

Solution chemistry in acid forest soils: Are the BC : Al ratios as critical as expected in Switzerland?

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Summary – Zusammenfassung

The molar ratio of base nutrient cations to total dissolved aluminum ($BC : Al_{tot}$) in the soil solution was measured at six forest sites in Switzerland in acid mineral soils to determine whether the ratio measured in the field was lower than the critical value of 1, as predicted by the mapping of exceedances of critical loads of acidity. The soil chemistry was then related to the soil solution composition to characterize the typical effective base saturation (BS) and BC : Al ratio in soil leading to critical $BC : Al_{tot}$ in the soil solution. The median $BC : Al_{tot}$ ratio in the soil solution never reached the critical value in the root zone at any sites for the whole observation period (1999–2002), suggesting that the $BC : Al_{tot}$ ratios measured in the field might be higher than those modeled for the determination of critical loads of acidity. The gibbsite model usually applied for the calculation of critical loads was a poor predictor of the Al^{3+} activity at the study sites. A curvilinear pH-p Al^{3+} relationship was found over the whole range of pH (3.8–6.5). Above a pH of 5.5, the slope of the pH-p Al^{3+} relation was close to 3, suggesting equilibrium with $Al(OH)_3$. It decreased to values smaller than 1.3 below a pH of 5.5, indicating complexation reactions with soil organic matter. The BS and the BC : Al ratios in the soils were significantly correlated to the $BC : Al_{tot}$ ratios in the soil solution. The soil solutions with the lowest $BC : Al_{tot}$ ratios (≤ 2) were typically found in mineral soils with a BS below 10 % and a BC : Al ratio in the soil lower than 0.2. In acid pseudogleyed horizons overlying a calcareous substrate, the soil solution chemistry was strongly influenced by the composition of the underlying soil layers. The soil solutions at 80 cm had pH values and $BC : Al_{tot}$ ratios much higher than expected. This situation should be taken into account for the calculations of critical loads of acidity.

Chemismus der Bodenlösung sauren Waldböden: Sind die BC:Al-Verhältnisse wirklich kritisch in der Schweiz?

Anhand von Modellen wurde berechnet, dass die Säurebelastung in großen Teilen der Schweiz so groß ist, dass mit schädlichen Wirkungen auf die Vegetation gerechnet werden muss, weil in der Bodenlösung der als kritisch erachtete Grenzwert des $BC:Al_{tot}$ -Verhältnisses von 1 unterschritten wird. An sechs Waldstandorten wurde die Bodenlösung in verschiedenen Tiefen untersucht, um das Ausmaß einer realen Gefährdung abschätzen zu können. Die Zusammensetzung der Bodenlösung wurde mit bodenchemischen Messgrößen verglichen. Damit sollte geklärt werden, ob bestimmte Beziehungen zwischen der Bodenmatrix und der Bodenlösung bestehen.

An allen Standorten wurde der Medianwert der $BC:Al_{tot}$ -Verhältnisse in der Bodenlösung für die Messperiode 1999–2002 ermittelt. Es wurde festgestellt, dass dieser an keinem Standort und in keiner Bodentiefe den kritischen Wert je erreichte oder gar unterschritt, wie dies aufgrund der Modellrechnungen hätte erwartet werden müssen. Die Gründe mögen daran liegen, dass die Gibbsit-Löslichkeit, welche den Modellrechnungen zugrunde liegt, die Aluminium-Löslichkeit nur sehr unbefriedigend wiedergibt, denn bei pH-Werten < 5.5 wird die Aktivität von Al^{3+} vorwiegend durch Komplezierungsreaktionen mit der organischen Substanz kontrolliert. Das $BC:Al_{tot}$ -Verhältnis in der Bodenlösung korrelierte dagegen recht gut mit dem $BC:Al$ -Verhältnis am Kationentauscher sowie mit der Basensättigung. Die tiefsten $BC:Al_{tot}$ -Verhältnisse in der Bodenlösung wurden in Böden mit einer Basensättigung $< 10\%$ und einem $BC:Al$ -Verhältnis am Kationenaustauscher < 0.2 gefunden. Allerdings wurde festgestellt, dass in einigen Fällen die Bodenlösungen in 80 cm Tiefe stark vom Chemismus des Unterbodens beeinflusst werden, was zu schwer interpretierbaren Resultaten führt. In der vorliegenden Untersuchung stammten solche Proben aus pseudovergleyten Horizonten über einem tieferliegenden kalkhaltigen Ausgangsgestein. Der Chemismus des Unterbodens sowie der Bodenwasserhaushalt sollte deshalb bei der Berechnung der "Critical loads of acidity" unbedingt beachtet werden.

Key words: BC : Al ratio / soil solution / aluminum / soil acidification / forest soils / base saturation

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1 Introduction

Atmospheric deposition of acidifying compounds such as SO_2 and NO_x has been shown to accelerate the acidification processes in the soil (e.g., Binkley et al., 1989; Ulrich and Sumner, 1991). Depending on the soil chemical characteristics, accelerated soil acidification may lead to a decrease in the soil pH, the leaching of nutrients (Ca^{2+} , Mg^{2+} , K^+) from the exchange sites, and the mobilization of Al species that can act as phytotoxic agents to plants (e.g., Sumner et al., 1991; Marschner, 1995). The molar $BC : Al_{tot}$ ratio in the soil solu-

tion (with BC corresponding to the sum of the concentrations of Ca^{2+} , Mg^{2+} , and K^+ , and Al_{tot} representing the total concentration of dissolved Al) is often used as critical chemical parameter, assuming that a $BC : Al_{tot}$ ratio ≥ 1 will protect trees from adverse soil acidification effects (Sverdrup and Warfvinge, 1993; Cronan and Grigal, 1995; Brunner et al., 1999). The ratios are usually calculated with total dissolved Al but the critical BC : Al mostly refer to the proportion of Al^{3+} and $AlOH^{2+}$ that are the most toxic forms of aluminum to roots (Foy, 1988; Løkke et al., 1996). Critical loads of acidic deposition for forest soils were calculated based on the $BC : Al_{tot}$ criterion to establish European abatement strategies (e.g., Sverdrup et al., 1990; Sverdrup and de Vries, 1994). The critical loads of acidity, calculated at 226 forest sites throughout

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Table 1: Forest site characteristics at the six study areas.**Tabelle 1:** Standortmerkmale an den sechs Orten der bodenkundlichen Untersuchungen.

