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Characterization of weak acidity in selected precipitation samples from a forest ecosystem

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ABSTRACT

In different incident precipitation and throughfall samples, it is shown that the CO_2-acidity (base neutralizing capacity up to pH 8.3) can be twice the H_3O^+-concentration. This fact can be explained only by the existence of weak acids (with the exception of $H_2CO_3^*$). The buffer capacity was determined by using an exact acid/base-buffer-titration. Assuming the existence of only one weak acid, the concentration and strength were calculated.

1. Introduction

In recent years, it has become apparent that an exact measure of total input of acidifying agents is important to obtain a good estimation of the acidification of soil and surface waters. From a water-chemical point of view, the acidity is strictly defined (Stumm and Morgan, 1981). In routine analyses of ecosystem data, the acidity input is normally directly calculated from the pH value (McColl et al., 1982; Hüser and Dunkel, 1985). However, this method always underestimates the acidity if hydronium ions are not the only acidifying species in solution.

Ulrich et al. (1979) and Ulrich (1983) developed a concept for calculating the acidic input in forest ecosystems with respect to canopy processes. In these papers, the acidic input by weak acids was neglected. However, the contribution of weak, probably organic acids to acidic input is more important if the precipitation passes through plant canopies and organic substances are washed off or leached (Tukey, 1970; Henderson et al., 1977; Ulrich, 1983; Cronan, 1984).

There are few quantitative investigations reported on the importance of weak acids for the total acid input (Hoffman et al., 1980; Keene et al., 1983). Therefore, the contribution of weak acids to the acidity of the rain and the throughfall in a damaged spruce stand was investigated and the importance for the acid input discussed.

2. Theoretical section

While the pH value is a measure of the activity of the hydronium ions,

$$\mathrm{pH} = -\log_{10} a_{H_3O^+}, \tag{1}$$

the acidity, according to Brønsted's theory, is defined as the concentration of all species which can deprotonate compared to a defined reference status minus the concentration of those which can accept a proton. The reference status is defined by a certain proton level (pH value). Hence, the acidity is equivalent to a certain base neutralization capacity, which is measured by titration with a strong base from the actual pH value of the solution of interest to the pH value of the proton level (Stumm and Morgan, 1981). If the reference status is equal to pH 7.0 and only strong acids ($pH_{actual} - pK_a > 2$) are present, the acidity can be calculated using eq. (2).

$$[\mathrm{Acy}] = [H_3O^+] - [OH^-] \simeq [H_3O^+]. \tag{2}$$

If, additionally, there is a weak acid (HA) present, the part of its protonated species which would deprotonate during titration to the refer-

ence status (pH_{level}) has to be added to the acidity (eq. (3)):

$$[Acy] = [H_3O^+] - [OH^-] + ([HA]_{pH_{actual}} - [HA]_{pH_{level}}). \quad (3)$$

The part $[HA]_{pH_{level}}$ is intentionally neglected in order to get an easy and usable interpretation of acidity data. Therefore, the proton levels have to be fixed as far as possible from the pK_a-values of the acids present.

The following proton levels and acidity definitions derived from the dissociation constants of the carbon dioxide–carbonate equilibria are ordinarily used (Stumm and Morgan, 1981):

—the mineral acidity with the proton level of pH 4.4;
—the CO_2-acidity with the proton level of pH 8.3;
—the total acidity with the proton level of pH 10.3.

Until now, the following methods have been employed for the determination of the acidity of precipitation water.

(a) Determination of Acy (pH) by using the pH value (eqs. (1) and (2)) (McColl et al., 1982; Hüser and Dunkel, 1985).
(b) Titrations to the mentioned equivalence points pH 8.3 (Schrimpff et al., 1984) and 10.3 (Bartels and Block, 1985), respectively.
(c) A more exact determination of the equivalent volumes is gained by a mathematical linearization of the titration curve (Gran, 1952; Johansson, 1970; Liberti et al., 1972). Johansson's $y1$-function (Johansson, 1970) is used to calculate strong acidity. It uses titration points before the equivalence point (mostly pH 7.0) for the determination of the equivalent volume. Johansson's $y2$-function can be applied to equivalent points pH 7.0, using titration points between pH 8.0 and pH 8.4 for neutralization acidity, and pH 10.3 using titration points pH > 11.0 for total acidity. Johansson (1970) and other authors (Lee and Brosset, 1978; Brosset and Ferm, 1978; Keene et al., 1983; McQuaker et al., 1983; Lindberg et al., 1984; Johnson and Sigg, 1985; Tyree, 1985; Keene and Galloway, 1985) have shown that partial dissociation of weak acids during the titration makes the functions nonlinear and so disturbs the exact determination of the acidity.

