Forest influence on the surface water chemistry of granitic basins receiving acid precipitation in the Vosges massif, France

A. PROBST
Institut de Géologie, ULP, 1 rue Blessig, F
67084 Strasbourg Cedex, France
B. FRITZ
Centre de Sédimentologie et de Géochimie de la
Surface (LP 6251 CNRS), 1 rue Blessig, F 67084
Strasbourg Cedex, France
B. AMBROISE & D. VIVILLE
Centre d'Etudes et de Recherches Eco-
Géographiques (UA 95 CNRS), ULP, 3 rue de
l'Argonne, F 67083 Strasbourg Cedex, France

ABSTRACT This study shows the influence of acid rain on
the chemistry of surface waters in two small basins. The
basins present similar altitudes and climates, only one
is forested, and the forest decline has been clearly
established. In both basins, rain water is polluted by
acids (H^+, SO_4^{2-}, NO_3^-). This acid input is neutralized in
soils but the efficiency of that neutralization varies
from one basin to another: (a) in the non forested
basin, the alkalinity of surface water dominates the
anionic charge, (b) in the forested basin, the strong
acid anions still dominate the anionic charge of a just
neutralized solution. The chemistry of surface water in
the forested basin cannot be explained only by the inci-
dent rainfall and its partial evaporation. There appears
to be a major input of pollutant through dry deposits in
throughfall.

Influence de la forêt sur la chimie des eaux de surface
de bassins granitiques soumis à des précipitations acides
dans le massif des Vosges, France
RESUME Cette étude montre l'influence des précipitations
acides sur la chimie des eaux de surface dans deux petits
bassins versants d'altitude et de climat similaires. Un
seul de ces bassins est boisé et sujet au dépérissement
des forêts. Dans les deux bassins, la pluie est polluée
par un apport d'acides (H^+, SO_4^{2-}, NO_3^-) neutralisé dans
les sols. L'efficacité de cette neutralisation varie
d'un bassin à l'autre: (a) dans le bassin non boisé,
l'alcalinité des eaux de surface domine la charge
anionique, (b) dans le bassin boisé, les anions d'acides
forts dominent encore la charge anionique d'une solution
tout juste neutralisée. La chimie des eaux de surface du
bassin boisé ne peut être expliquée par les pluies

incidentes et une évaporation partielle. Il faut
envisager un apport majeur de polluants sous forme de
dépôts secs dans les pluviolessivats.

INTRODUCTION

The acidity of rain waters has been clearly established in many
places of the Vosges massif and in the neighboring Rhine valley
(Bourrié, 1978; Fritz, 1982; Fritz *et al.*, 1984). This phenomenon
is part of a general pollution of the atmosphere in the Northwest of
Europe, and it was first studied in France for its effect on the
weathering of sandstones used in monuments and buildings (Gross,
1978; Fritz & Jeannette, 1981). Recent works were initiated for
studying the effect of that pollution on forested areas (National
Program DEFORPA "Dépérissement des Forêts Attribué à la Pollution
Atmosphérique"). The Vosges massif is largely forested, mostly by
conifers, and these forests present now the evidence of a recent
decline: 24.2% of white fir, 12.8% of spruce and 18.5% of Scots
pine have lost more than 25% of their needles. Moreover, yellowing
needles is the other decline symptom particularly obvious on
spruces. This paper presents a comparative study of two basins,
respectively forested and non forested, to show the influence of
acid rain water on the chemical composition of surface water and
particularly the effect of a declined coniferous forest. The data
already available for comparison are limited to the geochemical
characterization of rain, spring and stream water. The research in
progress will try to establish the fluxes of chemical elements in
the basins.

THE STUDIED AREAS

The Strengbach basin (0.80 km^2) at Aubure and the Ringelbach basin
(0.36 km^2) at Soultzeren are located on the eastern and Alsacian
side of the Vosges mountains (eastern France), respectively 58 and
72 km SW from Strasbourg (Fig.1). These two small basins have
similar elevation range (respectively 883-1146 m and 748-1000 m
a.s.l.) and granitic bedrocks. Their shallow and coarse texture
soils belong to the brown and podzolic series, with hydromorphic
conditions in the valley bottom.

They have a temperate oceanic mountainous climate, with monthly
averages of daily mean temperature ranging from -2° to 14°C. The
mean annual precipitation is about 1200-1300 mm - ca. 15% as snow-
fall. Stream discharges are usually high in winter and spring, when
the snowmelt occurs, and low from August to October.

