

Assessing the Resilience of Soils to Acidification on Different Time Scales

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Abstract

To estimate the sensitivity of soils to naturally and anthropogenic induced acidification we measured Acid Neutralizing Capacities (ANC) of typical soils in West Germany. Measured values of ANC are strongly dependent on the procedure employed. We conducted three kinds of experiments to distinguish between 1. Short-Term Acid Neutralizing Capacity (STANC) due to exchange processes and dissolution of easily weatherable non-silicate minerals, on the scale of days to years, 2. Medium-Term Acid Neutralizing Capacity (MTANC) due to dissolution of easily weatherable silicate minerals, on the scale of decades and 3. Long-Term Acid Neutralizing Capacity (LTANC) considering the buffer capacity of stable minerals, on the scale of centuries. The experiments have been applied on soil profiles at forest and agricultural sites with soil parent material ranging from Holocene sediments, Pleistocene loess, and Devonian sedimentary rock (greywacke/shale). Calculated acid neutralizing capacities ranged from 12.9meq kg⁻¹ to 747meq kg⁻¹ (STANC) depending on target pH, 580meq kg⁻¹ to 3680meq kg⁻¹ (MTANC) and 2841meq kg-1 to 12233meq kg⁻¹ (LTANC). Only 11% to 19% of the MT- and LTANC can be explained by a release of basic cations (Ca, Mg, K, Na) and Mn. Thus, the remaining buffer capacity is associated with Al and Fe. These elements do not buffer protons until pH <4.8 (Al) and <3 (Fe), respectively. Because of the beginning Al-toxicity below pH 4.8 only the basic cation fraction of MTANC and LTANC should be taken into consideration when assessing soils in terms of acidification endangerment.

Keywords: Soil acidification; Soil degradation; Acid neutralizing capacity; Resilience; Buffer capacity

Introduction

Estimations show that worldwide 75% of the land is degraded [1] and besides physical and biological process, chemical degradation processes, including soil acidification, plays a significant role [2]. In that context, soil acidification, e.g. due to excessive N fertilization, is a major problem in intensive agricultural systems and is becoming increasingly serious [3-7]. Furthermore, according to the IPCC SRES A2 scenario for 2050, many soils, especially in Asia, are at risk for acidification damage due to sulfur dioxide emissions. In addition to the sulfur deposition Zaipeng Yu et al. [8] reported that regional Nitrogen deposition, warming, and decreasing water availability have contributed to a temporal decrease in pH and base cations in natural ecosystems. Even though a lot of research in the area of soil acidification is available, the acidification risk of soils developed on different parent material and different use need further understanding [9]. Accelerated weathering, mobilization of toxic elements and reduction of the cation exchange capacity are only a few potential impacts on soils and their productivity as a result of soil acidification. Soils have various mechanisms to buffer inputs of acidity [10-13]. These proton consumption processes have different kinetics and capacities and are associated with different soil components and pH ranges. According to Ulrich [10] and Schwertmann et al. [13] the most important buffer reactions and pH ranges of buffering are: dissolution of carbonates (pH 8 to 6.5) and cation exchange reactions (pH 8 to <3) resulting in a release of basic cations, protonation of functional groups of clay minerals (pH 6 to <3) and humic substances (pH >7 to <3) without a release of cations, dissolution of silicate minerals (pH <7) with a release of basic cations, Al, Fe and heavy metal cations and dissolution of Al (pH 4.8 to 3) and Fe oxides (pH <3) with a release of Al and Fe ions, respectively.

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Most attempts found in the literature to measure the Acid Neutralizing Capacity (ANC) of soils only address one or two of the buffer compounds mentioned. Most investigations were carried out with buffer substances with fast kinetics in order to assess the short time acid neutralizing capacity and thus the resilience of soils to acidification. This capacity is operationally defined as the amount of acid required to lower the pH of a soil sample to a reference pH value [14,15] or by a pH unit [16,17] during a defined reaction period using batch or titration experiments. Changes in pH and cation release due to addition of acids were measured by Schaller & Fischer [18], Bruce & Riha [19] and Kaupenjohann & Hantschel [20]. Yuan & Lavkulich [21] developed a procedure to calculate the acid neutralizing capacity related to extractable aluminum and Sato & Ohkishi [22] calculated the rapid ANC derived from carbonates, exchangeable base cations and sulfate adsorption. In contrast to the mentioned substances with fast buffer reactions some authors focused their research on buffer substances with slower kinetics but larger capacities. To estimate ANC in a toposequence of soil profiles on loess, Brahy et al. [23] measured the total contents of major alkaline and alkaline-earth cations as well as aluminum and iron occluded in silicates. The determination of ANC from selected rock forming minerals [24,25] is another possibility to obtain the buffer capacity due to dissolution of minerals during soil development.