Location	Altitude [m]	FAO soil type	Humus form	Geology (rock type)	Tree species
BEA	1510	Podzol	Raw humus	Sandstone	<i>Picea abies</i>
COP	650	Podzol	Moder	Gneiss	<i>Castanea sativa</i>
LAU	810	Dystric Cambisol	Mull	Calcareous moraine above calcareous sandstone	<i>Fagus sylvatica</i> , <i>Abies alba</i>
NOV	900	Podzol	Moder	Non-calcareous moraine above gneiss	<i>Quercus cerris</i> , <i>Castanea sativa</i> , <i>Betula pendula</i>
OTH	470	Haplic Acrisol	Mull	Calcareous moraine above calcareous sandstone	<i>Fagus sylvatica</i>
VOR	480	Dystric Planosol	Moder	Moraine above marl	<i>Abies alba</i> , <i>Quercus robur</i>

Europe with a steady-state model (SMB), were exceeded at about 30 % of the plots during the period 1995–1998 (de Vries et al., 2002). In Switzerland, the BC : Al_{tot} ratio was modeled at 770 sites using the steady-state PROFILE model (Kurz et al., 1998a). It was found that about 90 % of the forest area in the Swiss Plateau region and 60 % in the core region of canton Ticino in southern Switzerland received acidic deposition exceeding the critical loads (BC : Al_{tot} < 1) for the period 1986–1990. The BC : Al_{tot} ratio in the soil solution was also measured in the field at numerous intensive forest monitoring sites throughout Europe, providing indications whether the ratios were frequently below the critical limit or not. The proportion of sites with BC : Al_{tot} < 1 in the topsoil (0–40cm) was only 10 % in 1996 (de Vries et al., 1999) but increased to 30 % in 1997 (de Vries et al., 2003a). In Switzerland, there is very little information available on the BC : Al_{tot} ratio in the soil solution. The monitoring of the soil solution chemistry at one site in Southern Switzerland between 1987 and 1997 showed a significant decrease of the BC : Al_{tot} ratio over time (Blaser et al., 1999). However, the authors found that the ratio did not reach the critical value of 1 in the root zone, although the critical loads of acidity were exceeded between 1965 and 1985. As a result, it is still unclear whether the BC : Al_{tot} ratios have really reached the critical value in regions where exceedances of critical loads of acidity were predicted.

The purpose of the present investigation was to determine whether the BC : Al_{tot} ratio in the soil solution was below the critical limit in acid forest soils at six sites located in regions that received acidic deposition in excess of the critical loads (Kurz et al., 1998a). This study also attempted to relate the BC : Al_{tot} ratio in the soil solution to the soil chemistry (base saturation and BC : Al in soil) in order to determine the typical soil chemical properties leading to critical BC : Al_{tot} ratios in the soil solution. To get a better estimate of the risks of detrimental effects on tree roots, the BC : Al ratios were also calculated with the most toxic forms of aluminum (Al³⁺ and AlOH²⁺). The findings could serve as a simple approach to predict the BC : Al_{tot} ratio in the soil solution from the soil base saturation, provided that a sound relationship exists between both of them. The investigations were focused on acid mineral soils where low BC : Al_{tot} ratios in the soil solution were expected.

2 Materials and methods

2.1 Site description

Five study areas are part of a national forest monitoring network including 17 permanent plots established between 1994 and 1997 for the Swiss Long-term Forest Ecosystem Research project (e.g., Kräuchi, 1996; Cherubini and Innes, 2000; Thimonier et al., 2001). These sites belong to Level II plots in the ICP Forests network of the EC-UN/ECE (e.g., de Vries et al., 2003a). Three sites are located on the Swiss Plateau in Lausanne (LAU), Vorderwald (VOR), and Othmarsingen (OTH), one site on the northern slope of the Alps in Beatenberg (BEA), and one site in southern Switzerland in Novaggio (NOV). Each plot is about 2 ha in area and contains a 43 m × 43 m subplot (IM plot) that is used for the intensive monitoring of the forest ecosystem. The sixth study area is located in Copera (COP) in southern Switzerland. The characteristics of all study sites, including altitude, main tree species, and soil type, are described in Tab. 1.

2.2 Sampling methods and analytical methods

Soil properties in COP were characterized by taking samples from a profile near the site where the soil solution was collected. The analytical methods are described in Blaser et al. (1997, 1999). The methods used in the Level II plots are given in the manual for integrated monitoring of the UN/ECE (1993), and are fully described in Walthert et al. (2002). Soil samples in the IM plots were collected at 16 sampling points according to a regular grid. The four samples collected within each quarter of the IM plot were pooled together for each depth interval. The chemical parameters measured in soil samples included pH(H₂O), concentrations of exchangeable cations and protons. The pH value in soil samples was measured potentiometrically in deionized water (soil : solution ratio = 1 : 5, equilibration time 2 h). The exchangeable cations were extracted with 1M NH₄Cl (soil : solution = 1 : 10, extraction time 1h), and were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES; Optima 3000, Perkin-Elmer Corp.). Exchangeable protons were calculated by the difference of total and Al-induced exchangeable acidity (Thomas, 1982). The effective cation exchange

capacity (CEC_{eff}) was calculated by summing up the exchangeable cations (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Al^{3+} , Fe^{3+} , H^+). The base saturation (BS) was obtained by dividing the sum of base cations (K^+ , Na^+ , Ca^{2+} , Mg^{2+}) by CEC_{eff} . The BC : Al ratio in the soil was calculated by dividing the sum of the exchangeable base cations (Ca^{2+} , Mg^{2+} , K^+) by the exchangeable Al, expressed in $mmol_c\ kg^{-1}$.