The methods listed so far are not suitable for providing exact information on the content and strength of weak acids, which are partly dissociated at the actual pH value. To determine this, the titration curve has to be recorded more exactly. This can be done using a mathematical method to get a segmentation and linearization of the titration curves (Seymour et al., 1977), but this iterative method is very expensive.

Another way to measure the content and strength of weak acids by computing an acid/base-buffer-titration curve according eq. (4) (Stumm and Morgan, 1981; Liljestrand, 1985) produces some indications of the discussed problems:

$$\beta_{\Delta pH} = \frac{\Delta C_{tit}}{\Delta pH}; \quad (4)$$

ΔC_{tit}: amount of strong base or acid added to the solution in mol l^{-1};
ΔpH: resulting change in the pH value;
$\beta_{\Delta pH}$: buffer capacity in eq. l^{-1}.

While $\beta_{\Delta pH}$ is calculated from titration data, the buffer capacity β_{pH} can be computed if the composition of the solution is known. If the solution contains several monoprotic acids, the buffer capacity β_{pH} is defined according to eq. (5):

$$\beta_{pH} = 2.3\left([H_3O^+] + \frac{K_w}{[H_3O^+]} + \frac{C_1 K_{a,1}[H_3O^+]}{(K_{a,1} + [H_3O^+])^2} + \ldots + \frac{C_n K_{a,n}[H_3O^+]}{(K_{a,n} + [H_3O^+])^2}\right) \quad (5)$$

K_w: ion product of water;
$K_{a,n}$: dissociation constant of nth acid;
C_n: concentration of nth acid (protonated and deprotonated species).

In the presence of only strong acids ($pH_{actual} - pK_a > 2$) and $[H_3O^+]$ is assumed to be greater than 10^{-6} M, the buffer capacity is:

$$\beta_{pH,s.a.} \simeq 2.3[H_3O^+]. \quad (6)$$

In the additional presence of one weak acid ($|pK_a - pH_{actual}| < 2$), the buffer capacity will be higher by the amount $\Delta\beta_{pH,w.a.}$:

$$\Delta\beta_{pH,w.a.} = 2.3 \frac{C_{w.a.} K_a [H_3O^+]}{(K_a + [H_3O^+])^2}, \quad (7)$$

$C_{w.a.}$: concentration of weak acid,

which can be computed from the titration data with eq. (8) for small intervals ΔpH:

$$\Delta\beta_{pH,w.a.} \simeq \beta_{\Delta pH} - \beta_{pH,s.a.} \quad (8)$$

The buffer intensity of an acid is maximal when the activity of H_3O^+ is equal to the dissociation constant K_a of the acid. Consequently, at the titration point where $\Delta\beta_{pH,w.a.}$ is maximal, $pH = pK_a$ and therefore eq. (7) simplifies to:

$$\Delta\beta_{pH,w.a.} \simeq 2.3 \frac{C_{w.a.} [H_3O^+]^2}{4[H_3O^+]^2} \quad (9)$$

$$C_{w.a.} \simeq 1.74\, \Delta\beta_{pH,w.a.} \quad (9a)$$

The concentration of the weak acid can then be calculated directly from the titration data. This statement is only valid if one acid is present.

3. Sampling, storage and analytical procedures

The samples were collected in the 'Fichtelgebirge' (NE-Bavaria, FRG) near Oberwarmensteinach (11°47′30″ east longitude, 49°59′30″ north latitude, maximal altitude about 1000 m a.s.l.). These mountains are located in the center of Middle Europe and receive a high acidic and sulfur deposition (Verhoeven, 1985; Hantschel et al., 1985). Experimental plots were established in a 20–40 year old Norway spruce—*Picea abies* (Karst.)—stand on a weakly inclined SE-slope. These trees show symptoms of yellow tip-chlorosis and necrosis mainly caused by Mg deficiency (Zech et al., 1985—further site and symptom description Hantschel et al., 1985; Kaupenjohann et al., 1985).

