Brook Experimental Forest (HBEF), NH, United States in 1963, facilitated by advances in technology to electronically measure water solute concentrations quickly and inexpensively. This record at HBEF has continued uninterrupted since 1963 (Likens & Bailey, 2014). This catchment-scale mass balance technique was pioneered as a method for estimating rates of release of base cations such as $Ca^{2+}$, $Na^{+}$, etc., by dissolution of minerals in field settings (Johnson et al., 1968). As this approach evolved and was applied at other sites, a growing appreciation of dynamics in biomass and soil pools of some elements released by mineral dissolution was taken into account, thus refining estimates of mineral weathering and highlighting dynamics in response to disturbances in biotic and soil pools (Likens et al., 1996; Price, Rice, et al., 2013; Velbel & Price, 2007). Thus, the mass balance for an element $x$ at a catchment scale is determined by inputs of atmospheric deposition ($P_x$) and mineral weathering flux ($W_x$), stream output ($S_x$) and changes in ecosystem pools, including net biomass uptake ($B_x$), secondary mineral formation ($M_x$), and change in available soil pools ($\Delta A_x$) as expressed by

$$P_x + W_x = S_x + B_x + M_x \pm \Delta A_x \tag{7.1}$$

Note that at this site, typical of relatively undisturbed forested catchments of the region, erosion rates are very low. Catchment export of mineral-derived materials is

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primarily in a dissolved form; particulate export is relatively small (Likens et al., 1977).

Net catchment export of sodium (Na), calculated simply as streamwater export minus atmospheric input in bulk precipitation, has been interpreted as an estimate of $Na^+$ release by primary mineral dissolution, and has been shown to be attributable to plagioclase weathering in catchments underlain by soils and bedrock of a variety of lithologies (Price, Peresolak, et al., 2013; Price, Rice, et al., 2013; Stutter et al., 2002). The limited uptake of Na by plants (Kronzucker & Britto, 2011), resulting in minimum storage in biomass pools, and large ionic radius of $Na^+$, which makes it a poor competitor for soil ion exchange sites, and its absence as an essential component in secondary minerals, contribute to the simpler mass balance of this element (S.W. Bailey et al., 2003), facilitating the use of net Na export as an indicator of mineral dissolution, and in particular plagioclase weathering.

While the relatively conservative behavior of Na may facilitate its use as a weathering index, the other elements derived from plagioclase dissolution are critical to a number of ecosystem processes and functions. Calcium (Ca) and silicon (Si) are important nutrients, actively taken up by plants (McLaughlin & Wimmer, 1999; Ronchi et al., 2013). Limitations in Ca supply lead to health impacts in sensitive species, which include red spruce and sugar maple, two of the most ecologically and commercially important species in NE North America (Long et al., 2009). Silica drives productivity in marine environments, where its supply is derived from runoff from terrestrial sources (Ronchi et al., 2013). Aluminum (Al) is not a nutrient, and can be toxic to terrestrial and aquatic life in its free ionic form $Al^{3+}$ (Driscoll et al., 2001). However, in humid, temperate to subtropical portions of the world where podzolization is an important soil forming process, Al is responsible for mineral horizon carbon (C) sequestration, the dominant C store in Spodosols (Lundström et al., 2000). Thus indices of Ca, Si, and Al loss normalized to Na export may provide an important tool for understanding biogeochemical processing of these elements including dynamics in storage in vegetation and soil pools.

S. W. Bailey et al. (2003) proposed the use of a net ecosystem Ca/Na ratio, or the net loss of Ca from a catchment divided by the net Na loss, as a tool for evaluating temporal dynamics in ecosystem Ca pools, which may include net storage in aggrading vegetation or changes in weakly bound pools on the soil cation exchange complex. Unlike Na, ionic Ca pools in biomass and in soil are typically large compared to atmospheric inputs and streamwater outputs, and are potentially dynamic, responding to disturbances such as air pollution and vegetation loss, including biomass harvest during forest management. By normalizing net Ca loss to net Na loss, the effect of annual variability in mineral weathering flux can be removed, highlighting dynamics in ecosystem Ca pools. Elevation of net Ca flux relative to net Na flux, and subsequent declines have been interpreted as evidence for depletion of Ca from available soil pools, which peaked in the 1970s in response to anthropogenic acid deposition (S.W. Bailey et al., 2003; Watmough et al., 2016). Catchments at the HBEF that received various forest disturbance treatments, which included clearfelling trees, herbicide applications, and removal of forest biomass in tree boles or whole trees, showed further elevated net Ca/Na flux ratios relative to reference or unmanipulated catchments, suggesting additional losses of Ca in excess of weathering inputs, with treatment effects lasting decades and continuing through the record reported on by S.W. Bailey et al. (2003). As plagioclase feldspar is also a dominant mineral source for Al and Si, there is potential to interpret net ecosystem Al/Na and Si/Na export ratios relative to the stoichiometry of plagioclase similar to the approach that has been applied with Ca.

The objectives of the current study are to update the analysis of net ecosystem Ca and Na loss at the HBEF (S.W. Bailey et al., 2003) to determine if net Ca loss continues to decline relative to net Na loss in response to acid deposition, and to determine if experimentally treated catchments continue to follow a distinct trajectory from reference catchments, or if these trajectories have merged, suggesting that treatment effects on Ca export have ceased. The current study was also designed to expand this technique to evaluate net Si and Al loss from the same suite of catchments. This will elucidate processes affecting the export of these additional elements and infer potential dynamics in Si and Al ecosystem pools.

## 7.2. METHODS

### 7.2.1. Study Area

Hubbard Brook Experimental Forest is located in west-central New Hampshire, USA (43°56'N, 71°45'W; Figure 7.1) within the White Mountain National Forest. The climate is humid continental with a mean annual precipitation of 140 cm and stream runoff of 90 cm (A.S. Bailey et al., 2003). Much of the research is centered on nine headwater catchments located in the northern (W1–W6) and southern (W7–W9) portions of the experimental forest (Figure 7.1) where water and solute input and output is measured at a series of meteorological and stream gauging stations. This study focuses on catchments W3, W6, and W9, which are maintained in a natural, unmanaged condition and serve as reference catchments, and W2, W4, and W5, which have had various vegetation manipulation treatments, described below.

