PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY B BIOLOGICAL SCIENCES

Deposition-Plant-Soil Interactions [and Discussion]

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Deposition–plant–soil interactions

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Rainwater reaching the ground as throughfall beneath vegetation usually shows an increase in pH, except in areas where sulphur dioxide deposition can be presumed to be high. Stemflow, however, is almost always reduced in pH. The changed acidity in throughfall results from hydrogen-ion exchange for base cations at leaf surfaces, with evidence that potassium, calcium and magnesium are all involved. Amounts of base cations gained are much greater than the losses of hydrogen ions from bulk precipitation. Either other processes are involved, or the extra base cations exchange for acidity resulting from dry deposition of sulphur dioxide. Further interpretation is confounded by the lack of general agreement as to the relative contributions of dry deposition and of crown leaching to the sulphate gained by throughfall. Usually plants are able to replace leached cations, even when treated with very low pH rain. However, there are suggestions from Germany that exceptional rates of leaching of magnesium from tree foliage may be leading to growth decline and death. For such extreme losses to occur cell membranes must first be damaged, with gaseous pollutants, such as ozone and sulphur dioxide, and frost both being implicated. Because the base cations gained at leaf surfaces had previously been exchanged for hydrogen ions at the root–soil interface, exchange in the crowns is merely an extension of the soil exchange process and can be regarded as an acid stress upon the soil.

INTRODUCTION

There is general agreement as to which processes might lead to alterations in the chemistry of rainwater passing through vegetation, and reasonable concurrence as to the significance of these changes for subsequent soil–water interactions. However, although most studies of rainwater chemistry above and below a canopy have produced comparable results, interpretations in terms of the relative contributions of the different processes involved vary widely. At one extreme, some authorities suggest that the enrichment, or gain, of certain elements by rainwater is due largely, even entirely, to the acquisition of elements originally deposited on vegetation surfaces from the atmosphere, a process that Ulrich (1983) described as interception deposition. The other extreme is to ascribe much of the change to the acquisition of elements derived, by one means or another, from within the plant, a process now generally termed foliar or crown leaching (Tukey *et al.* 1958).

Vegetation will intercept fog, sea-spray, dry salts, and soil- and pollution-derived minerals and gases. This interception is dependent on turbulent transfer, which provides the momentum for a particle to penetrate the boundary layer, and on impaction of the particle on the vegetation surface without subsequent reinsertion into the atmosphere. It can be predicted, therefore, that input should increase with the aerodynamic roughness of the surface (Miller & Miller 1980) and that, by Stokes's law, interception should be greater on fine, needle-like, leaves than on larger obstacles. Indeed, there is recent evidence to suggest that the input of atmospheric strontium is larger to a spruce-fir stand than to a neighbouring aspen stand (Graustein & Armstrong 1983). It can also be assumed that where the capture is dependent on chemical reactions, as could be expected for gases at least, then the efficiency will be dependent on the rate at which metabolic processes regenerate the sink. Gases that are known to be captured include SO_2 (Garland & Branson 1977) and NH_3 (Tjepkema *et al.* 1981), but no doubt others can also be trapped, including nitric acid gas.

Crown leaching has been known for a long time, having been variously termed both excretion and recretion (Mes 1954). Using radioactive isotopes, Tukey *et al.* (1958) found that the relative ease of leaching was ^{22}Na, ^{54}Mn (amount leached equivalent to 25–45% of amount in leaf) more than ^{45}Ca, ^{28}Mg, ^{35}S, ^{42}K, ^{90}Sr–^{90}Y (1–10%) more than $^{55-59}Fe$, ^{65}Zn, ^{32}P, ^{36}Cl (< 1%). Subsequently, Tukey (1970) suggested that cations leached were derived both from the 'free space' between cells and through hydrogen-ion exchange at the leaf surface, little or no cations being leached from directly within the cell. Hydrogen-ion exchange at leaf surfaces results in a reduction in the acidity of throughfall water.

CHANGES IN ACIDITY

Although most reports are of an increase in pH as rainwater passes through trees, there are a number of pronounced exceptions. The available data from those studies that covered at least one full year are summarized in figure 1. This information would suggest that reductions in pH are largely limited to older (more than *ca.* 60 years) conifers, prime exceptions being the oak and birch studied by Skeffington (1983) at Tillingbourne, and, to a lesser extent, the beech at Solling (Matzner *et al.* 1982). At both these areas the incident pH was low, being 4.2 at Tillingbourne and 4.1 at Solling. These stands apart, there seems little reason to suggest that broadleaved species and young conifers (less than *ca.* 60 years) differ appreciably in their effects on throughfall pH. The series of 25- to 30-year-old Sitka spruce studied in Scotland would suggest a general tendency for pH changes to become more pronounced with increasing pH of incident rainfall.

