

# Modeling calcium and strontium cycling in northern hardwood forests

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Calcium is an essential nutrient for a forest ecosystem. Hubbard Brook Experimental Forest has been the site of many field studies documenting the flow of calcium in such an environment. This study is a synthesis of that data into a simple model of calcium cycling in northern hardwood forests. The calcium model is linked to a strontium model to determine the time evolution of Ca/Sr ratios of various ecological pools under different vegetation and weathering scenarios. The effect of forest harvest and ecological succession on the Ca/Sr ratio of the forest floor and mineral soil pools is also determined.

## Introduction

Calcium ( $Z=20$ ) is the most abundant alkaline earth metal found in the Earth's crust (Wedepohl, 1995). Similar to the other elements in this group (Be, Mg, Sr, Ba and Ra), the electron configuration of calcium is  $[\text{Ar}] 4s^2$  and the third-stage ionization energy is high (4912.4 kJ/mol). As a result, alkaline earth metals tend to be found as divalent cations (Huheey et al. 1993). Though common in the granitic rocks that make up the continental crust, calcium is found in much greater concentrations in the mafic rocks of the ocean floor. Aluminum-silicate minerals like pyroxenes, amphiboles and feldspars contain calcium in 8-fold coordination with the surrounding anions. Calcium is also found in sedimentary rocks like limestone, dolomite, gypsum and phosphorites (Bowen 1979).

Calcium becomes mobile through the weathering of minerals. It has been suggested that most calcium at Hubbard Brook Experimental Forest is supplied by the slow weathering of plagioclase into kaolinite (Likens et al. 1998). Weathering of apatite has also been suggested as a source of calcium (Blum et al. 2002). Additional calcium may enter the soil solution through release from the cation exchange complex or through soil organic matter. Once calcium enters the soil solution it can be used by plants and microbes, or can be transported within the soil column. Calcium can also adsorb onto negatively charged soil particles and organic matter, and considerable amounts of this "plant available" calcium can be stored in soils with a high cation exchange capacity (Bowen 1979).

In field studies of calcium biogeochemistry,  $\text{Ca}/\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios have been used to differentiate between calcium sources (Miller et al. 1993; Blum et al. 2008). This can be done because strontium is a divalent alkaline earth metal, and is therefore chemically similar to calcium. Strontium follows nearly the same biogeochemical pathways as calcium and can substitute for calcium in vegetation, though it has no known physiological function (Appelo & Postma 1993; Elias et al. 1982). Plant tissues for a given species can select for or against calcium in a constant ratio called the discrimination factor  $[\text{DF} = (\text{Ca}/\text{Sr}_{\text{plant tissue}})/(\text{Ca}/\text{Sr}_{\text{nutrient source}})]$  (Dasch et al. 2006). A  $\text{DF} > 1$  indicates that the given plant tissue is preferentially taking in calcium over strontium. There is no fractionation of strontium isotopes during plant uptake or other ecosystem processes (Graustein 1986; Blum et al. 2000). Blum et al. (2008) identified several caveats regarding the use of strontium as a tracer for calcium. These include variation of  $\text{Ca}/\text{Sr}$  ratios across tree species (Dasch et al. 2006) and in different tissues of the same tree species (Poszwa et al. 2000). Spatial variation in soil parent material and variation in mineral weathering rates also complicate such studies (Nezat et al. 2004).

## Motivation for a Modeling Approach

The availability of mobile calcium in a forest ecosystem is dependent on many factors. Landscape position and vegetation type have been identified as causes of high spatial variability in long-term weathering release of calcium at Hubbard Brook Experimental Forest (Nezat et al. 2004). Spatial and temporal variation in atmospheric calcium deposition, acid deposition and forest harvest also impact mobile calcium concentrations in ecosystem pools (Likens et al. 1998).

Calcium is fairly immobile once incorporated into living plant tissue, so vegetation represents an important biogeochemical reservoir of the element.

Since calcium is a necessary nutrient for many forest plant species, the health of a forest is dependent on its availability. Consequently, calcium deficiency has been linked to general declines in sugar maple forest health (Mader & Thompson 1969; Kolb & McCormick 1993; Horsley et al. 2000). Calcium also plays a role in organic matter decomposition, mycorrhizal infection, and recovery from winter frost injury (Reich et al. 2005; Hawley et al. 2006; Juice et al. 2006). Given that calcium can be removed from the system in large quantities through deforestation and leaching of the ion exchange pool due to acid deposition (Likens et al. 1996; Federer et al. 1989), it is important to understand the dynamics of calcium cycling. A simple reservoir-flux model can be useful in determining the effect of both natural and anthropogenic disturbances on the supply of mobile calcium. Such a model can also help constrain parameters like weathering rates and discrimination factors as well as aid in determining the sources of calcium to vegetation. Additionally, linking a calcium model to a strontium model allows for the calculation of Ca/Sr ratios of each reservoir throughout time. The model can therefore be used to make field-testable predictions of the Ca/Sr ratios of ecosystem reservoirs and test the response of the ecosystem to disturbances.

### The Calcium Model

Calcium transport has been monitored at Hubbard Brook Experimental Forest since 1963. Likens et al. (1998) synthesized the data collected between 1963 and 1992 into an overview of calcium biogeochemistry at this site and calculated yearly fluxes of calcium between ecosystem pools (Fig. 1).

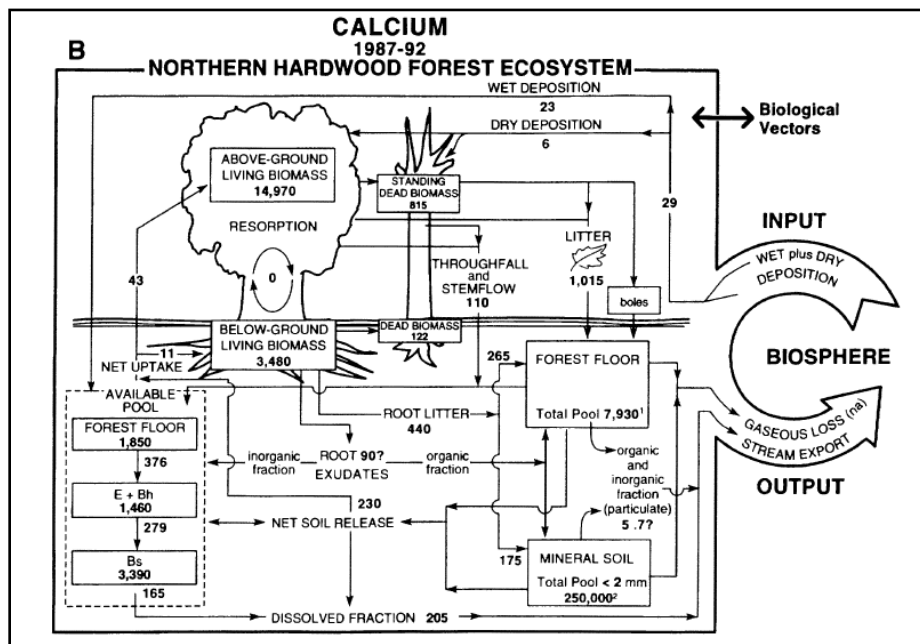


Figure 1: Reservoirs are in units of moles of Ca per hectare. Fluxes in mol/ha\*yr. (Likens et al. 1998)

This study is based on the Likens et al. (1998) ecosystem model with some simplifications to the conceptual model of the system. The simplified model has four pools, living above-ground biomass, forest floor, plant available (PA) soil, and mineral soil (Fig. 2). The forest floor is the Oie soil layer and the PA soil is the ammonium chloride exchangeable fraction of the mineral soil. Biomass receives calcium from the soil through PA soil uptake and forest floor uptake. An important assumption of this model is that litter calcium enters only the forest floor and not the PA soil pool. This assumption ignores the possibility for root litter to enter the PA soil pool. There is a flux between the forest floor and the PA soil that represents leaching of calcium down through the soil column. The mineral soil pool inputs calcium into the PA soil through weathering, which is assumed not to affect the forest floor. Stream export removes calcium from the PA and mineral soils and is also assumed to be independent of the forest floor. The model created in this investigation calculates the contents of each reservoir at a time step of one year. For a given reservoir, the input fluxes are added to and the output fluxes are subtracted from the previous year's contents.