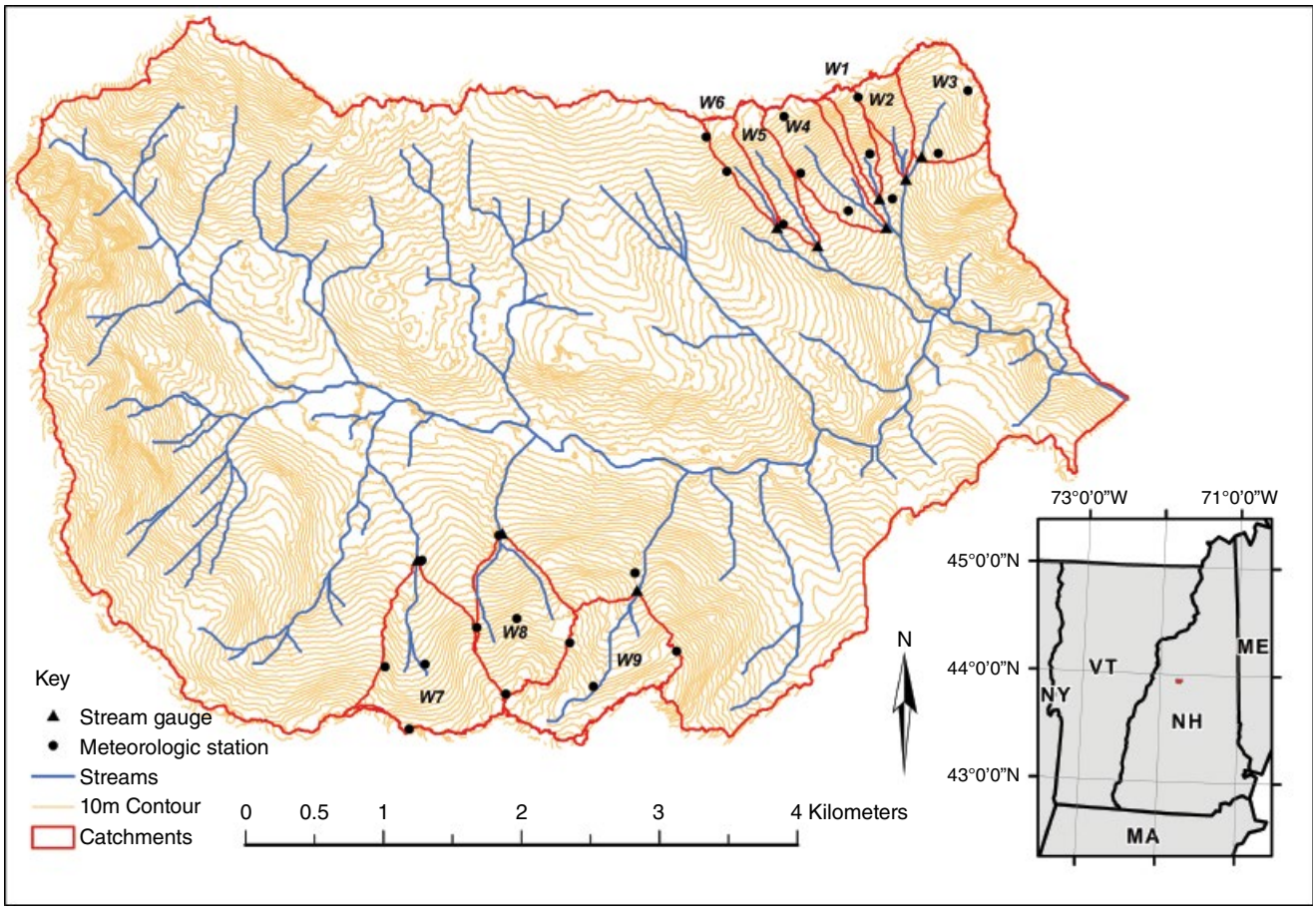


**Figure 7.1** Locus map of Hubbard Brook Experimental Forest.

Land cover at the HBEF is forest with northern hardwoods dominated by *Acer saccharum* Marsh. (sugar maple), *Betula alleghanensis* Britt. (yellow birch), and *Fagus grandifolia* Ehrh. (American beech) on deeper and better-drained soils; mixed conifers dominated by *Picea rubens* Sarg. (red spruce), *Abies balsamea* (L.) Mill. (balsam fir), and *Betula papryifera* var. *cordifolia* (Regel) Fern. (mountain paper birch) occupy wetter sites and areas where soils are shallow to bedrock. Forests on the reference catchments are mature, mostly second growth following partial cutting in the period of 1890–1920, and severe blowdown during a hurricane in 1938. Reference catchments (W3, W6, W9) have had no direct human disturbance or management since prior harvesting which ended in the 1910s. Treated catchments (W2, W4, W5) have aggrading forest following recent harvesting or deforestation experiments. Catchment W2 was clearfelled during the winter of 1965–1966 and herbicided to prevent regrowth during the growing seasons of 1966–1968; W4 was harvested in strips 25 m wide along contour during fall/winter 1970, 1972, and 1974, with one-third of the catchment harvested during each of the three years; and W5 was whole-tree harvested, removing all tops and stems > 5 cm diameter at breast height during the winter of 1983–1984.

Bedrock in the portion of the HBEF considered in this study is the Silurian Rangeley Formation, a sillimanite-grade metapelite consisting of mica schist with minor amounts of calc-silicate granulite (Burton et al., 2000). Bedrock is poorly exposed, cropping out mostly along ridges and in some stream channels, and is covered by a veneer of late Wisconsinan glacial drift. In the study watersheds, drift is thin and interspersed with exposed bedrock in the uppermost portion of the catchments, particularly along catchment divides, while it is up to 10 m thick in central to lower portions of the catchments. Catchment W9 is distinct in having much more bedrock outcrops while the majority of the catchment is underlain by thin drift, with bedrock less than 1 m deep.

