

## EFFECT OF SOIL ACIDIFICATION ON THE FORMATION OF Fe-, Al-, AND Mn-OXIDES AND THE STABILITY OF SOIL AGGREGATES

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**A b s t r a c t.** The effect of intensive soil acidification on the genesis of Fe-, Al- and Mn-oxides and their relation to the soil aggregate stability were investigated in the Vienna Woods. Analyses were carried out on soil samples of 2 sites at 4 depths (0-5, 5-10, 10-20, and 20-30 cm) taken from the infiltration zone of the stemflow (S) of beech trees, which is strongly influenced by acid atmospheric depositions (soil-pH KCl 2.5 to 3.0), and from non-contaminated reference areas (R) between the trees, where the acid input is much lower (soil-pH KCl 5.5). The extreme soil acidification in the infiltration zone of stemflow led to intensive weathering of primary minerals, to neoformation and accumulation of crystallized, amorphous and organic-bound Fe-oxides, to lower concentrations of Al- and Mn-oxides and to a high increase in soil aggregate stability, reflecting the aggregation effect of Fe-oxides, and the concomitant leaching of Mn and Al at a very low soil pH. Moreover, chemical extractions of the fine earth (water saturation extract and BaCl<sub>2</sub>-extraction) showed that Fe had accumulated in the strongly acidified soils also as water-soluble and exchangeable cation.

**K e y w o r d s:** soil acidification, soil aggregate stability, oxides

### INTRODUCTION

Pedogenical Fe- (Al-, Mn-) oxide minerals (comprising oxides, oxyhydroxides, and hydrated oxides), are the most abundant of the metallic oxides in soils. They cause the hues between red and yellow of most of the soils and reflect the pedoenvironmental conditions under which they formed [22]. Like in clay minerals, Fe-oxides are mainly present as very fine particles in the clay fraction (<2 µm) and

the Fe ion in the oxide mineral may be replaced by other metallic cations (isomorphous substitution). Substitution by Al occurs more frequently than by other cations.

Fe- (Al-, Mn-) oxides have the following properties relevant to soils:

a) On the hydroxylated or hydrated surface, a positive or negative charge is created by adsorption or desorption of H<sup>+</sup> or OH<sup>-</sup>. Because of its dependence on pH and ionic strength, this type of charge is called variable charge. The pH at which the net variable charge on the surface is zero, is called the point of zero charge (PZC). An excess of positive or negative surface charge is balanced by an equivalent amount of anions (A<sup>-</sup>) or cations (C<sup>+</sup>), respectively. For electrostatic (Coulombic) bonding, the adsorption is termed non-specific and depends only on ionic charge. Some anions and cations can, however, be held much more strongly (specific adsorption) on the oxide surface.

b) Fe-oxides also adsorb a wide range of organic compounds. Humic compounds such as humic (HA) and fulvic (FA) acids may be concentrated in Fe-oxide-rich horizons of soils under humid temperate conditions, such as B-horizons of Podzols. The amount of adsorbed FA and HA strongly increases with decreasing pH.

Amount and type of "free" oxides in soils are often the subject of investigation, because their formation and stability give informations about the intensity of genetic soil processes, including soil aggregation. One of the frequently used methods for the quantification of the total oxide content in soils is the chemical extraction of Fe, Al and Mn from the fine earth (<2 mm size) and/or from the clay fraction (<2  $\mu\text{m}$  size) by Na-dithionite-citrate-bicarbonate (DCB), [17]. Additional extractions by  $\text{NH}_4$ -oxalate [25,26] and Na-pyrophosphate [10] allow a further quantitative differentiation between poorly crystallized, amorphous and organic-bonded compounds. A qualitative distinction of the different pedogenical Fe-forms is possible using X-ray-diffraction and Mössbauer-spectroscopy.

Soil acidification, caused by natural and anthropogenical acid input, plays a decisive role in weathering processes, among them the formation and/or destruction of Fe-, Al- and Mn-oxides. The most relevant reaction inducing the neoformation of Fe(III)-oxides is the hydrolytic and oxidative decomposition of Fe (II)-containing primary minerals (Fe(II)silicates). From the degree to which this irreversible reaction has taken place, the degree of weathering, measured for example by the ratio of DCB-soluble Fe to total Fe ( $\text{Fe}_d/\text{Fe}_t$ ) or oxalate-soluble Fe to dithionite-soluble Fe ( $\text{Fe}_o/\text{Fe}_d$ ) can be deduced. Moreover, Fe-oxides are known as aggregating or cementing factors, due to crystal growth and to the attraction between positively charged Fe-oxide particles and negatively charged matrix particles, particularly clay minerals.