The effect of age of conifer stands is most marked. Indeed, in the series of stands studied at Glen Tanar only beneath the 110-year-old Scots pine was throughfall pH depressed, while there was a consistent increase beneath the 45-year-old stand of the same species only 500 m away. A similar effect of age has been recorded by Binkley *et al.* (1982) who found that over the summer months the pH of throughfall averaged 5.9 beneath 15-year-old Douglas fir as against 4.7 beneath a neighbouring 70- to 90-year-old stand comprising Douglas fir, western hemlock and western red cedar. The pH of the bulk precipitation was 4.5, so in this case even the old stand reduced the acidity of the throughfall, at least during the summer months. Generally, effects on throughfall pH are most pronounced in summer, even for evergreen coniferous species (figure 2), although for Sitka spruce, at least, removal of hydrogen ions continues throughout the winter. However, five years of data from six stands of this species in widely separated parts of Scotland and northern England suggest that where the average pH of the incident rain is low the throughfall develops an annual oscillation, neutralization reactions being least pronounced in the early months of the year and most pronounced in mid- to late-summer (Miller 1983). This pattern is quite unrelated to variations in the pH of incident rain at any one site and was not found at western sites where the rain pH is relatively high.

Other studies broadly confirm this pattern of a greater elevation of throughfall pH in the

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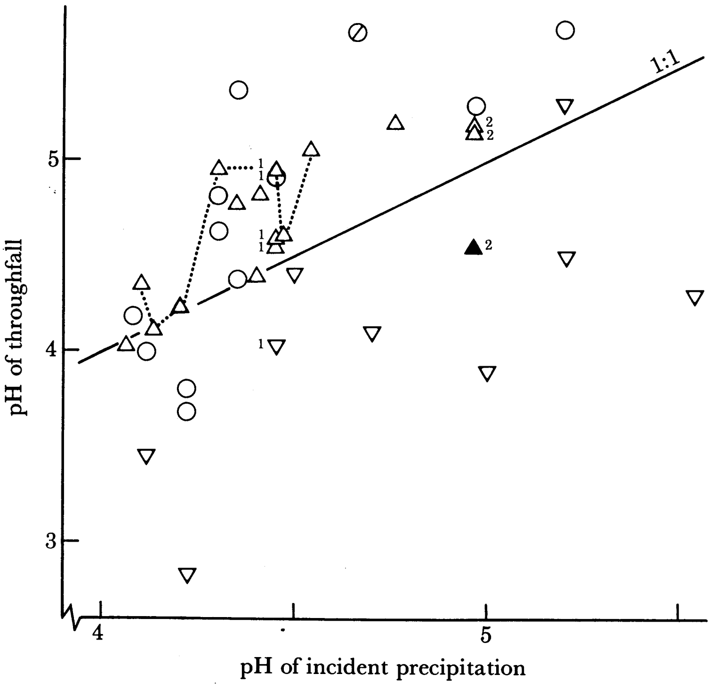

FIGURE 1. Throughfall pH as a function of that of incident precipitation, with data reported for studies that have covered at least one full year. Points represent: ○, temperate hardwood forests; ⊘, tropical hardwood forests; △, conifer forests of less than 60-year-old; ▽, conifer forests of more than 60-year-old; ▲, nitrogen deficient pine. Dotted line links seven stands of 25- to 30-year-old Sitka spruce studied with comparable techniques in Scotland (Miller & Miller 1980). Points identified 1 are from a study of a range of different species at Glen Tanar by the author and his colleagues whereas points identified 2 are for nitrogen deficient (closed triangle) and fertilized (open triangles) Corsican pine (Miller *et al.* 1976). Other data from Cole & Johnson 1977; Feller 1977; Hoffman *et al.* 1980*a*, Johnson *et al.* 1977; Mahendrappa 1984; Matzner *et al.* 1982; McColl & Bush 1978; Moore 1984; Nicholson *et al.* 1980; Nihlgård 1970; Olson *et al.* 1981; Richter *et al.* 1983; Robitaille & Laflamme 1984; Skeffington 1983.