The methods for the soil solution monitoring in the Level II plots were chosen on the basis of the manual for integrated monitoring of the *UN/ECE* (1993). Because of the strong temporal variability of the soil solution chemistry, the soil solution was monitored for a period of four years (1999–2002) to be able to determine the median chemical composition of the water at the six study sites. Soil solution was collected within the IM plots at eight sampling points according to a regular grid. It was sampled in the mineral horizons at three different depths (15 cm, 50 cm, and 80 cm), except in BEA where it was collected at 50 cm and 80 cm. Soil solution was sampled with ceramic suction cups (highflow porous ceramic cups, Soil moisture Equipment Corp., Santa Barbara, USA). The suction cups were cleaned with 0.1 M HCl, washed in deionized water prior to installation, and equilibrated in the field for three months at least. At the beginning of each sampling period, a vacuum of 500 hPa was applied to the suction cups. The lysimeters were connected to 1-l glass bottles that were stored in an insulated and light-protected box. The samples of soil solution were taken fortnightly. Volumes of collected soil solution were measured directly in the field. Immediately upon the arrival of samples in the laboratory, the samples were combined proportionally to form one composite sample for each depth.

The sampling methods used in COP are presented in *Blaser et al.* (1997, 1999). They are comparable to those used in the Level II plots. The soil solution was collected in the mineral horizons at a depth of 30, 57, and 110 cm.

All samples were filtered (0.45 μm , Schleicher and Schuell ME25, Germany) and analyzed for pH, electrical conductivity (EC), dissolved organic carbon (DOC), major cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Mn^{2+} , dissolved Fe, Al, and S species), and anions (Cl^- , SO_4^{2-} , NO_3^- , F^-). The subsamples for DOC determination were acidified with 7% HCl and for cation analysis with concentrated HNO_3 to 1.75 vol.-%. The samples were stored at 2 °C until they were analyzed. The pH and the EC were measured with a combined glass electrode (Meterlab PHM250 and CDM210, Radiometer). The DOC was analyzed with a TOC analyzer (Shimadzu TOC500, TOC5000 and TOC-V), the cations by Inductively Coupled Plasma Spectroscopy (ICP-AES OPTIMA 3000, Perkin Elmer), and the major anions by ion chromatography (DX-120, Dionex).

2.3 Calculation: chemical speciation in soil solution and exchange coefficients

Activities and concentrations of complexes in soil solution were calculated with WHAM 6.0 (2001), a chemical equilibrium model for waters. The activities were calculated using the Debye-Hückel equation (with mean soil temperature of

8 °C). The concentrations of fulvic acids were approximated by multiplying the DOC concentrations ($\text{mg}\ l^{-1}$) by 1.3 (*Tipping*, 2002). The speciation of Al was calculated by including complexation reactions with OH^- , SO_4^{2-} , F^- , Si, and fulvic acids. The solubility line for gibbsite and amorphous $Al(OH)_3$ adjusted at 10 °C were taken from *Adams et al.* (2000), using $pK_{(\text{gibbsite})} = 8.79$ and $pK_{(\text{amorphous } Al(OH)_3)} = 11.9$.

The exchange coefficient $K_{Al/Ca}$ for the cation exchange reaction between exchangeable Ca and Al can be defined according to *Gaines and Thomas* (1953):

$$K_{Al/Ca} = \frac{N_{Al}^2 \cdot [a_{Ca^{2+}}]^3}{N_{Ca}^3 \cdot [a_{Al^{3+}}]^2} \quad (1)$$

N_{Al} and N_{Ca} are the fractions of Al and Ca on the exchange complex, $a_{Ca^{2+}}$ and $a_{Al^{3+}}$ are the activities of Ca^{2+} and Al^{3+} in the soil solution. Since the $K_{Al/Ca}$ is not a true equilibrium constant and varies with the ionic strength and the distribution of ions in the solution and on the exchange complex (*Binkley et al.*, 1989; *Sauvé and Hendershot*, 1995), the $K_{Al/Ca}$ was calculated for each pooled soil solution sample. The coefficient was determined as long as the concentrations of cations in the soil solution were larger than 10 times the detection limit. The fractions N_{Al} and N_{Ca} were kept constant, assuming that the total amount of exchangeable cations and their distribution did not significantly change during the observation period (*Reuss and Johnson*, 1986). For a given $N_{Al} : N_{Ca}$ ratio on the exchange complex, the $a_{Ca} : a_{Al}$ ratio in the soil solution increases if $K_{Al/Ca}$ increases. $K_{Al/Mg}$ and $K_{Al/K}$ were calculated similarly.

3 Results

3.1 Soil and soil solution chemistry

The main chemical properties of the pooled soil samples and detection limits are summarized in Tab. 2. The mineral horizons were acid at all plots, with a $pH(H_2O)$ ranging between 3.7 and 5.0. The pH usually increased with depth. The CEC_{eff} in all sampled mineral horizons was lower than $135\ \text{mmol}_c\ \text{kg}^{-1}$. The BS was generally low, ranging between 3.4% and 27%, except in OTH where it reached 53%. The BS generally decreased from the topsoil to 40 cm of depth and increased again below 40 cm, except in BEA where the BS stayed below < 5%. The BC : Al ratio in the soil matrix varied between 0.04 and 1.26.

