# CONTENTS AND SOME PROPERTIES OF HUMIC SUBSTANCES IN A LONG-TERM WASTEWATER IRRIGATED SOIL

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The contents of humic and fulvic acids in a soil profile, the ratio of these two fractions of soil humic substances (HA : FA) and the extinction ratio of humic acids (E4 : E6) were determined in a sandy Cambisol which was almost 100 years irrigated with municipal wastewater. In samples from the upper layer (0–5 cm) of the irrigated soil, the contents of humic substances was about 100% higher than in soil samples from the control plot. Minor enhancements were detectable until 60 cm of soil depth. For the irrigated soil higher values of the HA : FA ratios were calculated. The values of the E4 : E6 ratios indicated a higher optical density of the HA preparations from the control plot. Analytical values obtained for humic substances extracted from soil which was since 20 years not irrigated resembled to those of the control soil site. It was concluded, (i) that the significant enhancement of the amounts of humic substances in a long-term irrigated sandy Cambisol may support the soil capacity in renovating the applied wastewater, and (ii) that both the quantitative and qualitative changes in humic substances could be useful as indicators of soil quality.

wastewater irrigation; humic substances; soil quality

## INTRODUCTION

The role of humic substances in a soil profile is multifarious. It includes the improvement of soil quality by increasing aggregation of mineral particles, affecting infiltration and retention of water, enhancing contents of nutrients, stabilizing soil buffering capacity and supporting the activity of soil microorganisms. Kerndorff and Schnitzer (1979) pointed on a negative correlation between structural characteristics of humic acids and soil pollution. Kovda (1990) indicated the soil dehumification resulting from

adverse anthropogenic activities as a risk for the bio-energetic regime not only of soils but of entire ecosystems. According to Bayer and Blume (1990), the amount of soil humus usually decreases under conventional farming. However, in soil samples deliberately polluted by organic compounds, an enhanced content of humic substances has been also observed (Filip, Müller, 1984; Griffith et al., 1989). In his investigations on a long-term wastewater irrigated sandy soil Hirte (1961) found an enhanced content of organic matter. In our recent paper remarkable differences in several microbiological and biochemical parameters of long-term wastewater irrigated soils were reported (Filip et al., 1999). The aim of our continuing investigations was to determine whether a long-term wastewater irrigation on a sandy soil would affect the content and some basic properties of soil humic substances, i.e., humic acids (HA), and fulvic acids (FA) which are of importance for the soil quality.

## MATERIAL AND METHODS

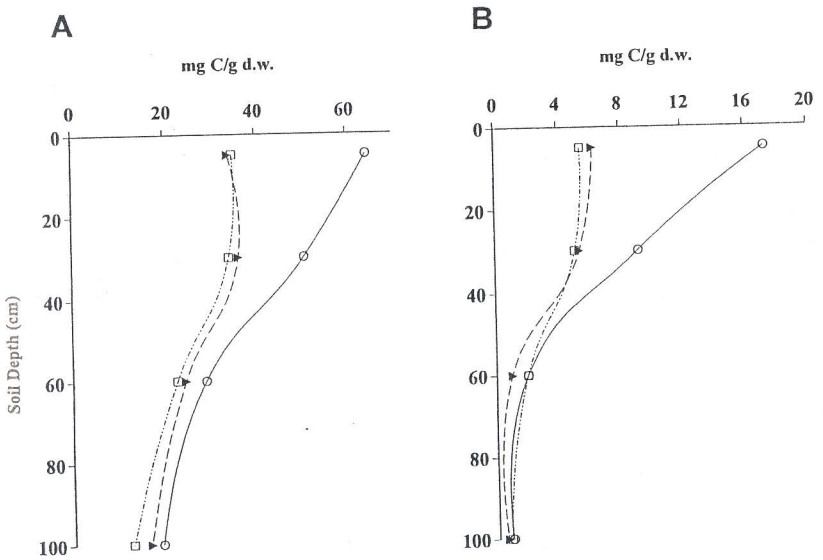
Soil samples were collected four times during a year from a sandy Cambisol in an outskirt of Berlin (Germany) using a cylindrical metal sampler which was driven into the soil to the desired depth. The individual plots were (i) irrigated with 2,000–7,000 mm.a$^{-1}$ of municipal wastewater (primary effluent) for about 100 years, or (ii) their irrigation was terminated 20 years ago. The control plot was never irrigated. The sampling area was covered by a mixture of natural and seeded grasses. The pedological characteristics of the soil site and also an information about the average composition of wastewater applied were reported earlier by Blume et al. (1980).