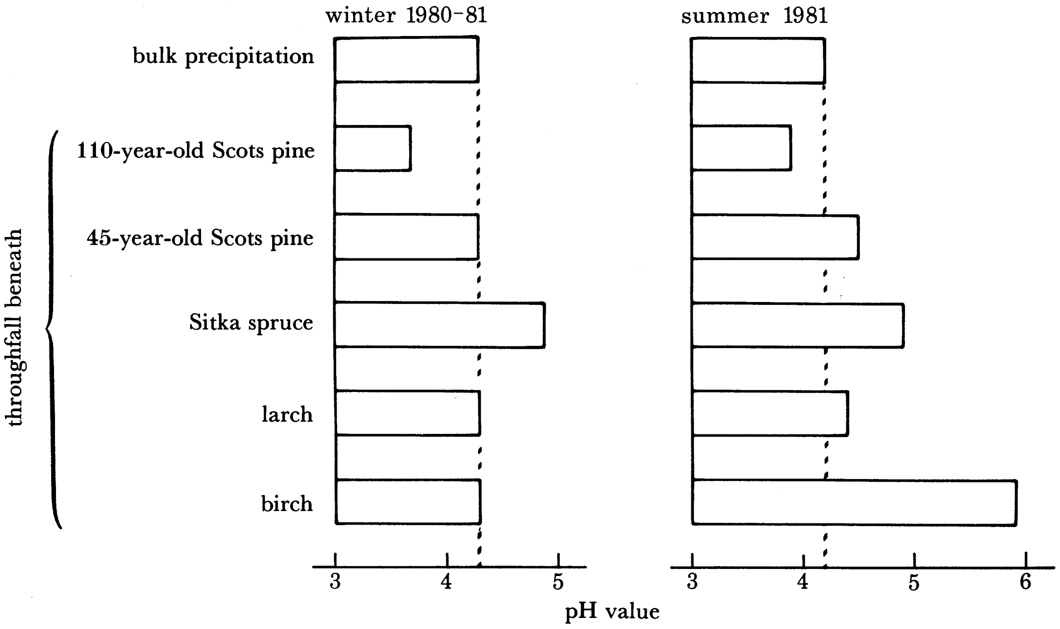

FIGURE 2. Seasonal effects on throughfall pH measured by the author and his colleagues beneath neighbouring stands of different species at Glen Tanar in northeast Scotland.

summer months, even for evergreen species, (Brinson *et al.* 1980; Hoffman *et al.* 1980*a*; Richter *et al.* 1983) suggesting that the rate of flux of base cations to the crowns may be an important factor. Richter (1983) found that throughfall acidity beneath two mixed hardwood stands was lower for the stand on the higher base status soil (table 1). It could then be expected that the application of base cations in fertilizers should increase the rate of hydrogen-ion exchange in the crowns. No such effect was found in six of the Sitka spruce stands identified in figure 1 in which paired plots had been treated with KCl and $Ca_3(PO_4)_2$, but neither did these treatments have any effect on growth so it may be that the supply of cations was never limiting. However, also identified in figure 1 are nitrogen deficient and fertilized Corsican pine from an experiment of the author and his colleagues at Culbin forest, in northeast Scotland. The pH of the throughfall beneath these nitrogen deficient trees was very much more acid than that of the received rain, this being the only example of acidification beneath young conifers in the data set used for figure 1. Following application of nitrogen fertilizer, however, the more typical removal of hydrogen ions from rainwater was observed, a change that was primarily matched by an increase in potassium ions in throughfall (table 2), perhaps reflecting the much enhanced potassium uptake stimulated by the nitrogen fertilizers (Miller *et al.* 1976). There was also a change from net foliar uptake of nitrogen in the deficient trees to a net release in the fertilized trees, but the changes in ammonium flux were largely balanced by changes in that of nitrate and are not sufficient to explain the observed effect on rainwater acidity.

TABLE 1. FLUX OF H^+ AND BASE CATIONS BENEATH MIXED HARDWOODS ON TWO SOILS OF DIFFERING BASE STATUS IN TENNESSEE (RICHTER *ET AL.* 1983)

(Units are kilomoles per hectare per year)

	H^+	base cations
bulk precipitation	0.60	0.47
throughfall		
Fullerton site (low base status)	0.24	1.25
Tarklin site (higher base status)	0.16	1.88

TABLE 2. EFFECT OF NITROGEN FERTILIZER ON GAINS OF H^+ AND BASE CATIONS IN NET RAINFALL BENEATH CORSICAN PINE (*PINUS NIGRA* VAR. *MARITIMA* (AIT.) MELV.)

	gains in unfertilized plots	change in gain in N fertilized plots
H^+	150	−190
K^+	180	+230
Ca^{2+}	200	−30
Mg^{2+}	350	−40
NH_4^+	−90	+110
NO_3^-	−60	+60

Rainwater also reaches the ground as stemflow. There are regrettably few reports of stemflow acidity but in almost all cases it is more acid than the received rainwater (figure 3). The data are insufficient to allow much useful speculation. The two reports from older conifers are the most acid of the data set in figure 3 and there is no difference in stemflow pH between the nitrogen deficient and fertilized pine. Although stemflow represents a relatively small flux of water it can exceptionally account for over half of the acidity reaching the forest floor (table 3). Furthermore, the acidity is concentrated in the small area around the base of the stem and this has been suggested to be the cause of the inverted saucer of enhanced podsolization sometimes found beneath old trees (see, for example, Skeffington 1983). It seems a plausible explanation, but it should also be borne in mind that increased podsolization could reflect the wetter environment in soil contiguous to stems (Gersper & Holowaychuk 1970).

