PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY B BIOLOGICAL SCIENCES

Solid Phase-Solution-Root Interactions in Soils Subjected to Acid Deposition [and Discussion]

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Solid phase–solution–root interactions in soils subjected to acid deposition

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[Plates 1 and 2]

In managed forests, biomass utilization means a discoupling of the otherwise closed ion-cycle. The rate of proton production caused by the utilization of the timber, however, is of the same magnitude as the rate of proton consumption during silicate weathering. Managed forests can thus be in a steady state and stable.

The input of acidity in forest ecosystems due to air pollution will in most cases exceed the rate of proton consumption by silicate weathering and thus result in soil acidification. Acidity can be accumulated as organic acids (mainly phenoles) and as cationic acids, that is, ions of sparingly soluble oxides (Al, Fe, Mn and heavy metals). The lower the pH, the higher is the solubility and toxicity of the acids existing. Owing to its high concentration and solubility, AlOOH produces the most important cation acid.

A soil is composed of microcompartments in which different reactions can occur at the same time. Also proton production can be spatially inhomogeneous for the following reasons:

(i) a considerable fraction of the input of acidity due to dry deposition of SO_2 is buffered by the leaves of the trees. It reaches the soil via the roots during ion uptake and thus acidifies the soil close to the root tips.

(ii) In acid soils, where the burrowing animals are missing, the soil organic matter formed from the root decomposition accumulates on the aggregate surfaces. It is thus in direct contact with the living roots. If during a temporal discoupling of the ion cycle (nitrification push) nitric acid is formed, this can acidify also, especially the soil close to the root surface. Thus in the direct vicinity of the roots, much higher Al-concentrations have to be expected than those which can be measured in equilibrium soil solution or in lysimeter solutions.

A direct effect of Al-toxicity on the root system of trees is the die-back of the young roots, which has been shown both *in vitro* and in field experiments to be the result of action of Al ions. The mechanism of this action was found to be the inhibition of uptake of Ca ions into the matrix of the cell walls, which changes the macromolecular and physical properties of the pectin molecules which form the primary cell wall of meristemic and parenchymatic tissues in the root tip region.

ACID LOAD AND ACID BUFFERING

The most simple chemical model of acidity in an ecosystem is the system CO_2–H_2O under low partial pressure of CO_2. From this model it is found that the optimum buffer range of soils lies in the pH range 5–6. Soils above pH 6 contain alkalinity in the form of bicarbonates; soils below pH 5 accumulate acidity. Acidity can be accumulated as organic acids (mainly phenolic, fulvic and humic acids), and as cationic acids, that is ions of sparingly soluble oxides (Al, Mn, Fe, heavy metals). The lower the pH, the higher is the solubility and toxicity of the acids. Soil acidification therefore results in an increasing potential of acid toxicity. Acid tolerance then becomes the deciding property of plant species for competition. Natural soil acidification is driven by the variation of weather conditions and occurs through a decoupling of the ion cycle in the ecosystem by hydrogen ions (Ulrich 1983*a*). It is accompanied by the leaching of nutrient cations (Mg, Ca, K) and anions (mainly NO_3) from the system. Soil acidification results therefore also in lack of nutrients.

TABLE 1. INTERNAL PROTON PRODUCTION AND DEPOSITION OF ACIDS IN SOLLING ECOSYSTEMS

(Units are kiloequivalents per hectare per year, mean values 1971–1981.)

		beech	spruce
1	production and leaching of organic anions	0.1	0.5
2	accumulation of cation excess in forest increment	0.7	1.5
3	accumulation of cation excess in the top organic layer of the soil	0.1	0.0
4	uptake of NH_4^+ from deposition	0.9	1.1
5	uptake of NO_3^- from deposition	0.7	0.1
6	buffering of deposited H^+ in the canopy	0.6	0.9
7	1+2+3+4+6−5 = ecosystem internal net proton production	1.7	3.9
8	deposition of H^+ to soil surface	1.4	3.0
9	deposition of cation acids (Al^{3+}, Fe^{3+})	0.3	0.4
	7+8+9 = total acid load	3.4	7.3
	because of acid deposition (directly and indirectly)	2.7	5.8
	because of biomass utilization	0.7	1.5

Ecosystems can be in a steady state with respect to the flux of cations through them, and thus stable as long as the mean rate of proton production by discoupling of the ion cycle is less than the rate of proton consumption connected with the release of alkali and alkaline earth cations during silicate weathering. The rate of silicate weathering does not exceed 2 keq H^+ ha^{-1} a^{-1} (Bache 1983; Ulrich 1983*b*); in most soils from sedimentary rocks it is below 1 keq H^+. In managed forests biomass utilization means a discoupling of the ion cycle. The rate of proton production caused by utilization of the timber is of the same order of magnitude as the rate of proton consumption during silicate weathering (Ulrich 1983*a*). Managed forests can thus be in a steady state and be stable.

The input of acidity in forest ecosystems caused by air pollution will in most cases exceed the rate of proton consumption by silicate weathering and thus result in soil acidification. This is shown by the mean value of an 11 year period for a beech (*Fagus silvatica*) and a Norway spruce (*Picea abies*) forest in the Solling in Central Europe (table 1). With 3.4 and 7.3 keq H^+ ha^{-1} a^{-1}, respectively, the total acid load exceeds by far the buffering capacity of silicate weathering; 80% of the acid load directly or indirectly relates to acid deposition. As soon as exchangeable base cations are replaced at the clay surface by H^+ and leached, the dissolution of oxides starts. The oxides react as bases in the sequence Mn (pH range 5–4), Al (pH range 5–3), and Fe (at $pH < 3.8$ in the presence of soluble organic acids, at $pH < 3$ in their absence). Owing to its high content and solubility, AlOOH represents the most important cation acid. The Al chemistry in soils is not yet completely understood. Polymeric hydroxo cations with a charge of about 0.5 per Al atom possess a low solubility and toxicity; they accumulate in the interlattice space of the swelling clay minerals (preferably in the pH range 5–4.2). The exchangeable Al is assumed to be Al^{3+}. In the presence of sulphate (from air pollution), Al-hydroxo-sulphates are formed (at pH around 4) that approach the composition $AlOHSO_4$. Together with AlOOH they form a perfect sink for H_2SO_4 according to the following equation (Prenzel 1983):

$$AlOOH^s + H_2SO_4 = AlOHSO_4 + H_2O.$$

If AlOOH is used up or its dissolution rate is too small, $AlOHSO_4$ dissolves and the concentration of Al ions can reach high values:

$$AlOHSO_4 + H_3O^+ = AlSO_4{}^+ + 2\,H_2O.$$

Taking into account the different ion species, the concentration of Al ions in solutions of acid soils follows fairly well the solubility product of gibbsite $Al(OH)_3$. There are, however, some important exceptions.

(i) The presence of dissolved organic acids results in the formation of metal–organic complexes. They can contribute more than 90% to the Al concentration in acid surface layers of soils (Nilsson 1983, personal communication). The concentration of Al in soil solution then exceeds the value predicted from gibbsite solubility. The complexes of Al with organic acids are less toxic, which explains why acid tolerant species can still root in very acid surface soil horizons.

(ii) The kinetics of Al ion release from AlOOH or Al hydroxo cations is rate limiting. This can happen in sandy soils, and in highly acidified soils where the Al hydroxo cations bound in the inter-lattice space of the clay minerals are already lost again. In this case the Al concentration in soil solution is less than the predicted value.

(iii) If the dissolution and leaching of Al hydroxo sulphate has started the Al concentration can then reach values up to 50 mg Al l^{-1} and exceed the value predicted from gibbsite solubility. This can happen in an acid soil as a consequence of an acidification push (see following section).

A soil is composed of microcompartments in which different reactions can occur at the same time. Proton production also can be spatially inhomogeneous for the following reasons.

(i) A considerable fraction of the input of acidity caused by dry deposition of SO_2 is buffered by the leaves of the trees. It reaches the soil via the roots during ion uptake, and will acidify the soil especially close to the roots. Table 2 gives values for some forests in northwest Germany.

