ACIDITY OF PRECIPITATION AS INFLUENCED BY THE FILTERING OF ATMOSPHERIC SULPHUR AND NITROGEN COMPOUNDS - ITS ROLE IN THE ELEMENT BALANCE AND EFFECT ON SOIL

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INTRODUCTION

The data presented here are based upon element balance investigations in a beech forest in Central Germany (Ellenberg 1971).

Being located in an altitude of about 500 m above sea level with an annual precipitation of about 1000 mm, and an acid soil with loess as the main constituent, the test site represents a typical environment for many Central European forests.

Situated apart from larger industrial centers or big cities, it may also - for Central European conditions - be considered as a clean air region with a relatively low level of air pollution.

METHODS

The methods used to measure the element stores and the element fluxes in the forest ecosystem were described in earlier papers (Mayer 1971, 1972; Ulrich et al. 1972a, b; Pavlov 1972). They included the use of

(a) faingauges for collection of wet precipitation (wetfall) and dry deposition (dryfall) beneath the tree canopy and on a non-forested area close to the forest test site.

(b) stemflow collectors

(c) funnels to collect the litterfall

(d) funnel lysimeters for collection of the element flux coupled with seepage water below the humus layer

(e) tension lysimeters for collection of the element flux below the root zone

(f) plant and soil chemical analysis to determine the element content of the different parts of the ecosystem.

RESULTS

Some results of the element flux measurements, expressed in kilograms per hectare per year and kiloequivalents per hectare per year, respectively, are given in table 1 and 2. Each flux was sampled continuously over 5 (or 3) years and analyzed monthly. These data were summed up for annual values.

Table 1 : Solling Beech Site - Annual Element Input
(Average Values 1969 - 1974)

	Water	H	Na	K	Ca	Mg	Fe	Mn	Al	Cl	S	P	N	NO_3-N
a.	l/m^2	kilograms per hectare per year												
(1) Non-forested area (above canopy)	1080	.90	8.2	3.8	13.9	2.2	.90	.6	1.2	17.9	24.5	.71	23.7	7.1
(2) Beneath canopy	796	1.21	12.5	22.9	26.0	3.7	1.2	3.0	1.5	31.6	44.2	.55	24.7	7.4
b.		kiloequivalents per hectare per year												
(1) Non-forested area (above canopy)		.90	.36	.10	.69	.18	.02	.02	.13	.50	1.53	.07	1.69	.51
(2) Beneath canopy		1.21	.54	.59	1.30	.30	.05	.11	.17	.89	2.76	.05	1.76	.53

Table 2 : Solling Beech Site - Annual Element Fluxes
(Average Values 1969 -1972)

	Water	H	Na	K	Ca	Mg	Fe	Mn	Al	Cl	S	P	N
a.	l/m^2	kilograms per hectare per year											
(1) Litterfall	-	-	.7	16.	16.2	1.6	1.8	5.1	.5	.8	3.2	4.0	49.4
(2) Seepage below root zone (100 cm)	531	.30	10.6	5.9	16.6	3.4	.1	5.6	12.7	33.	27.4	.05	6.
b.		kiloequivalents per hectare per year											
(1) Litterfall	-	-	.03	.41	.81	.12	.06	.19	.06	.02	.20	.39	3.53
(2) Seepage below root zone		.30	.46	.15	.83	.28	0.	.21	1.41	.94	1.71	.005	.43

For most elements the input by precipitation (wetfall plus dryfall) to the soil beneath the tree canopy is considerably larger than that to the canopy surface, as measured with the aid of raingauges on a non-forested area. Two effects may be responsible for this:

(1) Leaching of metabolites originating from the internal turnover of the trees, mainly from the leaf surfaces.

(2) Washing out of substances from leaves, branches and stems. The origin of these substances are airborne particles and atmospheric aerosols intercepted by the trees from the atmosphere.

From an ecological view this latter process is of main importance because it represents the filtering effect of the forest towards atmospheric substances. These substances have to be regarded as an input to the forest ecosystem in addition to the input measured as wetfall plus dryfall above the canopy surface or on non-forested areas.

For a judgement of the effectiveness of the forest in cleaning a polluted atmosphere, and of the impact of the filtered substances on the forest ecosystem itself, the magnitude of both fluxes - leaching and filtering - is required. Since there exists no experimental approach to separate the fluxes an indirect way for their assessment was proposed (Mayer et al. 1974).