The major differences between the two basins concern the vegeta-
tion. The Strengbach catchment, oriented W-E, is completely for-
ested with conifers (80%, spruce and white fir) and beech (20%),
which are affected by the recent forest decline. The Ringelbach
catchment, facing SW, is mostly covered by pasture (75%), with a
small Scots pine forest (25%) on the top.

FIG.1 *General location map of the two studied areas in Alsace (eastern France).*

MATERIALS AND METHODS

Hydrological equipment

The Strengbach catchment, which is studied since August 1985, and the Ringelbach study catchment, which is equipped since 1976 (ERA 569 CNRS 1982) have similar hydroclimatologic equipment (Fig.1): meteorological shelters and rain recorders both on the crests and the valley bottom, water level recorders on the stream (H-flume on the Strengbach, since July 1986, and 26.5° V notch weir on the Ringelbach). In addition, there is a network of rain gauges and (since October 1986) throughfall collectors under forests of the Strengbach basin.

Water sampling and measurements

Water is sampled in polyethylene bottles and filtered in the labora-tory (Millipore 0.45 μm filter). The major inorganic species were analyzed using mostly the classical techniques. Calcium, magnesium, sodium and potassium are analyzed by Atomic Adsorption Spectrophoto-metry; ammonium, chloride, nitrate, nitrite, sulfate, silica are analyzed by automatic colorimetry (Technicon apparatus). Alkalinity or acidity is determined by careful titration (near neutral solutions). Sampling methods are described and detailed in Krempp (1982).

In the Ringelbach basin, water samples were collected at springs and outlet approximately once a month from mid-1981 to mid-1982, with additional sampling during hydrological events. Seven monthly bulk samples of rain waters were collected during this period. After that period, samples were taken about every three months to confirm the range of variation of chemical composition.

Since August 1985, the samples in the Strengbach basin have been collected regularly twice a month, with additional sampling during flood events: (a) since August 1985 for rain, springs and stream waters, (b) since October 1986 for throughfall.

RESULTS AND DISCUSSION

Analytical results

The Strengbach basin is still in the process of being equipped for hydrological measurements. So, the comparison between the forested and the non forested basins is limited to the geochemical charac-teristics of the different surface waters (concentrations), with no discussion on chemical fluxes. For that reason, the chemical com-position will be presented and discussed using the most convenient units such as microequivalents per litre (μeq l^{-1}) and mg l^{-1}, the latter, with reference to the total dissolved solids (TDS).

Rain water   The chemical composition of acid rain waters for the two basins is very similar (Table 1). The concentrations are all very low (<50 mg l^{-1}) and slightly acid (mean pH = 4.5).

TABLE 1   *Chemical composition of rain water of the Ringelbach and Strengbach basins: minimum, mean and maximum values*

	Ringelbach basin (non forested) (PR:7 samples)			Strengbach basin (forested) (PS:19 samples)		
	min	mean	max	min	mean	max
pH* (labo)	3.91	4.53	6.46	4.09	4.48	6.36
NH_4^+ (μeq l^{-1})	1	26.3	60	1	24.9	110
Na^+ "	7	28.6	118	3	11.5	31
K^+ "	11	23.7	34	1	4.9	19
Mg^{2+} "	8	14.6	36	2	5.0	10
Ca^{2+} "	28	51.4	66	6	23.6	74
H^+ "	0.35	29.4	122	0.43	33.2	81
Alkalinity + H^+	8	15.0	36	0	6.1	49
Cl^- "	12	38.6	145	5	15.2	34
NO_3^- "	8	28.1	49	5	28.5	71
SO_4^{2-} "	54	82.3	110	18	52.5	130
H_4SiO_4 ($\mu mole$ l^{-1})	<1	<1	<1	<1	<1	<1
TDS (mg l^{-1})	11.4	7.7	16.6	3.2	6.8	15.1

mean pH is calculated as -log (mean H^+).

A Piper's diagram (Fig.2) shows how the major cations and anions contribute to the total ionic charge, using their respective percentage of charge. The rain waters (PS and PR) fall in the same area of very low carbonate alkalinity (alkalinity + H^+). The anionic charge is dominated by strong acid anions (SO_4^-, NO_3^-, Cl^-). H^+ and NH_4^+ are major cations, considering the concentrations in terms of equivalents or moles which characterize the chemical potential of the solution, instead of milligrams which only give the mass transfer, but will be used later for fluxes calculations.

