Reactions of sewage farm soils to different irrigation solutions in a column experiment. 1. Solid phase physicochemical properties

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This paper is dedicated to Prof. Dr. *Manfred Renger* on his 65th birthday

Zusammenfassung - Summary

Physicochemical properties of two sandy soils taken from a present and from a former sewage farm were studied during a 2.5 years column experiment, m which lime and irrigation water of various compositions were applied The amount of exchangeable bases and base saturation percentage in both soils changed markedly during the experiment. These changes were governed by changes in soil pH The specific surface area as well as the cation exchange capacity were closely related to the organic carbon content in the soil profile The surface charge density of both soils was roughly equal and independent of the soil depth

Key words: sewage farm soils / pH / surface area / surface charge / base saturation / column experiment

Veränderungen in Rieselfeldböden während eines Säulenversuchs mit unterschiedlichen Beregnungslösungen. 1. Physikochemische Eigenschaften der Festphase

In einem 2.5 Jahre dauernden Säulenexperiment wurden die physikochemischen Eigenschaften von zwei Sandboden, eines genutzten sowie eines ehemaligen Rieselfeldes, untersucht Die Boden wurden gekalkt, beziehungsweise mit unterschiedlichen Beregnungslosungen beaufschlagt Die Menge an austauschbaren basischen Kationen sowie die Basensättigung beider Boden veränderte sich deutlich wahrend des Experiments Diese Veränderungen wurden durch Boden-pH-Änderungen verursacht Die spezifische Oberfläche und die Kationenaustauschkapazität dieser Standorte hangen vom Gehalt an organischer Substanz im Bodenprofil ab Die Oberflächenladungsdichte war - unabhängig von der Tiefe - m beiden Boden gleich.

Introduction

During the past 150 years, sewage disposal onto agricultural land (sewage farming) and/or waste management farms was a common practice in many parts of the world *(Aboulroos* et al., 1989; *Moshiri,* 1993; *Smith,* 1996; *Siebe* and *Fischer,* 1996). In the vicinity of Berlin, a total area of about 20,000 ha has been treated with municipal wastewater for almost 100 years, resulting in changes of various soil properties and high accumulation of organic and inorganic pollutants *(Blume* et al., 1980; *Schlenther* et al., 1996). Stopping the wastewater supply induces intensive mineralization of organic matter, strong soil acidification and mobilisation of toxic elements and transport to the groundwater *(Hoffinann* et al., 1998; *Hoffmann* and *Renger,* 1998). To study the above processes in more detail, a column experiment with two soils taken from a former and a present sewage farm was performed. According to the author's knowledge, no long-term column studies with sewage farm soils are reported in the literature and most of our understanding of this subject comes from field and/or small scale laboratory experiments.

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The physicochemical properties of the solid phase of the soil govern most of the soil processes, e.g. ions exchange and transport, acid-base equilibria, organic matter behaviour as well as soil sorption, structural and water porperties. Thus, an investigation of the physicochemical properties constitutes a rational background to study other phenomena in soils. Therefore, the present study concentrates on soil physicochemistry and is meant as a general introduction to further reports on problems investigated in the column experiment performed, such as fate of heavy metals or leaching of dissolved organic matter (DOM).

Material and methods

The soils were taken from two sites situated in the surroundings of Berlin, Germany The first site, Buch, had been a sewage farm with municipal wastewater inputs of 3,000-10,000 mm per year until 1984 Afterwards it was ploughed and graded Since efforts to afforest the area failed, the present vegetation consists mainly of couchgrass *(Agropyron repens)* The soils at this site are generally Regosols (FAO Arenosols) developed in a sandy glacial till The depth of the Ah-horizon varies from 20 to 100 cm and organic carbon content from 3 to 15% due to the heterogeneous accumulation of sewage residues The pH of the topsoil varies between 4.5 and 5.5 and decreases with depth This decrease is attributed to the

