



Acidic deposition, nutrient leaching and forest growth

GEORGE H. TOMLINSON

80 Lyme Road, Hanover, NH 03755, USA; (e-mail: ghtomlinson@aol.com; phone: +1 603 643 7490)

Received 3 July 2002; accepted in revised form 24 April 2003

Key words: Acid deposition, Biomass growth, Calcium, Nutrient cations, Mineralization, Weathering

Abstract. Studies in Germany and confirmed in North America established that the forest decline that developed in the late 1970's and 80's resulted from a deficiency in one or more of the nutrient cations: Ca^{2+} , Mg^{2+} , and K^{+} . These nutrients are essential to the structure of the foliage, to photosynthesis and to the growth of the trees. The reactions and mechanisms involved in the entry of nutrients to the soil, their storage, and rate of transfer to the soil solution, and through it, to the fine roots and to the leaves at the top of the tree are reviewed. The continuing material balance studies carried out on a watershed at the Hubbard Brook Experimental Forest in New Hampshire allow a unique analysis of the changes caused in these nutrient transfers by acid rain. The nutrient cations are stored in the soil by adsorption on negatively charged clay, and the presence of an acid is required for their release to the soil solution. In pre-industrial times this acid was H_2CO_3 , which was subsequently displaced from the soil solution by H_2SO_4 and HNO_3 , as a result of acid deposition. The effect of the increased concentration of the negatively charged SO_4^{2-} and NO_3^{-} anions seeping through the soil, compared with that of the HCO_3^{-} that had been previously present, resulted in a substantially increased rate of transfer of an equivalent of Ca^{2+} and other positively charged nutrient cations from the soil to the soil solution. The increased concentration of Ca^{2+} in the soil solution resulted in both an initial increase in the rate of biomass growth and in a simultaneous increase in the rate of Ca^{2+} loss in the effluent soil solution from the watershed. It was found that this increased rate of removal of Ca^{2+} from the watershed soil had become greater than its rate of input to the soil from weathering and from dust and rain. As a result, the large Ca^{2+} inventory that had built up in the soil as a result of the reduced leaching in the years prior to the entry of acid rain, that started in about the 1880's, was eventually depleted in the hardwood forest at Hubbard Brook in the 1980's, about 100 years later. With insufficient Ca^{2+} available for its continuing transfer, net biomass growth on the watershed stopped. This resulted from the rate of tree mortality becoming equal to that of the small incremental growth of a few trees on the watershed. The future growth of forests is at risk from the long-term effects of acid deposition. The fundamental nature of the reactions involved indicates that similar growth anomalies are occurring in other forests impacted by acid rain. These changes from normal biomass growth can affect the amount of CO_2 stored in the biomass, of importance to our understanding of Global Warming.

1. The present concerns

In the late 1970's and 1980's unusual symptoms of forest decline involving discoloration and premature loss of foliage, leading to the death of many trees, were observed in certain areas of Germany, northern New England, and adjacent areas of Canada. Subsequently, these symptoms were observed in other regions of the industrial world. In the 1990's the trees in some locations appeared to have recovered, while in other areas increased new damage was still

being observed (Sharpe and Drohan 1999; Driscoll et al. 2001). Surprisingly, it was subsequently found that increased tree growth had apparently occurred in many forests of Europe and North America that had been impacted by acid rain. Of particular concern is the continuing acid leaching of nutrients from the soil that leads to deficiency in the trees. Relevant data in connection with four questions will be considered.

1. What was the primary cause of the forest decline and death?
2. Why have some trees recovered?
3. Why has the growth of many forests apparently increased as a result of acid deposition?
4. What is likely to occur in future years?

In a review of the literature in relation to answers to the above questions, it was found that the material balance studies involving the transfers of the calcium and other nutrients carried out on a watershed at the Hubbard Brook Experimental Forest were relevant, particularly to Questions 3 and 4 (Likens et al. 1996, 1998; Driscoll et al. 2001). These studies showed that the effect of acid rain seeping through the soil was to substantially increase the rate of removal of Ca^{2+} and other cationic nutrients from the soil, thus increasing their concentrations in the soil water. This in turn increased both the initial rate of biomass growth and the rates of loss of Ca^{2+} and of the other nutrient cations in the effluent draining the watershed soil. The acid rain results from gaseous combustion emissions and the rate of SO_2 discharged in the U.S., measured in millions of short tons per year, was already 9.9 in 1900, peaked at 31.7 in 1973 and decreased to 24 in 2000, while emissions of NO_x , in the same units, increased from 2.6 in 1900 to 24 in 1990, subsequently remaining at about 20 (Baker et al. 1993). It was found that the portion of the resulting H_2SO_4 and the HNO_3 deposited at the Hubbard Brook site from these emissions resulted in the depletion, by 1982, of the large inventory of Ca^{2+} that had built up prior to the period affected by acid rain. As a consequence, the rate of removal of Ca^{2+} from the soil had become greater than the rate of input, and therefore insufficient Ca^{2+} is now available on the watershed for the necessary increase in net transfer to biomass, essential for biomass growth. Although increased growth continued in some of the trees, this was balanced by the death of other trees. However the continuing mineralization of fallen leaves, wood, and dead roots provided the necessary Ca^{2+} and other nutrients, that has allowed the living trees to reestablish their foliage in this forest each year. Since the acid rain continues to remove a portion of the recycled Ca^{2+} and other nutrients resulting from mineralization, it is expected that although a living forest will continue for several years on this watershed, it will be with increasing dead wood and with a reduction of living biomass.

Because of the fundamental nature of the reactions and mechanisms involved, it appears logical that similar problems to that at Hubbard Brook are occurring, or will occur, in other forested areas affected by acid rain.

The deficiency of the specific nutrient involved, and the timing when it first appears, will be related to such factors as the nature of minerals in the soil, and the rate of acid input. In locations where large amounts of cationic nutrients accumulated in preindustrial times, biomass may still be growing at an excessive rate. Prior to the discussion of why the effects of acid rain are causing these serious changes in forest soils and biomass growth, relevant aspects of the following subjects, important to its understanding, will be discussed in: nutrient deficiency and its symptoms; chemical weathering and nutrient recycling; nutrient leaching; cation transfers; and the accumulation of large amounts of exchangeable nutrient cations in the soil during the period prior to acid rain.

2. Nutrient deficiency and the effect of fertilization

Hüttl (1985), and Zöttl and Hüttl (1986), Zöttl et al. (1989), noted that although most trees appeared healthy, seriously declining trees growing in certain areas of southern Germany showed different characteristic symptoms. Suspecting that nutrient deficiency was involved, they measured the nutrient content in the foliage and the cationic content of the underlying soil in three locations in which three different, and distinctive, decline symptoms were observed. The results are shown in Table 1. This study indicated that the tree decline in each location resulted from a deficiency of either Ca, Mg or K in the foliage, and that the specific ion causing the deficiency could be predicted from the analysis of the soil. This was found to occur in soils that had a very low concentration of the deficient ion and a relatively high concentration of an antagonistic ion that inhibits the uptake of the deficient ion. With conifers showing a deficiency of either or both of the divalent ions, Ca^{2+} and Mg^{2+} , which occurred in soils having a pH of less than 4.0 as measured in CaCl_2 , the antagonistic ion was found to be Al^{3+} . In calcareous soils, having a pH greater than 5.0, in which K^+ is the deficient ion, Ca^{2+} together with Mg^{2+} have an antagonistic effect on K^+ uptake. In each case the antagonistic ion, which was found to block nutrient ion uptake, has a higher valence than the deficient ion. They established that addition of an excess amount of a soluble salt of the deficient ion resulted in the recovery in the nutrient content of the foliage and in a rapid increase in the rate of growth of the tree. This not only increased the content of the deficient ion in the soil, but also markedly reduced, by mass action, the concentration of the antagonistic ion on exchange sites, resulting in its subsequent loss from the rooting zone in the seepage water from rain. These and many other related studies, which established that deficiency is the primary cause of these declines, led to large-scale helicopter fertilization of declining trees in Germany. Although other factors such as decreased rainfall and/or increased temperature may also be involved, nutrient deficiency has been shown to be the primary cause by the observation that test fertilized trees recover, while adjacent trees remain stunted and/or die.

Table 1. Comparison of the molar ratio of Ca^{2+} and Mg^{2+} with their antagonistic ion, Al^{3+} , and of K^+ with its antagonistic ion, Ca^{2+} , at 20–30 cm depth in the soil, found to cause nutrient deficiency in Norway spruce, and the effects of these cationic ratio imbalances on the nutrient content, in mg g^{-1} of the first year needles, thus identifying the cation causing the deficiency. From Hüttl (1985) and Zöttl (1986).

Site	*pH	Exchangeable ions in soil Molar ratio			Concentration in needles (Deficiency threshold)		
		$\text{Al}^{3+} : \text{Ca}^{2+}$	$\text{Al}^{3+} : \text{Mg}^{2+}$	$\text{Ca}^{2+} : \text{K}^+$	Ca	Mg	K
					(2.0)	(0.7)	(4.0)
Trees with Ca and Mg deficiency							
BadenBaden	3.6	88.1	35.1	0.2:1	0.9	0.4	10.0
Trees with Mg deficiency							
Elzach	3.2	23:1	61:1	0.5:1	3.0	0.3	8.6
Trees with K deficiency							
Ebnat	5.1	0:1	0:1	45:1	4.9	1.3	2.9

*The pH was measured with CaCl_2 .

Related studies in North America established that similar decline symptoms had developed in trees showing deficient levels of either Ca, Mg, or K in their foliage. These were found to occur, as in Germany, in areas where the soils had low concentrations of the affected ion and relatively high concentrations of the antagonistic ion. It was also found that the trees could be revitalized by fertilization with the soluble salt of the affected ion (Bernier and Brazeau (1980); Zöttl et al. (1989); Hendershot (1991); Ouimet and Fortin (1991)). These deficiencies resulted from acid leaching of the affected cations from the soil by the H_2SO_4 , HNO_3 and HCl in acid rain. Since HCl is normally present in only small amounts it will not be named each time with the other two strong acids.

3. Visible deficiency symptoms

The characteristic deficiency symptoms are related to the specific essential roles that the individual nutrient plays and it is in the foliage where the symptoms first appear in response to an inadequate transfer of that nutrient to the tree.

Magnesium is chiefly utilized inside the cells of the foliage, with about 25% being chemically combined in the chlorophyll, the green pigment that catalyzes the formation of sugars through photosynthesis. The balance is in the form of soluble salts of the enzymes present in the cytoplasm that control energy release, pH, etc. In conifers, when insufficient Mg^{2+} is available in the spring to supply the trees' needs, Mg salts move from the oldest needles to the youngest, which are located at branch ends and at the top of the tree. Only the oldest needles lose their chlorophyll and become yellow since the remaining carotene pigment is not affected, while the current year needles, with adequate magnesium to produce and retain their chlorophyll, stay green. As deficiency devel-

ops, the older needles, that are near the trunk and below the top, become brown and drop off, resulting in the 'subtop dieback' syndrome. In hardwood trees the Mg^{2+} is drawn back into the tree in August and the leaves become light green to yellow and then to golden brown between the veins, which remain green (Enders and Evers, 1997).