Table 2 also presents the median values of pH, DOC, BC, dissolved Al_{tot} , and BC : Al_{tot} ratios in the pooled soil solution samples collected in the mineral horizons (15, 50, and 80 cm of depth) during the entire observation period. The median BC : Al_{tot} ranged between 1.2 and 9.1, except at 80 cm in LAU, OTH, and VOR (BC : $Al_{\text{tot}} > 20$ and $pH \geq 5.9$). Two out of six plots had a BC : Al_{tot} ratio close to 1 (1.2 in BEA and 1.4 in COP) at least in one soil horizon. The median BC : Al_{tot} ratio at all plots was generally lowest at a depth of 15 cm and increased with depth, except in BEA where the ratio reached a minimum level at 50 cm and 80 cm. The median pH of the soil solution was the lowest between 15 cm and 50 cm of depth and increased at 80 cm. The Al_{tot} concentrations at all

Table 2: Median chemical composition of solid phase and soil solution samples at the six study sites.**Tabelle 2:** Chemische Messgrößen (Medianwerte) im Boden und in den Bodenlösungen an den sechs Untersuchungsstandorten.

Soil horizon	Sampling depth (cm)	pH(H ₂ O)	Solid phase					Soil solution						
			Exchangeable cations (mmol _c kg ⁻¹)			CECeff (mmol _c kg ⁻¹)	BS %	BC : Al _{soil}	Sampling depth (cm)	pH	DOC mg l ⁻¹	BC ^{a)} μmol l ⁻¹	Al _{tot} ^{b)} μmol l ⁻¹	BC : Al _{tot}
Detection limit			Ca, Mg:0.2 K: 0.4	0.2						0.50	Ca: 2.50 Mg: 0.82 K: 5.12	0.56		
BEA														
E3	20–40	4.1	1.5	17.1	4.0	23.5	8.2	0.10	Sampled from 08.99 to 12.02, n = 90					
Bs,h1	30–55	4.4	1.6	40.8	5.5	50	3.4	0.04	50	4.1	34.8	42	36.7	1.2
									80	4.4	23.6	44	38.7	1.2
LAU														
Asw3	10–20	4.5	4.2	38.9	6.4	51.3	8.5	0.11	Sampled from 01.99 to 12.02, n = 93					
Bsw1	40–60	4.7	6.2	34.6	4.7	46.8	13.2	0.18	15	4.6	4.6	143	39.8	3.4
Bsw1	60–80	4.8	9.0	34.9	4.6	49.7	18.3	0.26	50	5.0	1.2	136	20.5	5.8
									80	5.9	0.8	142	6.3	20.6
NOV														
Ah3+A	10–20	4.7	5.7	62.1	5.4	74.2	8.1	0.09	Sampled from 01.99 to 12.02, n = 81					
AB	40–55	5.0	1.4	5.9	0.3	7.7	18.2	0.27	15	4.8	6.6	58	29.5	2.0
B	55–90	5.0	1.4	4.1	0.6	6.3	23.4	0.41	50	5.3	2.3	42	13.3	3.1
									80	5.4	1.5	43	9.4	4.7
OTH														
AE1	10–20	4.4	6.8	44.8	5.4	58.6	12.5	0.15	Sampled from 11.98 to 02.00, n = 32					
Bt	40–60	4.7	29.8	44.9	5.0	81.2	32.8	0.66	15	4.3	12.9	313	60.1	5.4
Bt	60–80	4.9	52.0	41.4	4.8	99.5	52.8	1.26	50	4.7	4.1	282	32.5	9.1
									80	6.1	3.2	335	2.4	133.2
VOR														
ESW	10–20	4.4	1.8	46.5	5.6	55.2	3.9	0.04	Sampled from 01.99 to 12.02, n = 103					
Sw	40–60	4.5	5.6	46.1	5.7	58.8	9.1	0.12	15	4.9	5.2	46	23.6	1.9
Sd	60–80	4.6	9.1	49.4	6.3	66.5	13.9	0.19	50	5.0	1.0	69	18.9	3.6
									80	6.0	0.8	107	3.8	28.8
COP^{c)}														
(AE)	15–25	4.7	3.4	25.2	2.6	31.4	11.3	0.13	Sampled from 01.99 to 12.02, n = 86 ^{d)}					
(Bh)Bs	55–65	4.8	2.4	16.9	2.7	22.1	11.2	0.14	15	4.8	2.1	50	32.3	1.4
B(s)C	100–110	4.9	1.5	8.6	1.8	11.8	12.6	0.17	50	4.8	0.9	79	33.7	2.4
									80	5.1	0.9	65	28.6	2.3

^{a)} BC = Ca + Mg + K

^{b)} Al_{tot} = total dissolved aluminum

^{c)} Soil data in *Blaser et al.*, 1999

^{d)} pH between 10.2000 and 12.2001

plots were highest at a depth of 15 cm, except in BEA where they reached a maximum at 50 cm and 80 cm. The median DOC concentrations strongly decreased with depth at all plots, except in BEA where they remained high at 50 cm and 80 cm of depth (24–35 mg l⁻¹).

3.2 Al speciation and BC : (Al³⁺ + AlOH²⁺) ratio in the soil solution

Based on the results of the speciation with the WHAM model, the BC : Al ratio was recalculated considering the concentrations of the free ions in the soil solution (Tab. 3). The most toxic Al forms (Al³⁺ and AlOH²⁺) were used to calculate the BC : (Al³⁺ + AlOH²⁺) ratio. The Al³⁺ concentrations were smaller than the Al_{tot} concentrations, ranging between < 0.1 to 38 μmol l⁻¹, the proportion of Al³⁺ representing between 18 % and 76 % of the Al_{tot}. The concentrations of AlOH²⁺ were small (< 5.4 μmol l⁻¹). The median BC : (Al³⁺ + AlOH²⁺) ratios were greater than the BC : Al_{tot} ratios at all plots and higher than the critical value of 1. Below a pH of 5.9 in the soil solution, the median BC : (Al³⁺ + AlOH²⁺) ratios ranged from 1.6 to 15 and were related to the BC : Al_{tot} ratios (= 0.56 × BC :

Al_{tot} + 0.95; r = 0.87). Above a pH of 5.9, the BC : (Al³⁺ + AlOH²⁺) reached values higher than 300.