Table 1: Selected chemical and physical properties of the studied soils
Tabelle l: Ausgewählte chemische und physikalische Kenndaten der untersuchten Boden

| Horizont | Buch | | | | Gatow | | | | |
	Ah	C_2	C_3		Ah_1	Ah_2	rAh	Bv	C
Depth [cm]	0-20	20-50	50-75	75-100	0-12	12-30	30-50	50-80	80-100
pd [g cm^3]	1.21	1.46	1.58	1.54	1.08	1.31	1.49	1.54	1.60
Corg [w/w %]	3.12	0.23	0.15	0.09	5.09	2.58	0.44	0.18	0.06
pH $CaCl_2$	4.81	4.42	4.32	4.46	6.38	6.42	6.37	6.35	6.25
CEC [mmol$_c$ kg ']	83.5	34.27	29.78	22.31	223.7	251.0	39.1	27.2	15.8
BS [%]	49.3	49.8	76.8	81.6	97.9	98.1	99.1	99.3	99.4
SA [m^2 g ']	28.35				51.59	31.35	10.97		
Cd [mg kg$^{'1}$]	13.0	1.0	0.5	0.3	6.0	7.0	2.0	2.0	0.3
Cu [mg kg ']	129	12	9	6	80	70	13	8	5
Zn [mg kg ']	251	22	17	10	480	359	81	47	14
Pb [mg kg ']	220	13	8	5	590	717	60	12	4
Sand [%]	99.3	93.0	96.6	98.7	78.6	85.0	85.6	85.9	85.8
Silt [%]	0.4	6.5	2.6	1.1	14.5	11.9	10.3	11.4	11.8
Clay [%]	0.3	0.5	0.4	0.2	6.9	4.8	4.1	2.7	2.4

p_d = bulk density BS = base saturation SA = surface area
p_d = Lagerungsdichte BS = Basensattigung SA = Oberfläche

Table 2: Irrigation solution composition and its abbreviations for column treatments
Tabelle 2: Zusammensetzungen der Beregnungslösungen und verwendete Abkürzungen

| Irrigation solution composition | Buch | Gatow |
	treatment abbreviation	
Deionized water	OB	OG
1 mH HC1	SB	SG
Deionized water + liming	KB	KG
Sewage effluents from Ruhleben wastewater treatment plant	AB	AG

oxidation of sulfides accumulated m the elevated groundwater table during sewage farm activity (*Blume* et al 1980) High amounts of heavy metals accumulated m the upper soil layers

The second site Berlin Gatow is more loamy (Tab 1) and has been used for irrigation with municipal and industrial wastewaters for 90 years The present input of sewage waters reaches nearly 2,000 mm per year Every 5 years this site is ploughed to a depth of 30 cm and used as grassland (for more details cf. *Blume* et al 1980)

Some chemical and physical properties of both soils studied are presented m Tab 1

The samples of both sites were taken from the upper 100 cm of the soils in 5 cm layers The sieved (2 mm) and homogenized soil material was placed in polyacrylic columns of 1,000 mm length and 140 mm diameter in such way that field soil profiles were reconstructed At the base of the columns, leachate was collected beneath a 0 2 mm mesh V4A steel net In this way, 20 columns were prepared for each soil For column irrigation a self-constructed irrigation unit with 137 injection needles of 1.1 mm diameter and a peristaltic pump was used Twice a week the columns received 300 ml of irrigation solution at a rate of 16.8 mm h^{-1}

The experimental design consisted of four treatments with five replicates for both soils (Tab 2) In the lime treatments (KB and KG) the columns received two dosages of Ca/Mg carbonate a first dose of 9.24 g/column (6,000 kg/ha) was applied as a coarse powder at the beginning of the experiment and a second dose of 23.1 g/column (15 000 kg/ha) was applied as an aqueous suspension 700 days later This treatment was only irrigated with deionized water The other treatments included an acidic irrigation

(SB and SG) and an irrigation with treated wastewater (AB and AG) As a control deionized water was used (OB and OG)

Every 7 days the columns were drained and leachates were collected for further analysis The column experiment was conducted at 18-24°C in the dark

Every six months one column of each treatment was collected and the soil sampled in layers of 5 cm thickness in the humic horizons and 10 cm thickness in the underlying layers With these samples the following physicochemical measurements were conducted

The pH of the samples was determined in 0.01 M $CaCl_2$ solution

The exchangeable bases were calculated at the sum of basic cations extracted with l M ammonium chloride (AAS measurements)