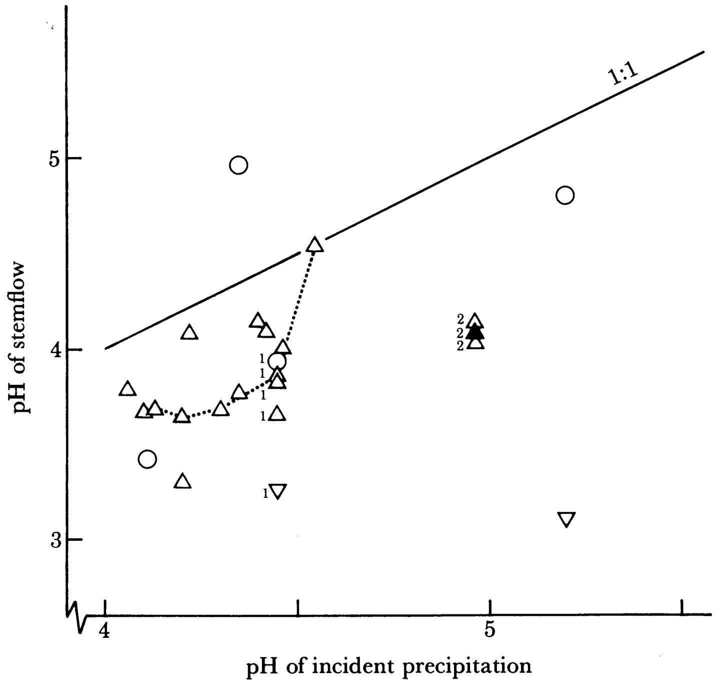

FIGURE 3. Stemflow pH as a function of that of incident precipitation, with data reported for studies that have covered at least one full year. For legend see figure 1. Data from studies by the author and by Matzner 1982; Nihlgård 1980; Olson *et al.* 1981; Robitaille & Laflamme 1984.

TABLE 3. DISTRIBUTION OF ACIDITY BETWEEN THROUGHFALL AND STEMFLOW OVER FIVE YEARS IN SIX *PICEA SITCHENSIS* STANDS IN SCOTLAND AND NORTHERN ENGLAND (MILLER & MILLER, UNPUBLISHED)

forest	throughfall eq H^+ ha^{-1} a^{-1}	stemflow eq H^+ ha^{-1} a^{-1}	stemflow as percentage of total
Leanachan	80	60	43
Elibank	200	70	26
Kilmichael	130	220	63
Strathyre	220	170	44
Fetteresso	380	150	28
Kershope	380	210	36

Stemflow amounts are found to be very variable, both between species and between sizes within the same species. Miller & Miller (1980) showed that for spruce the proportion of the incident rainwater that is channelled down stems increases with rainfall amount and decreases with tree height, to the extent that in the large spruce studied by Ulrich (see, for example, Ulrich 1983) at Solling there was no stemflow, despite copious amounts flowing down the adjacent beech.

FACTORS CONTROLLING THROUGHFALL ACIDITY

It is generally agreed that hydrogen-ion exchange occurs on leaf surfaces, although invariably the gain of base cations in throughfall greatly exceeds the amount of hydrogen ions lost from bulk deposition (table 4). Recently Ulrich summarized his views on the processes that may lead to enrichment of chemical elements in throughfall (table 5). On the basis of his observations in the field, supplemented with greenhouse experiments, he concluded that potassium and manganese are the only ions that are removed from within living tissue, that hydrogen-ions exchange exclusively for calcium and magnesium and that, apart from a limited leaching loss from senescent leaves, sulphur arrives entirely as interception deposition. This sulphur input would largely be as SO_2 and as such would be a source of introduced acidity in excess of that measured in bulk precipitation. Miller (1963), Nihlgård (1970) and McColl & Bush (1978) had all previously suggested, although without much supporting evidence, that interception deposition of SO_2 is important in explaining the elevated sulphate amounts they measured in throughfall. A more telling point is the observation of Richter *et al.* (1983) that the experimental reduction of inorganic sulphate levels in foliage, through application of urea, had no effect on the sulphate gain in throughfall, from which they concluded that a large proportion of the sulphate mobilized from the canopy was probably derived from atmospheric sources. The