Only a few attempts were made to measure buffer capacities of different kinetic and thus of different time-scales at once. Hodson et

al. [26] compared laboratory-determined short-term acid buffering capacities with the Skokloster classification (soil classes are defined primarily on the basis of soil parent material), based on the assumption that the majority of acidification neutralization is due to base cation release from mineral weathering. Based on chemical and mineralogical analyses, van Ranst et al. [27] distinguished between ANC of exchangeable basic cations, lattice basic cations, and Al. The present paper proposes an approach to calculate short-, medium- and long-term proton consumption processes of soils to produce a dynamic method of assessing soil acidification and recovery on different time-scales.

Materials and Methods

Soil samples

Samples were taken from soils developed on Holocene fluvial sand, Pleistocene loess and Devonian sedimentary rock (greywacke/shale) at forest and agricultural sites (Table 1). The spectrum of soil parent materials chosen represents the vast majority of soil landscapes in Western Germany. The soils developed on fluvial sand and greywacke/shale were classified as Cambisols (WRB). The loess soil is a stagnic Luvisol (WRB). Soil material was collected in depth of 0 to 30cm, 30 to 50cm and 50 to 100cm with a soil auger. The selected sample plots at the forest and agricultural sites were situated within a distance of 250m and shorter to ensure comparable exposition, precipitation, geology and hydrology. Thus, the influence of land use on soil acidification can be compared.

Table 1: Parent material (H=Holocene sediment, P=Pleistocene loess, D=Devonian sedimentary rock), land use (a=agriculture, f=forest), soil type according to World Reference Base for Soil Resources (WRB), sampling depth and sample identification of the studied locations.

Parent Material	Land Use	Soil Type (WRB)	Sampling Depth /cm	Sample Identification	
			0-30	Hf-1	
	forest	Cambisol	30-50	Hf-2	
			50-100	Hf-3	
Holocene sediment			0-30	Ha-1	
	agricult.	Cambisol	30-50	Ha-2	
			50-100	На-З	
			0-30	Pf-1	
	forest	Glayic Luvisol	30-50	Pf-2	
			50-100	Pf-3	
Pleistocene loess			0-30	Pa-1	
	agricult.	Glayic Luvisol	30-50	Pa-2	
			50-100	Pa-3	
			0-30	Df-1	
	forest	Cambisol	30-50	Df-2	
			50-100	Df-3	
Devoluan sedimantry FOCK			0-30	Da-1	
	agricult.	Cambisol	30-50	Da-2	
			50-100	Da-3	

Routine analysis

The soil samples were air dried, crushed and passed through a 2mm sieve. Particle-size distribution was determined by a combined

sieve and pipette method after removing organic matter by oxidation with H_2O_2 , removing Fe oxides by dithionite, citrate Bicarbonate (DCB) extraction and dispersion with sodium phyrophosphate.

The samples were analyzed for pH $(0.01M \text{ CaCl}_2)$ in a 1:2.5 (mass to volume) solution. Exchangeable cations were extracted with 1M NH₄NO₃. Soil Organic Carbon (SOC) was measured by means of a total-CNS analyzer. Total chemical composition was determined by X-Ray Fluorescence (XRF). Poorly crystalline Fe oxides were quantified by dissolution with ammonium Oxalate (Ox) buffered with oxalic acid at pH 3.3 [28], crystalline oxides by dissolution with dithionite, citrate and bicarbonate DCB method of Mehra & Jacksen [29]. Extracted elements were determined by Inductively Coupled Plasma Spectrometry (ICP-OES) and by Atomic Absorption Spectrometry (AAS). X-Ray Diffraction (XRD) was carried out with Ni-filtered CuK α radiation at 40kV and 40mA.