Glacial drift is dominated by granitic lithologies, transported from the north and west of the study catchments, with lesser contributions from local bedrock (S.W. Bailey et al., 2003), and is the parent material for soil development. Based on a review of published bedrock

**Table 7.1** Mineralogic contributions to Ca, Na, Al, and Si content (percent) of soil parent material

| Mineral | Ca | Na | Al | Si |
|---|---|---|---|---|
| Plagioclase | 75 | 98 | 73 | 24 |
| Minor silicates[a] | 15 | 2 | 3 | 1 |
| Apatite | 10 | 0 | 0 | 0 |
| Stable silicates[b] | 0 | 0 | 24 | 75 |

[a] Includes hornblende, diopside, epidote, actinolite, biotite.
[b] Includes quartz, K-feldspar, muscovite.

mineralogy, till lithologic sources, and direct microprobe analyses of soil minerals (S.W. Bailey et al., 2003, 2019; Hyman et al., 1998), plagioclase feldspar is of oligoclase composition ($Ca_{0.2}Na_{0.8}Al_{1.2}Si_{2.8}O_8$) and a dominant source of Ca and Na, as well as the most easily weathered source of Al and Si in the catchments (Table 7.1). Normalized to Na, the stoichiometry of oligoclase is 0.25Ca:1.5Al:3.5Si:Na. Thus, dissolution of this mineral is expected to produce 0.25 mol Ca, 1.5 mol Al, and 3.5 mol Si per mole of Na, resulting in index ratios that are useful for tracking the fate of solutes released by dissolution.

Where not confined by shallow bedrock, soils average 0.7 m to the top of the C-horizon, corresponding to the depth of major alteration of glacial drift by soil-forming processes, as well as the limit of the rooting zone (S.W. Bailey et al., 2014). Podzolization is a dominant soil-forming process, with organic acids leaching iron (Fe) and Al from surficial mineral soil layers (eluviation) and depositing them as organic Fe and Al complexes in lower mineral soil layers (illuviation). Soils vary in their expression of eluvial horizons, mineral soil low in organic matter, and illuvial horizons, with mineral surfaces coated by organic matter complexed by Al and Fe. Presence and thickness of eluvial and illuvial horizons depends on thickness of the soil parent material, subsurface drainage limitations, and upslope drainage area (S.W. Bailey et al., 2014).

### 7.2.2. Mass Balance

The small catchment approach was used to calculate water flux and element mass balance on an annual basis using a 1st June water year (S.W. Bailey et al., 2003). The experimental catchments are numbered consecutively by the date that monitoring began, with W1 established in 1956 to W9 established in 1995. Water inputs of rain and snow were measured at a series of meteorologic stations, with the two to four closest collectors to each catchment used to calculate an area-weighted water input. Water output via streamflow was measured at weir-controlled gauging stations at the base of each catchment. Gauging stations were installed on stream reaches with bedrock outcrops with a cement basin capturing all of the streamflow and directing it over a calibrated steel v-notch weir. Due to low density, nonintersecting orientation of fractures aligned primarily along foliation of tightly folded crystalline metamorphic bedrock, negligible water flux occurs through deep seepage (< 1% of atmospheric inputs) (Likens et al., 1977). Rain and snow were sampled for major solutes in bulk precipitation collectors open to wet and dry deposition and retrieved weekly. Streamwater major solute composition was measured from a weekly sample at the catchment outlet.

Instrumentation and analytical procedures for water chemical analyses are described fully in Buso et al. (2000). Chemical analyses were performed at the Cary Institute, Millbrook, NY through 2012 and then at the US Forest Service, Durham, NH from 2012 to the present. Similar methods were used at both laboratories and a year of overlap in the analyses was conducted in order to insure the integrity of the long-term record. Calcium, Na, and Si were measured on an ICP optical emission spectrometer (OES). Total dissolved Al was also measured by ICP-OES from 2012 onwards at the US Forest Service laboratory. Prior total dissolved Al measurements were made spectrometrically using the wet-chemical Ferron method (Buso et al., 2000). Inputs of dissolved Al and Si in rain and snow are negligible; although routinely measured, samples yield concentrations below analytical detection limits. Errors incorporated in the catchment mass-balance approach include error in annual water flux measured by gauges, estimated as ≤ 5% by Winter (1981) and determination of cation concentrations, estimated at ≤ 5% for precipitation and ≤ 1% for streamwater (Buso et al., 2000). Water flux and water chemical data used in this study are available in Campbell (2017a, 2017b) and Likens (2017).

## 7.3. RESULTS

### 7.3.1. Net Na Flux

Net Na flux from the reference catchments showed no long-term trend (Figure 7.2), with interannual variation largely reflecting wetness conditions (annual net Na flux vs. streamflow for W3, W6, and W9, $r$ = 0.93, 0.89, 0.77, respectively). The reference catchments, as well as the experimentally manipulated catchments outside of the immediate post-treatment periods, follow a consistent order with W4 and W3 having the greatest net Na flux while W9 had the least flux. The other three catchments, W2, W5, and W6 had Na flux similar to each other and intermediate to the other two groups of catchments (Figure 7.2). The reference and treated catchments follow similar trends and interannual variation (outside of the treatment periods). Thus, with regards to Na flux, there appears to be no difference in behavior between the reference and treatment catchments.