3.4 Effect of pH on Al solubility control

To obtain information on the solubility control of Al, the relationship between the pH in the soil solution and the negative logarithm of Al³⁺ activities (pAl³⁺) was investigated in all soil solution samples (n = 1065) (Fig. 1). The data showed a single curvilinear relationship between pH and pAl³⁺. Soil solutions with a pH > 5.5 were close to saturation with amorphous Al hydroxides. The slope of the regression line was 2.3 and fell between the amorphous Al(OH)₃ and gibbsite solubility lines. Below a pH of 5.5, the samples were clearly undersaturated with respect to amorphous Al hydroxides. The slope of the pH-pAl³⁺ relationship decreased to 1.3 in soil solutions with a pH between 4.7 and 5.5. This group of samples contained soil solutions from all sites. Below a pH of 4.7, the data strongly scattered, and the slope of the pH-pAl³⁺ relationship was on average close to 0. When considering the individual layers, the slope was 0.52 in LAU at 15 cm (r² = 0.19, P < 0.05) and 0.4 in OTH at 15 cm (r² = 0.39, P < 0.001). The corresponding constants of the regression lines were 2.13 in LAU and 2.67 in OTH. The samples in BEA showed a slope

Table 3: Chemical speciation of the soil solutions samples calculated with *WHAM 6* (2001). Input data: major cations and anions during the observation period (1999–2002). Output: median concentrations of BC ($\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+$), Al^{3+} , AlOH^{2+} , Al bound to fulvic acids (Al-FA), and median values of BC : ($\text{Al}^{3+} + \text{AlOH}^{2+}$). Median Gaines-Thomas exchange coefficients $K_{\text{Al/Ca}}$ and $K_{\text{Al/Mg}}$

Tabelle 3: Spezifizierung der Bodenlösung, berechnet mit *WHAM 6* (2001). Eingangsgrößen: Messwerte der Bodenlösung; Resultate: berechnete Medianwerte der Beobachtungsperiode 1999–2002. $K_{\text{Al/Ca}}$ und $K_{\text{Al/Mg}}$ Medianwerte der Gaines-Thomas-Koeffizienten.

Plot	Sampling depth	BC ($\mu\text{mol l}^{-1}$)	Al^{3+} ($\mu\text{mol l}^{-1}$)	AlOH^{2+} ($\mu\text{mol l}^{-1}$)	Al-FA ($\mu\text{mol l}^{-1}$)	BC : ($\text{Al}^{3+} + \text{AlOH}^{2+}$)	$K_{\text{Al/Ca}}$	$K_{\text{Al/Mg}}$
BEA (08.99–12.02)	50	35	6.5	0.3	29.6	5.1	0.98	1.08
	80	39	10.4	1.1	26.9	3.6	1.34	1.51
LAU (01.99–12.02)	15	138	23.4	3.3	6.8	5.2	1.41	1.44
	50	133	10.6	2.9	1.6	9.7	1.38	1.44
	80	138	0.1	0.3	1.2	332	–	–
NOV (01.99–12.02)	15	56	12.2	2.9	10.1	3.6	1.16	1.35
	50	40	3.6	2.1	3.6	6.7	0.74	1.21
	80	42	1.7	2.4	2.4	13.4	0.85	1.33
OTH (11.98–02.00)	15	308	37.9	2.2	15.1	7.4	1.45	1.59
	50	278	15.6	2.1	5.1	14.6	0.85	0.86
	80	323	<0.1	<0.1	1.8	> 1000	–	–
VOR (01.99–12.02)	15	44	8.1	2.3	7.9	3.6	1.72	1.80
	50	67	7.5	2.3	1.5	6.7	1.22	1.39
	80	104	<0.1	0.2	0.9	409	–	–
COP (01.99–12.02)	30	48	24.6	3.0	3.0	1.6	0.72	1.01
	57	76	24.6	2.7	1.3	2.8	0.88	1.67
	110	64	18.2	5.4	1.0	2.9	0.93	1.58

of 0.5 at 50 cm ($r^2 = 0.08$, $P < 0.05$) and a negative slope (–0.4) at 80 cm ($r^2 = 0.14$, $P < 0.01$). The constants of both regression lines were 3.32 and 6.99, respectively.

3.5 Relation between soil and soil solution chemistry

The median pH in the soil solution was similar or higher than the corresponding soil $\text{pH}_{(\text{H}_2\text{O})}$ in the mineral horizons (Tab. 2). In three horizons at 80 cm in LAU, OTH, and VOR, the pH in the soil solution was about one pH unit higher than the pH in the soil. In the other horizons, the pH difference could reach 0.5 units.