Acid Neutralizing Capacity (ANC)

The Short-Term Acid Neutralizing Capacity (STANC) of the soils was measured by adjusting soil samples with dilute acid to defined pH values. To accelerate the buffer reactions, enhanced temperatures during the equilibration period were chosen. Ten grams of air-dried soil were placed in 80mL polyethylene centrifuge tubes. After adding 50mL HCl solutions of different concentrations (0.03, 0.10, 0.30, 1.0, 3.0, and 10.0mM) the samples were equilibrated for 5 days at 90 °C in a water bath. At the end of the equilibration period the pH values were measured and a 10mL aliquot of the clear supernatant was removed, acidified with 0.5mL concentrated HNO₃ and stored in a cooling room for further analyses. The elements Ca, Mg, K, Na, Al, Fe, and Mn released into the solution at each acid addition level were used to measure the amount of acid consumed by the soil. We assume that this mild acid treatment at elevated temperature triggers buffer reactions with fast kinetics, which can be related to the short-term acid neutralizing capacity of the soil at defined pH values. The equilibrium pHs were used to calculate the acid consumption, referred to as the short-term

acid neutralizing capacity, at pH 5.0, 4.0, 3.0, and 2.0 by means of interpolation. Medium-Term Acid Neutralizing Capacity (MTANC) was measured using a method to determine weatherable P-, K-, Ca, and Mg-minerals [30]. Ten grams of air-dried soil were placed into 50mL of 30% HNO₃ and boiled for 1 hour using a Gerhard KT 20 digestion device. After a predefined cooling period, the suspension was filtered and the solution was analyzed for Ca, Mg, K, Na, Al, Fe, and Mn. MTANC was then calculated by the sum of cations released due to the digestion minus the sum of cations released due to STANC. According to van Breemen [12] the best way to estimate the total ANC of a soil is by component composition. Thus, Long-Term Acid Neutralizing Capacity (LTANC) was calculated from the sum of cations (see above) determined by means of a total elemental analysis using XRF minus cations released at MTANC. Because of the negligibly small amount of S, P, and Cl we have excluded these elements to simplify calculations.

Results and Discussion

Tables 2 & 3 present selected physical, mineralogical and chemical properties of the investigated soil samples. The soil texture becomes finer from the sediment to the loess and sedimentary rock soils. All samples were dominated by quartz. The content of feldspars ranged from 11% up to 30%. Phyllosilicates were detectable in the loess and sedimentary rock samples ranging from 1% to 19%. The pH covered a range between 3.44 and 6.85 with low pHs at forest sites (average pH 3.96) and high pHs at agricultural sites (average pH 5.96). Soil Organic Carbon decreased as expected with soil depth. Oxalate and dithionite extractable Fe, Mn, and Al as well as ammonia nitrate extractable cations are listed in Table 3. The average base saturation appears to be 45% at forest sites and 99% at agricultural sites.

	Sand	Silt	Clay	Quarz /%	Fsp	Phyllos.	SOC	pH (CaCl ₂)			
Holocene sediment											
Hf-1	85	9	6	n.b.	n.b.	bld	3.57	4.31			
Hf-2	89	7	4	68	32	bld	0.57	4.49			
Hf-3	89	8	3	72	28	bld	0.18	4.47			
Ha-1	71	19	10	83	17	bld	0.82	5.74			
Ha-2	67	21	12	79	21	bld	0.31	5.62			
Ha-3	78	12	9	70	30	bld	0.12	5.83			
]	Pleistocene loes	s						
Pf-1	11	70	19	76	23	1	5.96	3.44			
Pf-2	12	71	17	65	34	1	1.63	3.76			
Pf-3	8	63	29	65	29	6	0.4	3.98			
Pa-1	12	70	18	67	30	4	1.04	6.75			
Pa-2	13	65	22	67	27	6	0.39	6.85			
Pa-3	16	56	28	66	26	9	0.15	6.11			
	Devonian sedimentary rock										
Df-1	22	55	23	77	17	6	7.49	3.56			
Df-2	19	54	27	76	16	8	2.02	3.75			
Df-3	22	55	23	66	16	19	0.62	3.92			

Table 2: Physical (particle size distribution), mineralogical (soil silicates) and chemical (SOC and pH) characteristics of the soil samples, bld=below limit of detection).