Calcium is present in the foliage as calcium pectate, the polymer which forms the cell walls and the veins that comprise the structural parts of the foliage. Ca is also present in combination with protein and lipids in the membranes that line the cell wall. As the tree grows, Ca^{2+} moves up from the fine roots to the ends of the branches and to the top of the tree and, as deficiency develops, the youngest needles contain the lowest concentration of Ca, and these needles show the first symptoms. As deficiency develops in red spruce, fewer and smaller needles develop at the top of the tree and the ends of the branches, and during the winter, Ca^{2+} can be leached from them, without replacement, by the acidic frost that collects on the foliage. This can explain why, with inadequate buffering, the youngest needles turned brown in the late winter and dropped off in the late spring or early summer on the high mountains of the northeast United States in the 1970's and 80's. This led, in a few years, to 'top dieback' with bare terminal branches, the exact opposite of the symptoms resulting from Mg deficiency (Tomlinson (1987, 1990)). Ca deficient hardwoods have smaller leaves that develop early senescence and leaf fall.

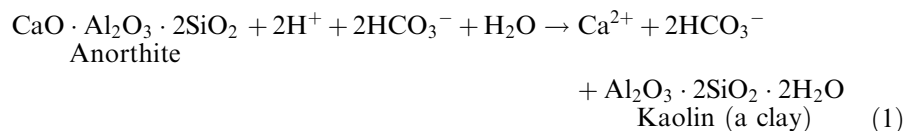
Potassium deficiency in conifers results in sparse and smaller needles that gradually turn yellow throughout all needle age classes. With hardwoods the leaves are small and change color in August. The coloring is similar to that developing in normal trees a month or two later and is referred to as the 'early autumn syndrome'. Leaf drop occurs a month or two before normal, leading to bare branches at the top of the tree. (Zöttl et al. 1989). K is present only in the form of soluble salts that move from cell to cell in the cytoplasm. Examples of these K-salts are the hormones: indole acetic acid, that each year initiates annual radial growth, and abscisic acid that terminates it. About 45% of the sugar produced is utilized in the energy required in producing, from the balance of the sugar, the proteins, fats, hormones, enzymes, vitamins, and the polymers such as starch, calcium pectate, hemicellulose, cellulose and lignin. The Ca, Mg and K salts are essential to the production of these and many other biochemicals that are required to insure the trees continuing long-term growth. These nutrients are vital to other plant and also to human and to other animal life.

4. Chemical weathering and nutrient recycling

The primary source of the nutrient cations is as constituents of insoluble silicates, and/or other minerals that may be present in the rocks, in which they are present in an inert form. The continuing entry of the nutrients to the soil solution in forest soils, over many thousands of years, has resulted from the

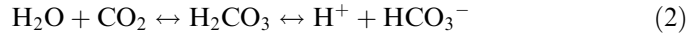
slow chemical weathering of the minerals present in the rock that had fragmented over very long periods of time. The reaction of these minerals with the H^+ ions from carbonic or other acids present in the soil, releases the cationic ions: Ca^{2+} , Mg^{2+} and K^+ to the soil solution. Because of their positive electrical charge the cations are immediately stored, as they enter solution, both on adsorption sites of negatively charged clay particles and as salts of humic acids that have been previously formed as an intermediate product of rotting foliage, roots and wood. It is from these storage sites that the cations are subsequently taken up through the soil solution by the fine roots of the trees, and to which, when trees die and decompose, the recycled cations return. A major requirement for the nutrient cations is in the foliage, and the recycling of the nutrients, released from the decomposition of fallen leaves, forms a major part of the trees annual nutrition. Likens and Bormann (1995) reported that the trees in a hardwood forest contained, in 1964–1969, a total of 384 kg ha^{-1} of calcium in above ground biomass. A total of 49.5 kg ha^{-1} of Ca^{2+} had fallen to the forest floor each year in throughfall, stemflow, and in fallen leaves and litter. This included 2.2 kg ha^{-1} deposited each year on the canopy in dust and rain, bringing nutrients from other geological areas, containing other nutrient elements that may have otherwise been lacking in the forest soil, Jenny (1980). After decomposition from the rotting of this fallen organic matter, all of this calcium, together with the other nutrients, are eventually released by ‘mineralization’ and recycled to the trees.

In order to assess the problems causing forest decline it is useful to first consider the mechanisms by which the trees obtain their nutrients, why many acidic soils contain Al^{3+} , and also to determine how these processes can be affected by continuing acid inputs to the soil. Ulrich (1986) pointed out that the chemical weathering of silicate minerals forms a major source of the nutrient cations entering the soil in the form in which they can be taken up by the trees. As an example, the slow reaction of the mineral anorthite with H^+ ions, resulting from the presence of carbonic acid, H_2CO_3 , or other acids in the soil, releases Ca^{2+} , leaving insoluble kaolin clay, as shown in irreversible Reaction (1).



The kaolin clay formed as a product of this reaction has a negative charge and provides cation exchange sites for storage of the released nutrients. Similar chemical weathering reactions result in the release of Mg^{2+} and K^+ from other silicates and minerals that contain these elements. The soaking of kaolin with the water in the soil that occurs over very long periods causes a reaction forming insoluble $AlOOH$ and SiO_2 . At least portions of the $AlOOH$ are subsequently converted to an organic complex (Johnson et al. 1981; Tyler et al. 1987). Over very long periods of time, insoluble Al_2O_3 is formed from $AlOOH$.

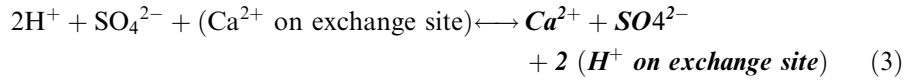
Carbonic acid is formed from CO_2 and H_2O that dissociates into H^+ and HCO_3^- ions as shown in reversible Reaction (2). The CO_2 is formed in the soil as a result of the rotting of the dead roots and the respiration of bacteria, worms and insects.



H_2CO_3 is a very weak acid and at a pH less than 5, as is now the case in the soil solution as a result of acid rain, the H^+ ion resulting from the strong H_2SO_4 drives the reaction to the left, the SO_4^{2-} ion replaces the HCO_3^- ion, and H_2CO_3 is eliminated from the soil solution as the CO_2 returns to the atmosphere. As a result, weathering now results from the action of the H_2SO_4 , rather than from the H_2CO_3 involved in pre-industrial times.

5. Nutrient adsorption and leaching

As the nutrient cations are released to the soil solution in chemical weathering, they are immediately taken up by the tree's fine roots or stored on adsorption or other cation exchange sites in the soil (Ulrich and Matzner 1986). The Ca^{2+} and other adsorbed nutrient cations remain fixed on the exchange sites and are only released to the soil solution when they exchange with an equivalent of H^+ ions such as in H_2SO_4 that enter the system. The H^+ takes its place on the exchange site as illustrated in reversible Reaction (3). A similar exchange occurs when the H^+ releases Ca^{2+} from calcium humate where it is held as a salt (Since the cationic nutrients are held in storage sites by ion exchange in both adsorption on clay, and as insoluble humate salts, the term (Ca^{2+} on exchange sites) signifies that either or both are involved.)



As the dilute H_2SO_4 and HNO_3 that are present in acid rain enter the soil solution, and seep through the soil, their H^+ ions displace, by exchange, an equivalent of nutrient cations from their storage sites, where they were previously adsorbed on negatively charged clay or held as salts of humic acid. *The negatively charged SO_4^{2-} and NO_3^- anions in the soil solution automatically balance their negative charge with the positively charged Ca^{2+} , Mg^{2+} , K^+ , and Na^+ cations that are displaced from their exchange sites in the soil by the H^+ ions, thus forming an 'electrically neutral equilibrium'.* About 90% of the H^+ ions exchange with the cations on the exchange sites and the remaining H^+ , together with the Al^{3+} , that is released from an organic complex in the soil, also participate in the 'electrically neutral equilibrium' with the other cations. The relative amount of each of the cations entering the soil solution is related to its relative

proportion on exchange sites, on its valence, and on its atomic weight (Sparks 1986). The negatively charged SO_4^{2-} and NO_3^- anions seep through the soil in the soil solution and it is as a result of this equilibrium, that these cationic nutrients are leached from the soil, as the soil solution drains from the watershed. Likens and Bormann (1995) have measured the concentrations of each of the ions present in the dust and rain and in the soil water draining the hardwood forest on Watershed 6 at Hubbard Brook in New Hampshire on a continuous basis since 1963. Their data for the cations and anions in Dust and Rain, (collected in open containers) and in the soil solution, as measured in the Outlet Stream from Watershed 6 for two periods, 1963–1974 and 1992–1993 are shown in Table 2. The units in this Table have been calculated in terms of $\text{eq ha}^{-1} \text{ year}^{-1}$ allowing a comparison of the relative changes in the concentrations of the individual ions, on a comparable basis. Data in the Outlet Stream show how the relative concentrations of each of the cations that enter the soil solution had been adjusted by the ‘electrically neutral equilibrium’ between anions and cations prior to their removal in the leachate from the Watershed soil. The reduction in the ionic inputs from the Dust and Rain between these two periods resulted largely from the reductions of the acidic and the particulate emissions from combustion gas as well as from the reduction of dust as a result of road paving. The concentration of the nutrient cations in the watershed soil had been reduced between the two measurement periods as a result of their uptake by biomass, and by their continuing loss to the Outlet Stream, carried with the anions that entered the watershed from acid deposition. The relative concentrations of the divalent Ca^{2+} and Mg^{2+} were found to decrease at a rate greater than that of the monovalent K^+ . In contrast to the decreasing concentration of the nutrient cations in the soil solution, the concentration of the trivalent Al^{3+} was found to be increasing, apparently resulting from its mobilization by the increased acidity of the soil solution. This is undesirable since Jorns and Hecht-Buchholz (1985) found that the concentration of Ca^{2+} in the foliage decreases as the $\text{Al}^{3+} : \text{Ca}^{2+}$ molar ratio increases above about 1:1.

The increase in the amount of SO_4^{2-} in the Outlet Stream, compared with that entering in Dust and Rain, resulted from the dry deposition of SO_2 on the foliage and bark where it was oxidized by the air to H_2SO_4 and independently reached the soil solution in the throughfall. This amount was estimated to be $420 \text{ kg ha}^{-1} \text{ year}^{-1}$ (Likens and Bormann 1995). Nitrogen is a nutrient essential for the production of protein in the leaves but unfortunately an excess is presently entering the soil in rain and is depleting the supply of the cationic nutrients. Nitrogen is recycled from fallen litter and can be taken up by the tree from both the NH_4^+ and NO_3^- ions. Nitrogen is accumulated in the humus and is partially released as HNO_3 following the rewetting of the soil after a hot dry summer (Ulrich 1986). This causes a periodic lowering of the pH of the soil solution and an increase in the loss of nutrients.