The cation exchange capacity (CEC) was calculated as the sum of the exchangeable bases and soil acidity The latter was determined by a single buffer method with l M calcium acetate at a soil water ratio of 1:2.5 (*Schachtschabel* 1951)

The organic carbon and nitrogen were measured with an ANA 1500 Carlo Erba C-N analyzer The surface area of the samples was calculated from water vapor desorption isotherms using the standard model of Brunauer Emmett-Teller, BET (*Oscik,* 1982) and assuming that a single water molecule occupies $1.08*10^{-19}m^2$ The desorption isotherms of all samples were measured twice at 298.0 + 0.2 K using a vacuum chamber method The soil samples were placed m a vacuum chamber above sulfuric acid solutions of stepwise increasing concentrations (decrease of the relative water vapor pressure p/po) The amounts of water present in the samples at a given p/p_0 were measured by weighing after 48 h of equilibration

Results and discussion

During the experiment marked pH-changes were observed in the 0-5 cm soil layers of both soils (Fig 1)

These changes were dependent on time and composition of the irrigation solution At the beginning of the experiment, the pH changes were most pronounced in the wastewater and acid treatments (Fig 1) The pH drop under distilled water irrigation was more or less uniform over time Adding lime to the columns did not result in a marked pH-increase
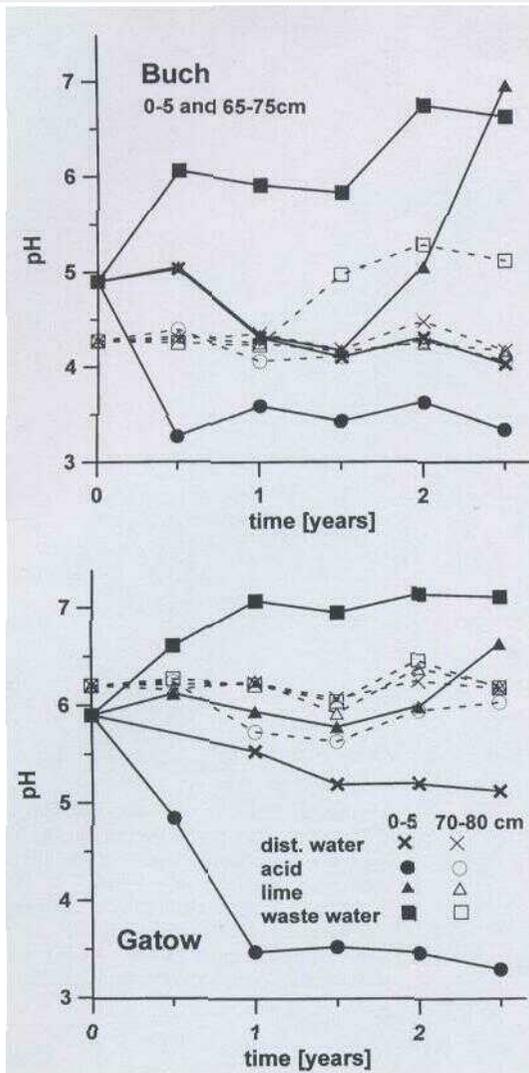
Figure 1: Changes of soil-pH after 2.5 years under various irrigation treatments in Buch and Gatow soil columns Top horizon = solid line, subsoil horizon = dashed line

Abbildung l: Veränderungen des Boden-pH nach 2,5-jährigen Säulenversuchen bei unterschiedlichen Behandlungen m Buch und Gatow Der oberste (massive Linie) sowie der tiefste Horizont (gestrichelte Linie) wurden exemplarisch dargestellt

after the first dose. However, the pH increased significantly after the second lime addition after two years. In the deeper soil layers, pH changes were less pronounced, indicating that the buffering capacity of the upper soil layers is high enough to protect the deeper layers against marked pH-changes. In both soils, the amount of exchangeable bases changed during the course of the experiment (Fig. 2).