All of the fluxes are derived from the Likens et al. (1998) interpretation of data from 1987-1992 at the Hubbard Brook Experimental Forest. Some of the major uncertainties identified in this model are associated with weathering rates, leaching rates and the ratio of calcium taken by vegetation from the forest floor to the amount taken from the plant available soil pool.

To test the weathering and leaching rates determined by Likens et al. (1998) the model was run for a range of weathering and leaching rates (0 to 1000 mol/ha\*yr). A comparison of the results indicates that the most reasonable scenario is one in which weathering occurs at a rate of 200-300 mol/ha\*yr and leaching occurs at a rate of 350-400 mol/ha\*yr. These rates are reasonable because they will not cause more than a 1% annual gain or loss of calcium in either the forest floor or the PA soil pool. The weathering and leaching rates (shown on Fig. 2) determined by Likens et al. (1998) fit within these ranges and were used in the rest of the model calculations in this study.

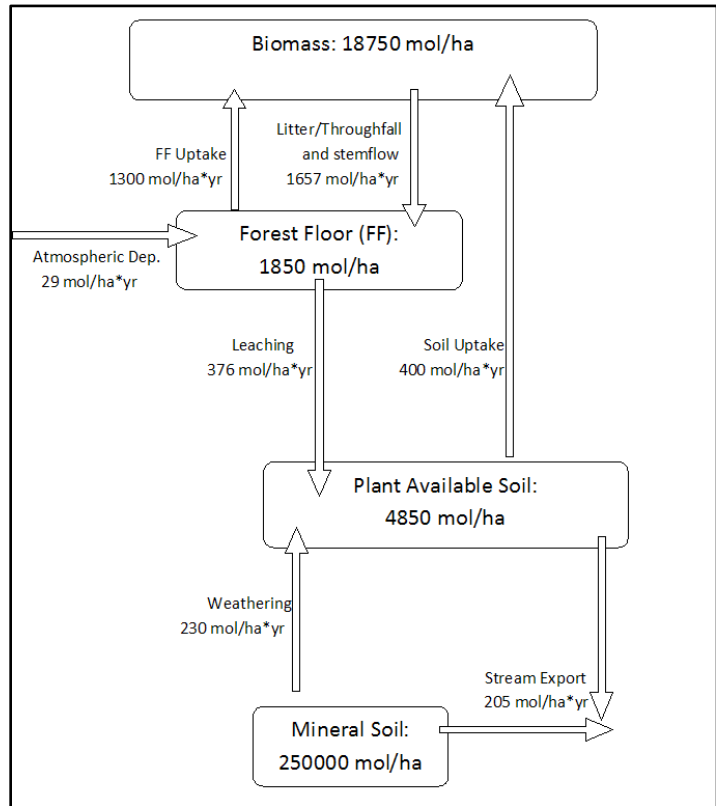


Figure 2: Simplified Ca model. Numbers in reservoirs indicate initial calcium contents

To constrain the relative importance of calcium sources to vegetation the model was also run for a variety of uptake ratios. This study defines the parameter “uptake ratio” as:

$$U = FF \text{ Uptake} / PA \text{ Soil Uptake}.$$

Assuming a nearly stable forest floor (0.5% annual growth), the fluxes determined by Likens et al. (1998) could only be supported by an uptake ratio of 3.25, meaning 76% of calcium taken up by vegetation comes from the forest floor.

Given the fluxes shown in Figure 2, vegetation will accumulate calcium at a rate of 43 mol/ha\*yr, which is a 0.2% annual increase. The forest floor accumulates calcium at a rate of 10 mol/ha\*yr (0.5% increase) and the plant available soil pool will gain 1 mole of calcium/ha\*yr (0.02% increase). The mineral soil pool is assumed to be large enough that any gains or losses in calcium content are considered negligible.

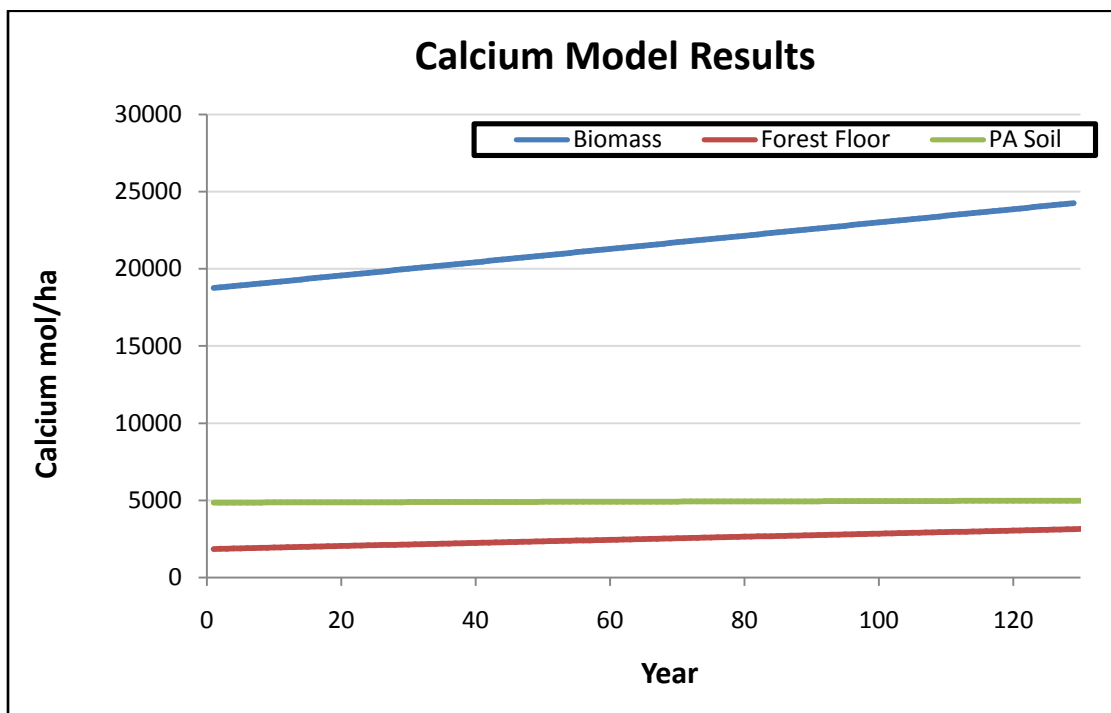


Figure 3: Calcium in main ecological reservoirs over time based on fluxes in Fig. 2