The aggregation effect of Fe-oxides has been demonstrated in various ways:

- a) by a significant correlation between the percentage of water-stable aggregates or related structural properties and the content of Fe-oxides [2,12,15];
- b) by the dispersion of aggregated soils after removal of Fe-oxides with a reducing agent [16];
- c) by the aggregating effect of added synthetic Fe-oxides [4,13,24].

These data indicate that Fe-oxides are the more effective in aggregating silty, e.g., loessial soils, the lower their crystallinity and the higher their oxalate solubility, i.e., the higher their  $\text{Fe}_o/\text{Fe}_d$  ratio is. Therefore, very small, highly charged Fe-oxide-polymers were found to be particularly effective in binding soil particles together [23].

The aim of this work was to determine the influence of soil acidification on the formation and behaviour of Fe-, Al- and Mn-oxides and their relationship to the water stability of soil aggregates.

## MATERIAL AND METHODS

### Site description and sampling procedure

The NE part of the Vienna Woods, mainly beech forests, is strongly polluted through urban and industrial depositions. In this area, the canopies of beech trees filter high quantities of air pollutants and acid rain, which are finally leached and concentrated through stemflow onto a limited soil compartment. Studies were carried out on 2 sites (Rieglerhütte, Jägerwiese) of the NE-Vienna Forest, situated at 500 m a.s.l. The soils in question are acidic Cambisols, according to the FAO-system [9], developed on calcareous sandstone of the Flysch zone and highly polluted with heavy metals, see Tables 1 to 3.

At each site, disturbed bulk soil samples (from an average of 10 trees) were taken at 4 depths (0-5, 5-10, 10-20, and 20-30 cm) in the contaminated infiltration zone of stemflow (S-area) and in the non-contaminated reference soils (R-area) between the trees, at 5-10 m distance from the stem, homogenized, air-dried, sieved at 2 mm (= fine earth), dried at 105 °C and analyzed as indicated below.

### Physical and micromorphological analyses

- Particle size distribution by wet sieving and sedimentation with Köhn-pipette method.

**Table 1.** pH-values, total carbon (Ct), total nitrogen (Nt), total sulphur (St) and Cation Exchange Capacity (CEC) of the investigated soils

Depth (cm)	pH (KCl)		Ct (%)		Nt (%)		St (%)		CEC (meq/kg)	
	S	R	S	R	S	R	S	R	S	R
Rieglerhütte										
0-5	3.3	4.5	22.4	6.3	1.3	0.4	2220	450	135	220
5-10	3.0	3.6	15.0	2.9	0.9	0.2	1510	240	120	141
10-20	2.9	3.5	5.3	1.6	0.3	0.1	580	150	106	125
20-30	3.1	3.6	2.1	1.1	0.1	0.1	230	60	105	120
Jägerwiese										
0-5	3.1	5.1	15.7	5.6	0.8	0.4	1460	440	155	333
5-10	2.8	4.6	7.1	3.7	0.4	0.3	690	250	132	272
10-20	2.7	3.7	2.8	1.9	0.2	0.2	260	150	152	201
20-30	3.1	3.9	1.6	1.6	0.1	0.1	140	100	163	188

S - infiltration zone of stemflow, R - reference area.

**Table 2.** Pb, Zn and Cu contents in the aqua-regia-extract of the investigated soils

Depth (cm)	Pb (mg/kg)		Zn (mg/kg)		Cu (mg/kg)	
	S	R	S	R	S	R
Rieglerhütte						
0-5	745	77	407	99	111	15
5-10	373	45	106	74	47	12
10-20	158	33	65	59	21	10
20-30	63	28	49	55	10	11
Jägerwiese						
0-5	555	63	236	102	74	19
5-10	218	53	114	91	36	18
10-20	95	34	78	69	23	15
20-30	41	30	76	67	18	15

Explanations as in Table 1.

**Table 3.** Particle size distribution of the investigated soils in weight %

Depth (cm)	Sand (2000-63 µm)		Silt (63-2 µm)		Clay (<2µm)	
	S	R	S	R	S	R
Rieglerhütte						
0-5	8	15	54	34	38	48
5-10	13	16	57	39	30	45
10-20	17	18	48	37	35	45
20-30	18	18	44	41	38	41
Jägerwiese						
0-5	7	8	52	41	41	51
5-10	8	9	46	40	45	51
10-20	10	11	34	34	56	55
20-30	9	13	34	48	57	40

Explanations as in Table 1.