The data can be summarized as follows. Coniferous species on soils in which aluminium is the main buffer (soils with low base saturation, cf. Ulrich 1983*b*) buffer 20% of the protons deposited in the canopy. Beech forests on similar soils buffer 30%. Beech forests in soils with medium base saturation buffer in the region of 50%. In soils containing $CaCO_3$ in the fine earth, the percentage of buffering in the canopy may be considerably higher. This indicates that in buffered soils the acidification of the soil may start not only from the surface of the soil exposed to the atmosphere, but to a greater extent from the surfaces of the soil exposed to the root.

(ii) In acid soils, where soil-burrowing animals are missing, the soil organic matter formed from root decomposition accumulates on the aggregate surfaces. It is thus in direct contact with the living roots. If during a temporal decoupling of the ion cycle (an acidification push) nitric acid is formed, this can acidify also especially the soil close to the root surface.

There is therefore a high probability that especially under the influence of acid deposition, acidification pushes can lead to strong proton formation in a soil fraction which is in touch

TABLE 2. TOTAL DEPOSITION OF ACIDITY, DEPOSITION OF H^+ AND H^+ BUFFERING IN CANOPY IN SOME FORESTS IN NORTHWEST GERMANY

(For methods see Ulrich 1983*c*; units are kiloequivalents of H^+ per hectare per year.)

	Göttingen 1981–1982	Solling 1969–1981		Lüneburg 1980–1981			Hamburg 1981–1982		
	beech	beech	spruce	oak	pine	birch + beech	beech	oak + beech	pine
total deposition of acidity	1.6	3.2	5.4	1.6	2.3	2.7	2.0	1.9	3.6
deposition of H^+	1.0	2.0	4.0	1.0	1.3	2.0	1.3	1.2	2.5
H^+-buffering in canopy	0.5	0.6	0.9	0.5	0.3	1.1	0.6	0.4	0.5

with the roots. During such events, Al concentrations in the soil solution may be reached that exceed considerably the ones measured in equilibrium soil solution or in lysimeter solutions.

Acidification pushes

In a cool wet climate like that of northern Europe, temperature is the factor that limits microbial activity and mineralization in soil. A dry year, which is usually also a warm year (in most years either warm–dry or cool–wet conditions appear simultaneously), influences the ecosystem not only by drought, but also by increased mineralization. If the rate of nitric acid formation by nitrification exceeds the rate of nitric acid (nitrate) uptake by the plants, an acidification push results. Such acidification pushes can be expected in warm years. Cool wet years may lead to de-acidification phases. To assess these climatically induced changes of acidification pushes and de-acidification pushes, which have been postulated on the bases of theoretical deductions (Ulrich 1980), soil solution was collected at regular intervals since 1981 by using ceramic cups in different forest ecosystems (Matzner & Thoma 1983). The year 1981 was cool and wet, 1982 was warm and dry. Some of the results are presented in table 3.

There was a strong increase in nitrate concentration in all soils during summer 1982. In the soil with the highest base saturation (Harste) the main cations that accompanied NO_3 were Ca, and Al to a smaller degree. In the soil with 10% base saturation the nitric acid released more Al than Ca as was to be expected. In the spruce soil of the Solling the main fraction of the protons produced during nitrification remained in the solution, decreasing the pH. A small fraction was buffered by the release of almost equivalent amounts of Al and Ca. In the soil of the beech forest in the Solling, the release of cations did not balance nitrate formation, but led to a decrease in sulphate concentration. This indicates that $AlOHSO_4$ has been formed according to the reaction mechanisms already discussed. These four examples demonstrate quite well the different manifestations of acidification pushes in soils depending on the chemical soil state (and the strength of the acidification push). The Solling spruce example indicates an almost complete loss of buffering capacity. If this soil dries out after the acidification push, quite high concentrations of strong mineral acids and correspondingly low pH values should result. Figure 1 shows for this example the time course of nitrate concentration, pH and living as well as dead fine root biomass (data from Murach 1983). The opposite time course of nitrate and pH becomes very clear: nitrate formation lowers pH (acidification push), whereas nitrate consumption (ion uptake) increases pH (de-acidification phase). The effects have been much

TABLE 3. DIFFERENCE IN ION CONCENTRATION IN SOIL SOLUTION BETWEEN THE DATE OF HIGHEST AND OF LOWEST NITRATE CONCENTRATION IN 1982

(Values in milliequivalents per litre; X^S_{Ca} is the base (Ca) saturation.)

	Solling		Spanbeck	Harste
X^S_{Ca}	4% beech	4% spruce	10% spruce	25% beech
soil depth/cm	0–10	0–10	10–20	0–10
H	−0.05	+0.41	+0.04	+0.06
Ca	+0.07	+0.17	+0.35	+0.48
Al	+0.24	+0.22	+0.45	+0.20
NO_3	+0.51	+0.52	+0.56	+0.69
SO_4	−0.2	+0.13	+0.21	+0.11

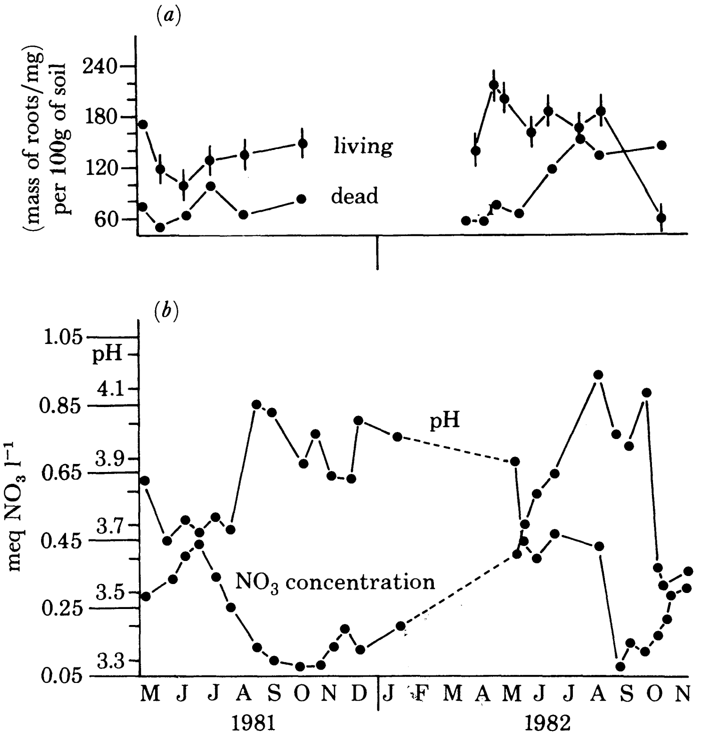


FIGURE 1. Acidification push during autumn 1982 in a spruce forest, Solling. (*a*) Fine roots, living and dead. (*b*) pH (inner scale) and NO_3-content (outer scale) in the soil solution.

larger in 1982 (warm–dry) than in 1981 (cool–wet). The living root biomass follows the changes in pH and drops down in autumn 1982 after a drop of pH to below 3.3. The fine root necromass increases correspondingly, suggesting a causal relation. All other possible explanations of the root die-back have been falsified (Murach 1983). The data show that the suggested acidification pushes and de-acidification phases actually occur under the predicted climatic conditions. The acid produced was buffered in such a way that only in the Solling spruce example could acid toxicity to the roots have occurred. We expect that the current warm year 1983 will again initiate an acidification push which probably cannot be buffered as well as in 1982 by Ca release. Therefore in 1983 a higher release of Al ions can be expected, and, as a consequence, a much larger root die-back if acid (Al) toxicity has effect. This should lead to the development of needle losses and other crown damage, which are the symptoms of spruce die-back, now also in the Solling.

CONSEQUENCES OF SOIL ACIDIFICATION FOR THE RHIZOPHERE IN FOREST ECOSYSTEMS: ROOT NECROSIS

The most prominent consequences of the constant input of acid into central European forests for the soil chemistry are the following ones:

(*a*) leaching of nutrient cations (Mg, Ca, K) and anions (mainly NO_3) from the system, which results in a lack of nutrients;

(*b*) high solubility of cation-acids: Al, Mn, Fe, heavy metals. Of these, Al is the one reaching the highest concentration in most soils and could have toxic effects. Our research has therefore been focused on the physiology of aluminium action with regard to forest trees.