Rain samples were collected with 2 polyethylene tubs (0.125 m^2 area). Collecting time was limited to a maximum of 12 h during a precipitation event to exclude dry deposition (Galloway, 1978). Samples were taken during the following weather situations:

15 May 1985: after 6 days of dryness and winds turning from NE to S during a moderate precipitation event;
12 June 1985: after rain events lasting for 7 days and winds from W to SW;
27 July 1985: after 2 days of dryness and winds from NE to SE, as a heavy western thunder-shower started.

The samples were frozen in polyethylene bottles prior to analysis. The element concentrations in the samples were measured with a flame photometer (Eppendorf) for Na, an atomic absorption spectrometer (Perkin Elmer 420) for Fe, Ca, Mg, and Mn, a flow injection analyzer (Tecator Fiastar 5022) for NH_4^+ (method Tecator application note AN 65/83), and a ion chromatograph (Abimed with Vydac anion column) for NO_3^-, SO_4^{2-}, and Cl^- (Small and Miller, 1982; Cochrane and Hillman, 1982; Bierl, 1985 personal communication). The pH measurements were all made with a glass electrode with sleeve diaphragm (Ingold 405-88-S7). The electrode was calibrated in HCL solutions and in buffer solution pH 9.0 (Merck 9461). The electrode does not show any measurable streaming potential ($\ll 1$ mV) in stirred solutions and the difference of liquid junction potential at the reference electrode in solutions having different ionic strengths (10^{-4} M $< I < 10^{-2}$ M, adjusted with NaCl), was < 2 mV. Acids and bases were made by usage of 0.1 M HCl (Merck 9931) and 0.1 M NaOH (Merck 9959) diluted with double-distilled water. This water was kept CO_2-free by cooling after distillation under N_2-atmosphere. The titer factor of the NaOH was determined as 1.00. 100 ml of each sample were bubbled with N_2 for 20 min and then titrated under N_2-atmosphere to about pH 3.2 with 0.2 M HCl. The subsequent isothermal titration to pH 10.0 was done in 0.05 pH-steps with a $5 \cdot 10^{-3}$ M NaOH and a titrator (Metrohm Dosimat 655). Titration points higher than pH_{actual} were used to calculate strong and CO_2-acidity. An additional 50 ml of each sample was titrated with 0.1 M NaOH to pH 12.0. The methods used to calculate the different acidities and the buffer capacity are described in Section 2.

The $\beta_{\Delta pH}$ data points have an inherent error

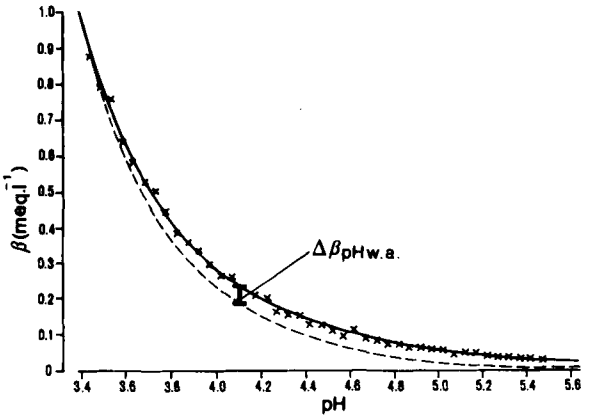

Fig. 1. Buffer capacity titration points (×), fitted function of throughfall sample of 27 July, 1985 (——), $\beta_{pH,s.a.}$ (---), and $\Delta\beta_{pH,w.a.}$

(c.f. Fig. 1) which can be explained by the precision of the pH electrode (the best precision of electrodes using liquid junctions is about ± 0.01 unit (Camman, 1979)), and by the precision of the titration (smallest additions were 2 μl). Therefore, a curve-fitting program, based on the method of the least squares (Durner, 1985; personal communication), was used to best describe the data points in order to provide a determination of pK_a and concentration of weak acids.