- Separation of the clay fraction (<2  $\mu\text{m}$ ) by wet sieving, sedimentation and lyophilization.
- Optical evaluation of the micromorphology and the degree of aggregation by means of thin sections, according to Čurlík [8] and Jongerius [11].
- Determination of the Soil Aggregate Stability (SAS) according to Murer *et al.* [19].

### Chemical analyses

- pH-value, potentiometrically (KCl).
- Total contents of C, N, S by gas chromatography.
- Total contents of Pb, Zn, Cu in aqua-regia-extract, according to Blum *et al.* [5, 6].
- Exchangeable  $\text{Fe}^{3+}$  and effective cation exchange capacity (CEC) through 0.1 M unbuffered  $\text{BaCl}_2$ -percolation, according to Blum *et al.* [5,6].
- Fe-content in different rain water fractions, collected weekly over a period of one year at the site Jägerwiese, according to Rampazzo [20].
- Fe-content in the water saturation extract (WSE) according to Meiwes *et al.* [18].
- Total Fe-content ( $\text{Fe}_t$ ) of the fine earth (<2 mm) and the clay-fraction (<2  $\mu\text{m}$ ) in NaOH-melt at 600 °C, according to Rampazzo [20].

- Determination of Na-dithionite-citrate-bi-carbonate (DCB)-soluble,  $\text{NH}_4$ -oxalate-soluble and Na-pyrophosphate-soluble contents of Fe, Al and Mn, according to various authors [1,3,10,14,25,26].

### Mineralogical analyses

- Qualitative analysis of Fe-oxides in powder patterns of the clay fraction (<2  $\mu\text{m}$ ) by X-ray diffraction using Cuka-radiation, according to Brindley and Brown [7].

### RESULTS AND DISCUSSION

Previous studies showed that the investigated areas of the Vienna Woods are affected by strong air pollution and acid rain, mostly concentrated in the stemflow of beech trees [21]. The soil infiltration zone of stemflow consequently undergoes an extremely high acidification (pH 2.5-3.0) and partially irreversible chemical-mineralogical changes, like accumulation of C, N, S (see Table 1) and heavy metals (see Table 2), decrease of the  $\text{CEC}_{\text{eff}}$  and of the base saturation, increase of the Al-saturation, dissolution of the "secondary" (Al)-chlorites and loss of layer charge of the expandable clay mineral components [21]. In all the investigated extracts, the acidified stemflow areas show a higher Fe content than in the reference areas, as shown in Table 4.

**Table 4.** Fe-contents of the fine earth in the water saturation extract (WSE), in the unbuffered  $\text{BaCl}_2$ -extract and in the NaOH-melt

Depth (cm)	WSE (meq Fe/l)		$\text{BaCl}_2$ (meq Fe/kg)		NaOH-melt (weight % Fe)	
	S	R	S	R	S	R
Rieglerhütte						
0-5	0.73	0.34	12.3	0.2	3.2	1.6
5-10	n.d.	n.d.	12.7	0.6	2.4	1.9
10-20	n.d.	n.d.	8.7	0.5	1.7	1.7
20-30	0.10	0.13	4.5	0.1	1.5	1.5
Jägerwiese						
0-5	0.93	0.07	11.5	0.3	2.8	2.1
5-10	n.d.	n.d.	13.5	0.3	3.1	2.4
10-20	n.d.	n.d.	10.9	0.2	2.8	2.1
20-30	0.06	0.06	4.4	0.2	2.4	1.8

n.d. - not determined.

Other explanations as in Table 1.

The same tendency was observed in the distribution of the Fe-oxides in the fine earth, which were highly accumulated in the infiltration zone of stemflow, as shown in Table 5.

In order to assess the origin of the accumulated Fe, different rain water fractions (stemflow, influencing the S-soil area, and canopy throughfall, influencing the R-soil area) were investigated. The results at the site Jägerwiese showed that the Fe input through stemflow was lower than the one caused by canopy throughfall, see Table 6 and [20]. Thus, the accumulation and neof ormation of Fe-oxides in the infiltration zone of stemflow can be deduced from weathering processes.