The drastic change which the soils in most parts of northern and central Germany seem to have undergone becomes most evident by following the fate of young beech-seedlings. The seeds produced in 1976 (the last year with a high seed production of beech) germinated rather well at nearly all suitable places in the following spring, but eventually died off in most parts of the region in the years thereafter. Especially conspicuous is the pattern of die-back in those areas where part of this natural regeneration has survived: the areas around the stem bases of dominant old beech trees are devoid of young trees, whereas in the regions between the trees or in the vicinity of suppressed trees, the seedlings still survive (figure 2). It is well known that more than 20% of precipitation and acid deposition in a beech forest occurs via the stem-flow of the trunk of the trees. Therefore the acidification in those ecosystems starts from the stem base of the dominant trees (Glatzel 1982; Glatzel *et al.* 1983). It has been shown in addition that microbiological and biochemical soil parameters in the region of the stem base are completely different from those in the region in the middle between the trees, where the least acid deposition occurs (Hüttermann & Gehrmann 1982). If these young beech trees are dug out and freed very carefully from the adherent soil, the following macroscopic picture always is found: living roots are only to be found in the top soil and upper layer of mineral soil. The deeper roots have died off (figure 3 gives examples of what can be observed repeatedly). The assumption that this root die-back is the result of soil toxicity due to soil acidification is supported rather strongly by the results of the following experiment. In 1981, beech seeds were sown at four different sites in Nordrhein-Westfalen and Niedersachsen, where the regeneration of beech has been observed to fail before. For a test of possible soil toxicity caused by cationic acids solubilized by soil acidification, the following treatments were applied: O, unchanged control; B, topsoil mixed with the mineral soil; BK, same treatment as B but with additional liming; E, soil monolith was removed altogether and replaced by Einheitserde (soil prepared comercially for greenhouses and plant nurseries). The results obtained after the second vegetation-period are shown in figure 4. Most of the seedlings in the untreated plots (O) have died; the survivors had roots only in the organic top soil. The mixing of the organic layer with the mineral soil (B) has resulted in a much deeper rooting. The root system is much better developed in the plots with lime added (BK), and the best roots were observed, as was to be expected, in the Einheitserde (E). (For details of the results see table 4 and Gehrmann & Ulrich

FIGURE 2. Die-back of natural regeneration of beech at the base of dominant trees (Eggegebirge, N.R.W.).

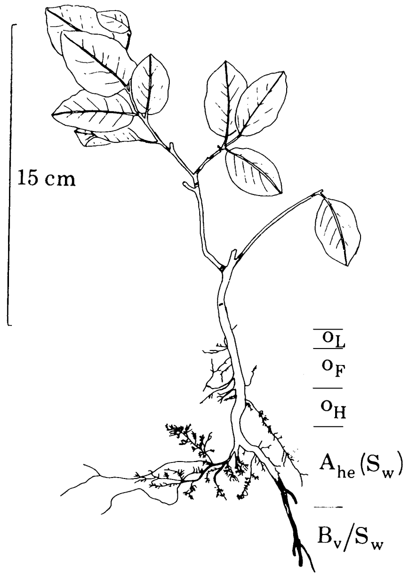
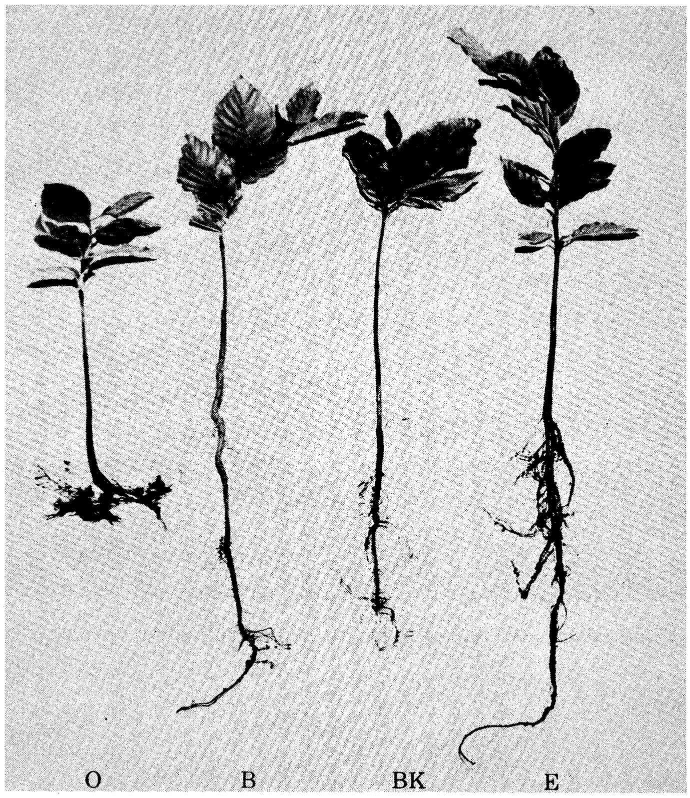


FIGURE 3. Young beech tree from the natural regeneration 1977, dug out 1981. Living roots are visible only in the uppermost layers of the mineral soil and top soil. Roots going deeper die off.

(1982), Hüttermann *et al.* (1983) and Gehrmann (1983).) S.e.m.-microscopy of the dying roots reveals that the most prominent symptom of damage arguing for soil toxicity is a necrosis in the region between the cortex and the central cylinder of the young primary roots (figure 5, plate 1). Similar symptoms have been found in young spruce-roots from acid soils, which show macroscopically the features of die-back (figure 6, plate 1).



(Experiment was done in the Haard (see Gehrmann 1983). The results given are the mean of 60 plants for each treatment.)

soil treatment	root length/mm
unchanged (symbol O)	130±37
top soil mixed with mineral soil (B)	174±50
top soil mixed with mineral soil and limed (BK)	212±45
soil replaced by nursery soil (Einheitserde, E)	249±53

ALUMINIUM TOXICITY AS CAUSE OF ROOT NECROSIS

The results of these experiments together with others suggest that Al toxicity is the main factor responsible for the observed root necrosis. For a direct test of this assumption, young spruce seedlings were grown in water cultures of different pH values in a medium that was optimal for spruce (Ingestad 1959) and in the presence and absence of Al ions (the Ca/Al ratio in the Al media was in the range between 2 and 0.5). Details of these studies are given in Tischner

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DESCRIPTION OF PLATE 1

FIGURE 5. S.e.m. picture of a root of a 140 d old beech seedling grown in acid soil.

FIGURE 6. S.e.m. picture of a fine-root of spruce collected in June 1981 in a stand grown on acid soil.

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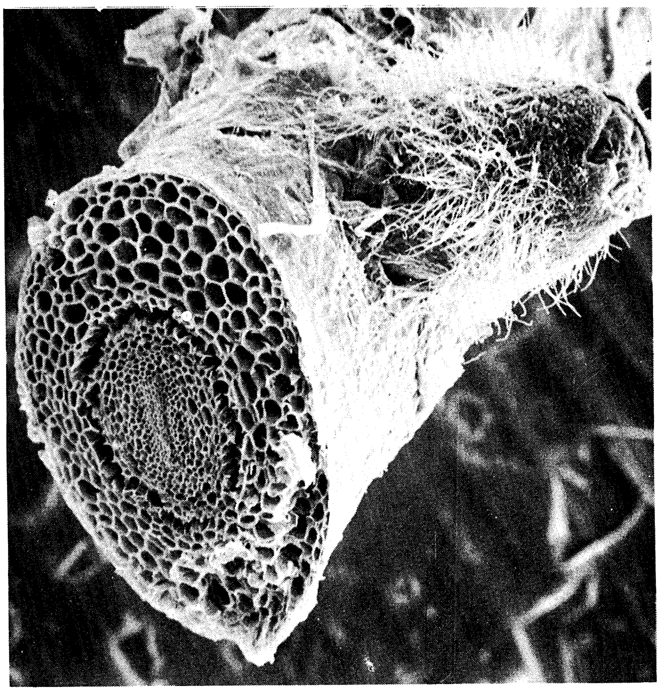