The changes in exchangeable bases, similar to those in pH, are related to the different irrigation solutions and to the duration of the experiment. After 2.5 years, irrigation with wastewater led to an increase of the exchangeable bases down to about 25 cm in both soils. Liming did not increase exchangeable bases, but prevented the decreases observed in the distilled water- and acid-treatment (Fig. 2). Within the first half year of the experiment, the irrigation with acid led to a decrease of exchangeable bases in the upper layers

and an increase of exchangeable bases in deeper layers of the Gatow soil. This may be attributed to the displacement of basic cations with protons from the upper layers and their transfer down the column. In the course of the experiment, the exchangeable bases decreased in deeper layers as well. For acid treated Buch soil, having lower exchangeable bases and CEC (Tab. 1), the exchangeable bases decreased in all layers from the beginning of the measurements. Generally, the distilled water treatment resulted in a decrease of the exchangeable bases of the whole profile of both soils.

It seems that the CEC was not influenced by either pH or time. The CEC for both soils is closely related to the organic carbon content in the respective soil layers, as shown in Fig. 3. As already stated, the variability of the column material was rather high, which may additionally mask the effect of time on CEC. The CEC is largely determined by organic matter in these sandy soils as shown in Fig. 3. The data fit well into one common regression line for both soils. However, the individual line for Gatow is slightly steeper than for Buch soil. The separate data for linear regression fit for both soils and are presented in Tab. 3.

The separate data show that the intercept values are approximately equal for both soils, indicating that the input of inorganic solid phase to CEC of both soils is similar and small, equal to about 34 $mmol_c$ kg^{-1}. This depicts that the clay fraction, especially of Gatow soil with a higher clay content, either does not contain large amounts of 2:1 clay minerals (but is composed mainly of e.g. fine quartz or 1:1 clay minerals) or that parts of organic matter enters the clay fraction during determination of the particle-size distribution.

Knowing the exchangeable bases and CEC values, the base saturation percentage was calculated for both soils studied. The base saturation *vs.* pH dependence is presented in Fig. 4.

The base saturation increases with the pH, however, the regression line is not very well fitted to the data. In case of the above relationship, an S-type dependence should be preferred *(Jozefaciuk* et al., 1994). However, our efforts to find a good S-fit failed because of very weak correlations as documented in Tab. 3.

The surface area *vs.* organic carbon dependence for both soils is presented in Fig. 5.

The above data show trends similar to those of the CEC and organic carbon relationship. The surface area input of inorganic soil compounds calculated from the regression equation in Fig. 5 is about 5 m^2 g^{-1}. It is slightly higher in Gatow, when calculated separately for both soils (Tab. 3). Due to this close relationship, the surface area of soil organic matter can be calculated after subtracting the contribution of mineral particles from the total surface area, and dividing the remaining value by the organic carbon content. This specific surface area (S/C) is around 10-14 m^2 $g^{-1}C$ in the topsoil in both soils (Fig. 6). In Buch there is an
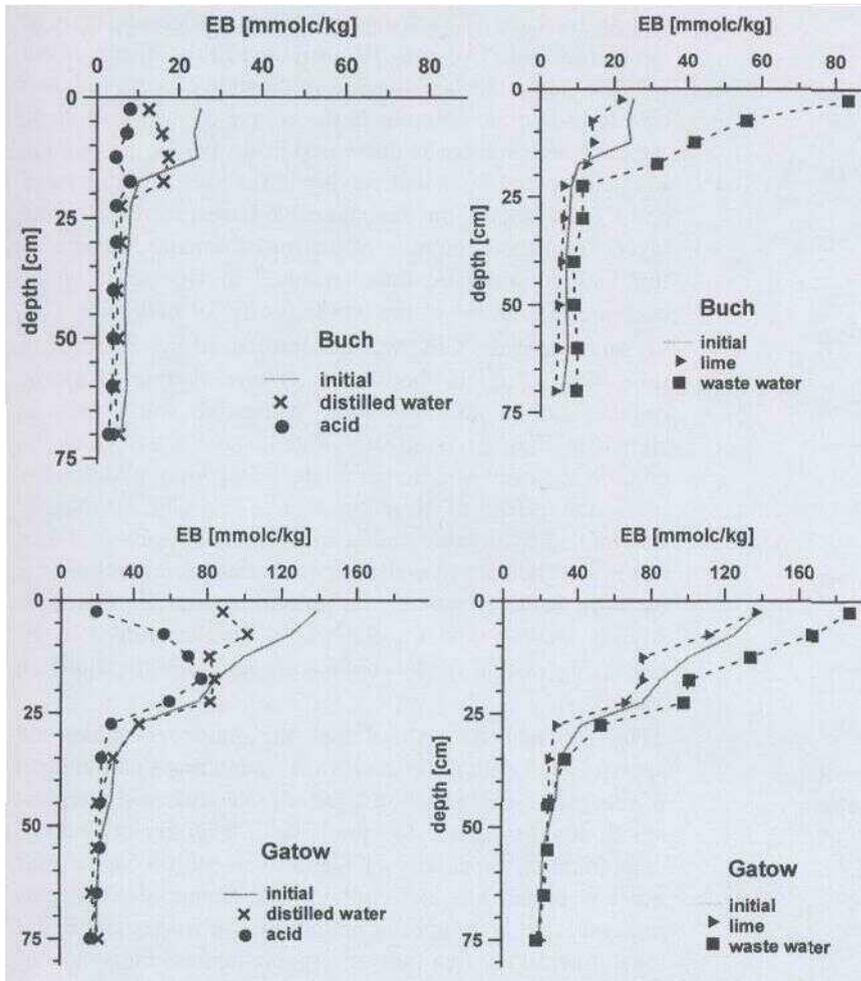
Figure 2: Changes of exchangeable bases (EB)[mmol$_c$ kg^{-1}] with depth m Buch and Gatow soil columns under various irrigation treatments after 2 5 year