### The Strontium Model and Ca/Sr Ratios

The strontium model was made using the calcium model along with data from Hubbard Brook Experimental Forest on the Ca/Sr ratio of each soil pool (Fig. 4) and discrimination factors. Dividing the initial calcium content of each pool by the Ca/Sr ratio of that pool gives the initial strontium content. Each initial strontium flux was calculated by dividing the corresponding calcium flux by the Ca/Sr ratio of the nutrient source and the discrimination factor (see below). The initial Ca/Sr ratio of vegetation was determined by dividing the sum of the calcium fluxes into biomass by the sum of the initial strontium fluxes into biomass (as calculated

using the Ca/Sr of the nutrient source and the  $DF_{veg}$ ). The Ca/Sr ratio of atmospheric deposition is assumed to be 193 based on the measurements of Miller et al. (1993).

$$Sr \text{ Flux} = \frac{Ca \text{ Flux}}{Ca/Sr \text{ of nutrient source} \times DF}$$

$$DF = \frac{Ca/Sr \text{ of plant tissue}}{Ca/Sr \text{ of nutrient source}}$$

Once all the initial values are calculated, the model advances by one time step (1 year) by adding and subtracting the fluxes to and from each reservoir. As the model moves forward in time, new Ca/Sr ratios and strontium fluxes are recalculated at each time step. Ecological processes that select for either calcium or strontium affect the Ca/Sr ratio of the reservoirs, which affects strontium fluxes for the next year.

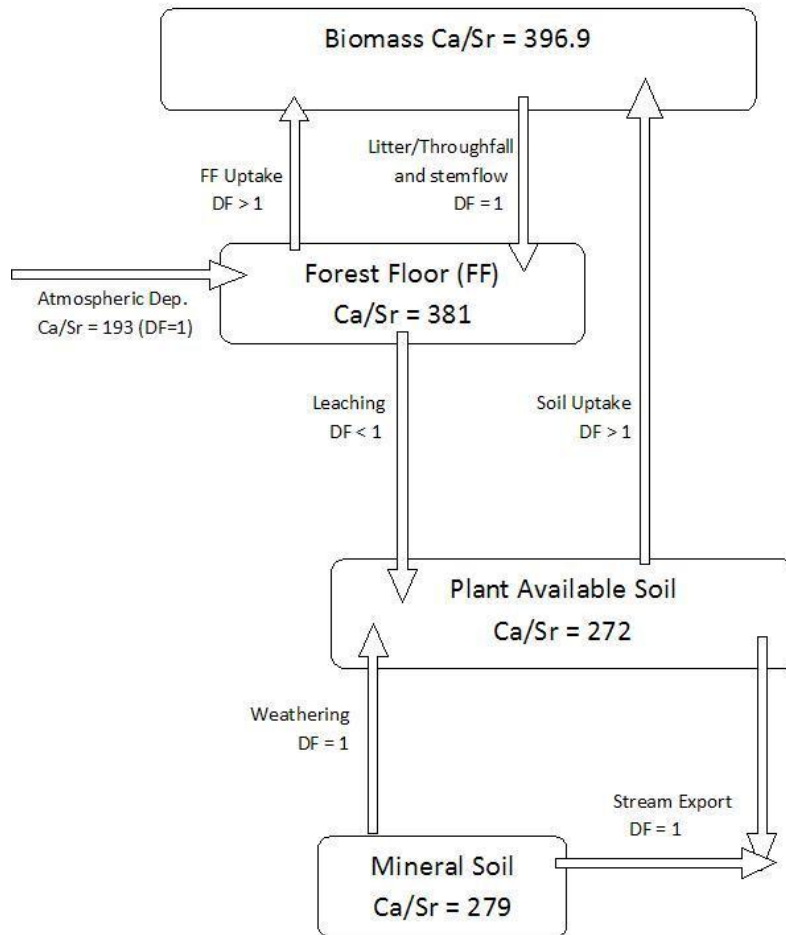


Figure 4: Initial Ca/Sr ratios from Blum et al. 2002

Discrimination occurs in the soil column and in plant tissue. It is estimated that the discrimination factor of leaching from forest floor to the plant available pool is 0.7, as indicated

by decreasing Ca/Sr ratios with depth (Blum et al. 2008). Discrimination factors vary widely by species of vegetation and by plant tissue within a species (Poswa et al. 2000; Dasch et al. 2006). For example, a forest composed entirely of sugar maple foliage would (ignoring discrimination in roots) have a  $DF_{\text{foliage}}=1.14 \pm 0.12$  (Dasch et al. 2006). The Ca/Sr ratios of vegetation, the forest floor, and the plant available soil pool would evolve as shown in Figure 5.

In this model calculation, the Ca/Sr ratio of vegetation initially increases, yet after 18 years it begins to decrease. This implies that sugar maple’s discrimination for calcium is not enough to overcome the lower Ca/Sr ratios of the nutrient sources. The forest floor also shows an initial increase in Ca/Sr ratio followed by a decrease in this ratio after about 18 years. The increase in forest floor Ca/Sr ratio is the result of leaching removing more strontium than calcium (leaching  $DF=0.7$ ). However, the low Ca/Sr ratio of atmospheric deposition eventually drives the forest floor to a lower Ca/Sr ratio. For both the vegetation and the forest floor, the rate of decrease in Ca/Sr slows with time. Vegetation selects for calcium over strontium, which dampens the effects of the low Ca/Sr ratio of nutrient sources. The decrease in Ca/Sr ratio of the forest floor is slowed by the recycling of calcium and strontium through litter as well as the discrimination that occurs during leaching. The leaching discrimination also causes the decrease in Ca/Sr in the plant available soil pool. The rate of this decrease also slows with time, which is the result of the higher Ca/Sr ratio of the mineral weathering input.