The nutrient cations plus Na^+ (which is not a foliage nutrient), are referred to as the base cations, and as they are replaced by H^+ , the soil pH (as measured in NH_4Cl solution) drops, as shown in Figure 1. In soils having a pH of

Table 2. Flux of ions in bulk precipitation, and in the outlet stream, to and from watershed 6 at Hubbard Brook, in the periods 1963–1974 and 1992–1993. From Likens and Bormann (1995).

	1963–1974 (eq ha ⁻¹ year ⁻¹)		1992–1993 (eq ha ⁻¹ year ⁻¹)	
	Dust + Rain	Outlet Stream	Dust + Rain	Outlet Stream
Cations				
Ca ²⁺	108	684	44	351
Mg ²⁺	48	257	25	165
K ⁺	23	48	15	37
Na ⁺	69	315	63	259
Al ³⁺	—	208	12	286
NH ₄ ⁺	161	19	167	15
H ⁺	969	103	720	107
Total cations	1378	1634	982	1220
Anions				
SO ₄ ²⁻	799	1120	556	863
NO ₃ ⁻	317	275	358	32
Cl ⁻	198	141	78	93
Total anions	1314	1536	992	988

*In addition to the SO₄²⁻ entering the system in bulk deposition, SO₂, equivalent to 420 eq ha⁻¹ year⁻¹, has been estimated to be dry deposited on the trees (Likens and Bormann, 1986).

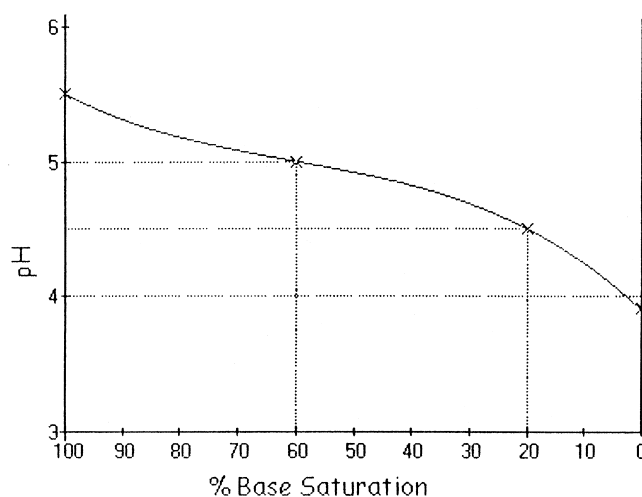


Figure 1. The relationship between soil pH and % base saturation. Adapted from Coote et al. (1981).

5.5, essentially 100% of the exchange sites are occupied by the base cations. In the pH range between 5.5 and 4.2, the soil is buffered by one or more of the base cations. When the continuing acid input has reduced the pH to a value of

4.2, the exchange sites are occupied by H^+ ions and in addition, because of the decreased pH, by Al^{3+} ions. At pH 4.2 the $AlOOH$ enters solution as $Al_2(SO_4)_3$ and the soil solution becomes buffered by the Al^{3+} ion. In most locations the drop in pH to a value below 4.2 can require very many decades. This is because the rate of entry of H_2SO_4 to the soil each year is relatively very small in relation to the large quantity of Ca^{2+} and other cations, that had been initially accumulated in the soil, and that are ultimately displaced by exchange. Although at pH values of around 4 most of the previously stored nutrient cations have been removed from exchange sites, their continuing recycling from rotting wood provides, for many years, a continuing supply. The leaching loss of cations from the soil is a major concern, and Tyler et al. (1987), found that the weathering rates of the minerals in the soil of Skåne in south Sweden, were unable to 'keep pace with the rate of acid input in recent decades'. They estimated that half the Ca^{2+} , Mg^{2+} , and K^+ formerly present in south Swedish soils in 1948–1953 had been replaced by H^+ and Al^{3+} in 1958. Driscoll et al. (2001) stated that at the Hubbard Brook Experimental Forest the available Ca pool in the soil appears to have declined 50% over the last 50 years.

6. The vascular system and cation transfers

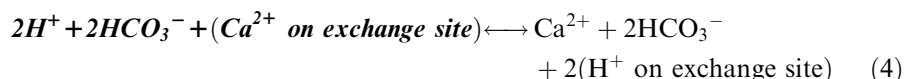
In a healthy forest, the soil, the fine roots, and other parts of the tree have remarkable interrelated ion exchange properties that allow the storage of the nutrient cations and their transfer, back and forth, between soil and tree (Ledin and Wiklander 1974). The nutrient cations, together with water, are required in the foliage, where the many reactions essential for the trees' growth and survival take place. The vascular system in conifers consists of hollow inter-connecting wood fibers, called tracheids, providing passages of about 10μ diameter for the movement of water and nutrients from each of the fine roots, through the main roots, the trunk, and the branches, to each leaf or needle in the tree's crown. In hardwoods the corresponding water-conducting units are called vessels and these have a similar function to that of the tracheids. The internal walls of each of these passages are lined with the calcium salts of hemicellulosic acids, which provide an ion exchange column from the fine root tips, where the Ca^{2+} enters, to the top of the tree (Timell (1965); Simson and Timell (1978)). As the tree grows in height, the vascular system is extended, and the H^+ ions, formed in the hemicellulose acids that line the inner walls of each new connecting tracheid, exchange with the Ca^{2+} ions in the tracheid to which it has just become attached. The H^+ ions simultaneously move down to the fine roots to the soil solution, step by step, as an equivalent of Ca^{2+} , released from its exchange site in the soil, moves up in response (Bell and Bidulph (1963); Shear and Faust (1970)). Calcium pectate, a tough flexible polymer, is the principal constituent that forms, in the leaf's cells and veins, an extension of the exchange column from that in the wooden twig. Synthesis of the pectic acid, in the position of the leaf it will occupy, occurs at the same time as it

reacts with the Ca^{2+} to form its solid calcium salt, since unreacted pectic acid would form a viscous acidic solution and not provide the structure to the leaf. The two H^+ ions released in the reaction are immediately exchanged with the Ca^{2+} discharged from the pectate molecule previously formed, and these move down the exchange column as the Ca^{2+} moves up. As the H^+ ions enter the soil solution they exchange with the Ca^{2+} on adjacent exchange sites, allowing Ca^{2+} to move up the exchange column as the H^+ ions come down. The trees' use of the ion exchange column for transfer not only prevents the buildup of acidity in the crown, but also provides the H^+ ions that release the required Ca^{2+} from the exchange sites in the soil. It also allows the H^+ ions to move down the walls of the vascular passageway as the transpiration water moves up. The transfer of sugars and nutrients from the foliage to the fine roots is through the sieve elements, located in the phloem (inner bark) which contains a high concentration of calcium pectate providing the flexibility to respond to the trees increased diameter (Painter and Purves 1960). The sieve elements deliver sugars to the cambium where new radial growth takes place and to the ray cells where sugars and nutrients are stored. The divalent Mg^{2+} transfers from the soil to the foliage in the same way as that described for Ca^{2+} . In contrast, the monovalent K^+ , with its single valence, enters and moves up the tree in the transpiration water (Bell and Bidulph 1963), with any excess being excreted from the foliage and washed to the forest floor in rain. The PO_4^{3-} and other anionic nutrients are not directly affected by acid rain and they also enter the tree's fine roots with the transpiration water.

7. The pre-industrial accumulation of nutrients in the soil

Unfortunately no measurements of the transfer of the cationic nutrients between the soil and tree had been made in the late 1800s when the emissions of SO_2 and NO_x in the United States were becoming significant during the development of the industrial age. However it is known that the world's virgin forests had been able to reproduce on the same sites, from generation to generation, for many thousands of years. It is also apparent, from presently known chemical reactions, that the trees had established chemical mechanisms for their growth using the byproducts from their own key reactions, thus guaranteeing their continuing survival. It had appeared that the forest growth could continue indefinitely. The acid needed for weathering was H_2CO_3 , formed in the soil from H_2O and the CO_2 released from the respiration and decomposition of roots (Ulrich 1986). The nutrients and micronutrients that may have been in low concentration in the native soil were brought in from other geological areas in dust and rain. These, together with the cations released in weathering and in mineralization, were concentrated, for future generations of trees, by ion exchange on the clay (Ulrich and Matzner 1986), and with salts of the humic acid, that had formed as byproducts in the reactions of the forest soil. When required for new growth by the tree, for instance

in the production of Ca pectate, Ca^{2+} from exchange sites in the soil transferred, in a series of exchanges, through the soil solution to the fine roots and up the ion exchange column in the tree where it exchanged with the H^+ ions formed in the nascent pectic acid. It is apparent that no outside source of acid was required for the transfer of the Ca^{2+} from the soil to the crown of the tree. By exchanging the H^+ ions, generated in the tree's crown, with the exchange sites in the soil vacated by the Ca^{2+} , the sites again became available for storage of the Ca^{2+} regenerated in the mineralization of rotting wood. The presence of H_2CO_3 established the pH and the Ca^{2+} and HCO_3^- concentrations in the soil solution as shown in reversible Reaction (4).



H_2CO_3 is a very weak acid with a dissociation constant of only 4.3×10^{-7} compared with 1.2×10^{-2} for H_2SO_4 . Because of the lower dissociation constant of H_2CO_3 , compared with that of H_2SO_4 , the availability of the H^+ and HCO_3^- ions in pre-industrial soil solutions was very substantially less than that with the present H^+ and SO_4^{2-} that now dominate the soil. The equilibrium of Reaction (4) is largely on the left hand side, resulting from its weak dissociation, as is indicated by italics. This resulted in a low concentration of Ca^{2+} in the soil solution and therefore a low rate of Ca^{2+} loss in the outlet stream from the soil. The closed recycling in the virgin forest resulted in the large accumulation of Ca^{2+} and other cationic nutrients on exchange sites requiring only a low nutrient input available from chemical weathering. This had allowed the forest to reproduce on the same soil, over very long periods of years, without exhausting the critical nutrient cations released from the rock. *Comparison of Reaction (3) with Reaction (4), which differ in the dissociation constants of the acids driving the reactions, illustrate why acid rain increased the Ca^{2+} in the soil solution resulting in the increased loss of Ca^{2+} to the effluent stream. This explains how the input of H_2SO_4 and HNO_3 , as shown in Reaction (3), with their higher dissociation characteristics, has reversed the mechanisms that previously controlled forest growth.* As will become apparent from the discussion of the data from Hubbard Brook, the effect of the strong acids has not only resulted in the leaching of the Ca^{2+} from its previous large inventory but is now removing, to the stream, the recycled Ca^{2+} and other nutrients released in mineralization.

8. The watershed study at Hubbard Brook

The continuing experimental studies carried out by Likens et al. (1998), involving the measurements of the nutrient cation and H^+ ion transfers to and

from the soil of Watershed 6 at the Hubbard Brook Experimental Forest, started in 1963. In addition, the transfer rates of Ca^{2+} to the forest biomass, together with biomass growth, were measured, in intervals of five years or more. These studies also established the chemical weathering rates of Ca^{2+} and other nutrients that, together with those present in the dust and rain, control the continuing entry of cationic nutrients to the soil. With the information obtained from their studies Likens et al. (1996, 1998) established, by means of material balance calculations, at intervals of 5 years or longer how acid rain, over many decades, has affected the changes in biomass growth and in nutrient loss from the soil.