Spring water   The spring waters from the two basins (SS, RS_1 and RS_2) are slightly more concentrated than the rain waters - TDS ranging from 35 to 65 mg l^{-1} - and always nearly neutral (Table 2). They differ however from one basin to another:

(a)   In the non forested Ringelbach basin, the original acidity of the rain water has been clearly neutralized, the influence of the weathering process can be seen on Fig.2 (RS_1 and RS_2), with an increase of the carbonic alkalinity (HCO_3^-, CO_3^{2-}) in the anionic charge and the disappearance of H^+ in the cationic charge (Table 2). In the Piper's diagram (Fig.2), these waters fall in the normal area for spring water in crystalline rocks (RS_1, RS_2) for either anions and cations.
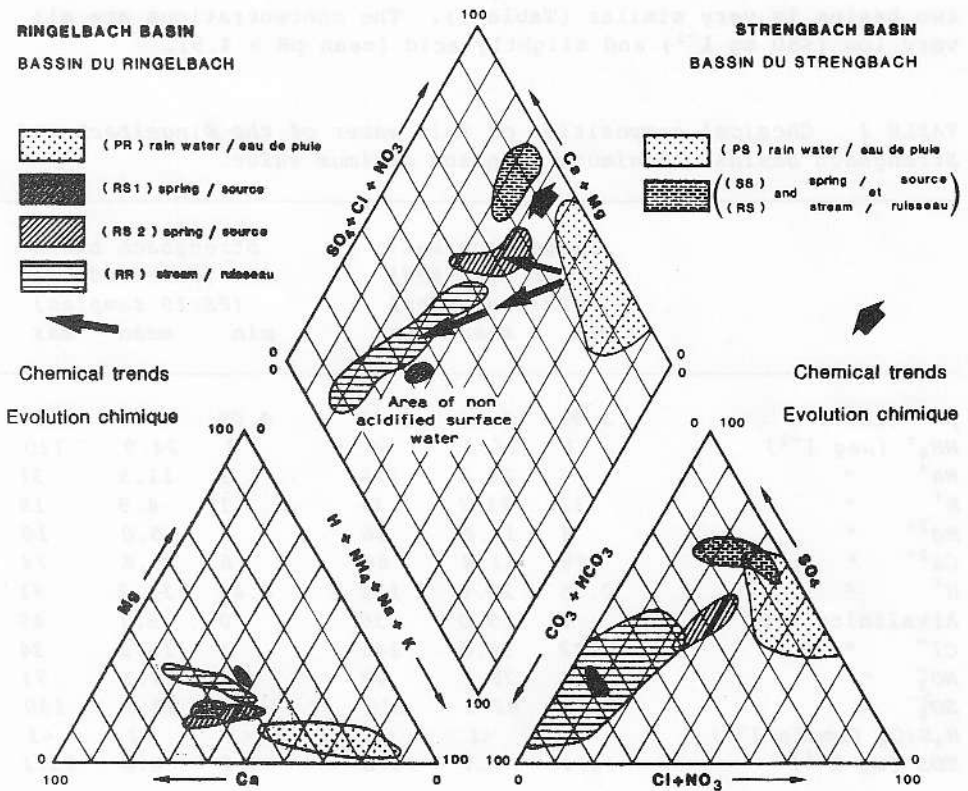
FIG.2   Piper's Diagram: Percentage of cations and
anions respectively in the cationic and the anionic
charge for rain, spring and stream water of the two
basins.

(b)   In the forested Strengbach basin, the acidity has also been
neutralized, but the anionic charge remains dominated by the strong
acid anions (SO_4^{2-}, NO_3^-, Cl^-) as seen in Fig.2 (SS).

Stream water at the outlets   The tendencies observed in spring
water are confirmed in the stream water sampled at both outlets.
This is true for the total dissolved solids (TDS between 30 and
65 mg l^{-1}) and the neutralization of original rain water acidity
(Table 3):
(a)   In the Ringelbach basin, the stream water composition shows
an obvious trend (Fig.2, RR) between the most concentrated low water
(HCO_3^-, Ca^{2+}, Mg^{2+}) and a more diluted end member influenced by rain
water (HCO_3^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+). This corresponds respectively
to the two types of spring waters found in the basin: one is more
representative of groundwater (RS_1) while the second is highly
influenced by the precipitation (RS_2).
(b)   In the forested Strengbach basin, the stream water (RS) has
a chemical composition very similar to that of spring water (SS)
(Fig.2).