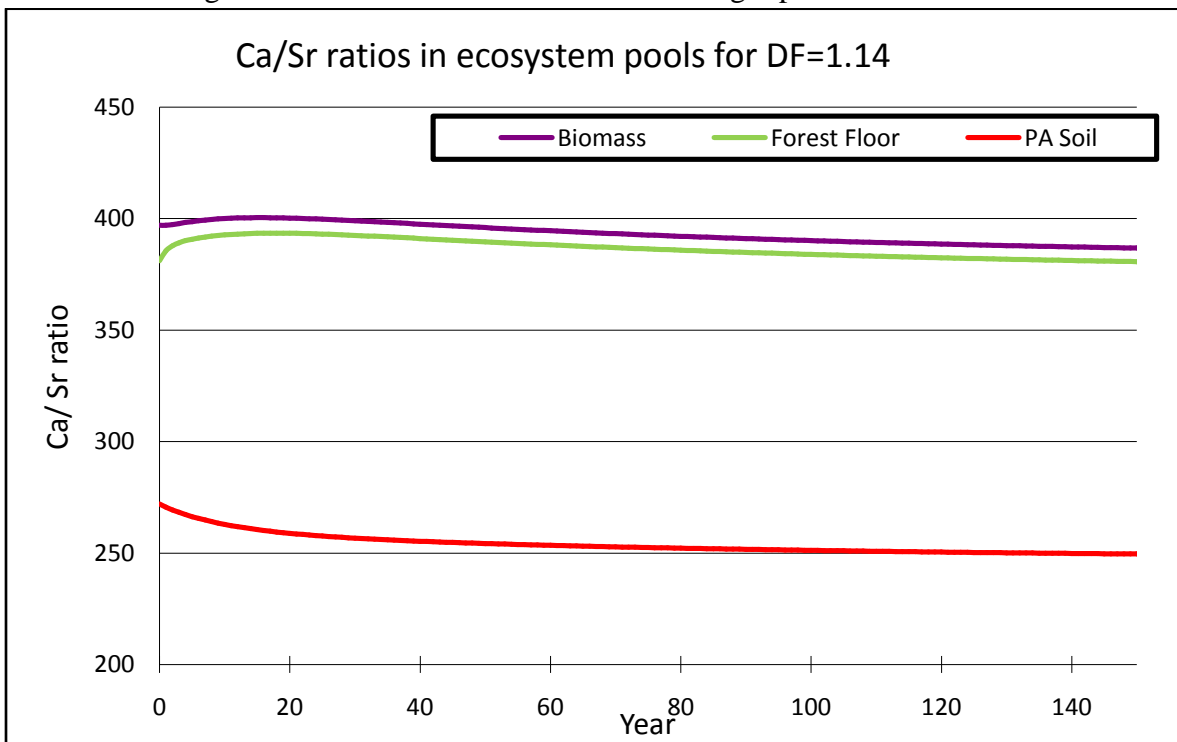


Figure 5: Ca/Sr ratios in main ecological reservoirs for a forest composed entirely of sugar maple

### Discrimination in Vegetation

The discrimination factor of vegetation ( $DF_{\text{veg}}$ ) is a key parameter in this model, as it varies widely in the natural world, and greatly affects the outcome of the model calculations. To

determine the relationship between  $DF_{veg}$  and the Ca/Sr ratio of each reservoir the model was run for a range of  $DF_{veg}$  values (0.8, 1.00, 1.14, 1.30, 1.60 and 1.90). The calcium fluxes for these runs were those shown in Fig. 2 and the strontium fluxes were calculated as described in the previous section. The results of this experiment are shown in Figures 6, 7 and 8, each of which show the evolution of the Ca/Sr ratio of a given reservoir over time for the different  $DF_{veg}$ .

The Ca/Sr ratio of vegetation is directly related the discrimination factor of the vegetation. The initial Ca/Sr ratio of this pool therefore increases linearly with  $DF_{veg}$ . For  $DF_{veg}=1.00$ , meaning no discrimination, the Ca/Sr ratio of the vegetation decreases over time. This is because the net input of calcium into vegetation is constant through time, but the net input of strontium decreases. The net input of strontium decreases as the Ca/Sr ratio of the leaf litter decreases, indicating that more strontium leaves the vegetation than in past years. If the  $DF_{veg}=0.8$ , there is an even stronger decrease in the Ca/Sr ratio of vegetation since strontium would be preferentially taken up compared to calcium.

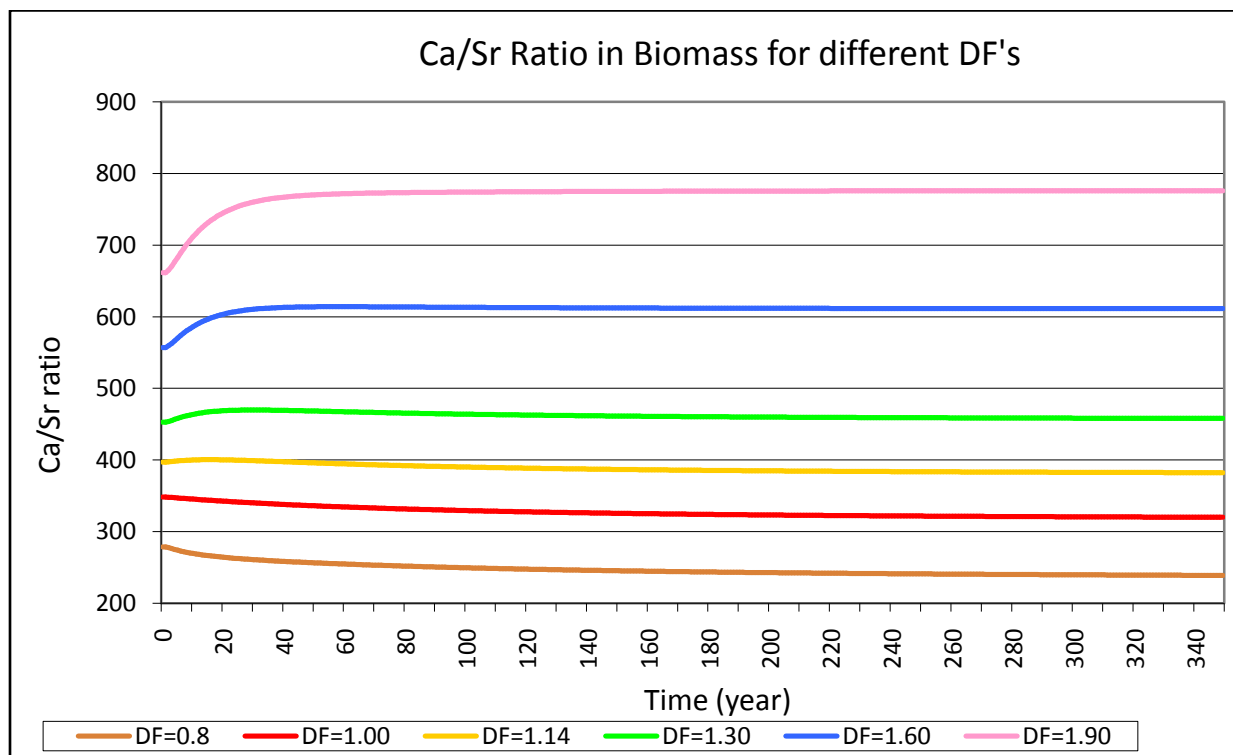


Figure 6: Ca/Sr ratios in vegetation over time

In contrast, if the vegetation in a forest has a discrimination factor that is greater than 1.00, then there will be an initial increase in  $Ca/Sr_{veg}$  due to selection of calcium over strontium by the vegetation. As  $DF_{veg}$  gets larger, there is an increase in the length of time over which the increase in  $Ca/Sr_{veg}$  occurs. There is a subsequent decrease in  $Ca/Sr_{veg}$ , which is the result of low Ca/Sr ratios in the nutrient sources as well as recycling of calcium and strontium back into the forest floor via litter. For a high enough  $DF_{veg}$  the discrimination for calcium is enough to continue the increase in  $Ca/Sr_{veg}$  despite low Ca/Sr ratios in the source pools.



The Ca/Sr ratio of the forest floor is a function of atmospheric deposition as well as exchange with vegetation and the plant available soil pool. For vegetation with no discrimination, the forest floor shows a decrease in  $\text{Ca/Sr}_{\text{ff}}$  with time. This is the result of atmospheric deposition having an extremely low  $\text{Ca/Sr}_{\text{atm dep.}}=193$ , Miller et al. 1993). The rate of decrease slows with time due to discrimination during leaching; the forest floor tends to retain calcium with respect to strontium during this process. A forest with  $\text{DF}_{\text{veg}} < 1$  shows a strong decrease in  $\text{Ca/Sr}_{\text{ff}}$  which is most likely the result of recycling between vegetation and the forest floor through litter. On the other hand, a forest with  $\text{DF}_{\text{veg}} > 1$  shows initial increases in  $\text{Ca/Sr}_{\text{ff}}$  which also implies that recycling through leaf litter plays an extremely important role in determining the Ca/Sr of the forest floor. However, all scenarios except  $\text{DF}_{\text{veg}}=1.9$  show an eventual decrease in  $\text{Ca/Sr}_{\text{ff}}$ .