Their studies established, as discussed in Section 5, and indicated in Reaction (3), that the effect of SO_4^{2-} and NO_3^- anions entering the soil solution had been to initially increase the concentration of Ca^{2+} and other nutrient cations in the soil solution that seeps through the watershed soil to the outlet stream. In addition, the greatly increased nutrient concentration in this solution, shown in the 1963–1974 period of Table 2, simultaneously increased the rate of transfer of Ca^{2+} and other nutrients to the biomass resulting in a fertilizing effect that led to its initially increased rate of growth. These studies also established that the combined increased rates in the transfer of Ca^{2+} to the stream and to the biomass exceeded the rate of replenishment of the soil from weathering, mineralization, and from dust and rain. This inevitably led to the depletion, over very many decades, not only of the very large initial reserve of Ca^{2+} that had previously accumulated on exchange sites in the soil, but also of the Ca^{2+} that had been mineralized during the same period from the organically combined calcium in rotting roots and other woody material in the soil. *The data in Table 3(A), showing the Ca^{2+} content of the biomass at the intervals at which it was measured, indicates that its continuing transfer to the biomass all but stopped in 1982* (data in Table 3 adapted from Table 7 of Likens et al. (1998)).

As the inventory of the Ca^{2+} on exchange sites became depleted in the 1970's, the rate of growth of biomass on Watershed 6 also decreased, leading to the absence of further incremental growth in the periods following 1982, as shown in Table 3(B). The forest on Watershed 6 had been harvested and the growth of the present forest started in 1915. Thus net biomass growth stopped when the trees were only 67-years old. Although some trees on the watershed showed continuing growth, this was offset by the death of other trees and branches. As noted in this regard in the Likens et al. (1998) paper, only standing dead wood was measured, and it is possible that the loss of biomass as a result of death of unmeasured fallen branches could have been greater than recorded. When trees die, the organically combined calcium and other nutrient cations contained in the foliage, the fine roots, and the above- and below-ground parts of the tree, all eventually become mineralized and recycled. The exchangeable cations thus formed become available to the neighboring trees, which can, or already share, overlapping space in the soil for their fine roots. However, when the nutrients are released by dying trees at a rate greater than they can be immediately taken

Table 3. Calcium content of live and dead standing trees (A). Total above and below ground biomass on Watershed 6 at Hubbard Brook (B). From Likens et al. (1988).

	1965	1977	1982	1987	1992
A. Calcium in Biomass (kg ha^{-1})					
Live					
> 9.6 cm	445	652	704	699	711
1.6–9.5 dbh	38	–	25	31	40
Dead					
> 9.6	–	26	29	35	40
1.6–9.5 cm dbh	–	–	1.0	1.4	1.1
B. Biomass ($\text{kg } 10^3 \text{ ha}^{-1}$)					
Live					
> 9.6 cm	149	218	235	234	237
1.6–9.5 cm dbh	11	–	8	10	12
Dead					
> 9.6 cm	–	10	11	14	15
1.6–9.5 cm dbh	–	–	0.52	0.62	0.45

* In calculating the amount of Ca^{2+} in biomass, and the increase in biomass, only the trees greater than 9.6 cm diameter than breast height for the years 1965, 1977 and 1982 were used.

up by neighboring trees, the surplus nutrients are not washed away. They are held in the soil on exchange sites and are subsequently utilized in new growth. The resulting effect of this ‘fertilization’ that has been observed a few years later, explains the apparent recovery following a period of serious forest decline. Only the nutrients, removed at the rate controlled by the rate of flow of the SO_4^{2-} and NO_3^- are lost in any given period of years. This results in a relatively constant total amount of live plus dead biomass on the watershed (Likens et al. 1998). Since the biomass growth has now become limited to the cationic nutrient content in a given area of soil, it does not allow the forest to increase its biomass, per hectare, to a value greater than that attained immediately prior to the period of decline.

The measurement of the Ca^{2+} content of the biomass was carried out in each period after the foliage had formed on the trees. Thus the difference between the values obtained in successive 5 year measurement periods gives the change in the *net* transfer of Ca^{2+} to biomass. This value is the difference between the Ca^{2+} transferred to biomass including the foliage, in successive periods, and therefore does not accumulate the quantities of Ca^{2+} taken up to supply the leaves each year since this quantity is cancelled out when the leaves fall from the tree in the autumn. The calcium content of the foliage amounted to 24.8 kg in 1992 and the substantial amount of sugars required in the production of this foliage can only be produced when photosynthesis is taking place. This normally occurs in August and September of the previous year, when the sugars, and other nutrients required for the foliage and for replenishing the fine roots, are prepared and stored in the ray cells. These cells,

which are provided for this storage, are located radially in the trunk and are fed from the leaves through the sieve elements which extend from the leaves to the fine roots through the phloem or inner bark, and also provide for the delivery of the sugars and nutrients to the stems and branches the following spring.

It might be assumed that a knowledge of the amount of the cationic nutrient formed by mineralization each year would be essential for calculating a material balance but unfortunately this cannot be obtained directly. However, Likens et al. (1998) established that it is possible to estimate the rate of depletion of the calcium in the soil, for any fixed period of years, by measuring the difference between a and b

a = the rate in which Ca^{2+} was removed in biomass and in stream water and
 b = the rate in which Ca^{2+} was replenished from weathering and in dust and rain.

When calculated in this way, the depletion rate includes the Ca^{2+} formed from the organically combined calcium that was mineralized from rotting wood and foliage during this period and removed, by exchange, together with that portion of exchangeable Ca^{2+} previously available in the soil, that was simultaneously removed during this period. This made possible the data in Table 4. This reports the Ca^{2+} depletion and transfer data calculated in terms of $\text{kg ha}^{-1} \text{ year}^{-1}$ and in addition, the biomass formed, in metric tons $\text{ha}^{-1} \text{ year}^{-1}$ (data adapted from Tables 2 and 5 of Likens et al. (1998)). These data, in which the rate of mineralization is included in the material balance, are plotted in Figure 2, and they allow important insights into the successive changes caused by acid deposition that have occurred over long periods of time, in the forest and its soil. The rates of depletion and of transfer of Ca^{2+} shown in Table 4 and Figure 2 add important clues as to the past history of the soil processes that occurred in the forest and in its soils in Watershed 6 prior to the Hubbard Brook study. The very serious rate of depletion of Ca^{2+} , that had resulted in a drop of from 25.53 to $6.4 \text{ kg ha}^{-1} \text{ year}^{-1}$ in the 17 years between 1965 and 1982, as shown in Table 4, clearly demonstrates that in an earlier period, prior to this study in the 1960's, the rate of transfer of Ca^{2+} to the biomass and to the stream water had definitely increased at a substantial and unsustainable rate. This resulted from the flow of H_2SO_4 and of HNO_3 in the rain.

As is apparent from the discussion of Table 3(A) and (B), the growth of biomass depended on the amount of Ca^{2+} taken up by the trees roots. As described in Section 6. The effect that the uptake of Ca^{2+} has on biomass growth results from its ability to initiate the synthesis by the tree of organic acids, such as pectic acid, from which it forms Ca pectate, the main constituent in the leaves, the phloem (inner bark), and the fine root cortex. As each divalent Ca^{2+} ion reacts with pectic acid in the formation of the leaves, two H^+ ions are released, and these provide the necessary means of transfer of Ca^{2+} by

Table 4. The change, with time, that occurred in the Ca^{2+} balance on watershed 6, indicating the depletion of the pre-industrial inventory of exchangeable and organically combined calcium, and on net Ca^{2+} uptake by net biomass, and its effect on the change in biomass growth while the Ca^{2+} loss to the stream continues. Adapted from Likens et al. (1988).

	Units	1965–77 (1971)*	1977–82 (1979.5)	1982–92 (1987)	1992–93 (1992.5)
1. Ca depletion from soil inventory	kg/ha/year	25.53	16.20	6.41	
2. Ca^{2+} taken by net biomass**	kg/ha/year	17.23	10.50	2.18	
3. Ca^{2+} lost from soil in stream water	kg/ha/year	12.86	9.56	7.79	7.03
4. Live net biomass** formed	kg/ha/year $\times 10^3$	4.9	5.0	0.6	
5. Ca^{2+} entering soil from weathering	kg/ha/year	2.56	2.56	2.56	2.56
6. Ca^{2+} entering soil from dust/rain	kg/ha/year	2.0	1.3	1.0	

* The midyear in each period is used in plotting the data in Figure 2.

** Net Ca^{2+} taken up by biomass is the difference in uptake between successive years.

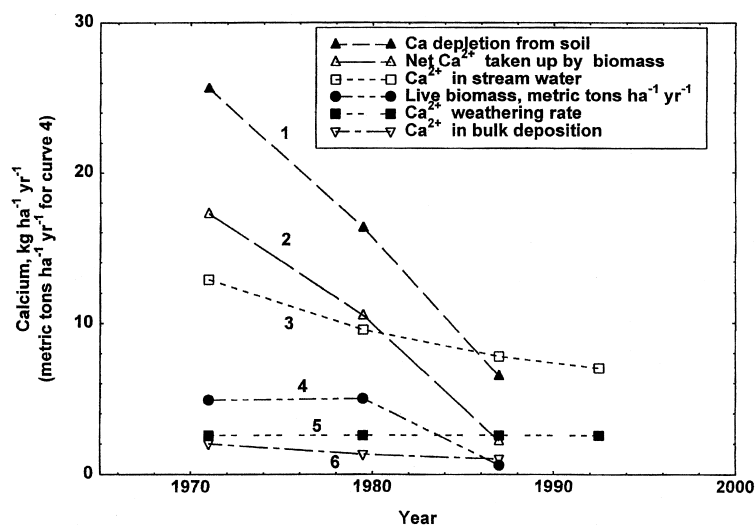


Figure 2. The effect of Ca^{2+} depletion on net Ca^{2+} transferred to biomass, in $\text{kg ha}^{-1} \text{ year}^{-1}$, and its effect on biomass growth in $\text{metric tons ha}^{-1} \text{ year}^{-1}$. Adapted from Likens et al. (1988).

ion exchange, from its exchange site in the soil to the crown of the tree, as the H^+ ions move down, step by step in the opposite direction. The rate of transfer in the ion exchange column between the fine root and the leaf, by maintaining electrical neutrality, is virtually instantaneous. However this transfer will temporarily stop if the Ca^{2+} in the soil solution adjacent to the root tip,

because of a low initial Ca^{2+} concentration in the soil solution, becomes depleted. As indicated in Reaction (4), the concentration of Ca^{2+} in the soil solution was substantially lower in pre-industrial times and yet it is known that the trees had grown at a reasonable rate. Trees have a very large fine root system that developed, by recycling mineralized nutrients during the pre-industrial era, and produced very large inventories of Ca^{2+} on the exchange sites, thus compensating for the low concentration of Ca^{2+} ions in the soil solution that then resulted from H_2CO_3 acidification.