$\pm 30\text{-}40\%$  of the total Fe is still non-oxidic  $[(\text{Fe}_t\text{-Fe}_d)/\text{Fe}_t]$ . Moreover, the amount of organically-bound Fe in the infiltration zone of stemflow is much higher than that in the reference area ( $\text{Fe}_p/\text{Fe}_o$ ), according to the high Ct-accumulation measured in the S-area [21].

X-ray diffraction analysis of the clay fraction did not show any qualitative differences between the S-area and the R-area. In both soil compartments a goethite-like mineral is recognizable (0.27 nm-peak) after treatment with  $\text{NH}_4$ -oxalate in the dark [26] which disappears after extraction with DCB [25], as shown in Fig. 1.

The IR-analysis of the same materials confirms the similar crystallization type of the

**Table 5.** Dithionite- $(\text{Fe}_d)$ , oxalate- $(\text{Fe}_o)$ , and pyrophosphate  $(\text{Fe}_p)$  soluble Fe contents in the infiltration zone of stemflow (S) and in the reference area (R) of the investigated soils. Contents in mg/kg fine earth

Depth (cm)	$\text{Fe}_d$		$\text{Fe}_o$		$\text{Fe}_p$	
	S	R	S	R	S	R
Rieglerhütte						
0-5	22000	10500	9625	3475	8100	1295
5-10	15800	11300	8300	3935	6350	1755
10-20	12100	10400	5800	4570	3570	1525
20-30	10000	11200	4830	4205	2050	765
Jägerwiese						
0-5	20500	10900	7236	4580	5450	1290
5-10	16800	11200	7560	4910	4865	1465
10-20	14000	10900	6300	4960	3065	1670
20-30	11700	11200	5399	4890	2255	1435

Explanations as in Table 1.

**Table 6.** Yearly Fe-input from rain precipitation, collected as stemflow and canopy throughfall at the site Jägerwiese

Site	Stemflow (g Fe/ha)	Canopy throughfall (g Fe/ha)
Jägerwiese 0-5	171	201

Fe-fractions, crystallization- and weathering indices of the clay fraction ( $< 2 \mu\text{m}$ ) and of the fine earth confirm this hypothesis, (see Table 7) and show that a high amount of the total Fe in the S-areas is already pedogenically neoformed ( $\text{Fe}_d/\text{Fe}_t$ ), but still amorphous or weakly crystallized ( $\text{Fe}_o/\text{Fe}_d$ ), whereas in the R-areas

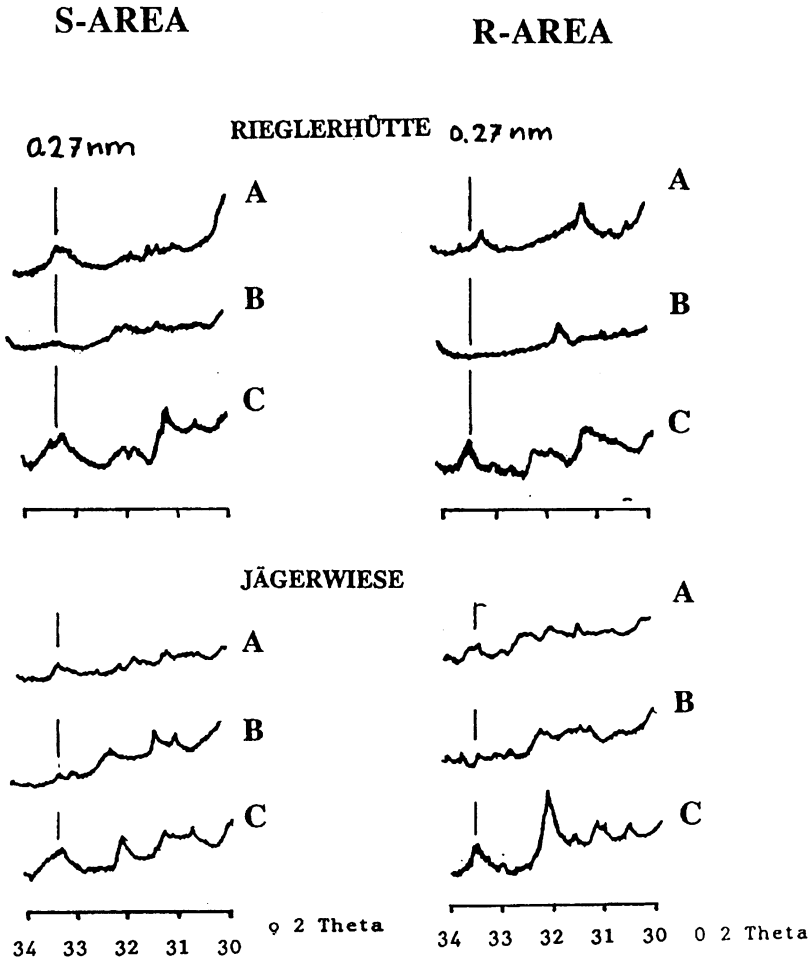
Fe-oxides formed in the infiltration zone of stemflow as well as in the reference area. The slight difference of the peak intensity and position as compared with a synthetic produced goethite shows that the crystallinity of pedogenic neoformed Fe-oxides almost differ from those pure types, synthesized in the laboratory, as shown in Figs 2 and 3.