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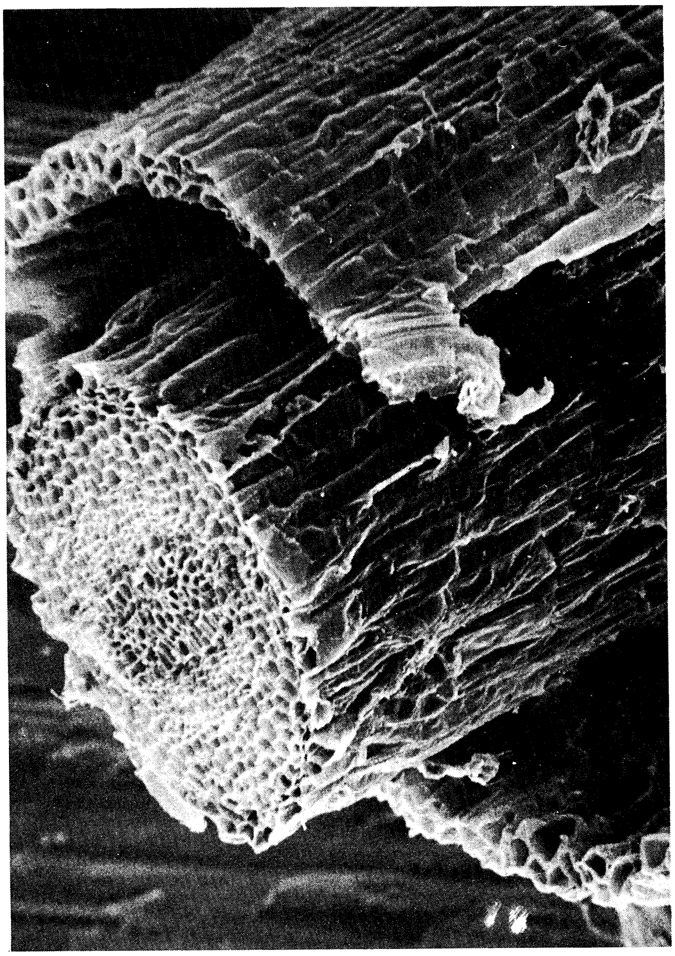

FIGURES 5 AND 6. For description see opposite.

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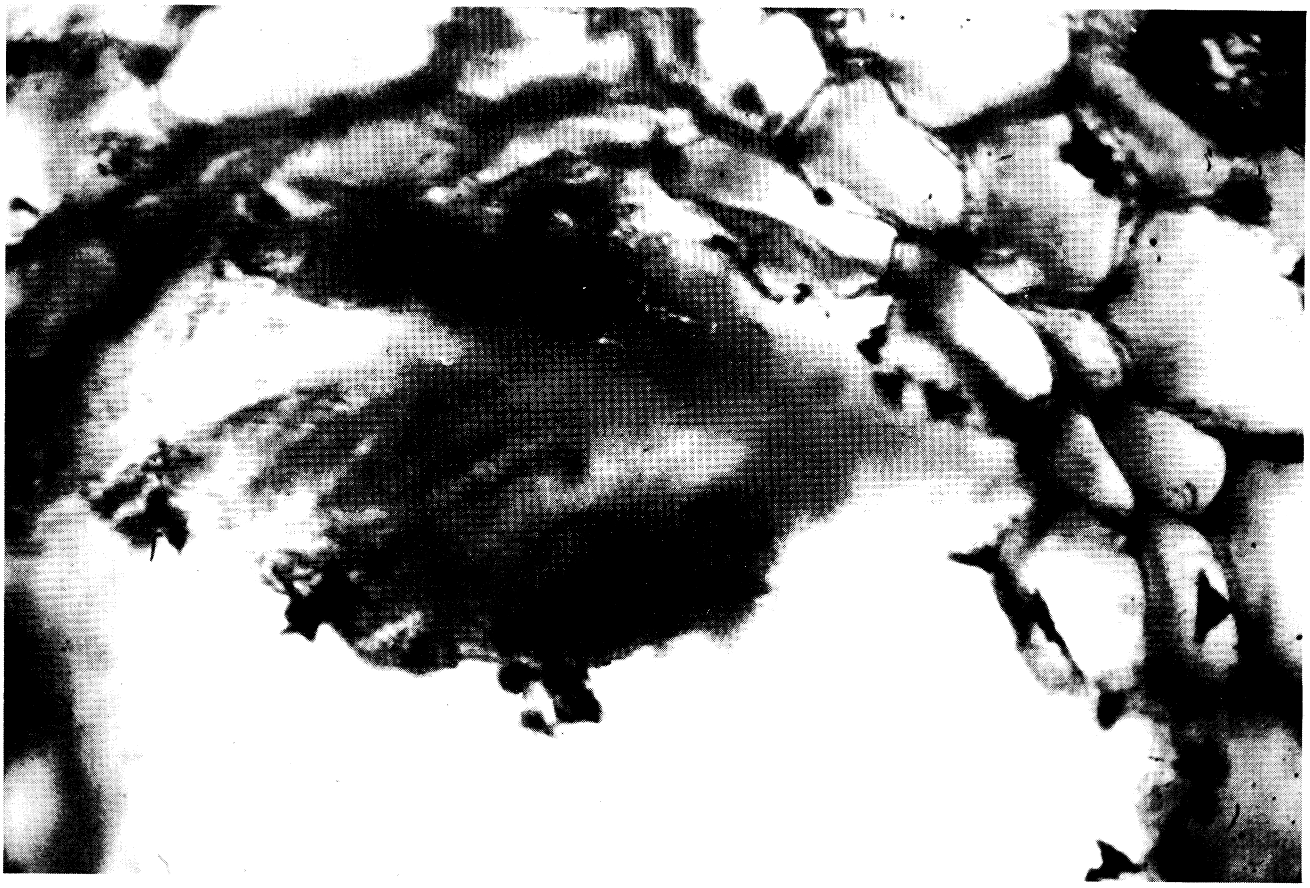

Figures 7 and 8. For description see opposite.

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et al. (1983). The nutrient solution had the following composition: 0.044 g KH_2PO_4, 0.0713 g KCl, 0.219 g $CaCl_2$ (6aq), 0.154 g $MgSO_4$ (7 aq), 0.05 g $FeCl_3$, 0.6 mg $MnCl_2$, 1 mg H_3BO_3, 0.4 mg $ZnCl_2$, 0.0 mg $CuCl_2$, 0.007 mg Na_2MoO_4 (2 aq), 101 mg KNO_3. The pH value was adjusted daily to the value given in the figures. After 6 weeks of growth of the young seedlings in the water cultures, changes in the root morphology were observed only in the cultures that had pH values below 4.2 and, in addition, Al ions in the medium. Microscopical examination of these roots revealed necrotic lysis of the part between the cortex and the central cylinder (figures 7 and 8, plate 2). Serial cuttings made from roots embedded in paraffin revealed another zone of heavy distortions owing to the presence of Al ions at low pH values: this was the meristem in the root tip. Here again the cells have undergone necrosis, rendering the meristem functionless. Thus the two main effects found in the root system of young trees growing in acid soils–die-back at the root tips and necrosis in the area between the root cortex and the central cylinder–could be reproduced in the laboratory under controlled conditions as an effect of the combination of Al ions and low pH. The effect was shown to be rather specific for Al ions. Manganese caused entirely different effects in the roots. When Al in the acidic media was chelated with EDTA, no detrimental effects on the root-system of young spruce trees were observed (Rost-Siebert 1983).

Mechanism of Al toxicity in young spruce roots

For an evaluation of the possible mechanism of action of Al on the physiology of young spruce roots, a series of experiments has been conducted, mostly in sterile water culture. A Ca/Al antagonism has been demonstrated by experiments done by Rost (see Ulrich 1982) who found that the most important factor for the manifestation of Al-toxicity is the Ca/Al ratio. Even at low pH values and high Al-concentrations in the medium, high Ca-concentrations can counteract the detrimental action of Al ions (figure 9.)

This mechanism has been investigated in more detail by Junga (1984). Using ^{45}Ca as a tracer, he has shown that the presence of Al at low pH inhibits the uptake of Ca into the roots (figure 10). The kinetics of this suggest that the majority of Ca is taken up rather rapidly by an ion exchange-type mechanism, which is completely inhibited by Al, whereas the much slower uptake, probably into the cells, is not affected. This interpretation is supported by a series of experiments with certain antibiotics (Junga, personal communication). The Ionophor-antibiotics, which act directly on cell membranes, did not affect Ca-uptake very much, whereas those compounds which chelate Ca ions, did have an influence on Ca-uptake into the roots.