Russell and Clarkson (1976) found that the Ca^{2+} uptake by the fine roots is confined to their tips, and it had been found by Clarkson (1969) that when the Ca^{2+} in the soil solution, adjacent to the tip, becomes exhausted, the fine roots develop branches with additional terminal tips, giving it a 'coral like' appearance. When one digs in the soil it is apparent that the soil solution does not form a body of liquid in which mixing by convection can take place, and in which ion exchange would be instantaneous. Instead the soil solution is distributed in a thin aqueous film that surrounds each grain of soil, between which the fine roots have penetrated. Since the fine roots are wedged between the soil grains, the volume of soil solution surrounding each fine root is greatly limited, and a reduced Ca^{2+} concentration in this critical zone can occur rapidly and independently of that in the main soil solution seeping through the soil. This results from the slow rate of diffusion of ions in thin liquid films such as those surrounding the fine roots, particularly when their concentration in the soil solution is low as was the case in pre-industrial times. In the absence of an adequate concentration of Ca^{2+} ions in the soil solution surrounding the fine root, its depletion at a fine root tip, would prevent transfer from that tip to the leaf, until Ca^{2+} from a non-depleted zone diffused in, or a new tip was formed on the fine root. Wood et al. (1984) examined the fine root system, which they separated from the soil in test cores taken from the Hubbard Brook Forest in 1977. Their data indicated that *under each square meter of soil, the total length of the elongated cylindrical fine roots, which had an average diameter of 0.6 mm, was $24.7 \pm 3.2 \text{ km}$ and that these carried 3.8 ± 0.6 million root tips*. This extraordinarily large system of fine roots and root tips, when combined with the very large Ca^{2+} ion inventory that accumulated in pre-industrial times, would have been developed by the tree to compensate for the low concentration of cationic nutrients in the soil solution and for the delayed nutrient transfers that can occur adjacent to the individual fine roots. Thus by shortening the distance the H^+ ions would have to travel between the root tips and the Ca^{2+} on exchange sites would allow a more rapid rate of transfer to the reaction site in the foliage and thus to the reasonable rate of biomass growth that took place in pre-industrial times. The entry of H_2SO_4 and HNO_3 to the soil in the late 19th Century resulted in the greatly increased concentration of Ca^{2+} and H^+ in the soil solution that, combined with the very large number of root tips and the very large inventory of Ca^{2+} that had built up on exchange site no doubt led to the initial increased rate of transfer to the fine roots. This indicates that this early effect of acid deposition resulted in the increased rate of growth on

Watershed 6 observed by Likens et al. (1998) during the 1960's and 70's. Unfortunately this increased rate of transfer of Ca^{2+} to biomass, together with the greatly increased loss to the Outlet Stream from 1880 to 1980, resulted in an unsustainable rate of growth. After approximately 100 years this resulted in the depletion of the very large reserve storage of Ca^{2+} that had accumulated on the exchange sites in the soil and to the cessation of net biomass growth on Watershed 6.

Fortunately the Watershed Studies by Likens et al. (1996) were initiated in the 1960s, prior to the period when the rate of depletion of Ca^{2+} had become greater than its rate of input from the exchange sites in the soil. This permitted an understanding of the serious resultant long-term sequence of the events that has resulted from the introduction of acid deposition to the forest ecosystem. This is illustrated in data from Lines 1 to 6 in Table 4 corresponding to Curves 1 to 6 in Figure 2. The values shown in the graph are the mid points of the measurement periods. As the inventory of Ca^{2+} in the soil became depleted (Line 1), the net Ca^{2+} taken up by biomass decreased (Line 2) and net biomass growth all but stopped (Line 4). The rate of Ca^{2+} entering the soil solution from weathering was found to be only $2.56 \text{ kg ha}^{-1} \text{ year}^{-1}$ (Line 5). When this is added to the $1.0 \text{ kg ha}^{-1} \text{ year}^{-1}$ entering in dust and rain in the 1982–1992 period (Line 6), the total rate of input from outside the Watershed amounts to $3.56 \text{ kg ha}^{-1} \text{ year}^{-1}$. The total rate of Ca^{2+} loss from the soil to the stream (Line 3), was $7.79 \text{ kg ha}^{-1} \text{ year}^{-1}$ in the same period, and therefore the net rate of loss from Watershed 6 was found to be $4.23 \text{ kg ha}^{-1} \text{ year}^{-1}$, this coming from recycled Ca^{2+} formed from mineralization of the fallen dead wood that will continue for many years. The rate of loss of Ca^{2+} to the stream is controlled by the rates of flow of SO_4^{2-} and NO_3^- multiplied by the percentage that Ca^{2+} constitutes of the total cations that are carried in the 'electrically neutral equilibrium' from the watershed. As shown in Table 2, the Ca^{2+} carried in the effluent, dropped from 12.86 to 7.01, from the 1963–1974 to the later period of 1992–1993. The strong acids will therefore continue to remove Ca^{2+} , and the other nutrient cations from the soil of Watershed 6 at a rate greater than they are replaced by their inputs from weathering and from dust and rain. This can be seen from the relative slopes of Curve 3 with that of Curves 2 and 4 in Figure 2, which indicates that the serious leaching of Ca^{2+} is continuing, regardless of the fact that there is no longer a sufficient supply on exchange sites to allow its transfer to net biomass. Unlike the organic acids that are synthesized in a fixed position in the tree, and therefore must attract the Ca^{2+} to them, the strong mobile anions, SO_4^{2-} and NO_3^- , will continue to preferentially carry Ca^{2+} and the other nutrient cations remaining in the soil, as long as these strong acids remain a significant constituent of the rain. The H^+ ions that enter the soil in the rain, and release an equivalent of cations from the exchange sites, are carried from the soil by the strong acid anions, while the H^+ ions, generated in the pectic acid, replace the Ca^{2+} ions from the exchange sites in the soil and are retained in the tree.

It appears that when the rate of loss of Ca^{2+} from the watershed exceeded that of its replenishment from weathering, and from dust and rain, hormonal

control directed the nutrients and sugars to the production of foliage, rather than to woody-matter, since without successive crops of leaves, the trees would die. Mineralization of litter-fall from the previous and earlier years, supplemented with Ca^{2+} recycled from dead wood, has provided the continuing supply for the leaves that reappear each year. Although there is no doubt still a substantial amount of organically combined Ca from dead wood remaining in the soil, without current net biomass growth, long-time storage of Ca^{2+} in wood, bark, and roots is no longer taking place, reducing the amount that will be available for foliage. As this eventually becomes depleted, less Ca^{2+} will become available for supplying the make-up for foliage each successive year. This appears to be already occurring, and the Ca content of the foliage on the watershed, as a % of its dry weight, has decreased since 1965. In the case of sugar maple, the value of 0.6% Ca in 1965 decreased to 0.52% in the 1992–1995 period. At the higher elevations of 715 m on the watershed, where mortality of maple had significantly increased between 1982 and 1992, the concentration was 0.38% indicating that deficiency in this zone is probably already involved (Likens et al. 1998). It is expected that as the trees on the watershed die, and release their Ca and other nutrients to exchange sites, the accumulated Ca^{2+} will be taken up by neighboring trees and in seedlings, and that the forest will continue to survive for many years. However, because of the continuing depletion of mineralized Ca^{2+} , living biomass will decrease as the portion of dead biomass increases.

The data obtained at Hubbard Brook has allowed an examination of the effects that H_2SO_4 and HNO_3 have had by displacing H_2CO_3 as the dominant controlling acid in the soil, indicating how this has greatly changed the present and future nature of a forest effected by acid deposition. Although Ca is the deficient element at this location, it is apparent from the properties of the Mg and K elements, in relation to these acids, that similar sequence of reactions are taking place in forest soils where, because of an initial low concentration in the native stone, a deficiency of these elements has, or will, take place. *The findings at Hubbard Brook have allowed an understanding of the serious changes now occurring in these forests and their soils that will continue until the emissions of SO_2 are greatly reduced.*

9. Related growth problems in the northeast USA

An important related series of experiments is being carried out adjacent to Whiteface Mountain in New York State, and the results of the first 10-year period were recently reported (Friedland and Miller 1999). This study illustrates the conditions that prevail when red spruce and birch gradually die and balsam fir utilizes the nutrients released. Experimental plots were established on the flank of Esther Mountain, a sub peak of Whiteface Mountain, in an area where the earlier decline and death of red spruce was less severe than on the main mountain. Miller and Friedland (1999) found that “The forest at the

Table 5. Comparison of data relating loss of Ca^{2+} from soil with growth of biomass on watershed 6 at Hubbard Brook and Esther plot on Whiteface mountain. From Likens et al. (1988) and Friedland and Miller (1999).

		Hubbard Brook (Watershed 6)	Whiteface (Esther plot)
Elevation, m		280–725 (525–625)	950–1150 (1050)
Acid input	$\text{kg ha}^{-1} \text{ year}^{-1}$		
H^+		0.72	1.27
SO_4^{2-}		26.7	54.9
NO_3^-		22.2	76.2
Live biomass	$\text{kg } 10^3$	243 (1982)	147 (1985)
		249 (1992)	150 (1995)
Biomass growth	$\text{kg } 10^3 \text{ ha}^{-1} \text{ year}^{-1}$	0.6	0.3
Ca^{2+} , live biomass	kg ha^{-1}	729 (1982)	339 (1985)
		751 (1992)	346 (1985)
Ca^{2+} uptake	$\text{kg ha}^{-1} \text{ year}^{-1}$	2.2	0.7
Ca^{2+} weathering	$\text{kg ha}^{-1} \text{ year}^{-1}$	2.56	8.6
Ca^{2+} dust rain	$\text{kg ha}^{-1} \text{ year}^{-1}$	1.0	3.3
Total input		3.56	11.9
Ca^{2+} to stream	$\text{kg ha}^{-1} \text{ year}^{-1}$	7.79	10.7

1050 m sampling site exhibited a gradual loss of mature individuals of red spruce, and to a lesser extent white birch, from 1985 to 1995. At the same time, vigorous growth of balsam fir stabilized the total leaf area of the stands over the period. Although this site did not constitute a watershed with an out-flowing stream, soil solution was continuously withdrawn from below the rooting zone, and the loss of the ions draining from the soil was calculated in terms of $\text{kg ha}^{-1} \text{ year}^{-1}$. A number of the variables that parallel those carried out at Hubbard Brook, and related data from the two sites, are shown in Table 5. At the higher elevation, the Esther Mountain site received slightly more than twice the amount of SO_4^{2-} and NO_3^- , while its biomass is only about 60% of that at Hubbard Brook. In both cases forest incremental growth has essentially stopped, being only 0.3 on the Esther Plot compared with 0.6 metric tons $\text{ha}^{-1} \text{ year}^{-1}$ on Watershed 6. The amount of Ca^{2+} transferred to the biomass on the mountain site is 46% of that at Hubbard Brook, while the annual input is just a third, only 0.7 kg ha^{-1} , in both cases an inadequate amount to promote increased growth. Although the weathering rate and inputs from dust and rain were higher on the mountain site, the higher rate of acid input, with the resulting correspondingly higher rate of Ca^{2+} outflow cancelled this advantage. It should be noted that the SO_4^{2-} and the NO_3^- continued to carry $10.7 \text{ kg ha}^{-1} \text{ year}^{-1}$ Ca^{2+} to the stream, leaving only $0.7 \text{ kg ha}^{-1} \text{ year}^{-1}$ for the biomass. Biomass growth all but stopped while the Ca^{2+} continued to drain from the soil, paralleling the situation at Hubbard Brook.