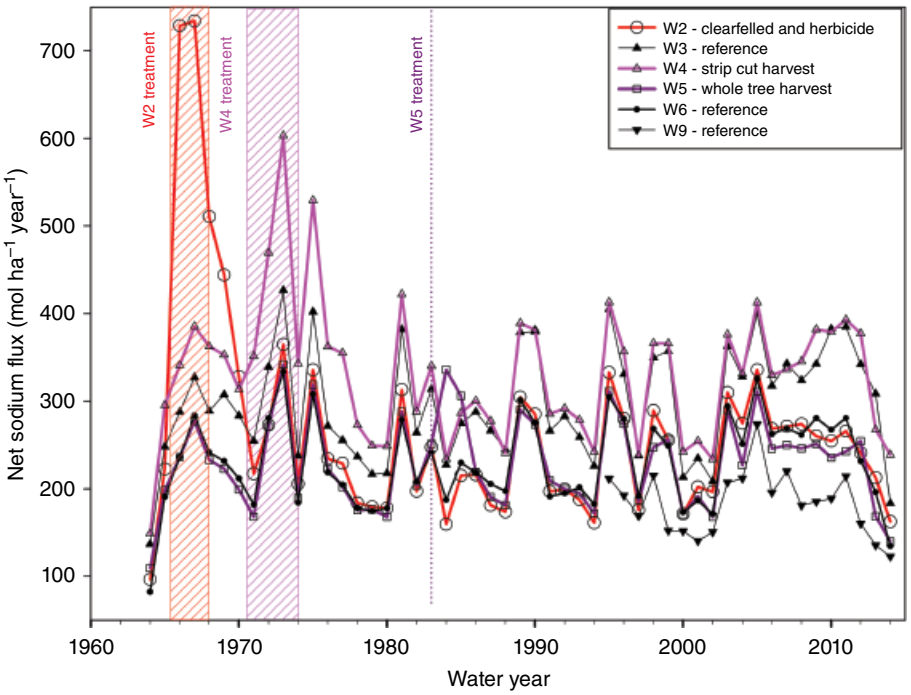


**Figure 7.2** Annual net Na flux calculated as stream export minus precipitation input. Reference catchments are shown with black lines while treated catchments are shown with colored lines. Symbols and colors for each catchment are consistent among all figures. Dashed vertical lines show the start of treatments in the experimentally manipulated catchments.

Compared to the other catchments, net Na flux was elevated following treatment with W2, which was devegetated for 3 years, showing the strongest response with increased flux for 5 years following treatment, and a maximum increase of about seven times over pretreatment conditions for the first 2 years following treatment. Whole-tree harvested W5 had an increase of net Na flux of about 40% for 2 years following treatment. Strip-cut W4 was harvested over a 6 year period, with a buffer strip left along the central stream. Thus, in contrast to the other two experiments, it maintained partial vegetative cover throughout the treatment and recovery period. This less severe treatment, coupled with W4's tendency to have the highest net Na flux throughout the record, make it somewhat more difficult to delineate a treatment response. However, net Na flux from W4 in 1973 of 603 mol ha$^{-1}$ year$^{-1}$ was the highest flux measured in any of the catchments except for W2 in the first 2 years of its treatment. Overall, the deviation in net Na flux in the treated compared to the reference watersheds was proportional to the severity of the disturbance.

### 7.3.2. Net Ca/Na Flux

The net Ca/Na flux ratio was always higher than that expected from stoichiometric plagioclase dissolution, with a minimum of 0.42 measured in W3 in 2011 and 2012, compared to a ratio of 0.25 in plagioclase (Figure 7.3). In contrast to the net Na flux, the net Ca/Na flux ratio showed a distinct long-term pattern with lesser interannual variation. The three reference catchments tracked each other closely, with net Ca/Na relatively low at 0.5 (W6) to 0.8 (W3) at the beginning of the record, increasing to a peak of 1.3 (W3) to 1.5 (W6) in the early 1970s, then decreasing steadily to 0.5 (W3) to 0.6 (W6) in 2000. The record in W9 began in 1995 with the net Ca/Na flux in W9 tracking the other reference catchments. Since 2000, which is beyond the limit of the record previously reported by Bailey et al. (2003), the net Ca/Na flux has been relatively steady in the reference catchments at values between 0.4 and 0.6 (Figure 7.3).

The treated watersheds followed a similar trend of net Ca/Na flux increasing to the early 1970s followed by a decrease, with deviations from the reference catchments following treatment, and continuing on trajectories distinct from the reference catchments until about 2011 (Figure 7.3). Similar to the relative treatment effects seen in net Na flux, the increase in net Ca/Na flux was greatest in W2, with lesser treatment effect seen in W5 and the least response in W4. In W2 and W5, the increase in net Ca/Na flux relative to the other catchments appeared immediately after initial treatment while the response in W4 was not apparent until about 1977, 7 years after treatment began and 3 years after