TABLE 4. PROPORTION OF BASE CATION GAIN IN WATER PASSING THROUGH A FOREST CANOPY THAT CAN BE EXPLAINED IN TERMS OF LOSS OF HYDROGEN IONS FROM BULK PRECIPITATION

New Hampshire: *Fagus*, *Acer*, *Betula* (Eaton *et al.* 1973)	27 %
Tennessee: *Quercus*, *Carya*, *Liriodendron* (Richter *et al.* 1983)	30 %
Scotland: 5 *Picea sitchensis* plantations (Miller & Miller, unpublished)	12 % 15 % 17 % 25 % 50 %

TABLE 5. SOURCES OF ELEMENTS THAT ENRICH RAINWATER PASSING OVER TREES AS SUGGESTED BY ULRICH (1983)

source	comment
interception deposition of Na, Cl, S	only source apart from minor leaching from senescent leaves
leaching from senescent leaves of Na, Mg, Ca, Fe, Cl, NO_3, SO_4	amounts small, not more than 2–7 % of flux in throughfall
leaching of K and Mn from living tissue	a result of metabolic processes
cation exchange, H^+ for Ca^{2+} and Mg^{2+} bound to acidic groups	particularly in stomata
dissolution of minerals in intercepted dust	

published estimates for interception deposition of sulphates (table 6) suggests that much depends on the method of assessment.

Undoubtedly much of the sulphate gain beneath trees in polluted areas must be derived from intercepted SO_2 and related gases. However, the original observation of Tukey *et al.* (1958) that ^{35}S is moderately easily leached counsels caution over ascribing all the sulphate gain to

Table 6. Reported contributions of different sources to S in net rainfall

	bulk precipitation	interception deposition	crown leaching
	eq S ha^{-1} a^{-1}	eq S ha^{-1} a^{-1}	eq S ha^{-1} a^{-1}
Ulrich (1983)[1]			
Fagus sylvatica	1470	1620	90
Picea abies	1470	1620	0
Nicholson *et al.* (1980)[2]			
Pinus sylvestris	740	1060	510
Lindberg & Harris (1981)[3]			
Quercus, *Carya*, *Liriodendron*	810	330	870
Bache (1977)[4]			
Pinus nigra and *P. sylvestris*	870	1820	220

[1] Assumes leaching only occurs from senescent leaves.
[2] Estimated from regression on deposition to inert surface.
[3] By expansion from measured deposition rate on inert surfaces.
[4] Micrometeorological measurements, v_g of 3.8 mm s^{-1}. Data expanded from 153 to 365 days.

Table 7. Effect of acidity of intermittently applied mist on leaching of base cations from pinto beans and sugar maple (Wood & Bormann 1975)

	K^+	Ca^{2+}	Mg^{2+}
	meq leached per square metre of leaf		
	pinto bean		
mist pH 5	0.050	0.025	0.015
mist pH 3	0.330	0.295	0.230
	sugar maple		
mist pH 5	0.010	0.045	0.005
mist pH 3	0.030	0.125	0.020

atmospheric inputs. Parker (1983), in a recent review of the literature on throughfall and stemflow, cites evidence that precipitation amounts strongly correlate with sulphate gain in throughfall as support for a leaching source. He concludes that in unpolluted areas foliar leaching could account for more than half the sulphate in throughfall. In current studies by the author, comparison of the pattern of variation in relative sulphate gains beneath an inert surface (Miller & Miller 1980) and beneath trees across various sites, believed to receive different pollution loads, does not seem to show the sort of change in sulphate fluxes that might be expected had the leaching component been negligible. An accurate, and simple, means of separating the leaching component from input has still to be developed. Until this is available speculation and differences in interpretation will continue.

Several authorities, including Ulrich (table 5), consider that hydrogen-ion exchange on leaf surfaces is primarily for calcium and magnesium. However, the results in table 2 would suggest a predominant role for potassium. When Wood & Bormann (1975) applied acidified mist to laboratory grown plants (table 7) the leaching losses of magnesium, potassium and calcium all tended to increase with increasing hydrogen ion concentration in the misting solution, although the relative losses of calcium and magnesium altered with species. More recently Scherbatskoy & Klein (1983) showed that both yellow birch and white spruce seedlings in a greenhouse lost increasing amounts of potassium and calcium as pH of an intermittently applied mist was lowered from 5.7 to 4.3 and to 2.8.