To test the described method, the following solutions were used:

—artificial rainwater (ARW); this water is equivalent to the average precipitation composition in this area (Verhoeven, 1985; see Table 1);
—ARW with $5 \cdot 10^{-5}$ M acetic acid;
—ARW with $1 \cdot 10^{-4}$ M formic acid.

The recovery of the acids used is shown in Table 1. The presence of a weak acid is indicated by a maximum of the $\Delta\beta_{pH,w.a.}$ function within the pH interval of the curve fitting. If the maximum is at the edge of the curve-fitting interval, no pK_a can be calculated. If in this special case an acid is present with a pK_a equal to any pH of the interval, its concentration is below the maximum × 1.74 (eq. l^{-1}) (cf. eq. (9a)).

Table 1 shows that the pH value of maximal buffering is measured with an estimated precision of ±0.1 unit and the concentrations with a precision of 20%.

4. Results and discussion

The chemical composition of our precipitation samples was dependent on the different weather situations. Their element concentrations, ionic strengths and the ion balances are listed in Table 2.

The ionic strength, as a rough measure for the amount of all dissolved ions, increases by about 45–115% after passing through the plant canopy. This observation has been reported by several authors (Clesceri and Vasudevan, 1980; Richter et al., 1983; Ulrich, 1983) and can be explained either by the washing-off of dry deposited particles from the plant surfaces (Fowler, 1980; van Breemen et al., 1982; Olson et al., 1981) or by the leaching of ions out of the plants (Eaton et al., 1973; Henderson et al., 1977; Ulrich, 1983; Matzner and Ulrich, 1984; Cronan, 1984; Kaupenjohann et al., 1985).

For the calculation of the ion balance, the most commonly measured and important ionic components were considered (Tyree, 1981; Munger, 1982; Kallend et al., 1983; Pratt et al., 1984). Nevertheless, all ion balances result with a positive excess charge. If the missing anions are conjugate bases of weak acids, they would influ-

Table 1. *Recovery of weak acids by the method of fitted buffer capacity functions*

	pK_a of weak acid		Concentration of weak acid		pH-interval of curve fitting
	theoretical	measured	employed (μM)	measured (μM)	
Artificial rainwater + HCOOH	3.75	3.66	100	100	3.4–5.0
Artificial rainwater + CH_3COOH	4.76	4.76	50	39	4.0–5.2
Artificial rainwater	–	–	0	<22	3.6–5.5

Table 2. *Amount, composition and hydrochemical parameters of precipitation samples*

Sample	N* l m^{-2}	pH	Na^+	K^+	NH_4^+	Ca^{2+}	Mg^{2+}	Fe^{3+}†	Mn^{2+}	Al^{3+}	CL^-	NO_3^-	SO_4^{2-}	PO_4^{3-}‡	I§ (μM)	IB¶ (μeq. l^{-1})
								(μeq. l^{-1})								
15 May 1985																
rain	3, 1	3, 85	14	11	156	120	22	4	<1	27	45	119	300	1	730	+38
throughfall	2, 1	3, 58	20	105	214	228	46	4	35	44	54	220	640	3	1459	+53
12 June 1985																
rain	8, 9	3, 98	13	4	63	40	6	<1	<1	6	22	79	94	<1	292	+44
throughfall	6, 4	3, 83	22	55	50	52	14	<1	12	8	33	70	194	1	474	+66
27 July 1985																
rain	8, 8	4, 36	8	19	106	64	12	<1	<1	11	45	57	90	<1	322	+73
throughfall	7, 6	3, 92	23	95	110	80	14	<1	10	9	44	122	210	2	589	+87
artificial																
rainwater	-	4, 10	40	10	110	30	15	0	0	0	45	99	140	0	377	± 0

* Amount of rainwater.

† Calculated as $Fe(OH)^{2+}$.

‡ Calculated as $H_2PO_4^-$.

§ Ionic strength, calculated from $I = 0.5 \sum_m z_m^2 [\text{ion}_m]$; z_m = charge number of ion_m; $[H_3O^+] \simeq 10^{-pH}$.