This method, applicable only on deciduous forests, is based upon the assumption that during the leafless winter time the internal turnover of the trees does not contribute significantly to the element content of the precipitation within the forest stand. In fact, most investigators describe the leaching process to take place at the leaf surfaces (Yamada et al. 1966, Tukey 1970). The difference between the element input coupled with precipitation to the forest soil and that to the forest canopy must be - during the state of defoliation of the trees - due to the filtering of atmospheric substances by the trees. For the summer months no similar procedure for calculation is available. A reasonable estimate for the filtering is received by using the same ratio between free area input and filtering for the winter as well as for the summer months. This assumption may be justified by the fact, that concentration of elements in the atmosphere affects both of these incoming fluxes in the same way.

On the other hand the estimate is rather on the minimum side for the same filter efficiency is assumed for the foliated as well as for the defoliated state of the trees.

Following this procedure, the filtering and leaching have been calculated on a seasonal base (winter: November - April, summer: May - October).

Average annual values are given in table 3.

Table 3 : Solling Beech Site - Annual Element Input by Filtering from the Atmosphere

	Na	K	Ca	Mg	Fe	Mn	Al	Cl	S	P	N	NO_3-N
(1) $kg.ha^{-1}.year^{-1}$	3.8	7.3	8.6	1.3	.5	1.5	.5	12.5	14.9	.09	4.8	1.4
(2) $keq.ha^{-1}.year^{-1}$	.17	.19	.43	.11	.02	.06	.06	.35	.93	.01	.34	.10

The input/output difference for the forest ecosystem gives the changes in the element stores within the system. The annual changes in the element stores (increments) of the trees have been measured (cf. Mayer 1971), results are given in table 4 (1).

Table 4 : Solling Beech Site - Annual Changes in Element Stores
(positive = gains ; negative = losses)

	H	Na	K	Ca	Mg	Fe	Mn	Al	Cl	S	P	N
a.	kilograms per hectare per year											
(1) In trees (bole)	-	.1	6.6	7.7	1.7	.7	3.4	.1	.1	.5	2.1	13.1
(2) In soil	1.7	-1.3	-1.4	-1.8	-1.6	.9	-6.9	-11.1	-2.9	11.5	-1.35	9.4
b.	kiloequivalents per hectare per year											
(1) In trees (bole)	-	.00	.17	.39	.14	.02	.13	.01	.00	.03	.20	.94
(2) In soil	1.7	-.06	-.03	-.09	-.13	.03	-.26	-1.23	-.08	.72	-.13	.67

It is now possible to calculate the annual changes in element stores within the soil, ΔCS, from

$$\Delta CS = IN_1 + IN_2 - OUT - \Delta CP$$

where IN_1 = input by wetfall plus dryfall (table 1 (1))

IN_2 = input by filtering (table 3)

OUT = output by seepage below root zone (table 2 (2))

ΔCP = changes in element stores in the trees (table 4 (1))

Results of this calculation are given in table 4 (2). Negative figures are standing for element losses, positive values for element gains.

DISCUSSION

To take a closer look on the effects of acidity some relevant figures are drawn from tables 1 - 4 and repeated in table 5, together with the input of hydrogen ions to the mineral soil as measured with the aid

Table 5 : Solling Beech Site - Annual Hydrogen Balance

	kiloequivalents per hectare per year		
(1) Precipitation input to canopy (wetfall plus dryfall)	.90	1.53	.51
(2) Filtering (sum of S plus NO_3- N)	1.03	.93	.10
(3) Precipitation input to soil surface	1.21	2.76	.53
(4) Buffering of H^+-ions within stand = (1) + (2) - (3)	.72		
(5) Input to mineral soil	2.00		
(6) H^+-ion production by litter decomposition = (5) - (3)	.79		
(7) Output with seepage below root zone	.30		
(8) Buffering of H^+-ions within mineral soil = (5) - (7)	.70		

of funnel lysimeters.

Under the conditions prevailing in the test area it may be assumed that most of the sulphate and nitrate found in the precipitation entered the atmosphere not as neutral salts but rather as sulphur dioxide and nitric or nitrous oxides. These oxides were then transformed by oxidation and dissolution to form finally sulphuric and nitric acid. In these processes each equivalent of nitrogen and sulphur requires one equivalent of hydrogen ions.