The BS and the BC : Al ratio in the soil (expressed in $\text{mmol}_c \text{kg}^{-1}$) were clearly related to the BC : Al_{tot} and the BC : ($\text{Al}^{3+} + \text{AlOH}^{2+}$) ratios in the soil solution (Fig. 2). When the three outliers identified above were excluded (samples indicated with “?” in Fig. 2), the Pearson correlation coefficients between the parameters in the soil (BS and BC : Al_{soil}) and in the soil solution (BC : Al_{tot} and BC : ($\text{Al}^{3+} + \text{AlOH}^{2+}$)) ranged from 0.81 to 0.84 (Fig. 2). The lowest BC : Al_{tot} ratios (≤ 2) were found in horizons with a BS $\leq 10\%$ and a BC : Al ≤ 0.2 in the soil. However, different horizons with similar BS or BC : Al ratio in the soil could have different BC : Al_{tot} and BC : ($\text{Al}^{3+} + \text{AlOH}^{2+}$) ratios in the soil solution. For instance, five horizons had similar BS (11%–13%) but different BC : Al_{tot} ratios, varying between 1.4 and 5.8. The exchange coefficients $K_{\text{Al/Ca}}$ and $K_{\text{Al/Mg}}$ were calculated in all pooled samples. The

median $K_{\text{Al/Ca}}$ varied between 0.7 and 1.7, with the lowest values in COP and in NOV (Tab. 3). The $K_{\text{Al/Mg}}$ were on average higher than the $K_{\text{Al/Ca}}$ (ranged between 0.9 and 1.8), and were correlated to the $K_{\text{Al/Ca}}$ ($r = 0.65$; Tab. 3). No reliable $K_{\text{Al/K}}$ could be determined, since the K concentrations in the soil solution were too low ($< 10 \times$ detection limit).

The three outliers characterized by high BC : Al_{tot} ratios and near-neutral pH values in the soil solution (Fig. 2) correspond to the horizons at 80 cm in LAU, OTH, and VOR. At the three sites, the subsoil below 1 m of depth was characterized by a strong BS increase, reaching values between 55% and 75%, and the soil at LAU and OTH was characterized by the presence of carbonates in the C horizon (Walthert et al., 2003). In VOR, the soil profile was 5.0 m deep, and did not reach the C horizon that presumably contains marl. In addition, there was evidence of hydromorphic features in the whole profile in LAU and VOR and below 90 cm at OTH, coming from the accumulation of rainfall due to the presence of slowly permeable layers (Walthert et al., 2003).

4 Discussion

4.1 BC : Al ratios in the soil solution

The median BC : Al_{tot} ratios in the soil solution at the six study sites never reached the critical value of 1, although all soils were acid and located in regions having received acidic deposition in excess of the calculated critical loads (Kurz et

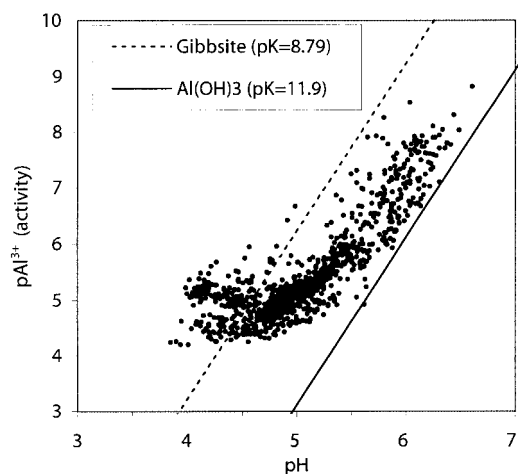


Figure 1: Relation pH-pAl³⁺ (-log(Al³⁺ activities)) for soil solution samples at the six study sites.

Abbildung 1: Beziehung zwischen pH und pAl³⁺ (-log(Al³⁺-Aktivität)) in den Bodenlösungen an den sechs Untersuchungsstandorten.

al., 1998a, b). When considering the toxic forms of aluminum (Al³⁺ and AlOH²⁺), the median BC : (Al³⁺ + AlOH²⁺) ratios were higher than the BC : Al_{tot}. Our findings suggest that the modeled BC : Al_{tot} ratios might be lower than those deduced from *in situ* measurements and that the critical loads might be higher than those calculated to date. It can be argued that, because the critical loads of acidity were calculated with steady-state models, the BC : Al_{tot} ratio in the soil solution has not yet declined below 1, but will probably reach the critical value of 1 at some time in the future. However, the application of a dynamic model (SAFE) to 622 Swiss forest sites indicated that the maximum BC : Al_{tot} threshold violation should have been reached or will be so in the next few years

(Kurz et al., 2001). The maximum occurrence of BC : Al_{tot} < 1 at 200 monitoring sites throughout Europe was found between 1980 and 1990 with the SMART model (de Vries et al., 2003b). In conclusion, it seems unlikely that the BC : Al_{tot} ratios at the study sites will reach the critical value of 1 in the next decade. The lowest ratios, that are still higher than the critical value, were found in the topsoil (15 cm) where acid loads have been the highest during the last decades. The BC : Al_{tot} ratio in the subsoil (> 50 cm) might decrease in the future if the proton buffer capacity decreases in the upper soil, due to depletion of reactive Al in the soil solid phase. In COP, the decrease of the BC : Al_{tot} ratios observed between 1987 and 1997 was much faster in the subsoil (110 cm) than in the topsoil (30 cm) (Blaser et al., 1999). Still the BC : Al_{tot} ratio did not reach the critical value of 1.

4.2 Control of Al solubility

Soil solution data showed that below a pH of 5.5, equilibrium with Al(OH)₃ was a poor predictor of the Al³⁺ activity in soil water. The slope of the pH-pAl³⁺ relation was much lower than 3, as predicted by the gibbsite model. It was about 1.3 for pH values between 4.7 and 5.5 and smaller than 0.6 for pH below 4.7. A non-integer value of the slope between 0 and 2 is typical of the reaction stoichiometry of Al released by equilibrium complexation reactions with soil organic matter (de Wit, 1992; Tipping and Hurley, 1992; Mulder and Stein, 1994; Prenzel and Schulte-Bisping, 1995; Wesselink and Mulder, 1995; de Wit et al., 1999). A similar pH-pAl³⁺ relation was found in forest soils in the Netherlands, Germany, and Sweden (pAl³⁺ = 0.16 × pH + 3.4) where it was shown that Al activities in soil solutions of acid mineral soils were mainly controlled by complexation reactions with soil organic matter (summarized in Wesselink et al., 1996). The curvilinear pH-pAl³⁺ relation over the whole range of pH (3.8–6.5) was also