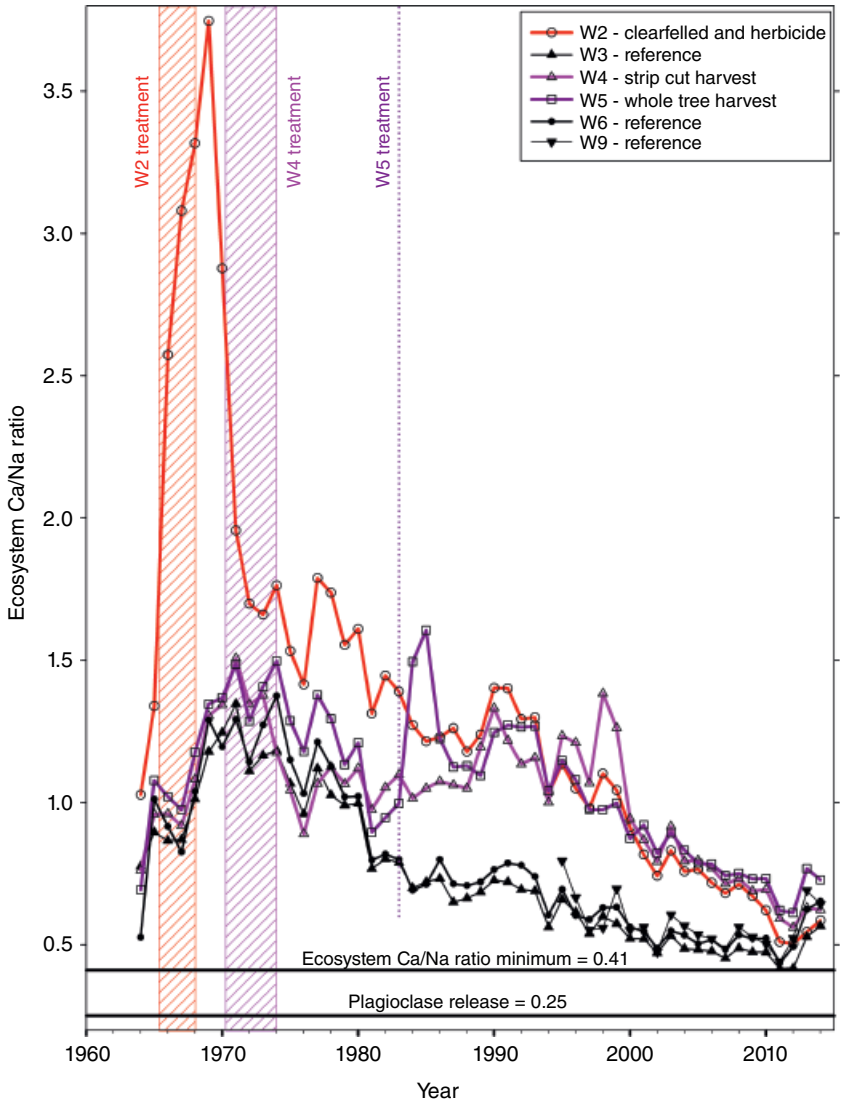


**Figure 7.3** Net Ca/Na flux ratio calculated as the net Ca flux divided by the net Na flux. The minimum value observed was 0.41, compared to a stoichiometric value for plagioclase of 0.25.

treatment was complete. In contrast to the shorter-lived, 5 year or less, response seen in net Na flux following treatment, net Ca/Na flux followed an elevated trajectory relative to the reference catchments until 2011. Net Ca/Na flux in the treated catchments tracked parallel but still slightly higher than the reference catchments in the last 4 years of the record. Taking 2011 as the end of treatment response in net Ca flux relative to Na, this suggests that elevated Ca following treatment lasted 45, 34, and 27 years in W2, W4, and W5, respectively (Figure 7.3).

### 7.3.3. Net Si/Na Flux

The net Si/Na flux showed no apparent long-term trends and perhaps the greatest interannual variation of any of the fluxes or flux ratios considered in this study (Figure 7.4). The catchments were all distinct from each other, with the exception of W3 and W6, the two reference catchments dominated by deeper soils and northern hardwood forests, which tracked each other closely in net Si/Na. The other reference catchment, W9, with shallow to bedrock soils and dominantly coniferous vegetation had distinctly higher Si/Na ratio. The net Si/Na ratio in W3 and W6 was generally less than the ratio of 3.5 expected from stoichiometric plagioclase dissolution, varying mostly in the range of 2.0–3.0. In contrast, the higher ratios observed in W9 were mostly greater than the ratio expected from plagioclase dissolution, varying mostly in the range of 3.5–4.5. Outside of the treatment periods, the treated catchments (W2, W4, and W5) fell generally between the Si/Na ratio of the reference catchments, with W9 at the upper end and W3 and W6 at the lower end.

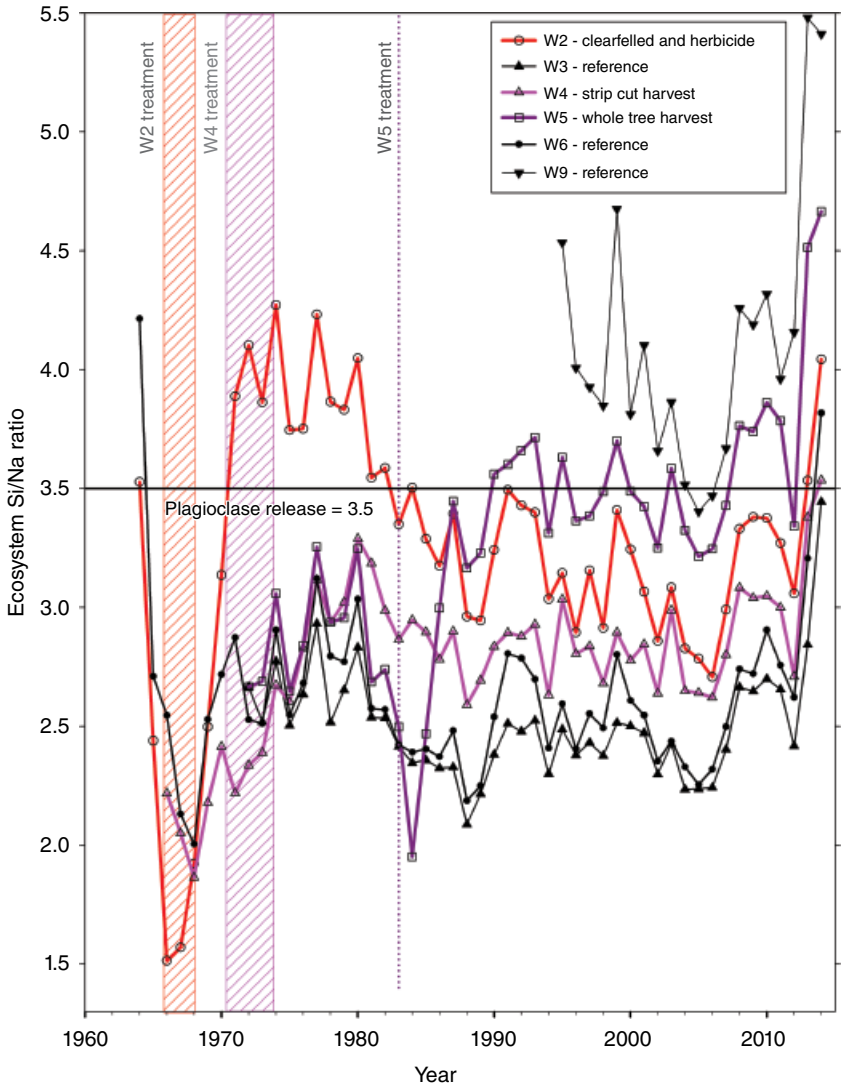


**Figure 7.4** Net Si/Na flux ratio calculated as Si output in streamwater divided by the net Na flux. Si input in atmospheric deposition was negligible. The measured values vary about the stoichiometric value for plagioclase of 3.5.