In the infiltration zone of stemflow of all investigated soils, lower amounts of Al-oxides were found compared to the reference areas, as shown in Table 8. In previous investigations [21] it was observed that in the clay fraction of the reference areas "secondary" Al-chlorite occurred, but not in the very acid stemflow zone with lower pH. The higher Al-contents in

**Table 7.** Fe-fractions ( $Fe_t$ ,  $Fe_d$ ,  $Fe_o$ ,  $Fe_p$ ), crystallization- and weathering indices in the clay fraction (\*) and in the fine earth (\*\*) of the infiltration zone of stemflow (S) and of the reference area (R) in a soil depth of 0-5 cm

Site	$Fe_t^*$	$Fe_d^*$	$Fe_o^*$	$Fe_p^{**}$	$\frac{Fe_o^*}{Fe_d^*}$	$\frac{Fe_d^*}{Fe_t^*}$	$\frac{(Fe_t - Fe_d)^*}{Fe_t^*}$	$\frac{Fe_p^{**}}{Fe_o^{**}}$
	(mg/kg)							
Rieglerhütte								
S	34300	34170	17115	8100	0.50	0.99	0.01	0.84
R	28900	19600	4400	1295	0.22	0.68	0.32	0.37
Jägerwiese								
S	32200	28597	13709	5450	0.48	0.89	0.11	0.75
R	30200	18500	7500	1290	0.40	0.61	0.39	0.28

$Fe_t$  - total Fe,  $Fe_d$  - DCB-soluble Fe,  $Fe_o$  - oxalate-soluble Fe,  $Fe_p$  - pyrophosphate-soluble Fe.



**Fig. 1.** X-ray patterns of the clay fraction of the infiltration zone of stemflow (left) and of the reference area (right) in a soil depth of 0-5 cm. A - untreated; B - DCB-treated; C - oxalate-treated (Cuka-radiation).