From these results it is apparent that Al acts at low pH values on the roots by replacing the Ca ions in the matrix of the cell walls. Since the rigidity of the cell walls is much affected by this exchange of ions (cf. Foy *et al.* 1978), it is obvious that the meristemic regions in the root should exhibit the highest sensitivity to Al ions. Our results are fully compatible with the work of Bauch (1983) who measured the element-content in cell walls of apparently healthy and

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Description of plate 2

Figure 7. Transverse section of a root of a spruce seedling grown for 6 weeks in a hydroculture containing 2.5 mM Al, at pH 5.0 (Ca/Al ratio 0.5)

Figure 8. Transverse section of a root of a spruce seedling grown under the same conditions as in figure 7, only at pH 4.0.

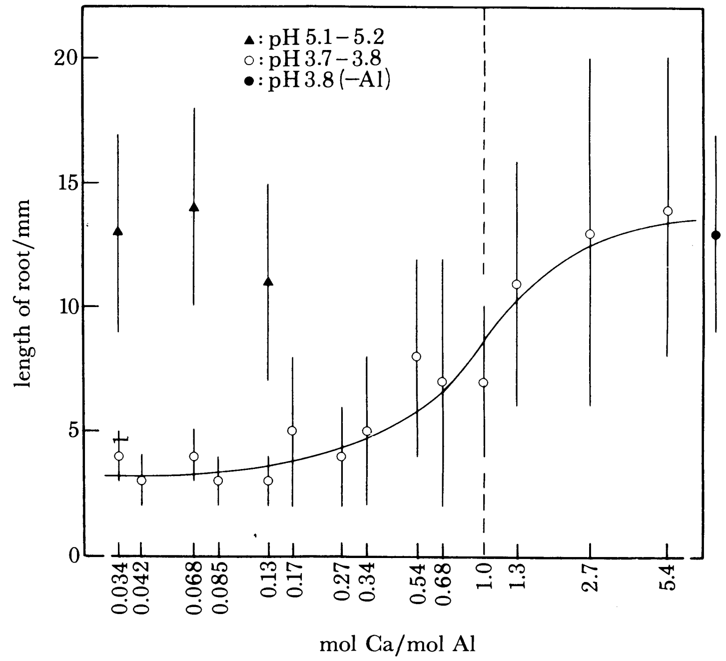

FIGURE 9. Influence of the Ca/Al ratio on the length of spruce roots at different pH values. The ordinate indicates the length of the roots in millimetres. The bars give the values of the standard deviation.

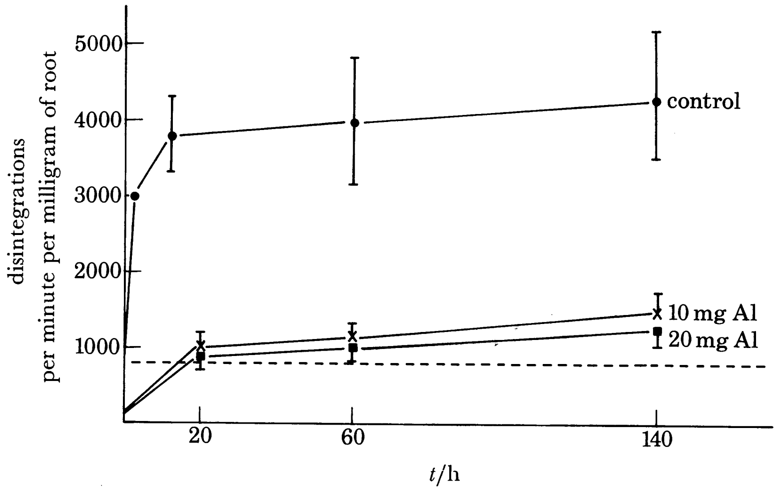

FIGURE 10. Inhibition of uptake of ^{45}Ca by Al ions. The dashed line indicates the amount of radioactive Ca present in the medium (value without any uptake at all is 4 mg l^{-1}).

diseased firs and spruce. He found a complete replacement of Ca ions in the cell walls of diseased trees by Al.

Murach (1983) followed the dynamics of the fine-root system with regard to different soil depth in two spruce forests growing on soil which differ in their chemical state by discontinuous measurements as has been demonstrated in figure 1. Simultaneously, the physical, hydrological and chemical soil parameters were followed. For an explanation of the observed fine root dynamics, Murach was able to exclude the following possible causes–soil temperature, soil humidity and drought, lack of carbohydrates and endogenous rhythms of the plant–as primary causes of the observed root die-back. The observed root die-back, however, followed the change in the chemical state of the soil with regard to soil acidity, an observation that is compatible with the interpretation presented in this paper that soil acidity is the main factor responsible for the observed root die-back.

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Ulrich, B. 1983*c* Interaction of forest canopies with atmospheric constituents: SO_2, alkali and earth alkali cations and chloride. In *Effects of accumulation of air pollutants in forest ecosystems* (ed. B. Ulrich & J. Pankrath), pp. 33–45. Dordrecht: Reidel.

Discussion

J. R. **Kramer** (*McMaster University*, *Hamilton*, *Ontario*, *Canada*). First, what procedures are used to relate the concentrations of biologically active species of aluminium in Professor Hüttermann's chemostat studies to measured natural levels?

Second, I understand that the soil–water aluminium analyses of natural examples referred to are made after centrifugation. Aquatic samples at pH 4.5 show only 10–30% of the aluminium concentrations found in 0.045 μm filtered water. It would appear that centrifugation would include 'particulate' aluminium in his analysis. Please comment.

A. **Hüttermann**. Owing to complete control of pH(3.5), only Al^{3+} can be present in our experiments (the reaction $Al(OH)_3 + 3H_3O^+ = Al^{3+} + 6H_2O$ obeys the mass law). The species of Al present in acid soil solutions is the subject of intensive study (see, for example, Driscoll 1980). The 'biological activity' of Al depends on the tolerance mechanisms of the plant species in question.

In answer to Dr Kramer's second question, the concentration in the soil solutions mentioned (20 mg l^{-1}) was determined in filtered samples. Unfiltered ones may contain up to 300 mg l^{-1} (e.g. in the E.S.S. of acid soils).

Reference

Driscoll, Ch. T. 1980 *Nature*, *Lond.* **284**, 161–164.

R. A. **Barnes** (*Esso Research Centre*, *Abington*, *Oxfordshire*, *U.K.*). Several papers were presented at a recent meeting in Lindau, Germany, which described the extent and rapidity of decline of forest vitality in the F.R.G. During the ensuing discussion, it was stated from the floor that many of the affected forests had been established soon after World War II on soils that did not naturally support forests. This was apparently achieved by application of fertilizers. It was further claimed that in the 1970s a decision was taken federally to cease applying fertilizer to these forests.

As is well known, several different pollutants and other external negative stimuli have been invoked in an attempt to explain the variety of damage symptoms observed. In the circumstances it is attractive to speculate that a range of explanations was developed because many of the forests have a major common stress factor: lack of fertilization. Such a hypothesis would also account for the general lack of similar observations outside the F.R.G. and the rapidity of their onset. Would Professor Hüttermann care to comment?

A. **Hüttermann**. *All* soils in the F.R.G. that are below the treeline have naturally supported forests since the ice ages. Many of those forests have been destroyed by excessive biomass utilization, resulting in soil acidification before the 19th century. All forests existing now have either been established during the time since or have survived this devastation. Virtually all are now in the 2nd or 3rd generation, depending on the tree species. Until the 1960s, fertilization was effective on forestations; howver, the unfertilized control stands developed to stable forests, too. Since then, fertilization studies that use the conventional load of fertilizer (below 1000 kg CaO ha^{-1}) showed no effect in virtually all cases.

R. A. Scriven (*Central Electricity Research Laboratories*, *Kelvin Avenue*, *Leatherhead*, *Surrey*, *U.K.*). We are told that the areas of damage to forests in West Germany all have altitudes above about 500 m. These areas do not coincide with the pattern of rain acidity, which is more uniform in distribution. Does Professor Hüttermann have any explanation for this?