TABLE 8. LEVELS OF MAJOR NUTRIENTS IN FIRST YEAR FOLIAGE COLLECTED FROM ADJACENT HEALTHY AND SICK 27-YEAR-OLD *PICEA ABIES* AT DREISESSEL, BAVARIA (BOSCH *ET AL.* 1983)

	adjacent trees		suggested deficiency level*
	healthy	sick	
	oven-dry mass (%)		
N	1.8	2.0	< 1.5
P	0.20	0.22	< 0.14
K	0.63	0.58	< 0.50
Ca	0.28	0.17	?
Mg	0.04	0.02	< 0.03

* Values for *Picea* spp. from Binns *et al.* 1980.

ACCELERATED FOLIAR LEACHING

Observations of an increasing flux of base cations in throughfall as rainfall pH declines also come from field experiments (Horntvedt *et al.* 1980), but until recently all evidence has been that these losses are easily replaced and that there is no decline in foliar nutrient levels (see, for example, Tveite 1980). Now, however, Rehfuess and his colleagues at Munich (Rehfeuss 1983; Bosch *et al.* 1983) are suggesting that an accelerated and unacceptable loss of foliar magnesium, and perhaps of calcium, may explain some, at least, of the forest damage presently of concern in Germany. They have compared adjacent healthy and sick trees at various sites (table 8). Both groups of trees seem well supplied with nitrogen, phosphorus and potassium but calcium levels are depressed and magnesium levels in the sick trees are invariably below the levels considered necessary for satisfactory growth. In addition the trees show the golden-yellow tips to older needles (Goldspitzigkeit) typical of magnesium deficiency.

According to Bosch *et al.* (1983) the progression of the disease is for the yellowing to first appear, and remain most pronounced, on the upper regions and more exposed side of the tree. The chlorosis is followed by needle necrosis, associated with invasion by secondary fungal species, and eventually premature shedding of older needles starts from the base and inner parts of the crown. Tree volume growth rapidly declines and within a few years death of scattered individuals or groups of trees occurs, while the matrix may remain green and apparently healthy. There are also indications of reduced root growth and impairment of the mycorrhizal association. Interestingly, as tree growth declines there is sometimes an increase in the vigour and spread of epiphytic lichens. Damage seems to be most severe on exposed ridge-tops and at high altitudes, but is found on a wide range of soil types, from moist and fertile brown earths to humus-iron podzols formed on acid rocks (Rehfuess 1983). Death has been reported of European silver fir, Norway spruce, Scots pine and European beech from sites including Fichtelgebirge, Frankenwald and Sudschwarzwald. In this context it should be noted that until now pronounced deficiencies of magnesium have been a rather rare occurrence in established forests, most reports being restricted to New Zealand and the northeastern United States, and even at these localities the damage is not severe and the symptoms are usually transient. Rehfuess (1983) notes that the symptoms on beech are reminiscent of those described for winter frost damage. Similarly Bosch *et al.* (1983) suggest that there was some agreement between the symptoms shown by damaged Norway spruce at high altitudes in the Bayerischenwald and those reported following late-winter frost damage to Sitka spruce in west Scotland.

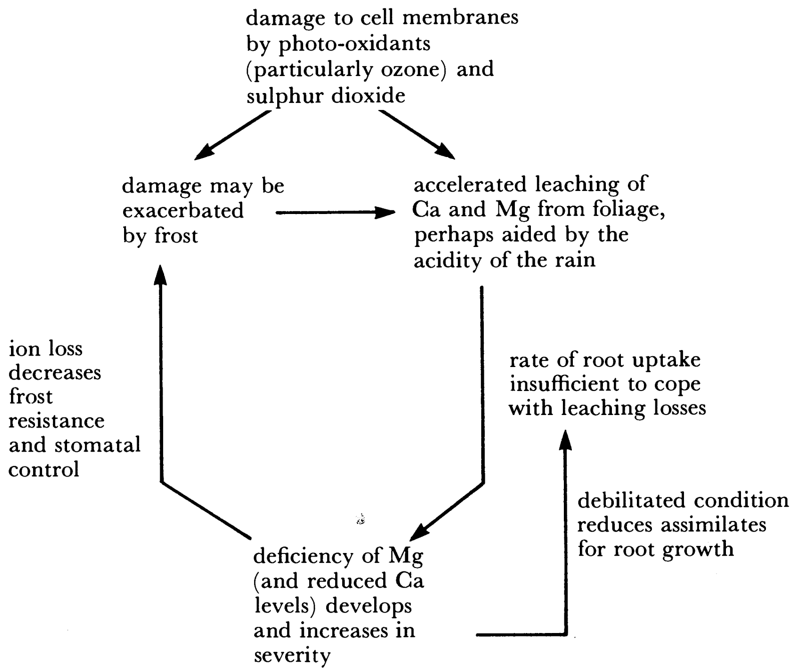

FIGURE 4. Possible explanation for the severe magnesium deficiency and consequent tree death observed in spruce forests of southern Germany as postulated by Bosch *et al.* (1983) and Rehfuess (1983).