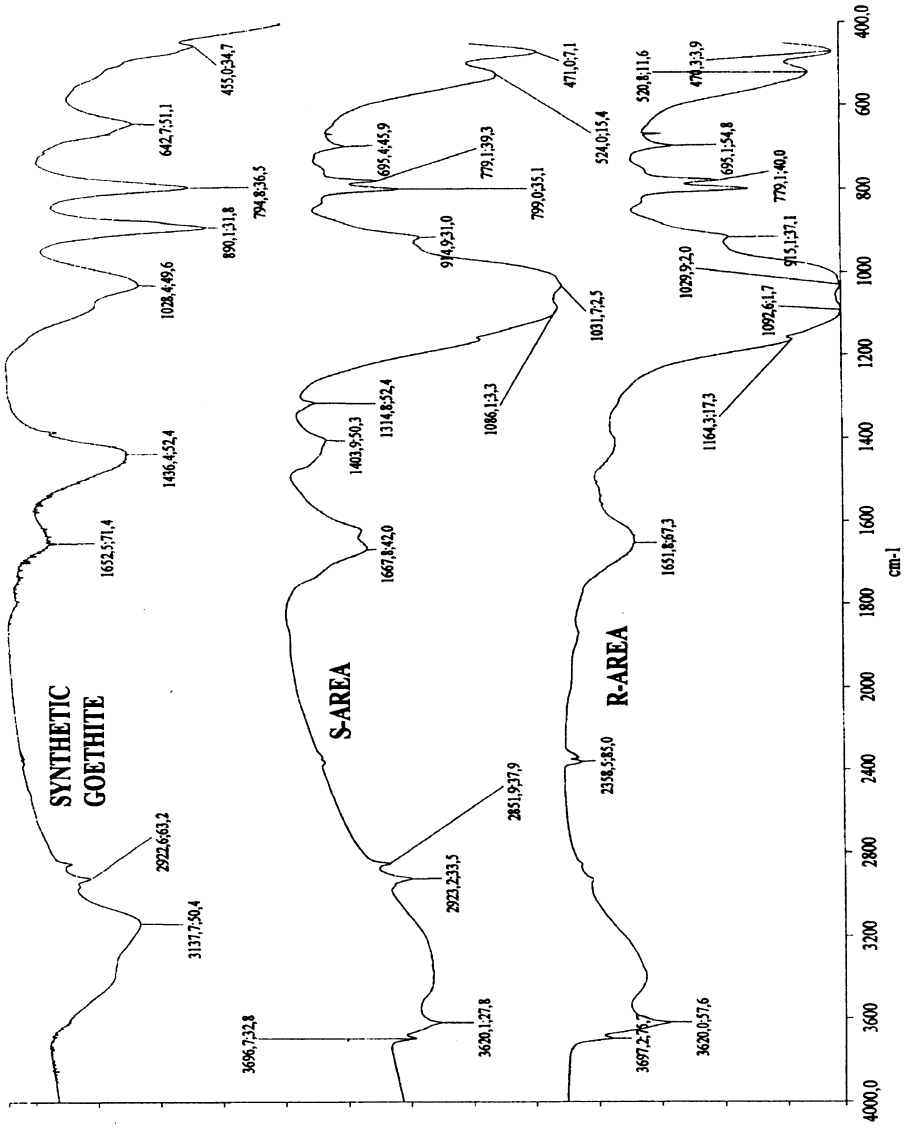


Fig. 2. IR-patterns of the soil Rieglerhütte (0-5 cm). Comparison between the infiltration zone of stemflow (S), the reference area (R) and a synthetic produced goethite. The values of each peak indicate the wavenumber (cm<sup>-1</sup>) versus the percentage of transmission (%T).