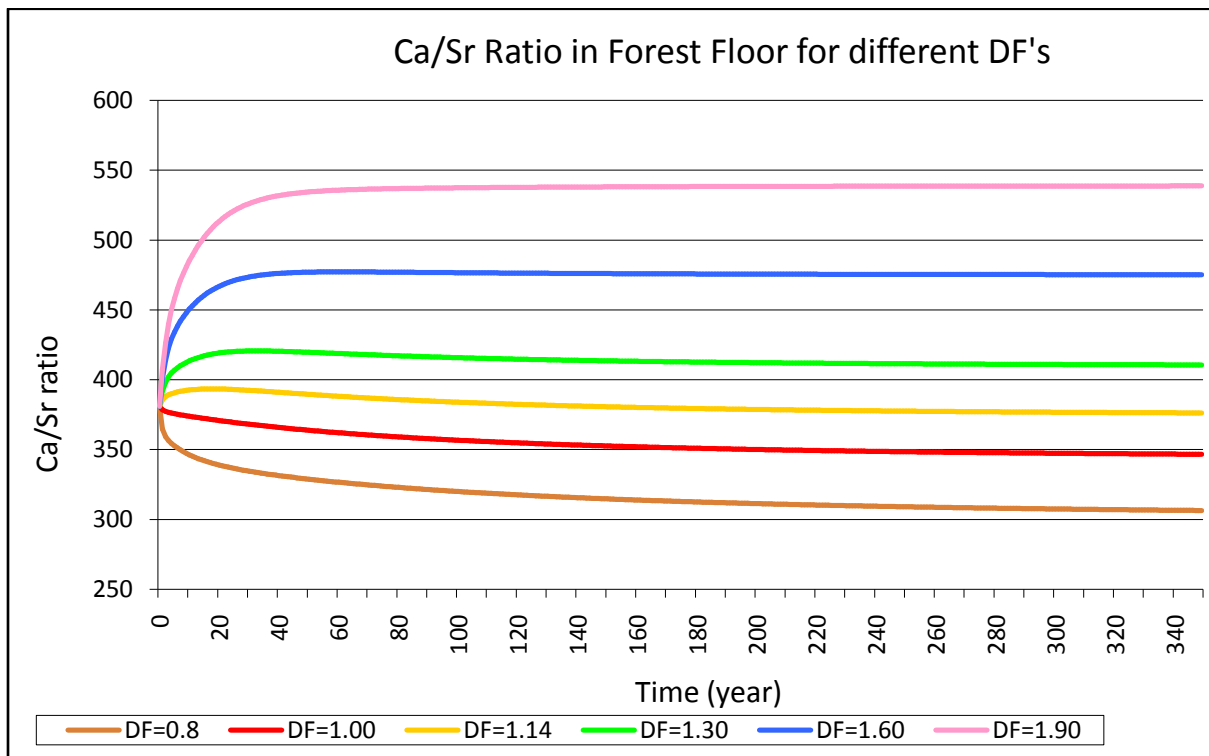


Figure 7: Ca/Sr ratios in the forest floor (Oie layer) over time

The Ca/Sr of the plant available soil pool decreases with time for a  $\text{DF}_{\text{veg}}$  that is greater than or equal to 1.00. This is because vegetation removes more calcium than strontium from this reservoir while leaching brings in more strontium than calcium. The highest  $\text{DF}_{\text{veg}}$  shows an eventual, gradual increase in  $\text{Ca/Sr}_{\text{pa}}$  which is due to the increase in  $\text{Ca/Sr}_{\text{ff}}$ . In contrast, for  $\text{DF}_{\text{veg}} < 1$ , there is an initial increase in  $\text{Ca/Sr}_{\text{pa}}$  since calcium is being “left behind” by vegetation in this case.

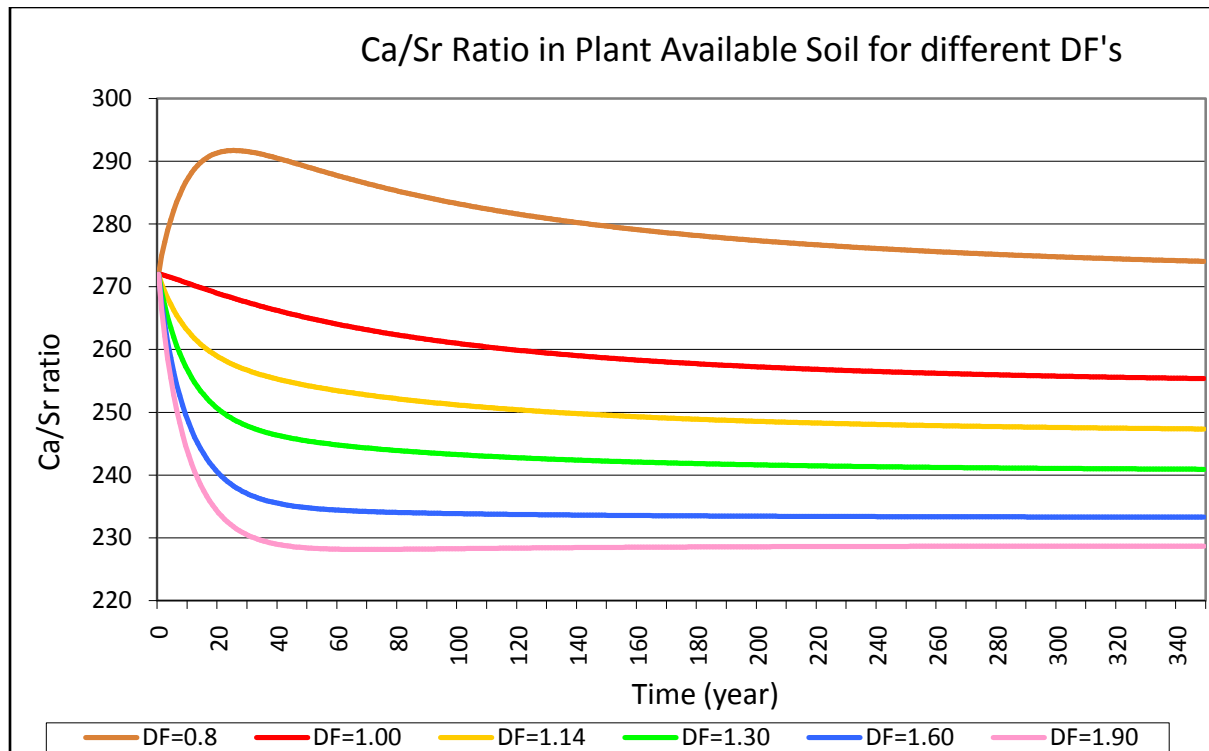


Figure 8: Ca/Sr ratios in the plant available soil pool over time

### Effect of weathering source and rate

The original model assumes the weathering input comes from weathering of silicates, predominantly plagioclase, with a Ca/Sr ratio of 279 (Blum et al. 2002). However, data from Hubbard Brook Experimental Forest show that present rates of silicate weathering and atmospheric deposition do not provide enough calcium to support rates of stream export (Likens et al. 1998). Increased silicate weathering rates could account for this difference, yet there is evidence that weathering of apatite provides a significant portion (~35%) of the calcium exported in streams (Blum et al. 2002). At Hubbard Brook Experimental Forest, the Ca/Sr ratio of apatite weathering is 2500 (Blum et al. 2002), so even a small input from this pool would affect the Ca/Sr ratios of ecological pools.