Comparing the sum of sulphate and nitrate in the incoming precipitation with the amount of hydrogen we realize that more than half of the respective acids are neutralized by bases, that is by other air contaminants like calcium oxide CaO.

In the same way the sulphur and nitrogen filtered from the atmosphere by trees and then washed out by rain contribute to the acidity. again the acidity is neutralized to a great extent by filtered air contaminants or by plant metabolites. The hydrogen ion input into the mineral soil as measured in lysimeters is 2 keq . ha^{-1} .$year^{-1}$, from which 60% = 1.21 keq . ha^{-1} . $year^{-1}$ originate from the precipitation input, 40% from the litter decomposition with mineralization of nitrogen and sulphur compounds.

While in calcareous soils nearly the total amount of hydrogen ions is neutralized, in the acid soil under consideration, where aluminium forms the buffer system for the soil solution, still more than 80% of the acidity is neutralized.

This buffering of the soil solution takes place in the upper 20 to 30 cm of the soil, most accentuated in the uppermost 1 to 2 cm of the mineral soil. Here pH values of as low as 3 are observed.

Comparing the input-output data from the Solling beech forest with those of a spruce forest in the same area, table 6, (Mayer et al. 1974), it can be seen that the hydrogen ion and sulphur fluxes in the spruce forest exceed the ones of the beech forest considerably, so that all effects associated with acidity of precipitation are expected to be more accentuated here.

Table 6 : Comparison Beech/Spruce

	kilograms per hectare per year			
	H		S	
	Beech	Spruce	Beech	Spruce
(1) Precipitation input to canopy (wetfall plus dryfall)	.9	.9	24.5	24.5
(2) Precipitation input to soil	1.21	2.61	44.2	75.4
(3) Output with seepage below root zone	.30	.35	27.4	43.

CONCLUSIONS

The element balance data allow to draw some conclusions regarding the effect of acidity of precipitation on the forest ecosystem:

The buffering of protons - and to a minor extent accumulation of Fe in the mineral soil balanced by the loss of Al, Mn and - to a smaller extent - Na, K, Ca and Mg. This is possible by the weathering of silicates, or - as in the case of K, Ca and Mg - by desorption from the exchangeable fraction.

These processes definitely change the soil chemical conditions in the uppermost 1 to 2 cm of the soil. While tree growth is probably not affected by the acidification of this layer, a disturbance of all plants rooting very close to the soil surface, as e.g. germinating plants, is to be expected.

Ulrich et al. (1968) have shown, in which way this could happen: In a germination experiment with oats they found evidence that the damage of plants grown on soils with pH around 3 or lower was due to an inundation with Al and Fe, and perhaps Mn. The high concentration of these elements in the soil solution at low pH led to a blocking of the phosphate transport from the seeds to the shoots. This process may be a sound explanation for the difficulties met in recent years in the natural reproduction of beech in Germany. Another effect of the acidity of precipitation is probably the accumulation of sulphur in the soil, which becomes evident from the element balance. The question in what form sulphate is accumulated is still under study. It may be tied up in only slightly soluble minerals of the alunite - jarosite group, known from acid soils (van Breemen, 1972). In this minerals of the type $AlOHSO_4$ each sulphate requires one equivalent Al.

The loss of Al, which is shown in table 4 (2) gives the amount annually set free by the weathering of silicates. It corresponds with 80 kg of clay minerals or plagioclase; or with 130 kg if the aluminum set free by weathering is partly tied up in newly formed sulphates. If we keep in mind that the acidification is effective mainly in the top 1 to 2 cm of the soil, this means an annual loss of about 1% of the total clay and plagioclase of the loess soil. From this reasoning a manmade podzolization of the upper A-horizons seems possible.

Finally the acidification of the soil and the associated loss of Mg may become a problem in the supply of this nutrient element in near future. A great number of recent leaf and needle analysis' point into this direction. The same is true for manganese. By the annual loss of nearly 6 kg/ha the total store in the upper 20 cm of the soil is depleted by 0.3%. As a consequence the Mn-concentration in rivers and in young river sediments reach considerable values.

ABSTRACT

Acidity of throughfall precipitation is increased by the filtering of sulphur and nitrogen from the atmosphere by trees. An element balance for a beech forest is given. As a consequence of acidification the soil chemical conditions are changed in a way, that plants rooting close to the soil surface are affected. Losses of nutrients may pose a problem in forest plant nutrition in the near future in Central European forests on light or medium textured acid soils.

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