Abbildung 2: Veränderungen der austauschbaren basischen Kationen (EB) [mmol$_c$ kg^{-1}] in den Saulenvarianten Buch und Gatow in Abhängigkeit von der Tiefe nach 2,5 Jahren

abrupt increase to 25-35 m^2 g^1 C^{-1} below 25 cm, while in Gatow, the positive depth gradient is more gradual, corresponding to the differences in profile development at the two sites (Tab. 1).

Treatment effects are only discernible in Buch, where the specific surface area of organic matter in the subsoil (>25 cm) is highest in the acid treatment (Fig. 6). This could be due to a preferential mobilization of low-molecular organic colloids at low pH, as also observed in acidified samples by *Marschner* (1998) and a subsequent immobilization of these high specific surface area-colloids in the less acidified subsoil horizons.

Taking into account the linear CEC and surface area dependencies on soil organic carbon (Tab. 3), the occurrence of linear dependence of surface area on CEC is rather obvious. This dependence is presented in Fig. 7.

The slopes of the regressions are almost identical for both soils (Tab. 3) while the intercept of the linear fit is much higher for Gatow (0.60 m^2 g^{-1}) than for the Buch soil (0.07 m^2 g^{-1}). This indicates that when the CEC value approaches zero, the soils still have some surface area coming from the small inputs of soil inorganic compounds with negligible CEC. A good example of such compound is fine quartz, the
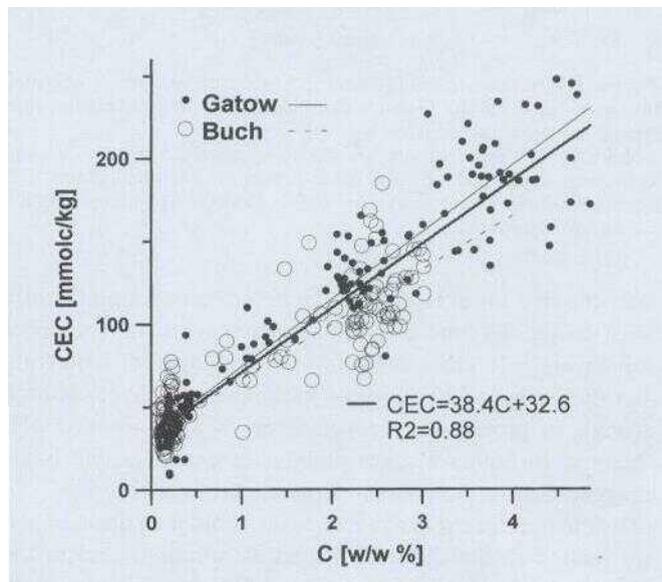

Figure 3: Dependence of cation exchange capacity (CEC) [mmol$_c$ kg^{-1}] on organic carbon content [w/w %] for all irrigation treatments The thick line is the linear regression plot for all data Thin lines are separate fits for the Gatow and Buch samples.