A. Hüttermann. Areas of damage to forests exist in West Germany at all altitudes, down to sea level. The damage is often most pronounced in altitudes where cloud formation and transport occur. Rain water is only one minor pathway of acid input to the forest ecosystem. Other pathways of greater importance are the dry deposition of SO_2 with subsequent acid formation, and the interception of acid fog and cloud water droplets by the forest canopy. Often there seems good agreement between forest damage and cloud water interception.

With regard to the question on whether photo-oxidants including ozone may play the decisive role in the currently observed 'Waldsterben' in West Germany, as was suggested by Prinz *et al.* (1982), the following answer can be given at the moment.

On the basis of published observations (Prinz *et al.* 1982) for Norway spruce, and studies concerning the kinetics of leaching of ions from needles (as indicators for 'cracks' in the cuticle as proposed by Prinz *et al.* (1982) to be the main mechanism by which ozone acts on spruce), we (i.e. the group at the Forstbotanisches Institut) can exclude photo-oxidants as the main cause of spruce die-back in our study area (Hils, Solling, Hamburg). We do find, however, evidence (especially in our SDS-polyacrylamide gel electrophoresis pattern) for a direction action and participation of air pollutants (which have to be identified yet) on the needles of many trees, especially in Hamburg. Here, perhaps, episodes of high pollution may be responsible for this change in protein pattern in the otherwise green needles.

Ulrich's basic theory does not in fact exclude such direct action of air pollutants on the needles or leaves. It merely states that the changes in the soil due to the constant input of acid load render the forest ecosystem more susceptible to all kinds of stress factors, which otherwise could be compensated or tolerated in a more stable ecosystem.

Reference

Prinz, B., Krause, G. M. H. & Stratmann, H. 1982 Waldschäden in der BRD. LIS-Bericht no. 28 Essen. ISSN 0720-8499.

M. W. Holdgate (*Department of the Environment*, 2 *Marsham Street*, *London SW*1*P* 3*EB*, *U.K.*). The data presented suggest that some of the changes now being described have built up over many years, if not decades. Do the models that have been developed give any indication of the extent to which these changes are reversible, and if so, what the likely timescale of response to reduced sulphate and nitrate inputs is likely to be?

A. Hüttermann. Knowing the rate of acid deposition and soil parameters such as the rate of silicate weathering and the cation exchange capacity, the rate of change occurring in the chemical state of the soil can be calculated. Such calculations show that the soil changes may go on for many decades.

The time of de-acidification (recovery) can be estimated also. It can vary from decades to centuries, depending on soil parameters and forest management. The de-acidification of the soils can be speeded up considerably by fertilizers, but only to the depth to which the basic fertilizer can be incorporated.

S. R. Elsden (*University of East Anglia, Norwich, U.K.*). It is clear from Professor Hüttermann's slide that there was very poor root formation in those beech seedlings grown in soil from a beech forest and that root growth was improved when the original soil was diluted or limed or replaced by garden soil. Assuming that the beech trees *per se* had not caused a deterioration of the forest soil – like that observed by Watt (1934) – what is the possibility that the poor root development he observed was due to the build-up of beech-specific infectious agents or pests in the forest soil? I ask this question (*a*) because I have been advised by a well known commercial grower, to his loss, not to replant my rose bed for at least two years after removing the original bushes, (*b*) because it is well known in the glass house industry that there will be a reduction in the yield of tomatoes if the compost is not either sterilized or replaced each year before planting out, (*c*) because, as with roses, it is inadvisable to replant an apple orchard the same year as you dig up the original trees.

Reference

Watt, A. S. 1934 *J. Ecol.* **22**, 230–270; 445–501.

A. Hüttermann. In most parts of Germany, especially where beech is still grown today, beech stands have been naturally regenerating for millennia.

R. A. Skeffington (*Central Electricity Generating Board, Kelvin Avenue, Leatherhead, Surrey, U.K.*). First, did the soil replacement experiments with beech seedlings take place under a mature beech canopy? In Britain at least there is evidence that on easily podsolized soil under beech the trees themselves create conditions that are unfavourable for seedling establishment (Tansley 1939). Perhaps this rather than acidification by acid precipitation could be an explanation of the poor establishment?

Second, British forests have levels of S deposition comparable with German forests, and broadly similar soils and climatic conditions. Where Al levels have been measured they are as high or higher than in the Solling (e.g. up to 9 mg l^{-1} at my own Tillingbourne site). At Tillingbourne the trees appear healthy and fine roots normal, and in British forests in general there is no evidence of the forest die-back afflicting Germany. Can Professor Hüttermann explain this discrepancy by his theory?

Reference

Tansley, A. G. 1939 *The British Islands and their vegetation*, pp. 361–424. Cambridge University Press.

A. Hüttermann. Problems with natural regeneration of beech increased after the fifties, concomitant with increased accumulation of organic top layers. This effect can be explained by acid deposition. To answer the second point, the most important factor in soil toxicity is the process of solubilization of Al in a toxic form. Without additional information on the state of the soils and the processes going on there, no further comment can be made for the time being. But, wait and see how the stand will develop in the years to come.

Gwyneth D. Howells (*Central Electricity Research Laboratories, Kelvin Avenue, Leatherhead, Surrey, U.K.*). Professor Hüttermann refers to presence of H_2S below decaying litter in the Solling

Forest. What were the concentrations, and were they at levels possibly toxic to roots or soil biota?

A. HÜTTERMANN. This refers to an observation which has been reported rather frequently, however, quantitative measurements are still lacking.

GWYNETH D. HOWELLS. What were the levels of aluminium observed in Solling soils: were they at concentrations (and in the forms) judged toxic to tree roots as shown by laboratory tests in hydroponic solutions to be of the order 10 and 20 mg Al l^{-1}?

A. HÜTTERMANN. These data are given as monthly values in 80 cm soil depth in Matzner (1982*a*) (for the years 1969 to 1979) and for 1980 and 1981 in Matzner (1982*b*). For the spruce stand, the Al concentration varied from 1972 to 1979 between 0.01 and 25.6 mg Al l^{-1}, with a median value of 11. In 1980 and 1981 the concentrations varied as a consequence of increased soil acidification to between 12 and 19 mg Al l^{-1}. The cation–anion balance of the solutions as well as occasional measurements of dissolved carbon make it probable that only a small percentage of this Al was organic bound. A greater fraction seems, according to mass action law calculations, to exist as $AlSO_4^+$ ions.

References

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Matzner, E. 1982*b* *Forsch.* 104 02 615 *des Vundesministers des Innern, Bonn.*

I. TH. ROSENQVIST (*Oslo University*, *Box* 1064, *Blindern*, *Oslo*). Professor Hüttermann spoke of 'buffering' processes. Surely *neutralization* would be a more appropriate term?

A. HÜTTERMANN. No. Following Brønsted's definition of acids, buffering means a reaction in which an acid of lower strength is produced. These can be cation acids like aluminium ions or organic acids. We preserve the term neutralization for reactions that lead to the formation of the acid with the lowest strength, that is water. Such reactions are the dissolution of carbonates and the release of alkali and earth alkali cations from the silicate lattice by protons.

SIR FREDERICK WARNER, F.R.S. (11 *Spring Chase*, *Brightlingsea*, *Essex CO*7 0*JR*, *U.K.*). Professor Hüttermann referred to H_2S produced by reduction of sulphates. But what about the effect on nitrate before this occurs? In water pollution, before anaerobic conditions set in and H_2S is produced, nitrate is available as an oxygen source, but is reduced to nitrite and when ammonia is present disappears as elemental nitrogen.

Loss of nitrogen in water can be massive. With regard to pollution in the Thames, in 1971 a large discharge of surplus activated sludge was made from the Southern Outfall sewage works. Within 24 h, 200 t of nitrogen disappeared by ammonium nitrite formation and decomposition.

A. HÜTTERMANN. With regard to the question about the fate of sulphur (= sulphate) in the forest-ecosystem after deposition, we have information although still preliminary (but from many observations in different forests, which have yet to be analysed quantitatively) that to a certain extent the conditions in our acidified forests get so anoxic that SO_4^{2-} is reduced to S^{2-} which then leaves the soil in the form of H_2S. This is to be considered as a possible way of proton export from these soils. The chain of events that is to be considered as leading to this increase in anaerobic episodes in these soils can be characterized as follows.