There remains the particular problems of explaining both why foliar leaching of calcium and magnesium should be so high in these forests, when rainfall pH is no lower than in many other northern regions, and why the damage should have appeared so suddenly. In this respect Bosch *et al.* (1983) noted both that there was the possibility of ozone damage to cells, this pollutant probably acting in conjunction with SO_2, and that a decrease in the starch–raffinose ratio in affected trees indicated decreased frost resistance. Accordingly they postulated the series of events summarized in figure 4. Certainly ozone is very damaging to leaf cells (Prinz *et al.* 1982), and is known to effect membrane permeability (Mudd & Kozlowski 1975). Experiments by Prinz *et al.* (1982) have confirmed accelerated leaching of magnesium from spruce needles after exposure to this gas. Similarly, it is widely accepted both that impairment of the ion balance of leaves may lead to increased susceptibility to frost damage (see, for example, Baule & Fricker 1970; Malcolm & Freezaillah 1975) and that such damage increases the permeability of cell walls (Tukey 1970). The concurrence of elevated ozone concentrations, acid fogs and radiation frosts at higher altitudes can then explain the distribution of the disease. Furthermore, it has been suggested that weather conditions in southern Germany during the late 1970s and early

1980s have been conducive both to unseasonal frosts (Rehfuess 1983) and to the formation of ozone (Prinz *et al.* 1982), for which the presumed precursor is NO_x, the levels of which have been increasing in the atmosphere fairly rapidly over the past decade.

There remain problems, and Rehfuess (1983) warns against uncritical acceptance of a single explanation for what might turn out to be a series of unrelated diseases. A particular difficulty is to understand why potassium is not lost to the same extent as the other base cations. Bosch *et al.* (1983) suggest that this may reflect the greater availability of potassium in the soil or acid-invoked root damage that is more critical for the uptake of calcium and magnesium than for the uptake of potassium. Nevertheless, this new hypothesis represents an important advance and will, undoubtedly, guide and stimulate new research.

TABLE 9. WEIGHTED MEAN CONCENTRATIONS IN BULK PRECIPITATION, THROUGHFALL AND STEMFLOW COLLECTED OVER FIVE YEARS AT A SITKA SPRUCE STAND IN WEST SCOTLAND

ion	bulk precipitation	throughfall	stemflow
	eq l^{-1}	eq l^{-1}	eq l^{-1}
NH_4	2	15	4
K	7	51	64
Ca	31	108	101
Mg	28	58	84
Na	170	283	350
H	28	8	27
NO_3	3	11	8
PO_4	<1	4	2
SO_4	88	203	242
Cl	169	299	353
mm water a^{-1}	1525	867	214

EFFECTS ON THE SOIL

Water reaching the soil beneath trees, or other vegetation cover, is considerably enriched in base cations and generally rather depleted in hydrogen ions (table 9), a process that may continue as the water passes through the soil litter layer (Richter *et al.* 1983). Some of these base cations are derived from hydrogen-ion exchange at the leaf surface, the exact proportion depending on the amount of additional hydrogen ions that result from dry deposited SO_2. These exchanged base cations have previously been taken up by roots from soil cation-exchange surfaces in contact with root hairs or associated mycorrhizal hyphae, an uptake that requires the reverse flux of hydrogen ions from the root to the exchange surface. In essence, therefore, the loss of rainwater acidity at the leaf surface through cation exchange entails acidification of the soil, an acidification that will accelerate with increasing hydrogen-ion deposition to the vegetation (table 7).

Should the foliage-derived base cations in throughfall then come into contact with the relevant soil exchange surface, it is feasible that hydrogen ions could be displaced by base cations returning to those exchange surfaces from which they were originally derived. In this event there is a closed cycle of base cations while the sulphuric acid introduced from the atmosphere is reformed to pass on to deeper soil horizons. In practice, however, not all the base cations will be exchanged. The mobile sulphate anions introduced from the atmosphere, therefore, pass through the immediate surface soil accompanied by base cations, derived from the vegetation, and by hydrogen ions, either those that have avoided exchange reactions or those that have been displaced from soil surfaces. In addition, there will now be soil-generated organic acids of varying strengths and degree of dissociation. Within the soil the hydrogen ions, from whatever source, may subsequently be exchanged for base cations, buffered by dissolution of aluminium, or neutralized by reaction with soil minerals.