Abbildung 3: Beziehung zwischen Kationenaustauschkapazität (CEC) [mmol$_c$ kg^{-1}] und organischem Kohlenstoff [Masse-%] Die dicke Linie zeigt die lineare Beziehung für alle Proben Die dünnen Linien beschreiben die Fits fur die Gatower und Bucher Varianten.

Table 3: Linear regression equations for the relations between the studied physicochemical characteristics for Gatow and Buch soils (for average regressions one should refer to the respective figures)
Tabelle 3: Lineare Regressionsgleichungen fur die untersuchten physikochemischen Eigenschaften der Gatower und Bucher Böden

Variables	x	Gatow R^2	Gatow linear regression equations	Buch R^2	Buch linear regression equations
CEC	C_{Org}	0.91	y = 40.3 x + 33	0.80	y = 32.2 x + 35.0
BS	PH	0.48	y = 15.5 x - 25.4	0.71	y = 21.9 x - 74
SA		0.92	y = 9.9 x + 59	0.90	y = 8.5 x + 4.7
SA	CEC	0.89	y = 0.22x + 0.6	0.82	y = 0.21 x + 0.07

Abbreviations BS = base saturation [%], SA = surface area [m g], CEC = cation exchange capacity [mmol$_t$ kg], C$_{org}$ = organic carbon content [w/w %], R^2 = coefficient of determination
Abkürzungen BS = Basensättigung [%], SA = Oberfläche [m^2 g 1], CEC = Kationenaustauschkapazität [mmol$_c$ kg-1], C$_{org}$ = organischer Kohlenstoffgehalt [Masse-%], R^2 = Bestimmtheitsmaß
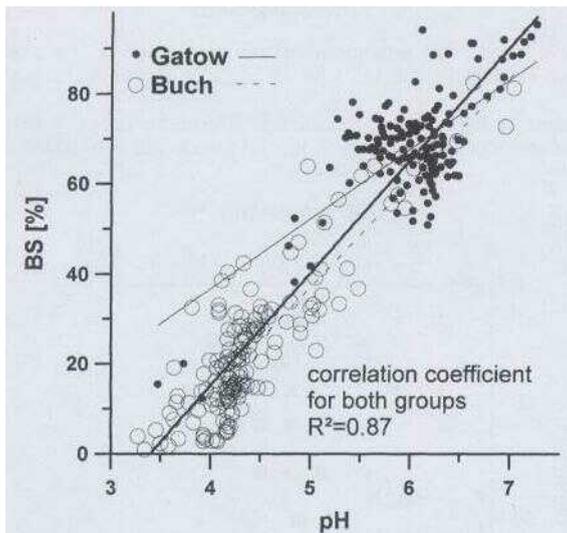
Figure 4: Relationship between base saturation (BS) [%] and pH for all irrigation treatments Legend as in Fig 3
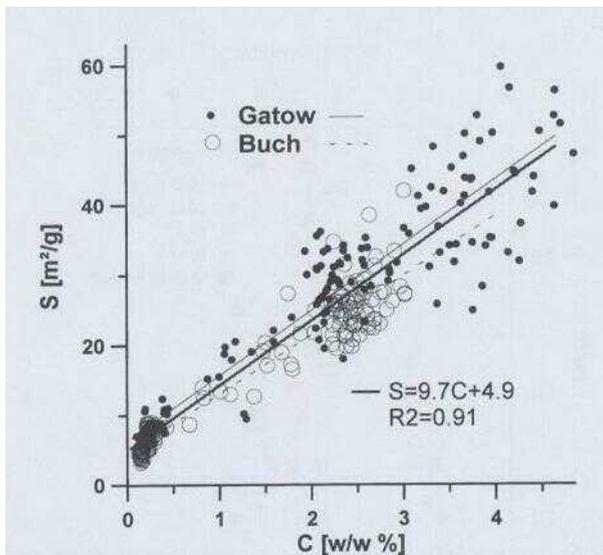**Abbildung 4:** Beziehung zwischen Basensättigung (BS) [%] und pH Legende wie in Abb 3