Da-1	40	30	30	80	15	5	3.8	5.72
Da-2	31	42	26	82	11	7	1.32	5.98
Da-3	15	49	36	69	13	18	0.44	5.01

Table 3: Pedogenetic Fe, Mn, and Al Oxides and exchangeable cations.

Oxalat/Dithionit-Extrac. Oxides/meq kg ⁻¹					NH ₄ NO ₃ -Extractable Cations/meq kg ⁻¹								
	Feo	Mno	Alo	Fed	Mnd	Ald	Са	Mg	К	Na	Al	Fe	Mn
Holocene sediment													
Hf-1	160	14	129	324	15	144	25.5	3.5	1.6	0.3	3.4	0.15	1.51
Hf-2	69	10	117	205	10	136	3.5	0.6	0.8	0.2	4	0.03	0.34
Hf-3	61	6	72	174	6	83	2	0.5	0.4	0.2	2.9	0.04	0.3
Ha-1	146	24	110	356	23	122	28.1	4.5	4.4	0.2	0.1	0.03	0.24
Ha-2	128	25	119	346	24	140	21.4	2.9	3.8	0.3	0.1	0.04	0.17
Ha-3	86	14	76	365	15	109	18	1.9	2.8	0.2	0.1	0.02	0.12
						Pleistoce	ene loess						
Pf-1	199	13	141	473	15	190	27.8	5	2.6	2.2	22.6	0.52	7.91
Pf-2	200	45	122	562	43	164	7.6	2.3	1.7	1.8	21.7	0.07	10.22
Pf-3	188	20	140	863	20	239	31.9	13.1	2.2	2.3	19	0.03	3.46
Pa-1	203	37	91	549	38	138	65.8	4.3	3.9	0.5	0.1	0.01	0.03
Pa-2	198	31	100	721	32	173	68.7	6	2.5	0.6	0.1	0.02	0.01
Pa-3	167	18	90	945	17	196	64.2	18.3	2.2	0.7	0.1	0.02	0.04
					Dev	onian sed	imentary 1	ock					
Df-1	330	70	325	803	66	389	18.4	2.8	2.6	0.9	57	0.31	15.63
Df-2	301	54	278	877	51	331	3.7	1.4	1.8	0.4	60	0.08	5.12
Df-3	335	33	201	1003	32	260	5.9	12.4	1.6	0.7	43.8	0.06	2.84
Da-1	375	65	204	852	61	274	98.4	15.1	3.7	0.7	0.1	0.03	0.82
Da-2	312	70	210	898	66	283	69.6	7.9	2.1	0.6	0.1	0.04	0.17
Da-3	270	30	159	1025	33	271	61.2	15.5	1.9	0.9	1.2	0.04	0.44

Short-Term Acid Neutralizing Capacity (STANC)

The STANC for each acid addition level can be described by the sum of cations released during the equilibration period. To make the results more easily compared, we calculated the STANC for pH 5.0, 4.0, 3.0, and 2.0 by interpolation. Buffer capacities lower than pH 5 were corrected by subtracting the released elements of the next higher pH. Thus, elements already released at pH 5.0, 4.0, and 3.0 were not taken into consideration the next lower pH unit. The results of STANC are shown in Figure 1. At the equilibration pH 5.0 only soil samples with an initial pH higher than 5.0 inevitably have a STANC in the range 12.9meq kg⁻¹ to 69.5meq kg⁻¹. These soils are solely agricultural soils with pHs>5.0 due to fertilization. The buffer capacity increases from the Holocene sediment soil to the Pleistocene loess soil and to the Devonian sedimentary rock soil. A decrease in STANC can be seen with soil depth. Most of the acid consumption at pH 5.0 could be accounted for by the release of basic cations (Ca, Mg, K, Na). At pH 4.0 (5.49meq kg⁻¹ to 71.5meq kg⁻¹), pH 3.0 (21.4meq kg⁻¹ to 216meq kg⁻¹), and pH 2.0 (83.1meq kg⁻¹ to 747meq kg⁻¹) the STANC increases with decreasing pH. However, the buffer capacity still decreases with soil depth. While the release of basic cations is still of importance at pH 4.0, the elements Al and Fe play a major role at pH 3.0 and 2.0. The most