At all events, it is important to appreciate that the initial hydrogen-ion exchange at leaf surfaces represents an acidification of the ecosystem and that this stress is ultimately placed upon the soil.

Hoffman *et al.* (1980*a*) added a new aspect to the model that suggested that it may be an over-simplification. They noted, as had been expected, a decline in strong acid content of throughfall passing through a mixed-hardwood forest canopy, but this was almost exactly matched by an increase in the flux of weak acids, which suggests that total acidity is conserved. Perhaps as much as 30% of the weak acids in throughfall were accounted for by metal ion hydrates, phosphates, sulphites and nitrites, the rest presumed to be organic in character. Certainly throughfall beneath trees is enriched with a wide range of organic compounds (Carlisle *et al.* 1966; Hoffman *et al.* 1980*b*). These weak acids may dissociate as the pH of drainage water increases with passing down the soil profile. As such, this represents an additional acid stress on the soil. It seems doubtful, however, that the quantities of weak acids involved are significant in relation to both the organic acids generated within the soil and the exchange acidity in the soil humus (Krug & Frink 1983).

Conclusions

As many of the processes involved in the collection and exchange of atn substances, including acids and acid forming gases, by vegetation are not amenable to direct measurement, definitive interpretation and extrapolation of results is not yet possible. Vegetation traps neutralizing and acidifying substances from the atmosphere. Of these, sulphur dioxide is clearly important but whether this is the only source for the measured sulphur gain in throughfall remains open to dispute. Undoubtedly there is hydrogen-ion exchange at leaf surfaces which leads to a reduction in the potential acid load in throughfall. However, perhaps this exchange should be viewed as merely an extension of the exchange reactions within the soil itself.

There are processes on and within leaves that lead to element loss in addition to that resulting from hydrogen-ion exchange. Such leaching is a natural and important component of the nutrient cycle but there are now indications that cell damage, resulting either from gaseous pollutants or frost or both, can lead to an unacceptable rate of leaching, at least of magnesium. The factors promoting such a catastrophe must be elucidated, as must the role, if any, of the acidity of the rain in the transfer of the nutrients. Until then no effective advice on control measures can be given. Clearly there is some urgency in seeking answers to these questions.

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Discussion

M. H. Unsworth (*Institute of Terrestrial Ecology, Bush Estate, Penicuik, Midlothian*). One hypothesis to explain tree deaths in Germany is that pollution stress increases the permeability of leaf surfaces and leads to excessive leaching of nutrients in throughfall. If the interception of wind-driven acid cloud and mist contributes to this pollution stress, one might expect to see more leaching from trees growing in upland sites than from lowland trees. Does Dr Miller have any evidence to support this view?

H. G. Miller. There are several reports to suggest that wind-driven cloud and mist water can be very acidic, at least close to pollution sources. We have collected interception deposition on artificial surfaces over five years at six sites around Scotland and have found that, at least at these remote sites, this water is not significantly more acid than is bulk deposition. However, there is a real possibility that in the German situation cloud water acidity may be involved in the observed tree death and, as mentioned in my paper, Rehfuess (1983) has suggested that the concurrence of elevated ozone concentrations, acid fogs and radiation frosts at high altitudes could explain the distribution of the disease.

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I. Th. Rosenqvist (*Oslo University, Box* 1064, *Blindern, Oslo*). Dr Miller's diagrams all showed SO_4^- as the anion in the water phase, but in Scotland, as in many other parts of the world, Cl^- is also an important anion and there does not seem to be a great difference in cation exchange processes depending upon whether the anion is Cl^- or SO_4^-.

H. G. Miller. I agree that we should not overlook the chloride content of rainwater and throughfall, particularly in Britain where, as can be seen from table 9, the levels of this element are particularly high. To find how much of the chloride drains from the soil as HCl, rather than NaCl, is clearly something that requires more work.

G. Abrahamsen (*Norwegian Forest Research Institute*, *Box* 61, 1432 *Aas-NLH*, *Norway*). Dr Miller's first slide indicated that NO_3^- and NH_4^+ were enriched in throughfall below conifers at different stations in Scotland. This is in contrast with Norwegian results where it is generally found that both NO_3^- and NH_4^+ are retained in the canopy. We believe this to be caused by the fact that N is in short supply in Scandinavian forests. What does Dr Miller think is the reason for the difference in results between Norway and Scotland?

H. G. Miller. I am aware that in Scandinavia, trees usually remove nitrogen from rainwater, indeed where we have studied nitrogen deficient forests we observe the same effect (cf. table 2). However, nitrogen deficiency is not, as yet, very common in the relatively young forests of Britain.