In the laboratory, coarse organic and mineral particles were removed from the collected soil, and air-dry soil samples were passed through a 2 mm sieve. Portions (50 g) were extracted under $N_2$ with 0.1M NaOH + 0.1M $Na_4P_2O_7$ (1 : 1 v/v) for 24 h (Kononova, 1966). The extraction was repeated up to 5 times until the extracts were only pale yellow. Soil residues were separated by centrifugation (5,000 x g, 15 min, 15 °C). The unified supernatants were adjusted to pH 1.5 with HCl and HA were allowed to precipitate overnight. Separately, the soil samples were also extracted with an ethanol-benzol mixture (1 : 1 v/v, 24 h) in the Soxhlet apparatus. Carbon contents of the FA fraction (acidic supernatant), of HA (solubilized in 0.05 M NaOH) and of an evaporated ethanol-benzol extract were determined by wet-combustion (Allison, 1965). Light absorption of HA was measured in a Perkin-Elmer, Typ 554 spectrophotometer; from the extinction values at 465 nm and 665 nm, a ratio E4 : E6 was calculated (Chen et al., 1977).



## RESULTS AND DISCUSSION

We reported earlier an accumulation of organic carbon and nitrogen in a sandy soil long-term irrigated with wastewater (Dizer et al., 1981). The carbon contents, e.g., in soil samples from a long-term irrigated soil taken from the soil depth of 0–5 cm, 5–30 cm, and 30–60 cm, respectively, amounted to 56.4, 20.5, and 16.1 mg.g$^{-1}$ (d.w.). The respective numbers of the control soil samples were only 16.1, 16.7 and 4.0 mg.g$^{-1}$ (d.w.). Our attempt here was not to present a total balance of carbon in the individual fractions of soil organic matter. Nevertheless, the vertical distribution of HA and FA as demonstrated in Fig. 1 shows the same development as the above mentioned carbon contents. In the upper layer of the long-term irrigated soil, the amounts of these fractions increased up to 3 times (for HA) in comparison with the control soil. With increasing soil depth, the differences gradually declined, and below 60 cm they were no more significant. The distribution




1. A vertical distribution of fulvic acids (A) and humic acids (B) in a sandy Cambisol irrigated with municipal wastewater for about 100 years

▲ no irrigation
□ since 20 years no irrigation
○ 100 years irrigation

of humic substances in soil which remained 20 years without irrigation resembled to that of the control site. Fulvic acids (FA) represented the main fraction of humic substances irrespective the soil treatment with wastewater.

In Table I total amounts of humic substances (HA + FA) extracted from the individual soil samples are listed. The data represent arithmetic means of four determinations. Since the calculated deviations were less than 25%, no other statistical evaluation was made. It is evident that the cumulative value of humic substances (HA + FA) from the top soil layers and up to 60 cm depth in the long-term irrigated soil (A) was 160.3 % of the control (C). On the other hand, differences were not found between the soil that remained without irrigation since 20 years (B) and the control soil.

Up to 30 cm depth (Ap1/Ap2 soil horizon), but especially in the top soil layer, the HA : FA ratios showed higher values indicating a relative increase in humic acids due to the wastewater irrigation. For the HA fraction, however, also higher values of E4 : E6 ratios were calculated. This indicates that the quantitative surplus in HA was accompanied by a decrease in the particle size and/or in molecular weight of this fraction of humic substances (Chen et al., 1977), i.e., the quality of HA slightly deteriorated in the long-term irrigated soil. HA preparations from the soil never irrigated and from that no more irrigated since 20 years did not differ substantially from each other in the both mentioned parameters.