fundamental mechanisms to neutralize protons on a short-time scale is the exchange of basic cations and the dissolution of Al-, Fe-, and Mn-hydroxides due to their fast buffer kinetic. The importance of exchange processes between pH 5.0 and pH 4.0 clarifies the comparison of exchangeable cations (Table 3) and cations released at STANC (Figure 1). According to Schwertmann et al. [13] variable charged buffer substances like clay minerals and humic substances are the main source for buffer reactions in this pH range. Thus, a decrease of organic carbon (Table 2) with soil depth explains the decrease of STANC with soil depth. The predominance of Al and Fe released at pH 3.0 and 2.0 can be explained by exchange processes and dissolution of hydroxides. Soil samples collected at forest sites were lower in pH and revealed a lower base saturation. Thus, the extent of exchangeable Al and Fe is higher compared with agricultural soil samples. These cations are part of the buffer mechanism at pH 4.0 and lower (Figure 1). Furthermore, Fe-, Al-, and Mn-hydroxides contribute to the STANC at pH 3.0 and 2.0. Soils high in Fe-, Al-, and Mn-hydroxides (Table 2) show high Fe-, Al-, and Mn release due to acidification (Figure 1). The higherthan-average Fe release of the top soil samples is remarkable. This could be explained by a combination of complex-forming organic compounds and increasing proton concentration.



Figure 1: Short-Term Acid Neutralizing Capacity (STANC) at pH 5.0, 4.0, 3.0, and 2.0 of soil samples derived from different parent material (H=Holocene sediment, P=Pleistocene loess, D=Devonian sedimentary rock), different utilization (a=agriculture, f=forest), and different depth (1=0-30cm, 2=30-50cm, 3=50-100cm).

Medium-Term Acid Neutralizing Capacity (MTANC)

The MTANC of the investigated soil samples ranged from 580meq kg⁻¹ to 3680meq kg⁻¹ (Figure 2). Like STANC the average MTANC increases from the Holocene sediment soil to the Pleistocene

loess soil and to the Devonian sedimentary rock soil. In contrast to STANC the MTANC increases with soil depth except for the Holocene sediment soil. The MTANC is based primarily on a release of Al and Fe and to a lesser content of Mg, K and Mn. Al- and Fe-hydroxides as well as Fe- and Mg-bearing alumosilicates like olivine, hornblende,

augite, biotite, and some clay minerals are known for their relatively high weathering rates. These minerals can be considered to contribute to the MTANC. Fe is the most important element to explain the increase of buffer capacity with soil depth. Looking at the Fed values of Table 3 and the Fe released in our experiment, a comparable tendency can be seen even within the Holocene soil samples. Furthermore, the content of phyllosilicates, involving biotite and Fe-bearing clay minerals, match with this tendency.

Long-Term Acid Neutralizing Capacity (LTANC)

The LTANC derived from total elemental analyses of the soil

samples minus the MTANC ranged from 2841meq kg⁻¹ to 12233meq kg⁻¹ (Figure 2). Forest sites show lower LTANC than agricultural sites. The average LTANC is lowest at sediment soils (3807meq kg⁻¹) followed by loess soils (7109meq kg⁻¹) and sedimentary rock soils (9182meq kg⁻¹) but still increases with soil depth. Al is the dominating cation at the LTANC. Furthermore, the cations Mg, K, Na, and Fe are part of the buffer capacity. This combination of elements reflects the buffer mechanism of silicate minerals with slow reaction kinetics. Table 2 shows that these are mainly feldspars and phyllosilicates like muskovite, and kaolinite. These minerals are known for their slow weathering rates [31-38].



Figure 2: Medium-Term Acid Neutralizing Capacity (MTANC) and Long-Term Acid Neutralizing Capacity (LTANC) of soil samples derived from different parent material (H=Holocene sediment, P=Pleistocene loess, D=Devonian sedimentary rock), different utilization (a=agriculture, f=forest), and different depth (1=0-30 cm, 2=30-50 cm, 3=50-100 cm).