Figures 9, 10 and 11 show how three weathering scenarios affect the Ca/Sr ratios of vegetation, the forest floor, and the plant available soil pool. Every flux except weathering in each scenario is the same as pictured in Figures 2 and 4, and each scenario has  $DF_{veg}=1.30$ . Scenario 1 is the control, in which the calcium weathering rate is 230 mol/ha\*yr and the Ca/Sr ratio of this input is 279. Scenario 2 uses the same Ca/Sr ratio but increases the weathering rate by 20% to 287.5 mol/ha\*yr. Scenario 3 also increases the weathering rate by 20%, but that extra portion comes from apatite weathering with Ca/Sr=2500. The Ca/Sr ratio of the weathering input for scenario 3 is therefore 723.2. It is clear that an apatite weathering input drastically increases the Ca/Sr of every pool in the model. The addition of this weathering input drives the Ca/Sr ratio of each pool approximately two times higher than Scenarios 1 and 2.

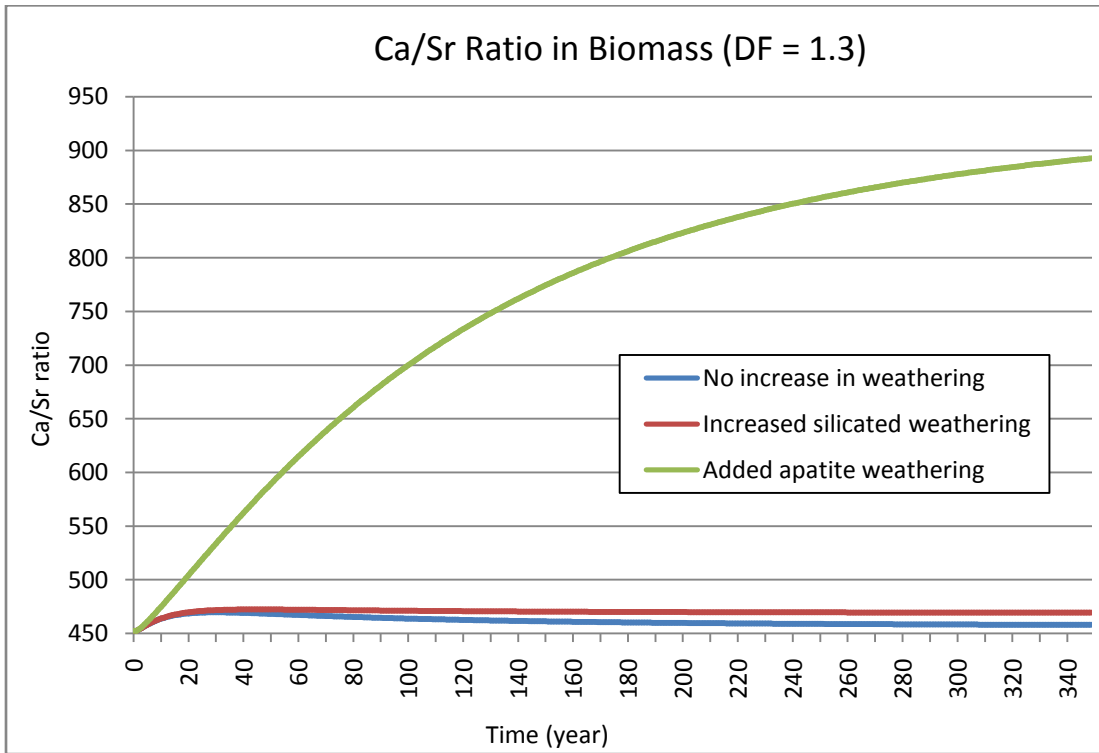


Figure 9: Ca/Sr ratios in biomass for three weathering scenarios

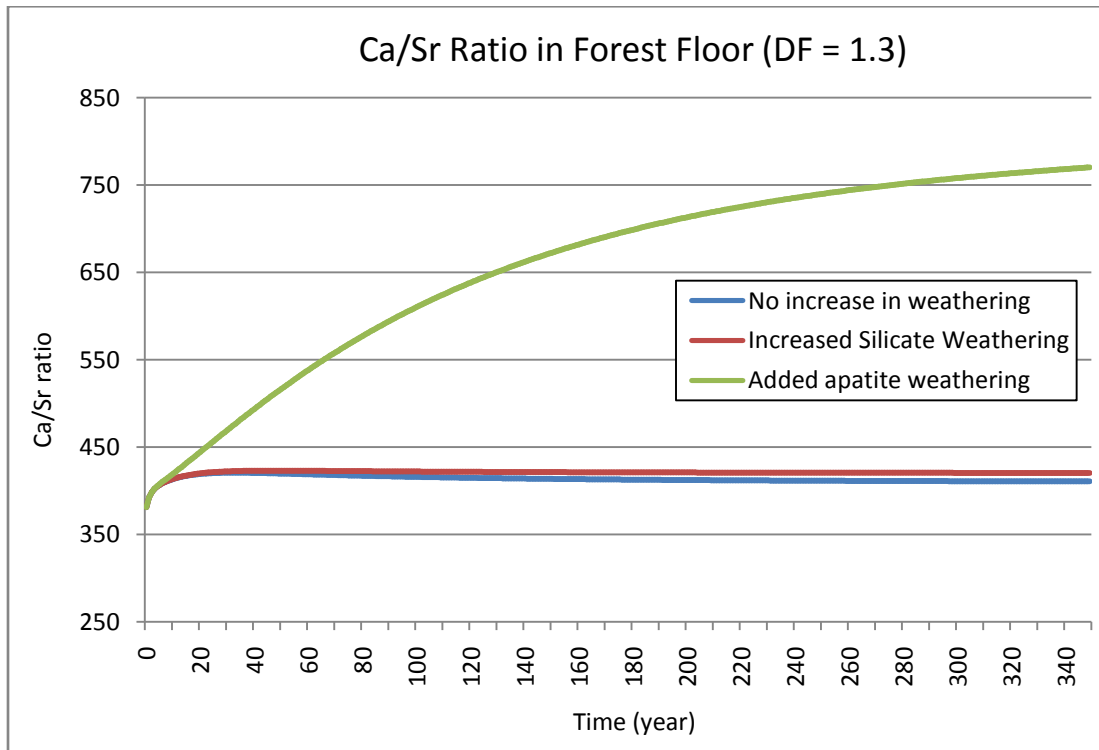


Figure 10: Ca/Sr ratios in the forest floor for three weathering scenarios

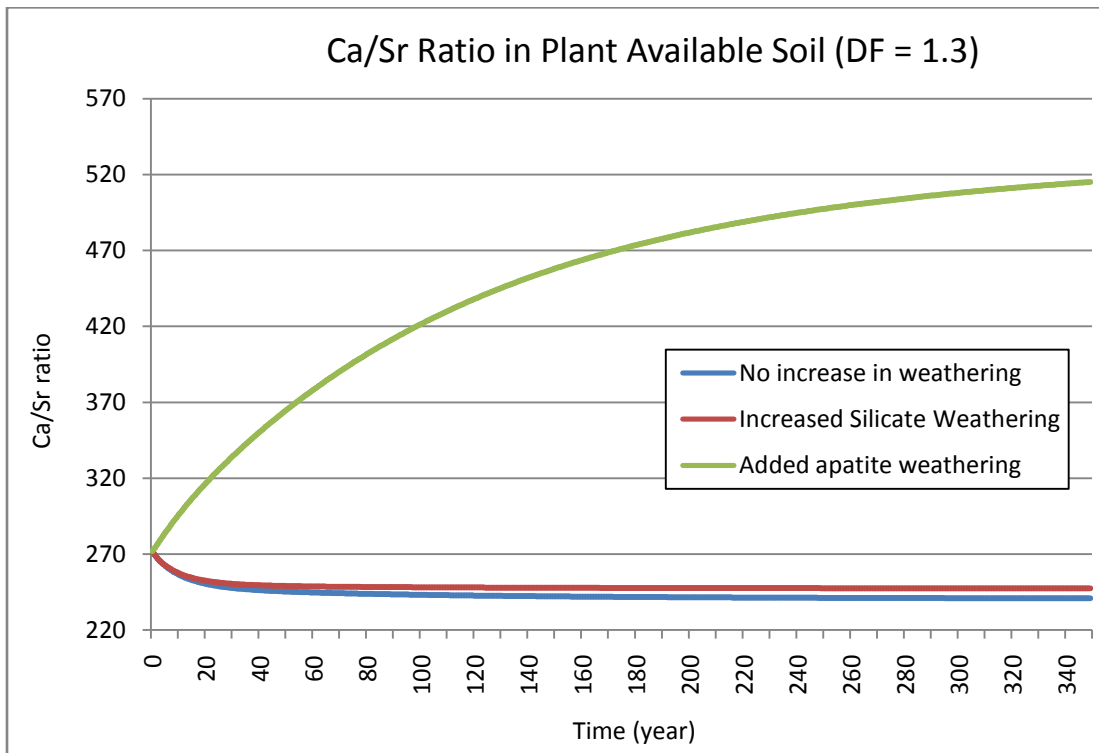


Figure 11: Ca/Sr ratios in the plant available soil pool for three weathering scenarios

### Impact of forest harvest and secondary succession

The next few plots show how the Ca/Sr ratio of each reservoir responds to a removal of vegetation, followed by a repopulation of the area by vegetation with a different  $DF_{veg}$ . For the first 349 years the vegetation has a  $DF_{veg} = 1.14$  and the weathering scenario is the original silicate weathering rate (Scenario 1). At 349 years the original vegetation is removed (whole tree harvest). The vegetation that takes over after the removal of the original has a  $DF_{veg} = 1.3$ , the discrimination factor of pin cherry trees which tend to dominate secondary succession after clear cutting in the Hubbard Brook region.

In all scenarios considered in this investigation, the Ca/Sr ratio of vegetation increased as vegetation with a higher discrimination factor began to grow. The forest floor showed a similar trend, mirroring vegetation due to the recycling of calcium and strontium in leaf litter. In contrast, the plant available soil pool behaved differently for the different weathering scenarios. During secondary succession, for no increase in weathering, the Ca/Sr of the PA soil pool dropped due to the removal of calcium at a higher ratio to strontium. Increasing the silicate weathering rate enabled the PA soil to recover from the initial decrease in  $Ca/Sr_{pa}$ , since the silicate weathering input has a higher  $Ca/Sr_{Si}$  ratio (279) than the PA soil at the time of logging (247.3). Similarly, adding an apatite input prevented a drop in  $Ca/Sr_{pa}$ . This is because the apatite brings the Ca/Sr ratio of the weathering input up to approximately 720.

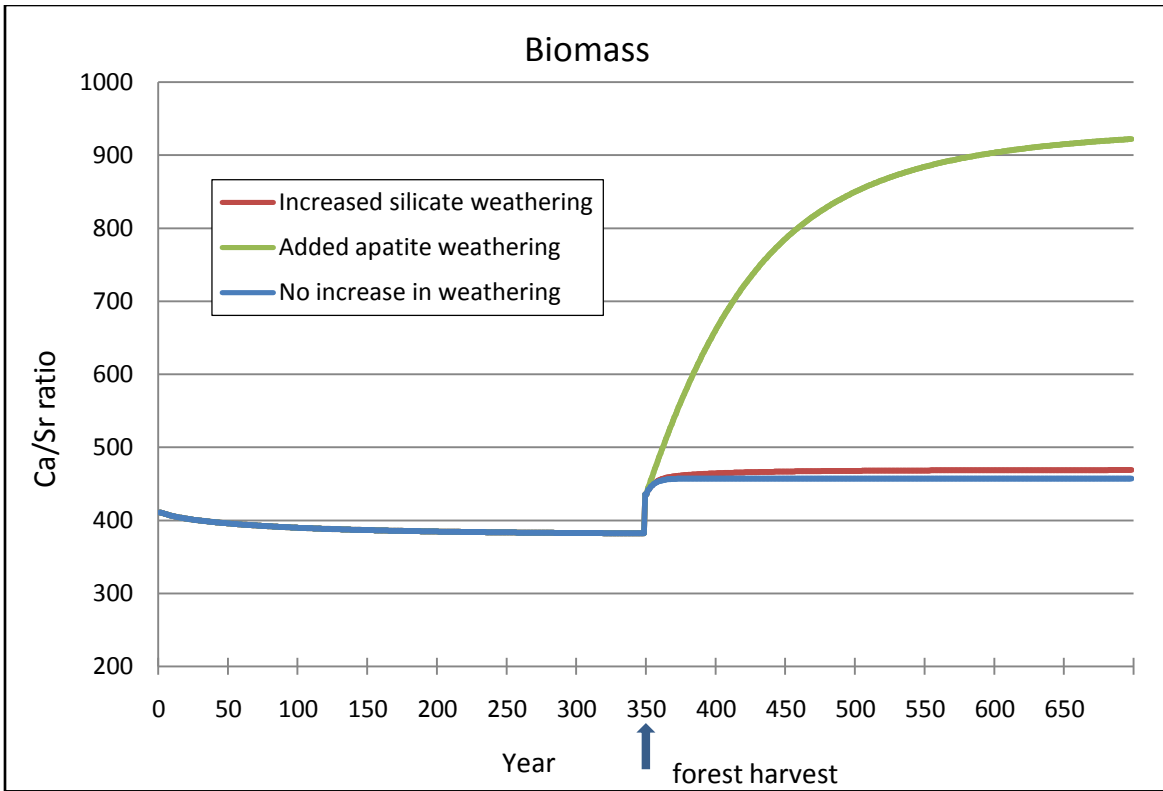


Figure 12: Response of vegetation Ca/Sr to forest harvest and secondary succession

