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

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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 (Hoffmann 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 properties. 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
The present input of sewage waters reaches nearly 2,000 mm per year. 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 CaCl₂ solution.
- The exchangeable bases were calculated at the sum of basic cations and exchangeable bases and soil acidity. The latter was determined by a single buffer method with 1 M calcium acetate at a soil water ratio of 1:2.5.
- The cation exchange capacity (CEC) was calculated as the sum of the exchangeable bases in ppm and soil acidity. The latter was determined by a single buffer method with 1 M calcium acetate at a soil water ratio of 1:2.5.

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 adsorption isotherms using the standard model of Brunauer-Emmett-Teller (BET, 1982) and assuming that a single water molecule occupies 1.08 × 10⁻¹⁹ m³. 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 in a vacuum chamber above sulfuric acid (H₂SO₄) at a given p/p₀. The amounts of water present in the samples at a given p/p₀ 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 treatment plant (SB and SG), and an irrigation with treated wastewater (AB and AG) as a control. Deionized water was used (OB and OG).

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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. 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 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 m² 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 m² g⁻¹C in the topsoil in both soils (Fig. 6). In Buch there is an

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.
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

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**Figure 2:** Changes of exchangeable bases (EB) [mmol kg$^{-1}$] with depth in Buch and Gatow soil columns under various irrigation treatments after 2.5 years

**Abbildung 2:** Veränderungen der austauschbaren basischen Kationen (EB) [mmol kg$^{-1}$] in den Saulenvarianten Buch und Gatow in Abhängigkeit von der Tiefe nach 2.5 Jahren

**Figure 3:** Dependence of cation exchange capacity (CEC) [mmol 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 kg$^{-1}$] und organismem Kohlenstoff [Masse-%]. Die dicke Linie zeigt die lineare Beziehung für alle Proben. Die dünnen Linien beschreiben die Fits für 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)

<table>
<thead>
<tr>
<th>Variables</th>
<th>Gatow</th>
<th>Buch</th>
</tr>
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<tbody>
<tr>
<td>CEC</td>
<td>R²</td>
<td>R²</td>
</tr>
<tr>
<td>BS</td>
<td>PH</td>
<td></td>
</tr>
<tr>
<td>SA</td>
<td>CEC</td>
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Gatow linear regression equations

- \( y = 40.3 \times + 33 \)
- \( y = 15.5 \times - 25.4 \)
- \( y = 9.9 \times + 59 \)
- \( y = 0.22 \times + 0.6 \)

Buch linear regression equations

- \( y = 32.2 \times + 35.0 \)
- \( y = 21.9 \times - 7.4 \)
- \( y = 8.5 \times + 4.7 \)
- \( y = 0.21 \times + 0.07 \)

Abbreviations BS = base saturation [%], SA = surface area \([\text{m}^2 \text{g}^{-1}]\), CEC = cation exchange capacity \([\text{mmol} \text{kg}^{-1}]\), Corg = organic carbon content \([\text{w/w}\%]\), \(R²\) = coefficient of determination

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 \(\mu\text{mol} \text{m}^{-2}\) below 10 cm depth, compared to 3-7 \(\mu\text{mol} \text{m}^{-2}\) 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
ploughing 15 years ago have initiated mineralization processes that result in the translocation of surface-active organic compounds.

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Abbildung 6: Veränderung der spezifischen Oberfläche des organischen Kohlenstoffs \([m^2 \cdot g^{-1}]\) in den verschiedenen Säulenvarianten Buch und Gatow nach 2,5-jähriger Versuchsdauer.

Abbildung 7: Einfluss der spezifischen Oberfläche \([m^2 \cdot g^{-1}]\) auf die Kationenaustauschkapazität \([\text{mmol}, \text{kg}^{-1}]\). Legende wie in Abbildung 3.

Abbildung 8: Tiefenprofile der Oberflächenladungsdichte (SCD) \([\text{µmol} \cdot \text{m}^{-2}]\) nach 2,5 Jahren unterschiedlicher Behandlung in den Bucher und Gatower Säulen.
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