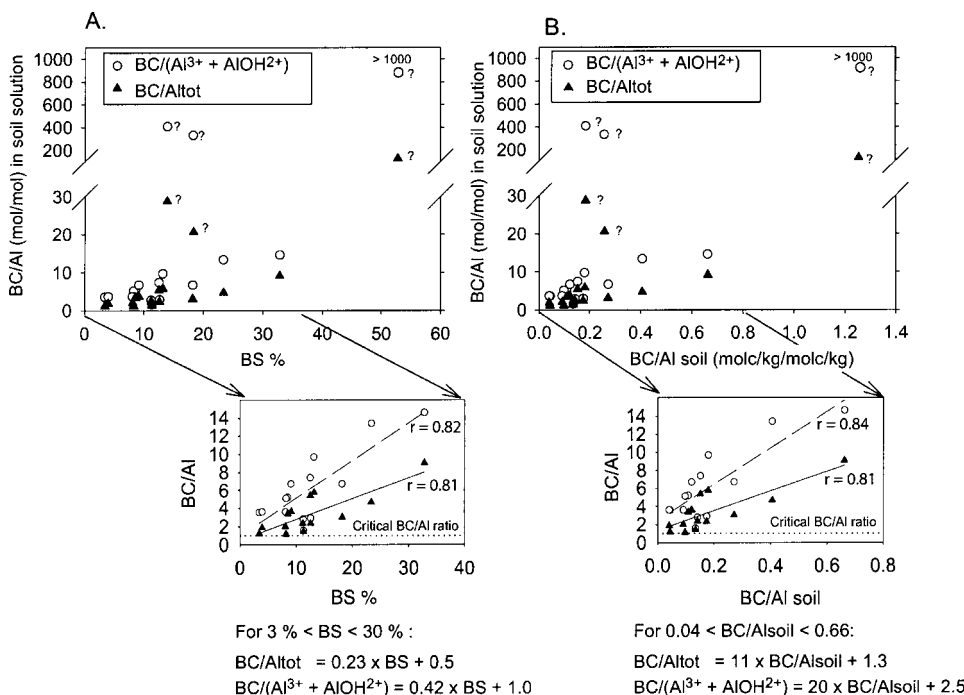


Figure 2: Relations between the soil and soil solution chemistry. (A) median base saturation (BS) vs. median BC : Al_{tot} and BC : (Al³⁺ + AlOH²⁺) in the soil solution; (B) median BC : Al ratio in soil vs. median BC : Al_{tot} and BC : (Al³⁺ + AlOH²⁺) in soil solution. “?” refers to outliers.

Abbildung 2: Beziehung zwischen chemischen Bodenparametern und der Zusammensetzung der Bodenlösung. (A) Basensättigung (BS) des Bodens vs. molarem BC : Al_{tot} oder BC:(Al³⁺ + AlOH²⁺)-Verhältnis in der Bodenlösung (Medianwerte); (B) BC:Al-Verhältnis im Boden vs. molarem BC:Al_{tot} oder BC:(Al³⁺ + AlOH²⁺)-Verhältnis in der Bodenlösung (Medianwerte). “?” bezeichnen die Ausreißer.

observed in different types of soils in New Zealand, and were interpreted as indicating two controls of Al solubility: $\text{Al}(\text{OH})_3$ at $\text{pH} > 5.5$ and soil organic matter at $\text{pH} < 5.0$ (Adams et al., 2000). The negative slope in soil solutions in BEA at 80 cm (Bsh horizon in podzol) is probably due to the decreasing contribution of organic acids to the aqueous acidity coupled to the increase in Al^{3+} activities.

4.3 Difference between in situ measurements and model results

Several reasons could explain the difference between our findings ($\text{BC} : \text{Al} > 1$ at all study sites) and the results of the national assessment of critical loads of acidity (Kurz et al., 1998a). First, internal element cycling of element was not considered in the model, since nutrient cycling was assumed constant over time (steady-state model). However, the study of 260 soil profiles in Switzerland showed that nutrient cycling influenced the base saturation of acid soils in the upper soil when calcareous material was present in the underlying layers (data not published). Acid soils with calcareous material at lower depth had a BS in the upper soil up to twice as high as soils developed from entirely acidic parent material, although the pH values in both cases were similar. The modeling of the soil solution composition in acid soils, based on soil mineralogy and weathering rates in the upper 50 cm (average thickness of the main root zone) probably underestimated the concentrations of exchangeable base cations, resulting in relatively low critical loads of acidity and frequent exceedances (for instance 90% of sites in the Swiss Plateau; Kurz et al., 1998a).

Secondly, the model did not take into account hydrological processes like periodic water saturation of soils and rises in perched water tables. In case of changes in the soil composition with depth (for instance large increase in BS), the composition of the soil solution in the transition zone (anaerobic/aerobic) might be influenced by the soil composition of the underlying layers due to the mixing of percolating and standing water. The soil solution at 80 cm in LAU, OTH, and VOR had pH values and $\text{BC} : \text{Al}$ ratios higher than expected when considering only soil pH and BS. The composition of the soil solution was probably influenced by the strong increase in BS to 60%–100% in the lowest part of the soil profile (Walthert et al., 2003) and the periodic accumulation of rainfall above the layers of low permeability. The presence of near-neutral water at 80 cm in LAU and VOR did not modify the BS because the exchange complex was mostly occupied by Al. Degassing of CO_2 during the collection with tension lysimeters could partly explain the relatively high pH at 80 cm (Zabowski and Sletten, 1991).