The decrease in litter decomposition (proven in many systems, e.g. Dr Skeffington's poster at this meeting) together with the disappearance of burrowing animals, especially lumbricids (work of Dr Schauermann in Göttingen) leads to, so far, unobserved stratifications in the humus layer of the forest floor and to the formation of hydrophobic layers (Professor von Buch, Hamburg, personal communication). After rainfall, this then will seal off the soil underneath and lead to much longer anaerobic episodes than occur in less acid soils. This, together with the decreased mixing of the soil, will lead to less aeration and more reducing conditions in the soil. It first leads to an appreciable amount of denitrification (work of Dr Beese in Göttingen) and in addition to sulphate reduction (observation by many colleagues all over northern Germany).

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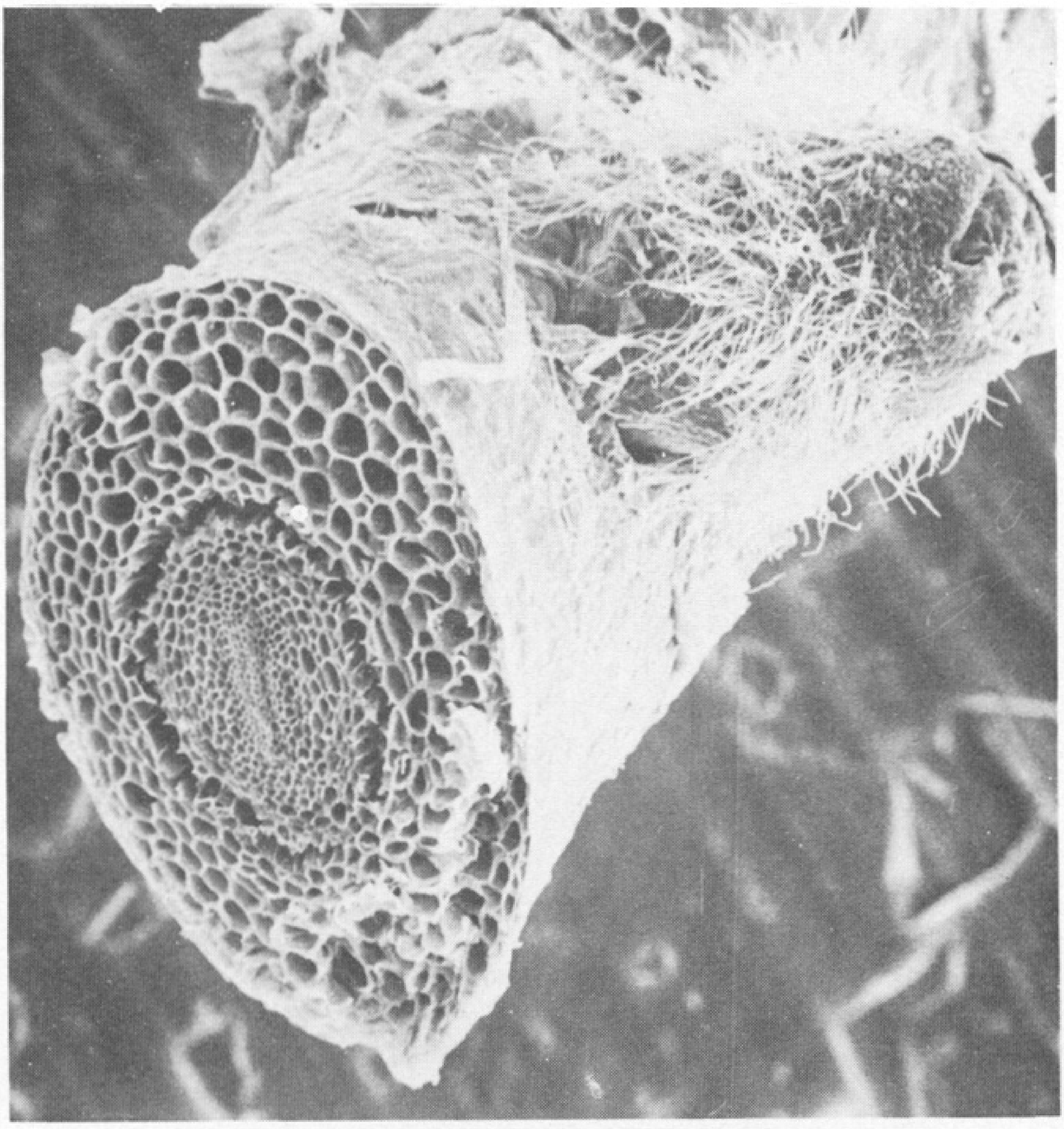
IGURE 2. Die-back of natural regeneration of beech at the base of dominant trees (Eggegebirge, N.R.W.).

(Experiment was done in the Haard (see Gehrmann 1983). The results given are the mean of 60 plants for each eatment.)

5



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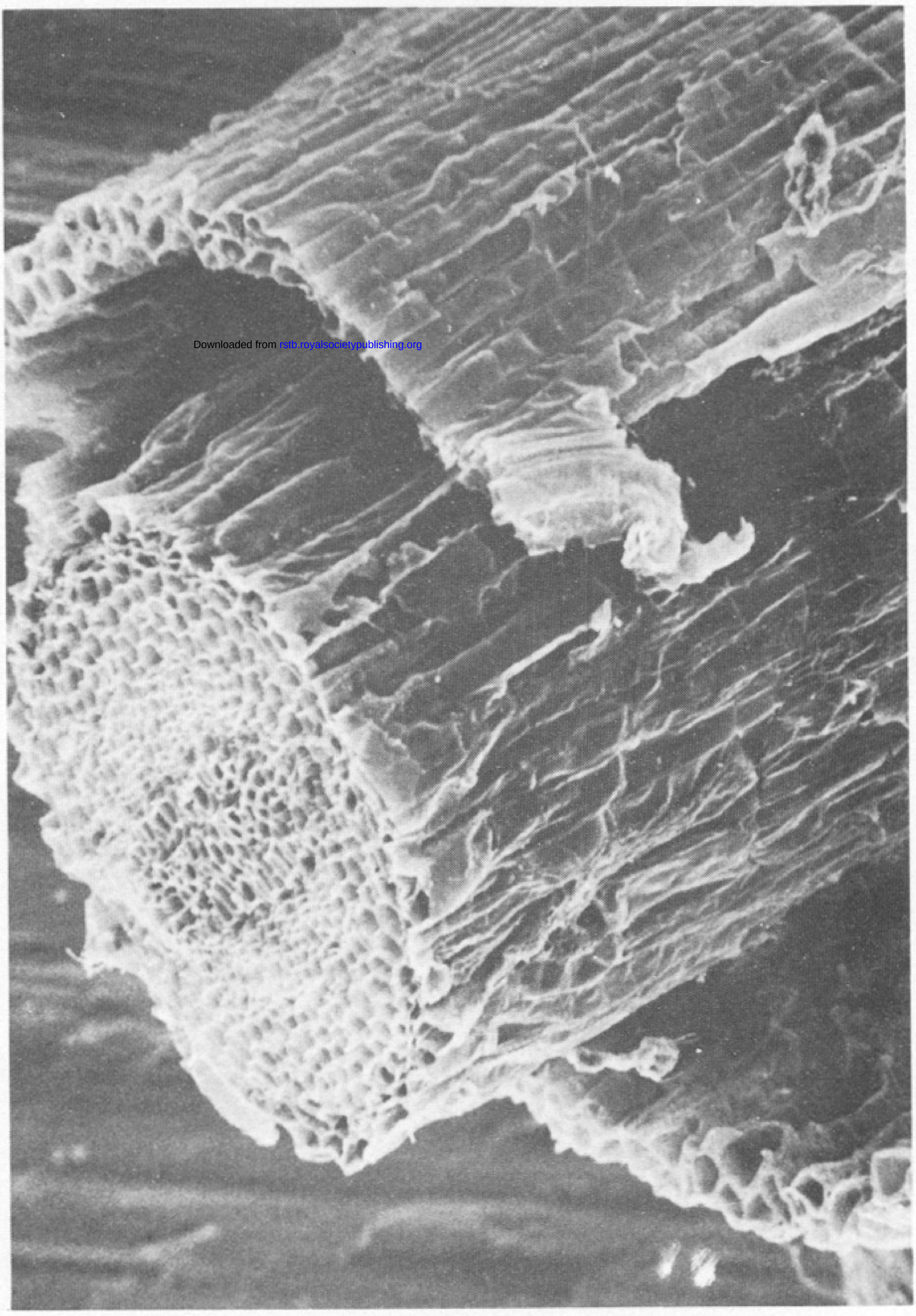

FIGURES 5 AND 6. For description see opposite.