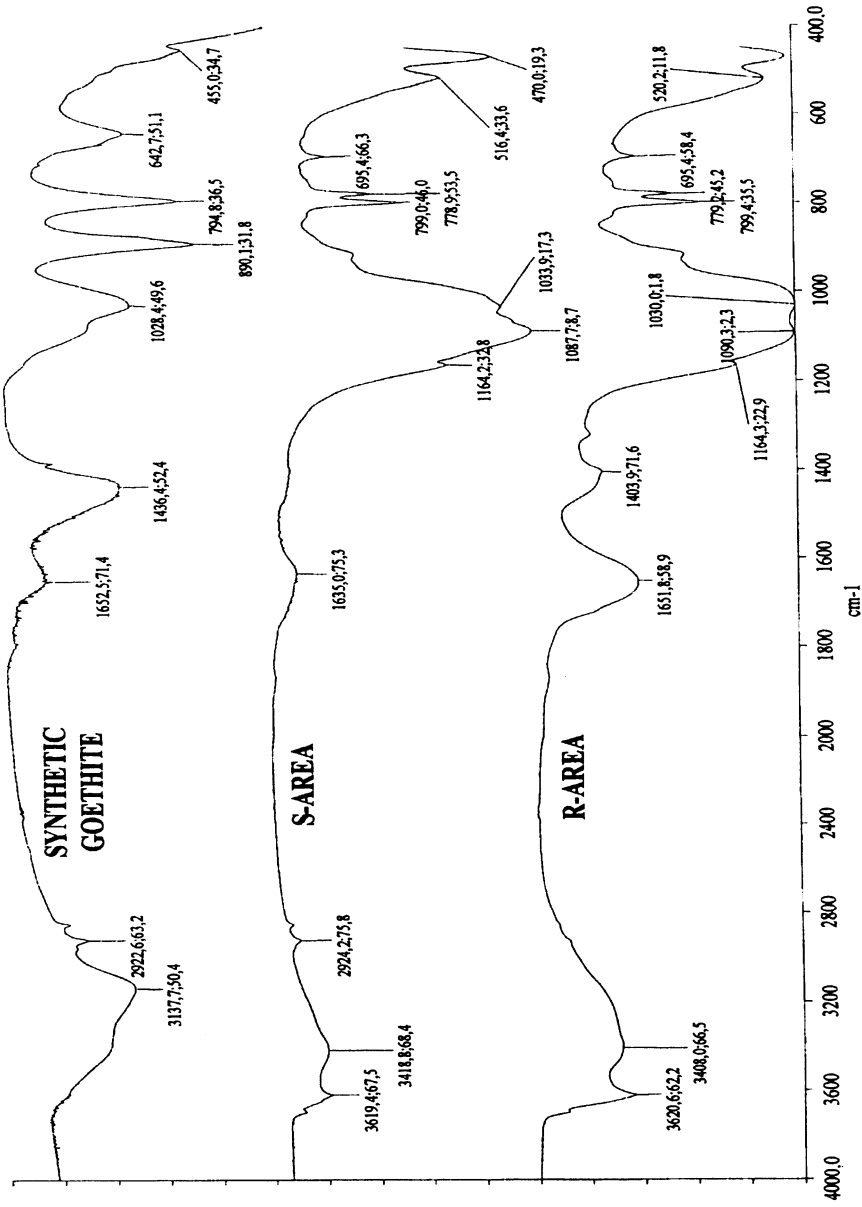


Fig. 3. IR-patterns of the soil Jägerwiese (0-5 cm). Comparison between the infiltration zone of stemflow (S), the reference area (R) and a synthetic produced goethite. The values of each peak indicate the wavenumber ( $\text{cm}^{-1}$ ) versus the percentage of transmission (%T).



**Table 8.** Dithionite-(Al<sub>d</sub>), oxalate-(Al<sub>o</sub>), and pyrophosphate (Al<sub>p</sub>) soluble Al contents in the infiltration zone of stemflow (S) and in the reference area (R) of the investigated soils. Contents in mg/kg fine earth

Depth (cm)	Al <sub>d</sub>		Al <sub>o</sub>		Al <sub>p</sub>	
	S	R	S	R	S	R
Rieglerhütte						
0-5	1160	1520	715	1210	715	770
5-10	1130	1710	730	1155	575	920
10-20	1280	1680	935	1155	670	805
20-30	1380	1620	1145	1070	720	412
Jägerwiese						
0-5	1370	1610	844	1210	705	680
5-10	1370	1650	980	1280	620	685
10-20	1550	1640	1162	1220	695	750
20-30	1910	1680	1566	1160	1245	660

Explanations as in Table 1.

the R-areas can be explained by the fact that DCB and oxalate also extract Al from the hydroxo-Al-polymers of „secondary“ chlorite and from goethite, where it substitutes Fe in the crystal lattice.

The amounts of Mn-oxides in the stemflow zone are very low, confirming the instability of Mn-oxides at low pH, see Table 9. Nevertheless, it is difficult to say if they are only leached into deeper horizons, or completely inhibited in their formation.

One aim of this study was to investigate, whether the strong acidification process, coupled with the above mentioned mineralogical changes, influence the structure type and the stability of soil aggregates. A micromorpho-

logical investigation at the site Jägerwiese by use of thin sections, taken from both stemflow and reference soil compartments, shows that the type of microstructure changes from a cracky-angular type in the reference area into a chamber-type in the infiltration zone of stemflow, due to intensive acidification and leaching processes, as shown in Fig. 4. A similar structure change was observed in other different acidified soils of the Vienna Woods [20].

Nevertheless, the soil aggregate stability of the topsoils in the contaminated area was much higher as compared with the reference area, as shown on Table 10.

This fact is strongly related with the chemical and mineralogical changes found,

**Table 9.** Dithionite-(Mn<sub>d</sub>), oxalate-(Mn<sub>o</sub>), and pyrophosphate (Mn<sub>p</sub>) soluble Al contents in the infiltration zone of stemflow (S) and in the reference area (R) of the investigated soils. Contents in mg/kg fine earth

Depth (cm)	Mn <sub>d</sub>		Mn <sub>o</sub>		Mn <sub>p</sub>	
	S	R	S	R	S	R
Rieglerhütte						
0-5	196	788	55	755	32	475
5-10	172	542	78	490	20	264
10-20	251	596	174	550	46	219
20-30	323	637	304	570	86	87
Jägerwiese						
0-5	299	1130	124	1090	64	600
5-10	334	1130	198	1085	58	505
10-20	423	875	240	850	78	339
20-30	625	934	463	830	192	218

Explanations as in Table 1.