Because of concern in relation to the decline of red spruce on the high mountains of the northeast, Hornbeck and Smith (1985) designed a study to see whether this species was declining in growth over its northern geographical

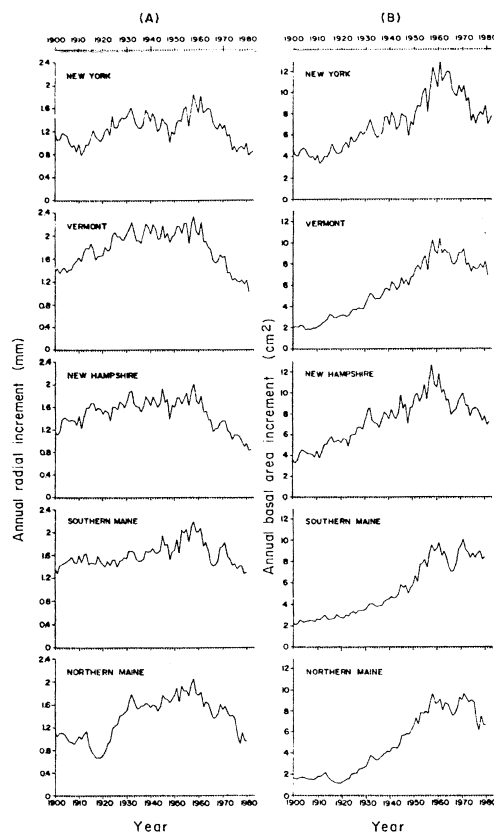


Figure 3. Mean radial increment (A), and basal area increment (B) of 3000 Red Spruce. NY, 224; VT, 302; NH, 391; North ME, 1691; South ME, 404. With permission, Hornbeck and Smith (1985).

range and if so when it began. They measured the mean radial increment of 3000 red spruce trees growing from northern New York State to Maine between the years 1900 to 1990 as shown in Figure 3(A). Based on these data they calculated the mean basal area increment, as shown in Figure 3(B) which, because it measures the area of the annual ring, rather than just its width, gives a better indication of net biomass incremental growth. This showed that the common pattern of a substantially increased growth was followed by a marked decrease in the 1960's, and it was suggested that the loss in growth might be related to acid rain. As has since become apparent, the EPA estimates (Baker et al. 1993) of sulfur dioxide and nitrogen oxides for the period from 1900 to 1990, shown in Figure 4 (A and B), follow a similar pattern, indicating that this may indeed be the case. Bondietti et al. (1990) considered the findings of Hornbeck and Smith and hypothesized that the anomalous increase in growth of red spruce prior to the 1960s', followed by the subsequent anomalous decrease, resulted from changes in the nutrient content of the soil solution caused

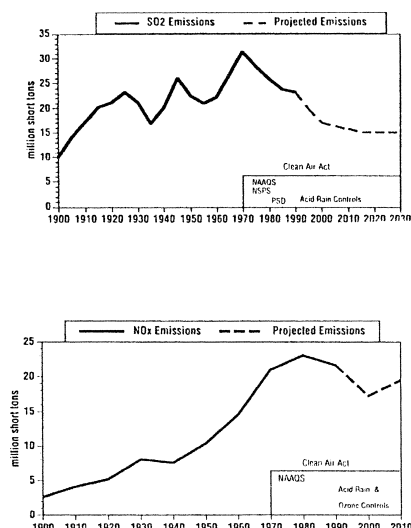


Figure 4. Annual emissions of SO₂ in USA (A). Annual emissions of NO_x in USA (B). From NAPAP Annual Report to Congress (1992).

by acid deposition. Reaction of the H₂SO₄ and HNO₃ with the Ca²⁺ on exchange sites would be expected to initially increase the concentration of the Ca²⁺ and other divalent cations in the soil solution, as shown in Reaction (3) and then, because of the prolonged leaching from the soil, the concentration would be reduced resulting in decreased growth. Since current measurements of foliage and soil solution cannot be used for establishing values in earlier years, they measured instead, the content of the divalent ions in the annual rings of the wood at 5 year intervals, starting in 1940. They found that in most cases the concentration of the divalent ions were consistent with their theory and concluded that an unsustainable amount of Ca²⁺ had entered solution as a result of the acid input to the soil, resulting in an initial increase in growth, and that the subsequent anomalous decrease in growth resulted from the loss of Ca²⁺ from the soil during the previous 'long period of enhanced mobilization'.

The hypothesis of Bondietti et al. (1990) was clearly justified by the subsequently published Hubbard Brook studies. These, and other studies, indicate that the problems caused by the leaching of nutrients by acid rain are widespread across the northeast, and probably well beyond. Rapid and more serious loss in growth was particularly serious at higher elevations. Vogelmann et al. (1988) reported on a series of ecological studies on Camels Hump Mountain in Vermont, where serious tree mortality occurred. This showed that the net biomass of red spruce at an elevation of 790–1035 m elevation had decreased from 1965 to 1986 by 74%, while that of sugar maple growing at 550–790 m had decreased by 27%, and that trees of other species were also affected. Tomlinson (1987) found that red spruce showing early signs of decline on

Camels Hump where deficient in both Ca and Mg. This serious damage is related to the increased acid deposition that occurs on mountains impacted by acid clouds. Johnson (1987), using data from Lovett et al. (1982), showed that the H_2SO_4 and HNO_3 input, including cloud drip, on Mt. Moosilauki (1400 m), are three and five times greater respectively, than the inputs at Hubbard Brook, just 12 km away. The fact that 26% of the red spruce biomass survived in 1986 was no doubt related to the self-fertilization resulting from the mineralization of dead and dying trees which were then being released at a rate faster than they were being leached by acid from the soil. It is apparent that at locations where mortality occurred over large areas, close to a major source of SO_2 emission, such as at the nickel smelters at Sarnia, Ontario, the rate of H_2SO_4 input to the soil had been greater than the rate of nutrient release from mineralization. This explains why the soil would not support vegetation without prior fertilization when tested in the laboratory as found by Hutchinson and Whitby (1977).

Although the timing of the reduction in growth in the early 1970's at Hubbard Brook coincided with the reduction in SO_2 emissions, it is probably related more closely to the initial inventory of calcium on exchange sites, the rate of acid input, the rate of weathering, and the tree species. In the higher mountain areas the growth reduction occurred in the early 1960's. The 1992 EPA data on SO_2 and NO_x emissions that appear to be closely related to the period of increased growth as measured by Hornbeck and Smith (1985) indicate that the problem of reduced growth of red spruce started about 70–80 years after acid rain entered the soil. Likens et al. (1998) estimated the loss to the stream of exchangeable Ca^{2+} and organically combined calcium, between 1962 and 1982, was of the order of 397–461 $\text{kg ha}^{-1} \text{ year}^{-1}$. Judging from the area of SO_2 emissions under the curve in Figure 4(A) the loss prior to 1960 was at least equal to, and probably 1.5 times greater, of the order of 400–600 $\text{kg ha}^{-1} \text{ year}^{-1}$, resulting in a total Ca loss of the order of 800–1000 kg ha^{-1} , from 1900 to 1982. Unfortunately, in spite of the fact that biomass growth has stopped at Hubbard Brook, the loss of Ca^{2+} to stream water is continuing, removing the Ca^{2+} formed in weathering, and deposited in dust and rain, and also resulting in a continuing drain on that formed on the watershed by mineralization of accumulated organically combined calcium that had been previously retained in biomass.

The same chemical reactions that have caused this loss will also lead to loss of biomass growth in any other area of the world impacted by acid rain where, because of the rate of acid input, the rate of loss of Ca^{2+} , or other cationic nutrient, is greater than its rate of input to biomass. This applies not only to forest soils but also to field and cropland, from which animals and humans obtain their nutrients, but because of the difference in biomass, a different time frame will be involved. In limestone and other calcareous soils there is an abundance of easily weathered Ca. However it is in such soils that potassium is likely to become deficient and the Ca^{2+} will act as an antagonist as occurred at Ebnat in southern Germany as shown in Table 1. The high molar ratio of Ca:K of 45:1 at this site resulted in K deficiency, the foliar value of K being

2.9 mg g^{-1} compared with the threshold deficiency value of 4.0 mg g^{-1} . Fertilization with K increased the value to 5.1 mg g^{-1} (Hüttel 1985). Although it is normal to fertilize crops where the profit will cover the cost, fertilization of the vast forests of North America is a virtually impossible task. However, small scale fertilization studies are of great value for diagnostic purposes.

10. Biomass growth and global warming

The earth is warmed from the sun by visible light that has wavelengths in the range of 4000–7000 Å units. Warmth is radiated from earth in the infrared range that has a wavelength of over 7000 units. Whereas the atmosphere is largely transparent to visible light, certain gases, chiefly carbon dioxide and water vapor, retain heat otherwise radiated from the earth through the atmosphere, the extent depending on their concentrations. Since the average water content of the atmosphere increases with its temperature, the concentration of CO_2 plays a key role in our climate. The combustion of carbon-containing fossil fuels is increasing, from year to year, the quantity of the total CO_2 in the atmosphere. The growing forests and their soils form an active sink for CO_2 , reducing its concentration during periods of growth and increasing it during periods of biomass death and decay. A detailed discussion of Global Warming is beyond the scope of the present paper. However, the results at Hubbard Brook appear to have some relevance to this problem and should be examined more closely. Fan et al. (1998) have pointed out that the concentration of CO_2 in the atmosphere passing over the North American continent actually decreases between the Pacific Ocean on the west coast and the Atlantic coast on the east. This indicates, surprisingly, that in North America a greater amount of CO_2 is being taken up in biomass growth than is presently being generated in emissions. Their data indicates that the increasing concentration of CO_2 in the Northern Hemisphere results from higher net emissions from the North Africa and the Eurasia continental areas that reach the North American west coast. They estimate that in North America $1.7 \pm 0.5 \text{ Pg year}^{-1}$ of CO_2 , calculated as C, are taken up by biomass ($\text{Pg} = 10^{15} \text{ g}$) compared with 1.6 Pg year^{-1} released in emissions. They suggest that this could result from an increase in growth of biomass resulting from a combination of increased NO_x deposition, warmer temperatures and increased CO_2 , as well as forest regrowth on abandoned farmland and in previously logged forests. Fan et al. (1998) acknowledge that there is considerable uncertainty as to the magnitude of the increase, and that the cause is unknown. They state that in addition to other requirements, ‘intensive atmospheric sampling, and ecological field studies to identify the location and cause of North American terrestrial CO_2 uptake’ are required. The possibility should be considered that in areas with higher initial concentrations of Ca^{2+} , or other nutrients in the soil, growth is still proceeding at an increased growth rate as a result of acid rain.