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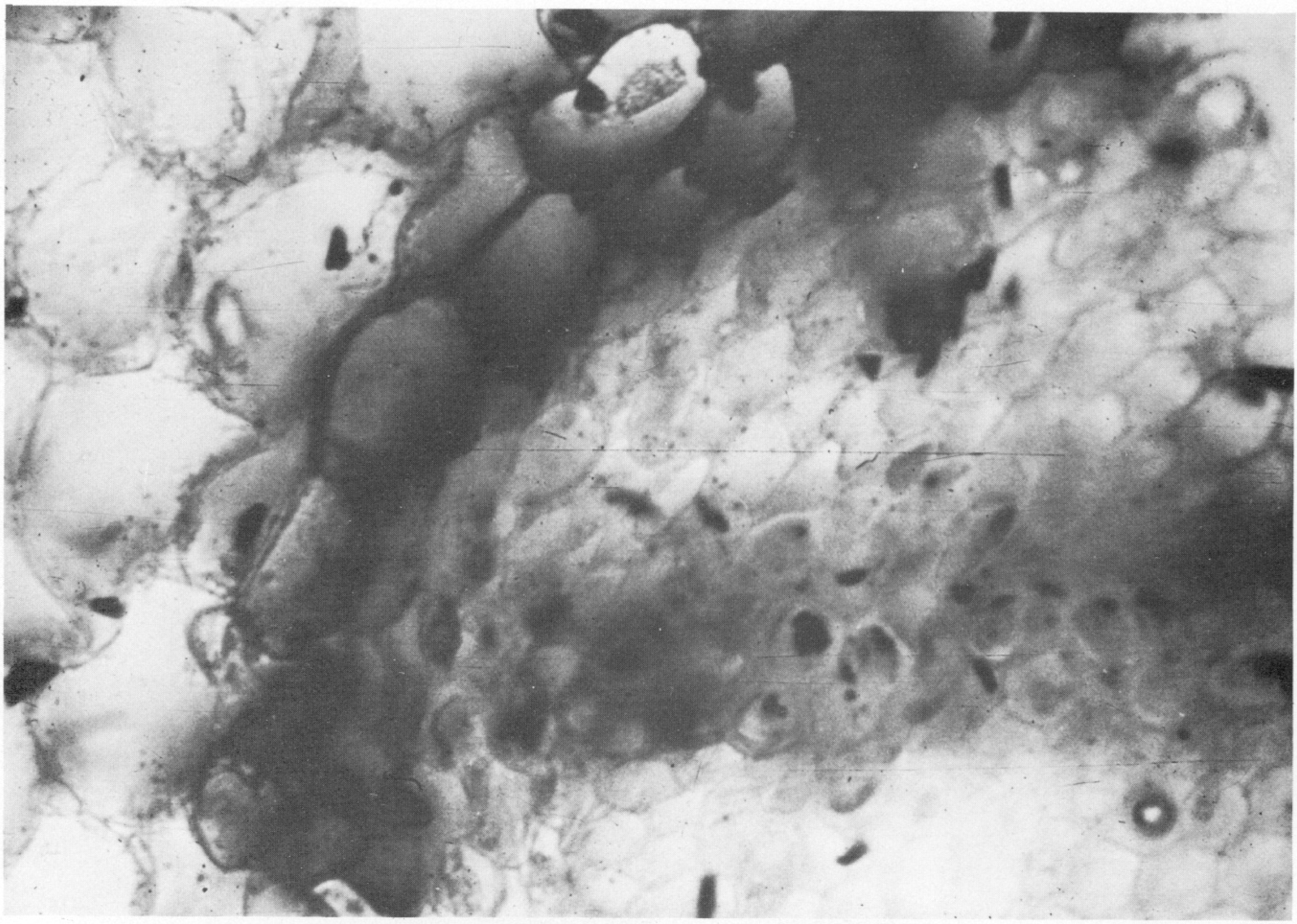

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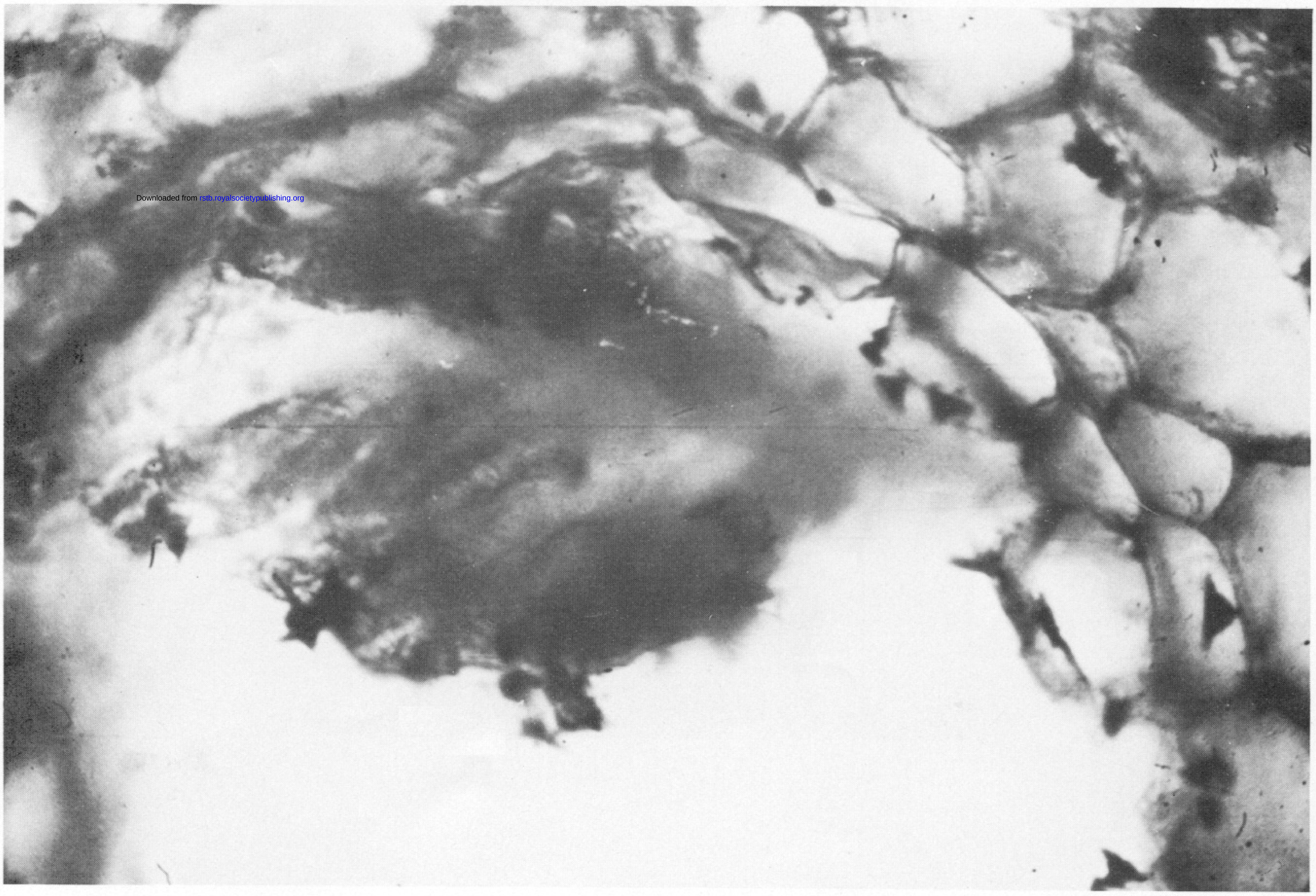

FIGURES 7 AND 8. For description see opposite.