Figure 5: Relationship between specific surface area [m^2 g^{-1}] and organic carbon content [w/w%] for all irrigation treatments Legend as Fig 3
Abbildung 5: Beziehung zwischen spezifischer Oberflache [m^2 g^{-1}] und Gehalt an organischem Kohlenstoff [Masse%] Legende wie m Abbildung 3

presence of which, especially in the clay fraction of Gatow soil, has been postulated already *(Sokolowska* et al., 1996).

Because the input of inorganic substances into charge and surface area can be neglected, one can apparently conclude that in lower soil layers the organic matter of both soils has higher CEC and surface area per unit mass. The values of surface charge density (SCD) for both soils, calculated as CEC divided by surface area, are hardly differentiated with depth in both soils (Fig. 8). The acid treatment in the Gatow soil is characterized by much lower surface charge densities around 2 (µmol$_c$ m^{-2} below 10 cm depth, compared to 3-7 µmol$_c$ m-^{2} in all other treatments. This may indicate, that organic matter of very low surface charge density (i.e. protonated organic acids or other uncharged molecules) was translocated into these horizons.

In the Buch soils, the lowest SCD-values were found in the lime treatment between 10 and 30 cm depth (Fig. 8). These results agree well with earlier investigations in a forest soil, where SCD was at similar levels and lowest values were in the limed plot *(Wilczynski* et al., 1993). This had been attributed to the increased microbial activity.

Conclusions

Significant changes in amounts of soil exchangeable bases and base saturation percentage observed during the column experiment were governed in general by changes in soil pH. The CEC and the surface area values reflected the organic carbon content in the soil profile and remained nearly unaltered in time.

The lack of profile differentiation in terms of surface charge density in both soils stands in contrast to other more natural soils (i.e. *Wilczynski* et al., 1993). High inputs of soluble organic compounds and year-round elevated soil moisture and soil temperatures probably favoured microbial activity in these soils and resulted in the rapid degradation of highly charged low-molecular compounds, such as organic acids. The degradation products therefore strongly contribute surface area, but not to surface charge. At the Buch site, the cessation of wastewater inputs and deep
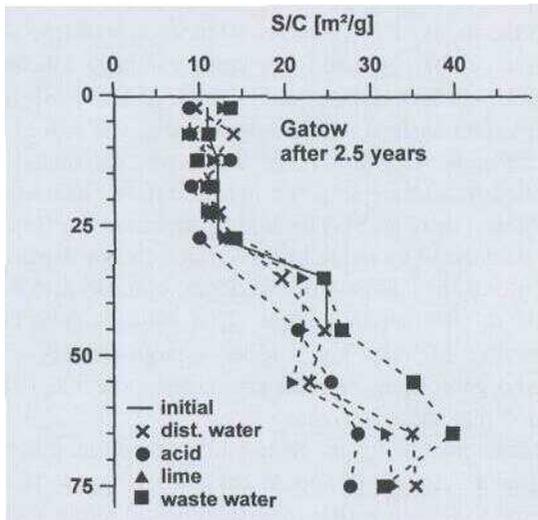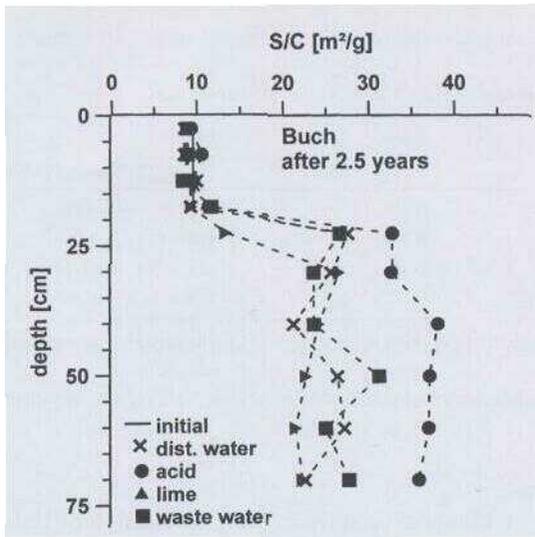
Figure 7: Relationship between specific surface area [m² g⁻¹] and cation exchange capacity [mmol_c kg⁻¹] for all irrigation treatments Legend as Fig 3
Abbildung 7: Einfluss der spezifischen Oberfläche [m² g⁻¹] auf die Kationenaustauschkapazität [mmol_c kg⁻¹] Legende wie in Abbildung 3