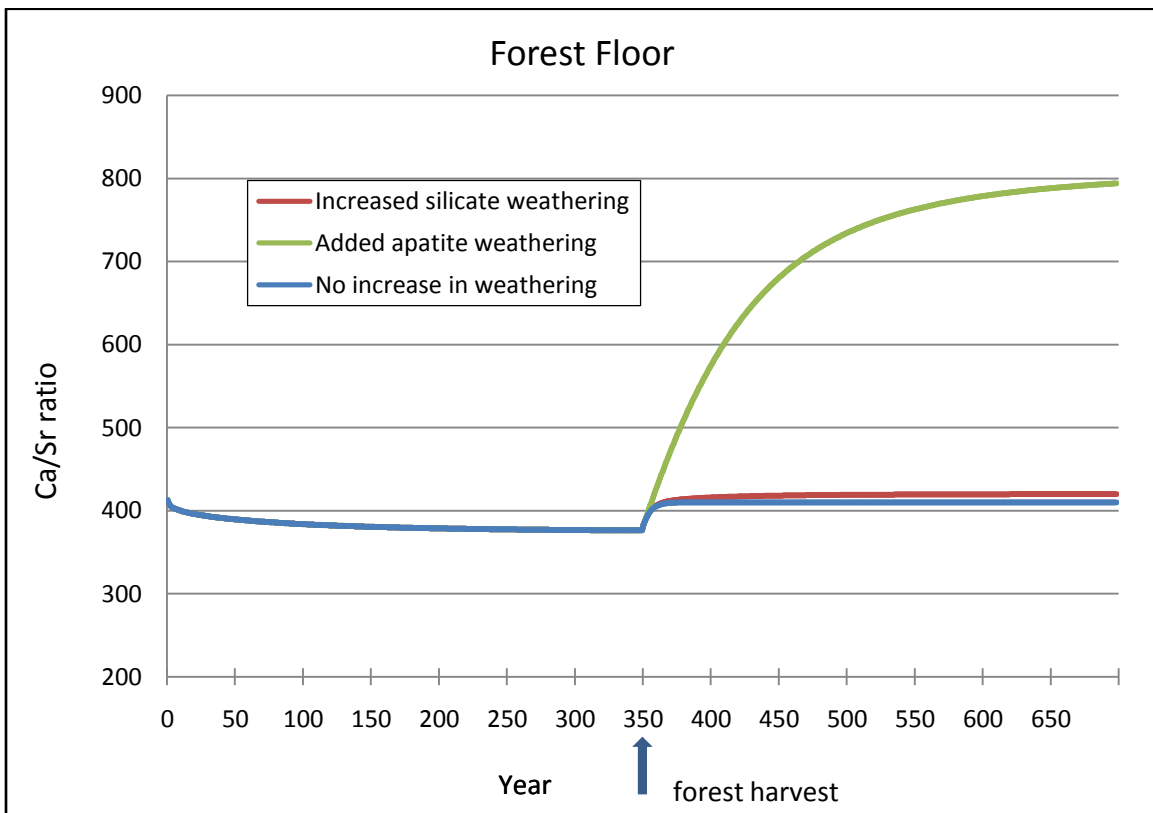


Figure 13: Response of forest floor Ca/Sr to forest harvest and secondary succession

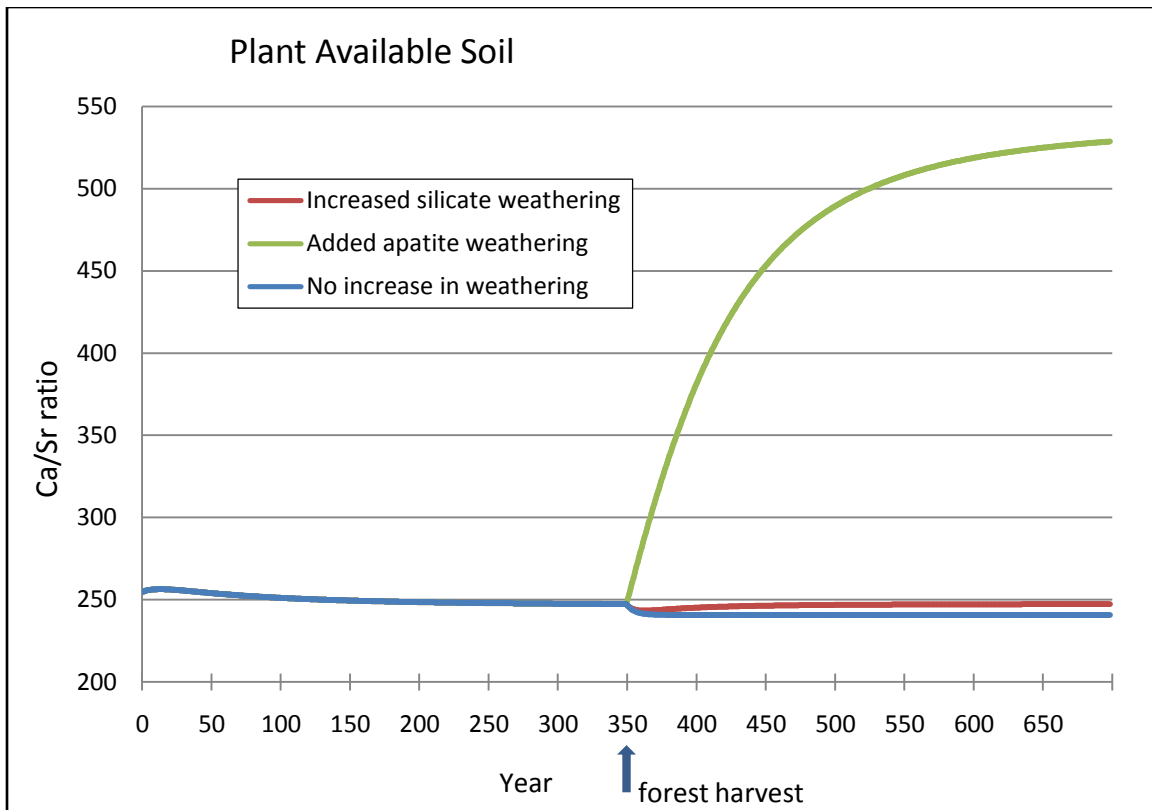


Figure 14: Response of plant available soil pool Ca/Sr to forest harvest and secondary succession

### Conclusions and future work

The calcium model created in this study provides constraints on two major fluxes in the system. Reasonable weathering rates were determined to be within 250 to 300 mol/ha\*yr and leaching rates were found to be between 350 and 400 mol/ha\*yr. The model also indicated that trees must be taking approximately 25% of their calcium from the plant available mineral soil pool. If this were not the case, the forest floor would either deplete rapidly or grow unchecked. The time evolution of Ca/Sr ratios in ecological reservoirs was determined by combining the calcium model with a strontium model. This is especially useful because it is much easier to measure Ca/Sr ratios compared to measuring absolute amounts of calcium or strontium in a given pool. As such, field studies typically use Ca/Sr ratios as tracers of nutrient sources. The model could be used in tandem with a field study to predict the behavior of this parameter under various conditions. Future work with the model includes correlating observations from differently aged sites at HBEF with the Ca/Sr ratios produced by the model. The model could be tuned to specific sites based on the vegetation found there, the bedrock geology and weathering rates, and the Ca/Sr ratios measured at those sites. The addition of a strontium isotope model would also be useful, since the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of an ecological pool has been used as a biogeochemical tracer. Another improvement on the model would be to split the biomass pool into a foliage pool, a root pool and an above-ground wood pool. In general, the simplification of the Likens et al. 1998 model was a useful approach toward understanding calcium cycling in northern hardwood forests.

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