TABLE 2 Chemical composition of spring waters of the Ringelbach and the Strengbach basins: minimum, mean and maximum values

| | | Ringelbach basin (non forested) | | | | | | Strengbach basin (forested) | | |
| | | (RS$_1$:8 samples) | | | (RS$_2$:17 samples) | | | (SS:24 samples) | | |
		min	mean	max	min	mean	max	min	mean	max
pH*	(labo)	6.55	6.67	7.04	5.50	6.14	7.02	5.52	5.82	6.41
NH_4^+	(μeq l^{-1})	<1	<1	<1	<1	<1	<1	<1	1	4
Na^+	"	104	108.5	112	44	47.6	54	78	89.2	103
K^+	"	55	58.6	66	13	25.4	37	20	21.7	27
Mg^{2+}	"	118	121.8	134	20	25.6	40	46	49.3	58
Ca^{2+}	"	174	182.0	198	64	79.2	126	174	184.8	226
H^+	"	0.09	0.2	0.3	0.1	0.7	3.2	0.4	1.5	3.02
Alkalinity + H^+	"	298	307.4	337	2	42.9	78	32	47.4	64
Cl^-	"	27	30.1	38	36	42.4	52	45	48.1	56
NO_3^-	"	<1	4.6	26	<1	9.2	19	6	41.2	59
SO_4^{2-}	"	106	115.3	124	58	79.5	144	200	207.6	220
H_4SiO_4	(μmole l^{-1})	196	213.6	298	74	87.1	95	112	139.5	171
TDS	(mg l^{-1})	53.4	56.1	63.3	19.7	20.9	22.5	33.8	37.7	42.6

*mean pH is calculated as -log (mean H$^+$).

The chemical evolution of waters from rain water to spring and stream water is different for the two basins as clearly shown in Fig.2 by the corresponding arrows.

Discussion

Due to the lack of reliable flow data it is not yet possible to compare the fluxes of chemical mass transfers in these two basins, however it appears clearly that the chemical composition of spring and stream water are significantly different, even if the initial rain water has almost the same composition.

In the forested basin, the initial rain acidity is still neutralized in the soils and does not appear in the spring water, as in the non forested basin (Fritz, 1982; Fritz et al., 1984). However, the characteristic strong acid anions (SO_4^{2-}, NO_3^-, Cl^-) remain dominant in all the waters sampled. Moreover, one may observe that the sulfate content is more important in spring and stream water than in rain water (Table 1 to 3). This could not be explained by an underground origin through weathering or by evaporation:

(a) The weathering origin cannot be taken into account in such a granitic environment with no evidence at all of sulfides oxidation (pyrites).

(b) The concentration induced by the evaporation process could perhaps explain part but not all of the phenomenon: stream mean sulfate/rain mean sulfate annual ratio up to four.

As a consequence, the only possible major source of sulfate must be searched in dry deposits (Likens et al., 1977; Hultberg et al., 1983; Dupraz, 1984; Lovett & Lindberg, 1984; Hultberg, 1985). The rain water described above has been sampled as incident bulk precipitation. So, it includes only the dry deposition captured by the rain collector itself and not the dry deposition to the surface of the conifer needles and twigs. First results from throughfall (October 1986, after a dry period) show that the sulfate content in throughfall samples is five to ten times that in the incident rainwater. These first results need to be confirmed over a period of at least a year but correspond to results obtained elsewhere (Mayer & Ulrich, 1980; Buldgen, 1984; Dumazet, 1983). In fact, Mayer & Ulrich (1980) think that another mechanism is added to the impaction of aerosols: adsorption of SO_2 in the water films adhering to the needles and oxidization to H_2SO_4 with the next rain.

The differences between the chemical composition of stream waters in the two basins appears very clearly in the calcium-bicarbonate and calcium-sulfate diagrams (Fig.3A,B). The correlation between these major constituents of the solutions are strictly opposite in the two basins:

(a) In the non forested Ringelbach basin, calcium and bicarbonate are positively correlated (r = +0.987), calcium and sulfate are negatively correlated (r = -0.800); this corresponds to an important neutralization of the original rain water acidity by the weathering process. Even when the alkalinity is minimum (>120 μeq l^{-1}), the sulfate is not dominant (<120 μeq l^{-1}).