Figure 6: Changes of specific surface area of organic carbon [m² g⁻¹] in Buch and Gatow columns after 2 5 years of different treatment
Abbildung 6: Veränderung der spezitischen Oberflache des organischen Kohlenstoffs [m² g⁻¹] in den verschiedenen Säulenvarianten Buch und Gatow nach 2,5 jahriger Versuchsdauer

ploughing 15 years ago have initiated mineralization processes that result m the translocation of surface-active organic compounds.

Acknowledgements

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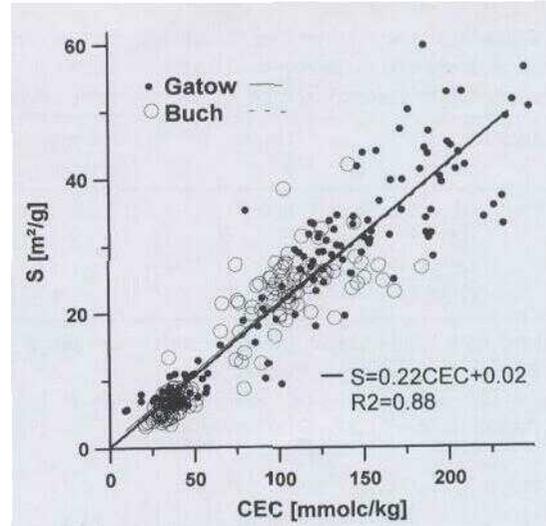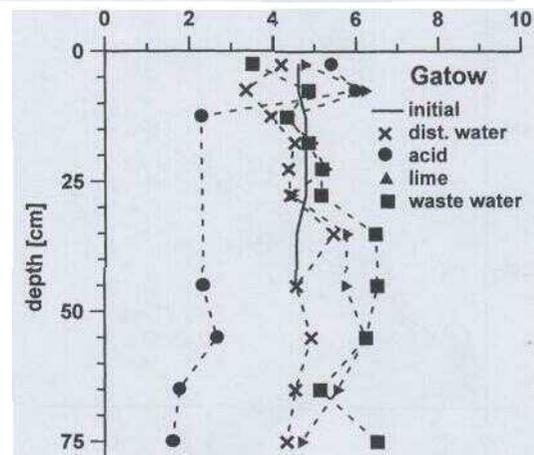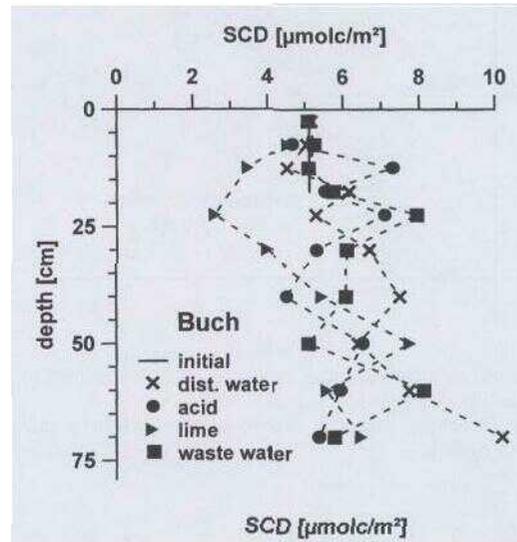
Figure 8: Depth profiles of surface charge density (SCD) [µmolc m-²] after 2 5 years different treatment in the Buch and Gatow columns
Abbildung 8: Tiefenprofile der Oberflächenladungsdichte (SCO) [µmol_c m-²] nach 2,5 Jahren unterschiedlicher Behandlung in den Bucher und Gatower Säulen.

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