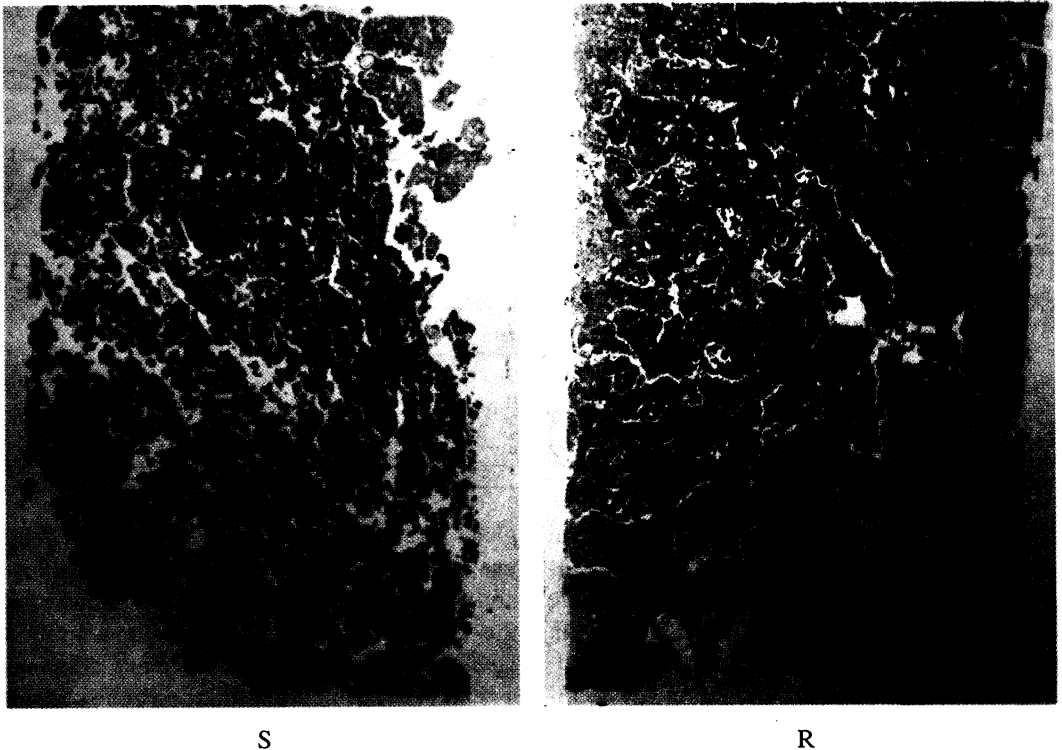


Fig. 4. Soil thin sections of the infiltration zone of stemflow (S) and of the reference area (R). Site Jägerwiese, natural size, horizontal view.

Table 10. Soil aggregate stability (SAS) in weight %

Depth (cm)	SAS (% ww)	
	S	R
Rieglerhütte		
0-5	83	47
5-10	80	52
Jägerwiese		
0-5	85	45
5-10	81	50

Explanations as in Table 1.

especially with the accumulation of organic carbon and Fe-oxides in the contaminated area. Because the charge of Fe-oxide particles is pH-dependent (variable charge), their aggregation effect is also pH-dependent. Fe-oxides have a zero point of charge (ZPC) at pH about 8 and become higher positive charged, the lower the pH from ZPC is. This leads to the conclusion that the Fe-oxides occurring in the extremely acidified infiltration zone of stem-

flow have a much higher positive electrical charge than in the reference soil area and therefore their aggregation effect with clay minerals is much higher.

#### CONCLUSIONS

The effect of intensive soil acidification on the genesis of Fe-, Al- and Mn-oxides and their relation to the soil aggregate stability were investigated in the Vienna Woods. Analyses were carried out on soil samples of 2 sites at 4 depths (0-5, 5-10, 10-20, and 20-30 cm) taken from the infiltration zone of the stemflow (S) of beech trees (*Fagus sylvatica*), which is strongly influenced by acid atmospheric depositions (soil-pH KCl 2.5 to 3.0), and from non-contaminated reference areas (R) between the trees, where the acid input is much lower (soil-pH KCl 5.5). The extreme soil acidification in the infiltration zone of stemflow led to intensive weathering of primary minerals, to neoformation and accumulation of crystallized, amorphous and organic-bound

Fe-oxides, to lower concentrations of Al- and Mn-oxides and to a high increase in soil aggregate stability, reflecting the aggregation effect of Fe-oxides, and the concomitant leaching of Mn and Al at a very low soil pH. This should be taken into consideration when studying the assessment of soil structure and its functions in the soil ecosystem. Soil aggregation and stability, as one of the most important pedogenetical process, can be strongly decreased if the aggregating agents, in this case mostly Fe-oxides, are affected.

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