The Si/Na ratio in the treated catchments was similar to the reference catchments before treatment and then showed complicated deviations compared to the patterns seen in the reference catchments (Figure 7.4). In W2, Si/Na decreased sharply to the lowest levels exhibited in the study for 2 years following treatment. This was followed by a sharp increase, with Si/Na ratios greater than that expected from plagioclase dissolution for the following 12 years. In whole-tree harvested W5, Si/Na also decreased sharply for 1 year following treatment, followed by a sharp increase. Net Si/Na flux in W5 fluctuated about the plagioclase value for most of the remaining record. The response in W4 was more subtle, without strong swings in the ratio following treatment. However, W4, which had exhibited Si/Na ratios less than the reference catchments W3 and W6 until treatment, has shown Si/Na ratios greater than those reference catchments since treatment (Figure 7.4).

### 7.3.4. Net Al/Na Flux

Routine monitoring of total dissolved Al in all HBEF catchments commenced in 2013. During 2013–2014, net Al/Na in two of the reference catchments, W3 and W6, as well as in all three of the treated catchments was very low, ranging from 0.08 to 0.40 (Figure 7.5). In contrast, W9, the reference catchment with shallow soils and coniferous forest had ratios of 1.2 and 1.4, much higher than any of the other measurements of net Al/Na except for W2 during the treatment period, and approaching the ratio of 1.5 expected from plagioclase dissolution.

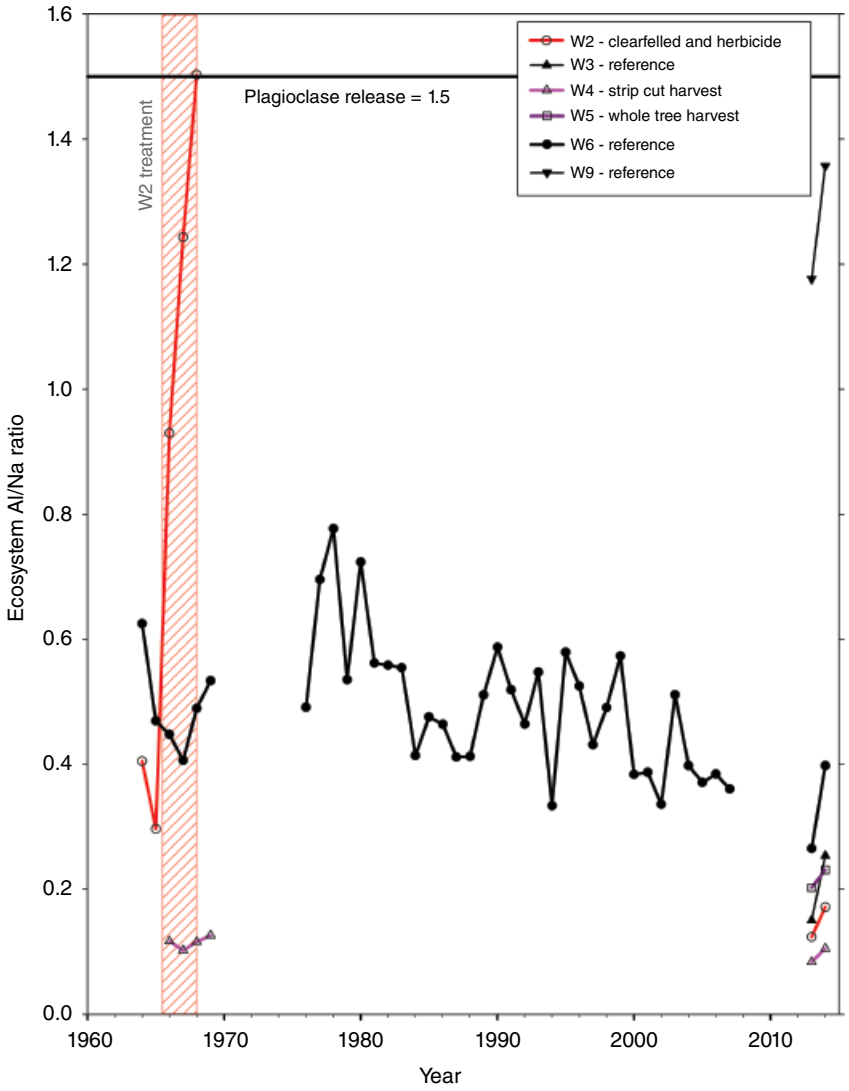


**Figure 7.5** Net Al/Na flux ratio calculated as Al output in streamwater divided by the net Na flux. The Al input in atmospheric deposition was negligible. The measured values are substantially less than the stoichiometric value for plagioclase of 1.5 except for W2 following treatment, and for reference catchment W9, where the measured values approach the plagioclase value.

The record of net Al/Na flux is limited by available data and is most complete for reference catchment W6. The Al/Na at W6 showed a slightly decreasing trend, at least from the late 1970s to the present (Figure 7.5). The measured flux ratio ranged from 0.78 in 1978 to 0.27 in 2013, all substantially less than a ratio of 1.5 expected from stoichiometric plagioclase dissolution. The only treated catchment with a record around a treatment period is clearfelled and herbicided W2, which showed Al/Na ratios slightly less than the W6 reference catchment in two pretreatment years, followed by strong increases during the year treatment commenced and the two post-treatment years for which data are available. The ratio of 1.5 measured in 1968 at the end of the herbicide applications equals that expected from plagioclase dissolution.

The level of analysis of Al/Na ratio is limited by available data. Monitoring of future trends will confirm and extend the findings presented here.