Wastewater irrigation on soil usually results in an accumulation of a greasy matter (lipids) in soil. These substances can be extracted by an ethanol-benzol mixture. The total amount of this type of organic matter in soil samples from 0 to 100 cm depth was very high, reaching 14.3, 4.22, and 3.1 mg $C.g^{-1}$ (d.w.) respectively, in the long-term irrigated, since 20 years no more irrigated, and the control soil. Greasy materials may cause clogging of the soil filter system,

I. Content and some other characteristics of humic substances in a sandy Cambisol irrigated with municipal wastewater for about 100 years

| Soil depth (cm) | Humic substances (HA + FA mg $C.g^{-1}$ d.w.) | | | HA : FA | | | E4 : E6 (HA) | | |
|---|---|---|---|---|---|---|---|---|---|
| | A | B | C | A | B | C | A | B | C |
| 0–5 | 81.6 | 40.5 | 40.4 | 0.27 | 0.16 | 0.18 | 4.2 | 3.8 | 3.4 |
| 5–30 | 59.8 | 39.2 | 41.6 | 0.18 | 0.15 | 0.15 | 4.3 | 3.4 | 3.4 |
| 30–60 | 30.8 | 24.5 | 25.4 | 0.07 | 0.09 | 0.04 | 3.8 | 3.5 | 2.9 |

A = 100 years irrigation
B = since 20 years no irrigation
C = no irrigation



while humic substances rather support the soil capacity to purify the infiltrating wastewater due to their large specific surface and a high cation exchange capacity.

In conclusion, the increase in the content of organic matter which was repeatedly described as a consequence of a long-term soil irrigation with municipal wastewater includes also a considerable enhancement in amounts of humic substances, i.e., HA and FA fractions. This effect, and especially the relative increase in the HA fraction may contribute to the purification capacity of the soil system. The lower optical density may indicate an enhanced mobility of the HA in soil profile. Only a little influence of the soil treatment on humic substances remained detectable 20 years after the wastewater irrigation was terminated. Until then, however, the quantity of humic substances, the ratio HA : FA, and the optical density of the HA fraction (E4 : E6 ratio) could be useful as specific indicators of the soil quality. Other specific characteristics of a long-term wastewater treated soils such as an accumulation of heavy metals and other pollutants should be carefully evaluated as shown in numerous examples presented recently by Renger et al. (1998).

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**Obsah a některé vlastnosti huminových látek v půdě dlouhodobě zavlažované odpadními vodami.**

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Huminové látky mají pro půdu mnohostranný význam. Přispívají ku příkladu ke zvýšení kvality půdy podporou agregace minerálních půdních částic, ovlivněním infiltrace a retence vody, akumulací rostlinných živin, stabilizací pufračního systému půdy a podporou aktivity mikroorganismů. Antropogenním zásahům do půdy je většinou připisován negativní účinek na obsah a kvalitu huminových látek. Nechybí však ani příklady pozitivních účinků. V předložené práci byl sledován vliv závlahy komunálními vodami, které byly aplikovány na písčitou půdu (Cambisol) na okraji Berlína v množství 2000–7000 mm ročně po dobu cca 100 let.

Huminové látky byly z půdních vzorků opakovaně extrahovány směsí 0,1 M NaOH + 0,1M $Na_4P_2O_7$ (1 : 1, v/v) 24 h. Huminové kyseliny (HA) byly vysráženy okyselením výluhu na pH 1,5 pomocí HCl. Obsah uhlíku v HA a ve fulvokyselinách (FA) byl stanoven spalováním za vlhka. Optická hustota preparátu HA byla měřena při vlnových délkách 465 nm a 665 nm.

Ve vzorcích půdy odebraných z povrchové vrstvy (0–5 cm) dlouhodobě zavlažované půdy se zvýšil obsah huminových látek cca o 100 % ve srovnání s půdou nezavlažovanou. Menší zvýšení byla zjištěna až do hloubky 60 cm; ve větší hloubce půdy byly rozdíly v obsahu huminových látek neprůkazné. V horních vrstvách zavlažované půdy vzrůstaly rovněž hodnoty vzájemného poměru huminových kyselin a fulvokyselin (HA : FA), zatímco optická hustota HA preparátů, posuzovaná podle extinkčního kvocientu E4 : E6, se snižovala. Výsledky analýz půdních vzorků odebraných z parcely, jejíž zavlažování komunálními odpadními vodami bylo přerušeno před 20 lety, se blížily hodnotám kontrolní půdy bez závlahy.

Ze studie lze vyvozovat, že dlouhodobá závlaha půdy komunálními odpadními vodami má příznivý účinek na obsah huminových látek v půdě. Tyto látky mohou druhotně pozitivně ovlivnit filtrační schopnost půdy a také další aspekty půdní kvality. Parametry zaměřené na obsah a kvalitu huminových látek v půdě mohou být užitečnými ukazateli účinku antropogenních vlivů na půdu.

zavlažování odpadními vodami; huminové látky; kvalita půdy

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