¶ Ion balance, calculated from $IB = \sum_m z_m [\text{cation}^+] - \sum_m z_m [\text{anion}^-]$

$$[H_3O^+] = \frac{10^{-pH}}{\gamma_{H_3O^+}}; \qquad -\log_{10} \gamma_{H_3O^+} = 0.5 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3\, I \right)$$ (Davies' approximation, Frevert, 1983).

ence the acidity of the samples and should therefore be investigated (Skiba et al., 1986).

It is important to approach the problem by using the adequate acidity concept (Morgan, 1982). The mineral acidity concept is not applicable to precipitation water because the pH values may be >4.4. The total acidity takes all weak acids into consideration, including very weak acids such as NH_4^+ ($pK_a = 9.3$) and partly HCO_3^- ($pK_a = 10.4$). From the ecochemical point of view, this is a doubtful measure, because there is no titration of precipitation water to pH 10.4 in a natural environment (soils, lakes). For that reason, HCO_3^- is a conservative anion, and NH_4^+ should be regarded in the same manner. On the other hand, under certain conditions, NH_4^+ can be partly or totally nitrified to NO_3^- by releasing 2 protons (van Breemen et al., 1982). Thus, the NH_4^+-ion has a potential acidification capacity. However, this concept is not appropriate to our problem, because it includes acids which do not dissociate at the actual pH values.

The CO_2-acidity and the neutralization acidity exclude very weak acids ($pK > 10.3$) and include 10% of the existing NH_4^+ and hence they are more appropriate concepts.

The different calculated acidities are listed in Table 3. The CO_2-acidity always roughly equals the neutralization acidity. This fact can be explained by the removal of CO_2 before titration. However, Table 3 further shows that the CO_2-acidity is always higher (up to a factor of two), than the strong acidity and the Acy(pH) which proves the existence of weak acids. Therefore, the Acy(pH) and the strong acidity cannot be an accurate measure of the acidity in our samples. The CO_2-acidity and neutralization acidity are appropriate concepts to describe the base neutralization capacity in systems like soils, plants or lakes.

The CO_2-acidity is, however, an insufficient measure of the strength of the acids involved. To get an indication of the acidification capacity of the precipitation in acidic soils or lakes, it is necessary to calculate the buffer capacity of the precipitation water. The results of the fitted functions and the parameters used for our samples are summarized in Table 4 and an exemplary plot

Table 3. *Acidity of precipitation samples calculated in different ways (μeq. l^{-1})*

Sample	Acy (pH)*	s. Acy†	CO_2-Acy‡	Neutr. Acy§	t. Acy¶
15 May 1985					
rain	148	167	227	228	340
throughfall	281	320	499	468	714
12 June 1985					
rain	109	106	124	126	197
throughfall	154	136	223	214	274
27 July 1985					
rain	45	64	109	96	312
throughfall	124	97	242	222	391

* $[\text{Acy}] = \frac{10^{-\text{pH}}}{\gamma_{H_3O^+}}$.

† Strong acidity according to Johansson's $y1$-plot.
‡ CO_2-acidity from end point titration until pH 8.3.
§ Neutralization acidity according Johansson's $y2$-plot for $8.0 \leqslant \text{pH} \leqslant 8.4$.
¶ Total acidity according to Johansson's $y2$-plot for pH > 11.

Table 4. *Fitted functions of buffer capacity titration curves*

Sample	Fitted function	Regression coefficient	$\text{pH}_{\text{max.diff.}}$*	Max. diff·1.74† (μeq. l^{-1})	A^-‡ (μeq. l^{-1})
15 May 1985					
rain	$\beta = 6.64\ \text{pH}^{-7.2783}$	$r = -0.9963$	4.25	83	24
throughfall	$\beta = 2.67\ \text{pH}^{-6.5218}$	$r = -0.9983$	4.10	150	35
12 June 1985					
rain	$\beta = 36.5\ \text{pH}^{-8.6430}$	$r = -0.9955$	(3.65§)	<22 for pH > 3.75	–
throughfall	$\beta = 27.9\ \text{pH}^{-8.3364}$	$r = -0.9983$	4.10	60	21
27 July 1985					
rain	$\beta = 8.98\ \text{pH}^{-7.5217}$	$r = -0.9978$	4.25	68	38
throughfall	$\beta = 7.06\ \text{pH}^{-7.3034}$	$r = -0.9986$	4.10	93	37
artificial rainwater	$\beta = 1.49 \exp.(-2.1792\ \text{pH})$	$r = -0.9990$	(3.45§)	<22 for pH > 3.80	–

* pH of maximal difference between fitted function and $\beta_{\text{pH,s.a.}}$; $\text{pH}_{\text{max.diff.}} = \text{p}K_a$ of weak acid with the assumption, that only one weak acid is present.