## 7.4. DISCUSSION

### 7.4.1. Long-Term Variation in Plagioclase Weathering

Shortly after recognition of acid deposition as an air pollution phenomenon, Johnson et al. (1972) questioned whether a switch from a carbonic acid buffering system to a dominance of sulfate as the major anion would result in

a change in mineral weathering rates. Lack of trends in net Na export (Figure 7.2), with Na fluxes correlating with streamflow (section 7.3.1) suggest a hydrologic driver of plagioclase weathering that has been insensitive to dynamics in acid deposition levels and water solute composition. Over the period of the HBEF record, there has been a sevenfold reduction in hydrogen ion concentrations in precipitation, with concomitant increases in surface-water pH and reductions in surface-water concentrations of base cations and Al (Likens & Bailey, 2014). These changes may counteract each other with respect to influencing weathering rates, with decreases in pH and dissolved Al, for example, expected to have opposing effects on weathering rates. Over the medium term, at decadal timescales, weathering of plagioclase shows no trends, responding only to interannual variation in wetness.

Differences in net Na flux between catchments appear to vary with soil depth. Bedrock outcrops are most common in W9, with intervening areas largely covered by glacial drift-based soils less than 1 m deep. Catchment W9 clearly has the shallowest soils, corresponding to the lowest net Na flux (Figure 7.2). The other catchments have bedrock outcrops mostly confined to catchment divides and existing soil surveys are insufficient to quantitatively compare soil depth between catchments. However, as W3 and W4 are wider relative to their length compared to the other catchments, it seems likely that soil depth could be deeper in these two catchments, especially in interior portions farther from a bedrock-controlled catchment divide. Better determination of soil thickness across the catchments, coupled with soil textural analyses, could be used to express net Na flux on a mineral surface area basis, rather than just a catchment area basis, and would improve our ability to compare weathering rate estimates measured in this field setting with those measured in laboratory experiments, which are routinely expressed on a mineral-surface-area basis.

Differences in plagioclase dissolution would also be expected from climatic differences related to temperature or moisture gradients (Dere et al., 2013; Williams et al., 2010). However, as the study catchments are in close proximity and within the same elevation range (Figure 7.1), they receive nearly identical precipitation amounts and have similar air temperature (A.S. Bailey et al., 2003). Thus it does not seem likely that climate accounts for differences between catchments in the relationship between net Na flux and streamflow. Differences in groundwater composition between the catchments could also account for differences in weathering flux. Catchments with groundwater of lower pH and higher dissolved organic carbon (DOC) would be expected to have greater dissolution rates (Hausrath et al., 2009). Groundwater chemistry at the HBEF has been shown to vary by soil type, with lower pH and higher DOC concentrations in groundwater in shallow soils associated with bedrock outcrops (Gannon et al., 2015; Zimmer et al., 2013), suggesting that dissolution rates might be expected to be highest in W9 with its distinctly shallower soils. However, W9 shows the lowest net Na export suggesting that limitations in soil depth and mineral surface area may outweigh increases in weathering rate due to acidity and organic acid complexation.

### 7.4.2. Soil Calcium Depletion

Dynamics in net Ca export relative to net Na flux, and in comparison to plagioclase stoichiometry, was a central basis that Likens et al. (1996) used to infer that acid deposition had depleted Ca soil exchange pools at the HBEF. This approach was modified by S.W. Bailey et al. (2003) who recognized that weathering of other minerals, such as hornblende and apatite was likely to contribute to catchment mass balance, and would release more Ca relative to Na than plagioclase. At the time of the S.W. Bailey et al. (2003) analysis, net Ca/Na flux was declining in all study catchments. Since 2011, net Ca/Na ratios have stabilized (Figure 7.3). This may signify that exchangeable soil pools of Ca have reached a new steady state, or have started to rebuild. In order to differentiate between these two possibilities, new studies of primary mineral depletion and contributions of minor minerals such as hornblende and apatite, would have to be undertaken to determine more quantitatively the Ca flux relative to plagioclase dissolution.

Watmough et al. (2016). also reported declining net Ca export coupled with steady net Na export. That net Ca/Na export has stabilized at a level slightly above that suggested by stoichiometric plagioclase dissolution is consistent with plagioclase being the primary weathering source of Ca, but with some contributions from dissolution of higher Ca/Na minerals such as hornblende, and/or non-Na bearing Ca minerals such as apatite (S.W. Bailey et al., 2003; Blum et al., 2002).

### 7.4.3. Ecosystem Silicon Dynamics

Net Si/Na flux from the catchments was mostly less than that expected from plagioclase dissolution, consistent with storage of Si in secondary pools. Both formation of clay minerals or their precursors, as well as net storage of biogenic Si (Table 7.2; Ronchi et al., 2013) may contribute to lower Si export than expected based on plagioclase stoichiometry. Export from reference catchment W9 was an exception to this pattern with greater Si export than expected from plagioclase dissolution. Presumably secondary clay and biogenic minerals are accumulating in W9 as well, adding to an unexpectedly high net Si flux in this catchment.

Plagioclase accounts for only about a quarter of the Si in primary minerals at the HBEF (Table 7.1), with the

remainder in minerals considered to be stable in weathering environments, such as muscovite, K-feldspar, and quartz. There has been some controversy as to whether quartz may be subject to enhanced weathering in the presence of higher concentrations of organic acids (Bennett, 1991; Drever & Stillings, 1997), based mostly on laboratory studies or theoretical considerations. Drainage waters from W9 stand out as being more acidic and with much higher DOC concentrations than the other catchments (Wellington & Driscoll, 2004), which is typical of shallow to bedrock soils (Gannon et al., 2015). A distinct Si cycling process in W9 is suggested by the net Si/Na ratio and provides an opportunity to investigate enhanced weathering of quartz and other silicates in a field setting.