Conclusion

To calculate critical loads of acid deposition or to predict element solubility due to soil acidification in the soil system, pH ranges of buffer compounds have to be considered. STANC measurement was carried out to cover the pH range that appears in soils. Thus, the laboratory-determined results can be transferred to field conditions. MTANC and LTANC have to be divided into different pH ranges. Using the pH ranges of buffering described in the literature, neutralization by basic cations due to dissolution of primary silicates and clay minerals takes place at pH <7 and <4.5 respectively. Neutralization of protons due to Al- and Fe-release can be considered at pH 4.8 to 3 (Al) and <3 (Fe). Taking this into account, the buffer capacity of MTANC and LTANC has to be divided into different pH ranges. The acid neutralizing capacities of basic cations (including Mn), Al, and Fe are listed in Table 4. The average MTANC calculated from the release of basic cations plus Mn (BC+Mn) of soils derived from different parent material is 133meq kg⁻¹ (Holocene sediment), 230meq kg⁻¹ (Pleistocene loess) and 333meq kg⁻¹ (Devonian sedimentary rock). Thus, only 11% to 13% of the total MTANC has its origin in basic cations and is available at pH>4.8. The remaining buffer capacity has to be considered to neutralize protons at pH<4.8 (Al; 43% to 57%) and at pH <3 (Fe; 30% to 44%). **Table 4:** Medium-term acid neutralizing capacity (MTANC) and long-term acid neutralizing capacity (LTANC) resulting from basic cations (BC = Ca, Mg, K, Na) + Mn, Al and Fe; share of the respective buffer capacity in %.

	MTANC/	meq kg ^{.1}	LTANC/meq kg ⁻¹							
	BC+Mn	Al	Fe	BC+Mn	Al	Fe				
	Holocene sediment									
Hf-1	99	452	195	589	2093	230				
Hf-2	80	358	179	577	2123	142				
Hf-3	62	305	212	712	2260	165				
Ha-1	179	683	366	831	3574	303				
Ha-2	188	872	403	780	3182	266				
Ha-3	192	747	472	850	3887	278				
%	13	57	30	19	75	6				
		Plei	istocene lo	oess						
Pf-1	126	604	305	855	4747	377				
Pf-2	170	727	689	907	4510	215				
Pf-3	307	1625	1314	1053	6215	480				
Pa-1	211	785	662	969	4887	412				
Pa-2	256	1015	977	1005	6061	442				
Pa-3	307	1142	1391	987	8128	404				
%	11	47	42	14	81	5				
		Devoniar	n sedimen	tary rock						
Df-1	289	970	598	824	5822	663				
Df-2	346	1242	1194	989	6818	505				
Df-3	394	1443	1842	1202	8632	629				
Da-1	278	878	777	981	6756	558				
Da-2	332	1047	1149	979	7011	490				
Da-3	356	1261	1461	1337	10233	663				
%	13	43	44	11	82	6				

The absolute amounts of BC+Mn in the LTANC are more than three to five times higher compared with BC+Mn in the MTANC even though the relative amounts are in a comparable range (11% to 19%). The results shown at Table 4 indicate an obvious dominance of Al in the LTANC (75% to 82%) whereas the absolute and relative amounts of Fe actually are lower compared to Fe at MTANC revealing the weathering stability of minerals included in this ANC. Although primary soil minerals represent a large source of potential acid neutralizing capacity, mineral weathering rates are relatively slow compared to rates of acid input due to acid deposition. Studies in Germany stated an annual acid deposition load of 3keq ha⁻¹ a⁻¹ to 4.5keq ha⁻¹ a⁻¹ for the Cologne-Bonn region. On the other hand, weathering rates are known for sandy soils of 0.2keq ha⁻¹ a⁻¹ to 0.7keg ha⁻¹ a⁻¹, for soils derived from loess of 0.35keg ha⁻¹ a⁻¹ to 1.72keq ha⁻¹ a⁻¹ and for soils derived from graywacke and shale of 0.49keq ha⁻¹ a⁻¹ to 2.49keq ha⁻¹ a⁻¹. Thus, the investigated forest soils with high MTANCs and LTANCs are acidified to pHs below pH 4.0 (Table 2) because of the high input rate of acids. Nevertheless, the methodology developed is a useful tool for predicting whether soils are recovering from acidification or are continuing to acidify under different H+ pollution scenarios. Furthermore, a beneficial

mobilization of basic cations or the danger of aluminization is predictable.

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