Finally, the model might have overestimated the Al^{3+} activities in the soil solution since they were estimated assuming equilibrium with gibbsite (Kurz et al., 1998a, b, 2001). Our soil solution data showed that below a pH of 5.5, equilibrium with $\text{Al}(\text{OH})_3$ was a poor predictor of the Al^{3+} activity in soil water. Several studies recommended to include Al complexation to soil organic matter in soil acidification models (e.g., Wesselink and Mulder, 1995; Holmberg et al., 2001; van der Salm

and de Vries, 2001). The regression coefficients of $\text{pH}-\text{pAl}^{3+}$ found at 15 cm in LAU ($\text{pAl}^{3+} = 0.52 \times \text{pH} + 2.13$) and in OTH ($\text{pAl}^{3+} = 0.42 \times \text{pH} + 2.67$) were similar to those recommended by Holmberg et al. (2001) for forest floor ($\text{pAl}^{3+} = 0.49 \times \text{pH} + 3.37$). The scatter of pH and pAl^{3+} data in Fig. 1 was likely due to errors related to Al_{tot} and pH analyses, especially in samples with $\text{pH} > 5.0$ and to assumptions made in the speciation calculations. The relative standard deviation of Al_{tot} analyses was smaller than 10% for concentrations higher than $5.6 \mu\text{mol l}^{-1}$ and $\pm 0.56 \mu\text{mol l}^{-1}$ between the detection limit ($0.56 \mu\text{mol l}^{-1}$) and 10 times the detection limit. Uncertainty associated with this level of precision is negligible compared with the scatter of data. The precision of pH measurements at $\text{pH} > 5.0$ was rather poor (± 0.15 pH unit), which contributed to the scatter of data. At lower pH values, especially in BEA (podzol), organic acids contributed to the aqueous acidity, resulting in a negative $\text{pH}-\text{pAl}^{3+}$ relation. Systematic errors arising from pH and Al_{tot} determination were insignificant, since certified reference materials were used to check the accuracy of measurements. The main uncertainties linked to the equilibrium speciation calculations were the soil temperature and the concentrations of fulvic acids, since they were not measured. Based on soil temperature measurements at different sites in Switzerland (Heim and Frey, 2004), a mean temperature of 8°C was assumed representative of the study sites. Concentrations of fulvic acids were estimated assuming 66% of dissolved organic matter (DOM = ca. $2 \times \text{DOC}$) being active fulvic acids (Tipping, 2002).

4.4 Relation between $\text{BC} : \text{Al}$ in solution and $\text{BC} : \text{Al}$ in the solid phase

The soil BS (range 3%–30%) and the $\text{BC} : \text{Al}$ ratio in the soil (range 0.04–0.66) were significantly related to the $\text{BC} : \text{Al}_{\text{tot}}$ in the soil solution. However, the $\text{BC} : \text{Al}_{\text{tot}}$ ratios in the soil solution differed in different horizons having the same BS. This is likely due to different exchange coefficients between Al and the main base cations (Ca, Mg). As a result of all parameters influencing the values of exchange coefficients (ionic strength, distribution of ions in the solution; Binkley et al., 1989; Sauvé and Hendershot, 1995), the median $K_{\text{Al/Ca}}$ and $K_{\text{Al/Mg}}$ varied between 0.7 and 1.8. These values are typical of those recommended by Holmberg et al. (2001; $K_{\text{Al/BC}} = 1.0$) in their tentative modifications for calculating critical loads of acidity. The outliers in Fig. 2 indicate that the prediction of the soil solution chemistry might be difficult in pseudogleyed soils with a strong BS gradient in the subsoil. Excluding these special circumstances, the clear relationship between the BS and the $\text{BC} : \text{Al}_{\text{tot}}$ ratio in the soil solution indicates that the lowest median $\text{BC} : \text{Al}_{\text{tot}}$ ratios (≤ 2) were measured in soils with a $\text{BS} \leq 10\%$ or a $\text{BC} : \text{Al} < 0.2$ in the soil. This finding supports the criteria of Binkley et al. (1989) who found that soils with $\text{CEC}_{\text{eff}} < 100 \text{ mmolc kg}^{-1}$, $\text{BS} < 10\%$, and soil solution $\text{pH} < 5$ were typical of soils sensitive to acid deposition, with respect to Al toxicity and deficiencies in base cations (low $\text{BC} : \text{Al}_{\text{tot}}$ ratios).

In order to use the relationship between the BS and the $\text{BC} : \text{Al}_{\text{tot}}$ ratio as a predictive tool, more data would be necessary to validate the regression line and the exchange coefficients.

The soil type and its chemical characteristics should be comparable to those investigated in this study, i.e., soils typically developed in a temperate climate. This relation would represent a pragmatic approach to identify the soils with a high probability of having low BC : Al ratios (< 2) in the soil solution.

5 Conclusion

1. The median BC : Al_{tot} ratio in the soil solution at the six study sites never reached the critical value of 1, although all soils were acid and located in regions receiving acidic deposition in excess of the calculated critical loads. The lowest BC : Al_{tot} ratio in each plot ranged between 1.2 and 5.4.
2. Below a pH of 5.5, equilibrium with Al(OH)₃ was a poor predictor of the Al³⁺ activity in soil water at the study sites. Al activities in soil solutions collected in acid mineral soils were mainly controlled by complexation reactions with soil organic matter.
3. The soil BS (range 3%–30%) and the BC : Al ratio in the soil (range 0.04–0.66) were significantly related to BC : Al_{tot} in the soil solution. The lowest median BC : Al_{tot} ratios in the soil solution (≤ 2) were found in soils with a BS $\leq 10\%$ or a BC : Al < 0.2 in the soil.
4. The chemical composition of soil solutions collected in acid pseudogleyed soils overlying a calcareous substrate was strongly influenced by the composition of underlying layers. These situations should be taken into account for the calculations of critical loads of acidity.

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