† max. diff.·1.74 = $C_{\text{w.a.}}$ with the assumption above.

‡ A^- = anion charge with the assumption above; $A^- = \frac{C_{\text{w.a.}} \cdot [H_3O^+]}{K_a + [H_3O^+]}$.

§ not interpretable because at the edge of fitting interval.

is shown in Fig. 1. The pH value of the maximal difference between the titration curve of the sample and $\beta_{\text{pH,s.a.}}$ determines the pK_a-value of one weak acid or the pH value of maximal buffering (apparent pK_a-value) of a mixture of different weak acids.

Table 4 shows that weak acids with concentrations >60 μeq. l^{-1} could be characterized in 5 of the 6 investigated environmental samples. The amount of weak acidity is always higher in the throughfall than in the incident precipitation. It is very remarkable that all throughfall samples and all rain samples show the same points of maximal buffering, pH 4.10 and 4.25, respectively. We cannot be sure that this shift is due to different mixing ratios of 2 (or more) acids

with different strengths. We have too little data to prove this difference statistically.

Assuming that only one weak acid is present in each sample, we can calculate its anion charge at the original pH value (Stumm and Morgan, 1981). The values are listed in Table 4 and should correspond to the net positive charge in Table 2. The agreement is about 50%. Furthermore, the concentration of the protonized species (max. diff. $\times 1.74 - A^-$) should correspond to the difference between the CO_2-acidity and neutralizing acidity on the one hand, and strong acidity and Acy(pH) on the other hand. The agreement is also about 50%.

These two results, which are gained by different methods, indicate that the weak acidity of our samples is caused by a mixture of several weak acids. Nevertheless, the apparent pK_a-value represents the pH of maximal buffering of this mixture.

We are assuming that the weak acid of the incident precipitation samples is caused by aerosol particles. The shifting of the maximal buffering in the throughfall samples is an indication of additional leaching of weak, organic acids out of the plants.

5. Conclusions

Calculation of acidity using pH values underestimates the real acidity by up to 50%. The rest of the acidity is caused by weak organic acids which have their origin mainly in aerosol particles and plant leaching. The buffer capacity of this mixture can be calculated using exact acid-base titration curves. We propose measuring the base neutralization capacity by titration up to pH 8.3 (CO_2-acidity) as an easy way to include this important part of the acidity.

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7. Appendix

Notation

[Acy]	= acidity (eq. l^{-1})
pK_a	= $-\log_{10}$ (dissociation constant of acid in M)
pH_{actual}	= original pH of precipitation sample
pH_{level}	= pH of proton level
$\beta_{\Delta pH}$	= buffer capacity measured by titration (eq. l^{-1})
ΔC_{tit}	= amount of strong acid or base added during titration (M)
ΔpH	= change in pH due to ΔC_{tit}
β_{pH}	= buffer capacity calculated (eq. l^{-1})
K_w	= ion product of water (M^2)
C	= concentration of acid (protonated and deprotonated species) (M)
s.a.	= strong acid, $pH_{actual} - pK_a > 2$
w.a.	= weak acid, here: $\lvert pH_{actual} - pK_a \rvert \leqslant 2$
$\beta_{pH,s.a.}$	= calculated buffer capacity of s.a. solution (eq. l^{-1})
$\Delta\beta_{pH,w.a.}$	= enrichment of buffer capacity due to w.a., calculated or measured by titration (eq. l^{-1})
IB	= ion balance (eq. l^{-1})
I	= ionic strength (M)
A^-	= anion charge of w.a. (eq. l^{-1}).

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