(b) In the forested Strengbach basin, these correlations are exactly opposites to those of the non forested basin, respectively

r = -0.887 and r = +0.950. The buffering effect of the weathering process remains weak and the alkalinity is always less than the sulfate concentration. A cationic exchange process in soils has replaced the protons by calcium ions (Pacès, 1985).
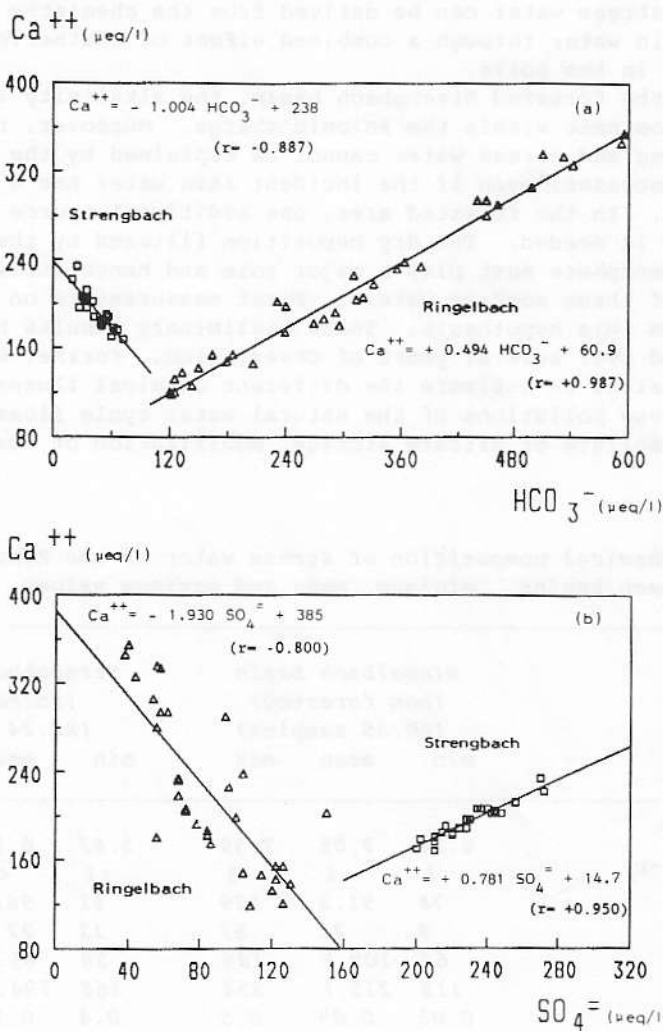

FIG.3 Comparison of the relationship between (a) calcium and bicarbonate (b) calcium and sulfate concentrations of stream waters for the Ringelbach (non forested) and the Strengbach (forested) basin.

CONCLUSION

The study of surface water chemistry in two similar drainage basins on a granitic bedrock has shown very clear differences. In both basins, the incident rainfall gives an acid rain water. This original acidity input is neutralized in the podzolic soils and is no

more present in spring water, where the strong acid anions are the only tracers of that pollution. However, the degree of that neutralization is very different for the two basins:

(a) In the non forested Ringelbach basin, the alkalinity (HCO_3^-) is throughout the year the dominant anion and the chemistry of the spring and stream water can be derived from the chemistry of the incident rain water through a combined effect of weathering and evaporation in the soils.

(b) In the forested Strengbach basin, the alkalinity is very low and never dominant within the anionic charge. Moreover, the chemistry of spring and stream water cannot be explained by the same combined processes, even if the incident rain water has a similar composition. In the forested area, one additional source of acidity and sulfate is needed. The dry deposition filtered by the conifers from the atmosphere must play a major role and hence influence the chemistry of these surface waters. First measurements on throughfall confirm this hypothesis. These preliminary results have now to be confirmed over several years of observation. Further measurements will allow to estimate the different chemical fluxes associated with these pollutions of the natural water cycle (loss of nutrients, sulfate or nitrate storage, mobilization of toxic ions...).