In a recent review, Wofsy (2001) in a discussion of papers on global warming by Pacala et al. (2001) and by Fang et al. (2001) published in the same issue,

headlined his paper “Where Has All The Carbon Gone?” He noted that more than 2 billion tons of carbon (25% of the carbon emitted by fossil fuel combustion) are being sequestered by forests each year. Although inverse models for studying atmospheric concentrations of CO₂ suggest that mid-latitude forests in North America and Eurasia are crucial carbon sinks, forest inventories indicate that they sequester much smaller amounts of carbon. Wofsy then states and asks “thus we have a mystery: if our forests are sequestering billions of tons of carbon annually, why can’t we find it?” He then suggests we look in the organic matter not considered commercially valuable, and points out that Pacalla et al. indicate that 75% of the carbon sequestered in the United States is not inventoried. In discussing the Fang et al. paper he noted that in China, by means of reforestation and afforestation, they had reversed a situation in which degraded forests had released 0.022 Pg of carbon per year from 1948 to 1980 to one in which they accumulated 0.021 Pg in 1998. They had not been measuring biomass and all their data had been based on timber volumes requiring relatively complex measurements and calculations to convert the inventories to biomass equivalents. Wofsey pointed out that we need to develop a ‘scientific basis for measuring and improving the properties of forest carbon sinks’.

Observations in Germany and other European countries have also indicated that a surprising increase in forest growth has been taking place without any clear explanation as to why (Spiecker 1996). The hypothesis that this increase could result from ‘acid fertilization’ presumably has apparently not yet been considered, and indeed this may seem hardly credible in view of the many observations of decreased growth which immediately preceded the death of red spruce and other species on Camels Hump as well as Norway spruce in certain areas of Germany. However, based on the assumption that the soil was first affected by acid rain in 1880, this decrease occurred on Camels Hump following approximately 85 years of increased growth, while at Hubbard Brook, incremental biomass growth slowed after about 80 years of increased growth and stopped after about 100 years. However it should be noted that an earlier forest on Watershed 6 had been harvested in about 1916, and that the present forest was only about 65 years old when growth stopped. These growth changes occurred on glaciated soils and it is possible that in other areas of North America and Europe, with higher exchangeable and organic calcium and other nutrient cations in the soil and/or, less acid deposition, a substantially longer period of increased biomass growth could precede a reduction and stoppage as occurred at Hubbard Brook. If this should prove to be the case, it can subsequently lead to a major increase in atmospheric CO₂ concentration when biomass growth stops as is, no doubt, already occurring on a much smaller scale in parts of the northeast US and adjacent areas of Canada.

Sterba (1996) observed that *trees in many areas of Austria and Germany have been growing at substantially higher rates than predicted from growth tables that had been prepared approximately 100 years earlier*. For instance on the Austrian Massif increases in the incremental heights of spruce were two and even three

times greater than that predicted by the 1896 Guttenberg Tables (Guttenberg, 1896). In another example he found that “the increment of dominant pines vastly exceeded the predictions for stem analysis at the very same site from which Guttenberg made in his 1896 Table”. He also compared the annual ring width of 120 year old and 80 year old spruce trees when they were each 30 years old with the values being 1.8 mm in 1887 and 2.5 mm in 1927. Sterba pointed out that in a number of cases in which it had been stated that trees showing decline symptoms were at the same time showing increased growth. *This latter appeared to be based on Growth Table values and that in most cases there was no evidence of actual incremental increase.*

The increased rate of forest growth in Europe paralleled that resulting from acid deposition in Hubbard Brook. Similar increased growth no doubt has occurred, or is still occurring throughout much of the U.S. and Canada where the impact of acid rain has been less, and /or the initial nutrient content of the soil was greater. The amount of incremental biomass growth and the period when growth slowed and stopped depends on the nutrient accumulated on storage sites in the pre-industrial era, the rate of acid deposition and other factors. Houghton et al. (1999) pointed out that large amounts of CO₂ were released in the U.S. during the 1800's due to forest clearing and fire and that the decrease in the CO₂ inventory during the 1900's results from forest re-growth. The possibility that missing carbon is also related to acid fertilization should be considered. This is important from the standpoint of the continuing loss of nutrients, which unless SO₂ emissions are greatly curtailed will, in areas less impacted by acid rain than Hubbard Brook, be still in the increased growth phase, and have yet to reach the period of zero biomass growth. Such forests, unless fertilized to replace the missing nutrients, will not again be able to become a sink for CO₂.

11. Summary and discussion

The effect of acid rain has been to greatly increase the loss of three elements of mineral origin from the soil: Ca, Mg and K. These originate in the rock fragments present in the soil where, while still imbedded in the rock, they are unavailable for plant life, but become available as a result of the chemical weathering reaction. As a result of the naturally occurring presence of H₂CO₃ in the soil during pre-industrial times, the positively charged cations Ca²⁺, Mg²⁺ and K⁺ were liberated from the minerals in which they were held and, because of their positive charge, were stored on exchange sites provided by the negatively charged clay particles produced as a byproduct of the weathering of silicate minerals. In addition, they formed salts with humic acid, a decomposition product of rotting woody matter. These cations are essential to all vegetable and animal life, and in areas where one or more of the minerals present in the soil are lacking in a nutrient cation, this has been brought in from other geological areas in dust and rain during past centuries. These

conditions, in the absence of significant losses from acid leaching in pre-industrial times, resulted in the accumulation of very large inventories of Ca^{2+} and other nutrient cations in the soil. Because of the low concentration of these nutrients in the soil solution the trees had developed a very large system of fine roots that allowed them to continue growth on the same land for many thousands of years.

Unfortunately the trees ability to survive made it difficult to recognize symptoms indicating the serious effect that acid deposition is having on the forest. The Hubbard Brook investigations have supplied extremely useful, but disturbing, information regarding its effects. With measurements of all of the transfers of Ca^{2+} in and out of the soil of a forested watershed, these studies have shown that the first effect of acid rain was to increase the Ca^{2+} concentration of the soil solution, to increase the growth rate of the trees and to increase the loss of Ca^{2+} to the stream at an unsustainable rate. What was surprising was that it took approximately 80–90 years before the growth rate slowed down, and another 10 or more before the net biomass incremental growth on the watershed came to a virtual stop. Since the trees continued to replace their foliage each year, this could not have been suspected without the evidence provided by these studies, (Likens et al. 1998). Particularly disturbing was the finding that, regardless of the stoppage of net biomass growth on the watershed, the SO_4^{2-} and NO_3^- ions in the soil solution continued to carry, in the 1982–1992 period, a total of $7.79 \text{ kg ha}^{-1} \text{ year}^{-1}$ of Ca^{2+} of which $3.56 \text{ kg ha}^{-1} \text{ year}^{-1}$ were supplied by weathering and by dust and rain, with the balance being supplied from the mineralization of recycled organic calcium. Friedland and Miller (1999) also established that incremental net biomass growth had virtually stopped on their Esther Mountain plot and that the effluent from the soil, sampled from below the rooting zone, carried away most of the Ca^{2+} that entered the soil from weathering and from dust and rain. The continuing absence of incremental net biomass growth on these, and related plots, with the soil being continuously denuded of the incoming Ca^{2+} , will result in a continuing decrease in the net biomass in these areas as well as in the ability of the forest to regenerate after harvest, unless and until acid emissions are greatly reduced.

Likens' studies, when coupled with those of Hornbeck and Smith (1985), of Bondietti et al. (1990) and of Friedland and Miller (1999), indicate that a similar sequence of increased growth at an unsustainable rate was involved throughout the northeast U.S. when acid rain first entered forest soils. Because of the very large initial quantity of Ca^{2+} on the exchange sites in the soil, it took 90 or more years before large numbers of trees on Camels Hump and Whiteface Mountain died. It is hypothesized, on the basis of strong chemical evidence, that the same mechanisms are involved in other areas subject to acid rain. As can be seen from the data in Table 2, passage of the acid rain through the forest soil, extracted not only Ca^{2+} , but also Mg^{2+} and K^+ , so that the continuing loss of any one of these nutrients, if it is limiting growth, can lead to deficiency, depending on its relative concentration in the soil and that of the antagonistic cation. In Table 2, one can compare the cation concentration of

the stream water with that of the corresponding input in rain, and note that each nutrient had continued to be extracted by the acid from the soil. Moreover, the SO_4^{2-} and NO_3^- anions will continue to extract the nutrient cations as long as they are still present in the soil. As stated in Section 9, it appears that approximately $800\text{--}1000 \text{ kg ha}^{-1}$ of Ca^{2+} had been lost from the soil in approximately 80 years. This can be compared with the 750 kg ha^{-1} of Ca^{2+} , the total amount that had been taken up by the net biomass on Watershed 6 by 1992, when its growth had stopped. In forests where there may have been more Ca^{2+} in the soil, or where there is less acid in the rain, it can be expected that depletion will occur years later than at Hubbard Brook. This question should be considered in forests now showing a high rate of growth, since once the transfer of a nutrient cation is depleted, incremental biomass growth, on an area basis, will cease. Conclusions in relation to the four questions that were asked at the start of this paper are as follows.

1. Studies in Europe and North America, including those in the northeast U.S. discussed in this paper indicate that *the primary cause of the forest decline is nutrient deficiency resulting from acid leaching of cationic nutrients from the soil*. The indication from symptoms that deficiency was involved, was established by analysis of the foliage, of the underlying soil, and by test fertilization studies.
2. It has been found that when several trees die within a few years, resulting in the opening of the canopy, relatively rapid growth of seedlings takes place, while in other cases when only a few trees die in a certain area, adjacent trees frequently lose their deficiency symptoms. In each of these cases *this results from the retention of the nutrients from dead foliage, fine roots, and other woody material on exchange sites and its subsequent transfer to new growth. This may suggest, erroneously, that the problem has gone away, or was unrelated to acid rain.*
3. The effect of acid deposition on the forest, when it first occurred in 1900 or earlier, was to increase the rate of transfer of Ca^{2+} and other nutrient cations from the exchange sites in the soil to the soil solution at a rate related to the rate of H^+ input. The resultant increase in concentration of Ca^{2+} in the soil solution resulted both in increased biomass growth and in its rate of loss in drainage water from the soil. Because of the earlier limited amount of H^+ ions resulting from H_2CO_3 acidification, the soil had accumulated a very large inventory of Ca^{2+} in pre-industrial times that was depleted at Hubbard Brook in the 1980's when biomass growth stopped. It is now apparent from the fundamental nature of the chemistry involved *that growth increase must have occurred in all forests that have received a significant amount of acid rain, and that it may be still occurring in areas where the initial nutrient content was higher or the acid input is less*. The effect on biomass growth was obviously not investigated when this change first occurred. This was also not initially understood in the 1970's and early 1980's when the problem of tree decline was being intensively studied. This has

now become apparent as a result of the studies described in this paper. The relatively rapid growth of trees in many areas, together with the indication of regeneration in areas where trees had died, erroneously suggested to many that the nutrient leaching from forest soils could not have caused the problem of forest decline. What had not been understood is that the depletion of the cationic nutrients takes many decades before deficiency symptoms occur, and that *the problem resulting in termination of net biomass growth will continue until acid emissions are reduced to the point where the rate of nutrient loss from the soil is less than its rate of entry.*

4. It is difficult to predict the timing of future events, but *it is important that emissions of SO_2 and NO_x be quickly and substantially reduced. It has been shown that once the inventory of Ca^{2+} that had built up in pre-industrial times is depleted, net biomass growth, on an area basis, stops, while the Ca^{2+} and other cationic nutrients entering the soil from dust and rain, weathering, and mineralization, will continue to be lost to the stream.* Because of the ability of trees to take up the nutrients that are released to exchange sites as neighboring trees die, the forest will no doubt remain green for many years. A rapid death of a large number of trees is not likely to occur on Watershed 6 since the leaching loss is controlled by the acid throughput. However, without fresh nutrient input and with the continuing loss of nutrients recycled from mineralization, the forest will become increasingly subject to a decrease in live biomass. *Without net biomass growth per hectare, the dying trees are a source, rather than a sink for CO_2 , as the organic matter rots away. This indicates a serious linkage between acid deposition and global warming that should be investigated.*

Acknowledgements

The author wishes to express his gratitude to Dr. Gene Likens for helpful discussions relating to this subject.