The treated catchments show a complex response of net Si/Na ratio following disturbance, with an initial reduction in Si export relative to Na for 1 or 2 years, followed by enhanced export for an extended post-treatment period. In general, the enhanced export is consistent with Conley et al. (2008) who reported increased dissolved Si loss in streamwater following all three harvesting experiments, with the magnitude of the response varying with the amount of detrital vegetation remaining after cutting. These results coupled with no detectable loss of amorphous Si soil pool, suggest that treatment response may be, at least partially, due to increased loss of biogenic Si from decomposing vegetation following treatment. Derry et al. (2005) showed that the Ge/Si ratio in drainage waters is sensitive to biogenic versus mineral weathering sources of Si export. This tool might be applied to archived samples of streamwater from the HBEF treated catchments to further elucidate mechanisms controlling treatment response in Si export. If stored pools of biogenic Si were contributing to Si export differentially to primary mineral dissolution, the Ge/Si ratio of drainage waters would be expected to reflect this dynamic.

### 7.4.4. Aluminum and Soil Development

Total dissolved Al was not measured routinely at the HBEF until 2012. Since that time, net flux of Al relative to Na is very low compared to plagioclase stoichiometry except for W9, where net Al flux approaches that expected from plagioclase dissolution. Shallow to bedrock soils in W9 are dominated by eluvial processes, with thick E horizons low in spodic materials or Al–organic-matter complexes (S.W. Bailey et al., 2014), whereas high concentrations of dissolved Al and dissolved organic carbon are exported downstream (Wellington & Driscoll, 2004). At the other five catchments considered here, net Al/Na flux is about 0.2 compared to a value of 1.5 for stoichiometric plagioclase dissolution. Given a typical value of net Na flux of 300 mol $ha^{-1}$ $year^{-1}$, this is equivalent to a net storage of Al of about 60 mol $ha^{-1}$ $year^{-1}$. To the extent that this storage of Al is due to spodic Al accumulation, a primary soil forming process in podzols, this flux is related to ongoing accumulation of C in mineral soil horizons. Other sources of Al accumulation include formation of secondary aluminosilicate minerals (Table 7.2). Bourgault et al. (2017) show concentrations of oxalate extractable Al < 1000 mg $kg^{-1}$ in shallow eluviated soils in the vicinity of bedrock outcrops, rising to 15,000 – 25,000 mg $kg^{-1}$ in deeper soils. These results suggest an opportunity to further evaluate mineral soil C storage. Quantification of Al stored as spodic organic–metal complexes, and as secondary minerals would provide a tool to evaluate long-term soil development processes that sequester Al. Comparison of secondary pools with net Al/Na catchment export may provide a tool to evaluate trends in C storage and dynamics as climate continues to change.

Although routine monitoring of streamwater Al and calculation of catchment fluxes was not instituted until 2012 (with the exception of W6), well after treatments applied to W2, W4, and W5, a four- to sixfold increase in

**Table 7.2** Catchment annual fluxes and pools. Fluxes are the range for the six study catchments for 2013–2014

| Flux/pool | Ca | Na | Al | Si |
|---|---|---|---|---|
| Atmospheric deposition (mol $ha^{-1}$ $year^{-1}$)[a] | 20–28 | 79–133 | Trace | Trace |
| Streamwater flux (mol $ha^{-1}$ $year^{-1}$)[a] | 98–196 | 214–424 | 22–166 | 514–904 |
| Biomass pool (mol $ha^{-1}$)[b] | 18450 | Trace | Trace | 579 |
| Soil exchange pool (mol $ha^{-1}$)[b] | 6700 | Trace | Substantial | None |
| Other soil pools (mol $ha^{-1}$) | None | None | Spodic materials, secondary minerals and precursers | Biogenic opal, secondary minerals and precursers |

*Note*: Adapted from Likens et al. (1998).

[a] Flux range calculated for all study catchments for the 2013 water year.

[b] Ca pools were quantified by Likens et al. (1998); Si biomass pool was quantified by Clymans et al. (in preparation).

total dissolved Al concentration in streamwater following whole-tree harvesting of W5 was reported by synoptic sampling conducted by Lawrence et al. (1987). Likens et al. (1970) reported an eightfold increase in streamwater Al export in the 2 years following harvest of W2 (Figure 7.5). Enhanced Al export as an impact of forest harvesting has been found to be most prevalent when > 40–68% of the tree basal area in a catchment is harvested (Siemion et al., 2011), as is certainly the case with the clearfelling/herbicide treatment at W2 and whole-tree harvesting treatment at W5. As such harvesting intensities in operational systems are rarely practiced at the catchment scale, the Al response due to the nonsilvicultural treatments at the HBEF may have limited applicability in a management context.

## 7.5. CONCLUSION

Although catchment-scale mass balance is a commonly used technique to understand the biogeochemistry of elements, this method is typically applied in studies of single elements. Utilizing the stoichiometry of an important ecosystem component, in this case the primary mineral plagioclase, allowed the coupled evaluation of multiple elements at once. Normalizing the biologically and pedogenically active elements Ca, Si, and Al to the relatively conservative Na enhanced the detection of dynamics in ecosystem pools in response to long-term trends in acid deposition as well as to pulse disturbance events such as harvesting experiments.

These results highlight uncertainties in understanding of ecosystem processes, or, in other words, opportunities for new studies to test hypotheses of catchment dynamics suggested by the net ecosystem flux ratio approach. In the last 2–3 years of record at the HBEF, net Ca/Na ratios appear to have stabilized relative to long-term declines in response to acid deposition and harvest treatment effects. Whether Ca soil exchange pools have reached a new steady state or are rebuilding following decades of depletion depends on the exact ratio of Ca/Na released from mineral weathering processes. More detailed studies of mineral weathering, perhaps aided by native isotopic or minor element tracers may determine the potential for soils to recover and the time frame involved. Similarly, net Si flux relative to Na is highly dynamic, especially in the first few years after vegetation disturbance, a response that is likely mediated by dynamics in biogenic Si pools. The net flux ratio tool also highlights the role of disturbance and pedogenic processes in Al dynamics, suggesting new methods to track rates of soil formation, including subsurface C storage dynamics. Thus, this tool to evaluate catchment input–output dynamics provides a framework for opening the black box with detailed studies of internal element pools and their controlling processes.

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