TABLE 3   Chemical composition of stream water of the Ringelbach and the Strengbach basins: minimum, mean and maximum values

	Ringelbach basin (non forested) (RR:35 samples)			Strengbach basin (forested) (RS:24 samples)		
	min	mean	max	min	mean	max
pH* (labo)	6.34	7.05	7.59	5.82	6.12	6.44
NH_4^+ (μeq l^{-1})	1	1	5	<1	<1	2
Na^+ "	74	91.5	129	81	96.0	119
K^+ "	7	23	57	13	27.7	41
Mg^{2+} "	62	109.8	186	58	65.9	80
Ca^{2+} "	118	215.1	354	168	194.9	234
H^+ "	0.03	0.09	0.5	0.4	0.76	1.5
Alkalinity + H^+	120	312.5	595	20	42.9	72
Cl^- "	6	31.4	94	44	66.4	117
NO_3^- "	<1	<1	3	1	34.9	67
SO_4^{2-} "	38	86.6	150	200	230.9	272
H_4SiO_4 ($\mu mole$ l^{-1})	64	123.3	145	103	127.4	146
TDS (mg l^{-1})	31.1	45.7	66.2	33.5	38.3	45.1

*mean pH is calculated as -log (mean H^+).

REFERENCES

Bourrié, G. (1978) Acquisition de la composition chimique des eaux en climat tempéré. Application aux granites des Vosges et de la Margeride. *Sci. Géol., Mém.* 52, Strasbourg.

Buldgen, P. (1984) Etude écosystémique de deux bassins versants boisés en Haute-Ardenne. Thèse Doc. Sci. Botaniques, Univ. Liège.

Dumazet, B. (1983) Modification de la charge chimique des eaux au cours du transit à travers trois écosystèmes distincts du Mont - Lozère. Thèse $3^{ième}$ cycle, Univ. Orléans.

Dupraz, C. (1984) Bilans des transferts d'eau et d'éléments minéraux dans trois bassins versants comparatifs à végétations contrastées (Mont. - Lozère, France). Thèse Doc. Ing., Géologie appliquée (hydrologie), Univ. Orléans, 363 p. et annexes.

ERA 569 du CNRS (1982) Structure et fonctionnement du milieu naturel en moyenne montagne: Bassins de la petite Fecht et du Ringelbach (Vosges, France). Rech. Géogr. à Strasbourg 19/20/21.

Fritz, B. (1982) Caractéristiques chimiques des eaux de surface d'un bassin versant des Vosges du Sud. *Rech. Géogr. à Strasbourg* 19/20/21, 179-184.

Fritz, B. et Jeannette, D. (1981) Pétrographie et contrôle géochimique expérimental de transformations superficielles de grès de monuments. *Sci. Géol. Bull.* Strasbourg, 34(4), 193-208.

Fritz, B., Massabuau, J.C. & Ambroise, B. (1984) Physico-chemical characteristics of surface waters and hydrological behaviour of a small granitic basin (Vosges massif, France): annual and daily variations. In: *Hydrochemical Balances of Freshwater Systems*, (Uppsala Symp., September 1984), IAHS Publ. no. 150, 249-261.

Gross, J.J. (1978) Caractérisation et évolution de l'altération des grès de la cathédrale de Strasbourg. Thèse de $3^{ième}$ cycle, U.L.P. Strasbourg, France.

Hultberg, H., Grennfelt, P., Olsson, B. (1983) Sulphur and chloride deposition and ecosystem transport in a strongly acidified lake watershed. *Wat. Sci. Tech.* (Copenhagen), 15, 81-103.

Hultberg, H. (1985) Budgets of base cations, chloride, nitrogen and sulphur in the acid Lake Gardsjon catchment, SW Sweden. *Ecol. Bulletins* 37, 133-157.

Krempp, G. (1982) Techniques de prélèvement des eaux naturelles et des gas associés. Méthodes d'analyse des eaux et des roches. *Notes techniques* No. 11, Institut de Géologie, Strasbourg, France.

Likens, G.E., Bormann, F.H., Pierce, R.C., Eaton, J.S. & Johnson, W.M. (1977) Biogeochemistry of a Forested Ecosystem. Springer-Verlag, New York.

Lovett, G.M. & Lindberg, S.E. (1984) Dry deposition and canopy exchange in a mixed oak forest as determined by analysis of throughfall. *Journal of Applied Ecology* 21, 1013-1027.

Mayer, R. & Ulrich, B. (1980) Input to soil, especially the influence of vegetation in intercepting and modifying inputs - a review. In: *Effects of Acid Precipitation on Terrestrial Ecosystems*, Hutchinson and Havas, NATO conference series, Series I: Ecology 4, 173-182.

Paces, T. (1985) Sources of acidification in Central Europe estimated from elemental budgets in small basins. *Nature* vol. 315, no. 6014, 31-36.