References

- Baker D.J. et al. 1993. National Acid Precipitation Assessment Program 1992 Report to Congress.
- Bell C.W. and Bidulph O. 1963. Translocation of calcium. Exchange versus mass flow. *Plant Physiol.* 38: 610–614.
- Bernier B. and Brazeau M. 1980. Foliar nutrient status in relation to sugar maple decline in the Quebec Appalachians. *Can. J. Forest Res.* 18: 754–761.
- Bondietti E.A., Momoshima N., Shortle W.C. and Smith K.T. 1990. A historical perspective on divalent cation trends in red spruce stemwood and the hypothetical relationship to acidic deposition. *Can. J. Forest Res.* 20: 1850–1858.
- Coote D.R., Siminovitch D., Singh S.S. and Wang C. 1981. Contribution 119, Land Resources Institute. Agriculture Canada Publishers Ottawa, pp. 1–25.
- Clarkson D.T. 1969. Ecological aspects of aluminum toxicity and some possible mechanisms of resistance. In: Rorison I.H. (ed) *Ecological Aspects of Mineral Nutrition of Plants*. Blackwell Scientific Publishers, Boston, pp. 381–397.

- Driscoll C.T., Lawrence C.B., Bulger A.J., Butler T.J., Cronan C.S., Eagar C., Lambert K.F., Likens G.E., Stoddard J.L. and Weathers K.C. 2001. Acidic deposition in the northeastern United States: sources and inputs, ecosystems effects, and management strategies. *Bioscience* 51: 180–198.
- Enders H.-P. and Evers F.H. 1997 In: Hüttl R.F. and Schaaf W. (eds) *Magnesium Deficiency in Forest Ecosystems*. Kluwer Academic Publishers, Boston, pp. 4–5.
- Fan S., Gloor M., Mahlman J., Pacala S., Sarmiento J., Takahashi T. and Tans P. 1998. A large terrestrial carbon sink in North America implied by atmospheric and oceanic carbon dioxide data and models. *Science* 282: 442–446.
- Fang J., Chen A., Changhui P., Shuqing Z. and Longjun C. 2001. Change in forest biomass carbon storage in China between 1949 and 1998. *Science* 292: 2320–2322.
- Friedland A.J. and Miller E.K. 1999. Major-element cycling in a high-elevation Adirondack forest: patterns and changes, 1986–1996. *Eco. Appl.* 9 (3): 938–967.
- Guttenberg A.V. 1896. Die Aufstellung von Holzmassen- und Geldertragstafeln von Stammanalysen. *Österr. Vierteljahresschr. Forstwes. Wien* 36: 203–237; 319–345.
- Hendershot W.H. 1991. Fertilization of sugar maple showing dieback symptoms in the Quebec Appalachians, Canada. *Fert. Res.* 27: 63–70.
- Hornbeck J.W. and Smith R.B. 1985. Documentation of red spruce growth decline. *Can. J. Forest Res.* 15: 1199–1201.
- Hutchinson T.C. and Whitby L.M. 1977. The effects of heavy rainfall and heavy particulates on a boreal forest ecosystem near the Sudbury smelting region of Canada. *Water Air Soil Poll.* 7: 421–438.
- Houghton R.A., Hackler J.L. and Lawrence K.T. 1999. The U.S. carbon budget: contributions from land-use change. *Science* 285: 574–578.
- Hüttl R.F. 1985. In: *Neuartige Waldschäden und Nährelementversorgung von Fichtenbeständen (Picea abies. Karst.) in Südwestdeutschland*. Thesis, Freiburger Bodenkundliche Abhandlungen, Vol. 16. Freiburg, Germany (See also Tomlinson and Tomlinson 1990. CRC Press Publishers, Boca Raton, FL, USA, pp. 34–39; 139–165)
- Jenny H. 1980. *The Soil Resource*. Springer-Verlag Publishers, New York, p. 87.
- Johnson A.H. 1987. Deterioration of red spruce in the northern Appalachian Mountains. In: Hutchinson T.C. and Meema K. (eds) *Effects of Atmospheric Pollution on Forests, Wetlands and Agricultural Ecosystems*. Springer Verlag Publishers, New York, p. 85.
- Johnson N.M., Driscoll C.T., Eaton J.S., Likens G.E. and McDowell W.H. 1981. Acid rain, dissolved aluminum and chemical weathering at the Hubbard Brook Experimental Forest, New Hampshire. *Geochim. Cosmochim. Ac.* 45 (9): 1421–1437.
- Jorns A. and Hecht-Buchholz C. 1985. Aluminiuminduzierter magnesium-und-calcium mangel in laborversuch bei Fichtensämlingen. *Allg. Forstz.* 40 (46): 1248–1252.
- Kirby E.A. and Pilbeam R.J. 1984. Calcium as a plant cell nutrient. *Plant Cell Environ.* 7: 7–405.
- Ledin S. and Wiklander L. 1974. Exchange acidity of wheat and pea roots in salt solution. *Plant Soil* 41: 403–413.
- Likens G.E. and Bormann F.H. 1995. *Biogeochemistry of a Forested Ecosystem*, 2nd ed. Springer-Verlag, New York.
- Likens G.E., Driscoll C.T. and Buso D.C. 1996. Long term effects of acid rain: response and recovery of a forest ecosystem. *Science* 272: 244–2246.
- Likens G.E., Driscoll C.T., Buso D.C., Siccama T.G., Johnson C.E., Lovett G.M., Fahey T.J., Reiners W.A., Ryan D.F., Martin C.W. and Bailey S.W. 1998. The biogeochemistry of calcium at Hubbard Brook. *Biogeochemistry* 41: 89–173.
- Lovett G.M., Reiners W.A. and Olson R.K. 1982. Cloud droplet deposition in subalpine balsam fir forests: hydrological and chemical inputs. *Science* 218: 303–1304.
- Miller E.K. and Friedland A.J. 1999. Local climate influences on precipitation, cloud water, and dry deposition to an Adirondack subalpine forest: Insights from observations 1986–1996. *J. Environ. Qual.* 28 (1): 270–277
- Ouimet R. and Fortin J.M. 1991. Growth and foliar nutrient status of sugar maple: incidence of forest decline and reaction to fertilization. *Can. J. Forest Res.* 22: 699–706.

- Pacala S.W. et al 2001. Consistent land- and atmosphere-based carbon sink estimates. *Science* 292: 2316–2320.
- Painter T.J. and Purves C.B. 1960. Polysaccharides in the inner bark of white spruce. *TAPPI* 43: 729–736.
- Russell R.S. 1977. *Plant Root Systems: Their Function and Interaction in the Soil*. McGraw-Hill Publishers, London.
- Sharpe W.E. and Drohan J.R. 1999. *The Effects of Acidic Deposition on Pennsylvania's Forests*. Environmental Resources Research Institute Publishers, University Park, PA 16802, USA.
- Shear C.B. and Faust M. 1970. Calcium transport in apple trees. *Plant Physiol.* 45: 670–674.
- Simson B.W. and Timell T.E. 1978. Polysaccharides in cambial tissue of *Populus tremuloides* and *Tilia americana*. 1. Isolation, fractionation and chemical composition of the cambial tissue. *Cell. Chem. Technol.* 12: 39–50.
- Sparks D.L. 1986. *Soil Physical Chemistry*. CRC Press Publisher, Boca Raton, FL, USA, pp. 56–63.
- Spiecker H. 1996. *Growth Trends in European Forests*. European Forest Institute Research Report No. 5. Springer-Verlag Publishers, Berlin.
- Sterba H. 1996. Forest decline and growth trends in Central Europe – a review. In: Spiecker et al. (eds) *Growth Trends in European Forests*. European Forest Institute Research Report No 5. Springer-Verlag Publishers, Berlin, pp. 189–199.
- Timell T.E. 1965. Wood and bark polysaccharides. In: Coté W.A. (ed) *Cellular Ultrastructure of Woody Plants*. Syracuse University Press Publishers, Syracuse, NY, pp. 127–156.
- Tomlinson G.H. 1987. Acid deposition, nutrient imbalance and tree decline: a commentary. In: Hutchinson T.C. and Meema K.M. (eds) *Effects of Atmospheric Pollution on Forests, Wetlands and Agricultural Ecosystems*. Springer-Verlag Publishers, New York, pp. 189–199.
- Tomlinson G.H. 1990 In: Tomlinson G.H. and Tomlinson F.L. (eds) *Effects of Acid Deposition on the Forests of Europe and North America*. CRC Press Publishers, Boca Raton, FL USA, p. 33 and pp. 133–135.
- Tyler G., Berggren D., Bergkvist B., Falkengren-Grerup U., Folkesson L. and Ruhling Å. 1987 In: Hutchinson T.C. and Meema K.M. (eds) *Effects of Atmospheric Pollution on Forests, Wetlands and Agricultural Ecosystems*. Springer-Verlag Publishers, New York, pp. 347–359.
- Ulrich B. 1986. Natural and anthropogenic components of soil acidification. *Z. Pflanz. Bodenkunde* 149: 702–717.
- Ulrich B. and Matzner E. 1986. Anthropogenic and natural acidification in terrestrial ecosystems. *Experientia* 42: 344–350.
- Vogelmann H.W., Perkins T.D., Badger G.J. and Klein R.W. 1988. A 21 year record of forest decline on Camel's Hump. Vermont, USA. *Eur. J. Forest Pathol.* 18: 240–249.
- Wofsy S.C. 2001. Where has all the carbon gone? *Science* 292: 2261–2263.
- Wood T., Bormann F.H. and Voight G.K. 1984. Phosphorus cycling in a northern hardwood forest: biological and chemical control. *Science* 227: 391–393.
- Zöttl H.W. and Hüttel R.F. 1986. Nutrient supply and forest decline in southwest Germany. *Water Air Soil Poll.* 31: 255–256.
- Zöttl H.W., Hüttel R.F., Fink S., Tomlinson G.H. and Wisniewski J. 1989. Nutritional disturbances and histological changes in declining forests. *Water Air Soil Poll.* 48: 87–109.