Effect of irrigation water quality on organic matter, Cd and Cu mobility in soils of central Mexico

A. Herre*, C. Siebe** and M. Kaupenjohann*

* Institut für Ökologie, TU Berlin, Salzufer 11-12, 10587 Berlin, Germany
(E-mail: andrea.herre@tu-berlin.de; martin.kaupenjohann@tu-berlin.de)

** Instituto de Geología, UNAM, Circuito Exterior s/n, Cd. Universitaria, C.P. 04510, México, D.F.
(E-mail: siebe@servidor.unam.mx)

Abstract Untreated wastewater has been used for irrigation since 1912 at the Irrigation District 03, Central Mexico. Accumulated heavy metals are dominantly bound to the organic soil fraction. In a field study we evaluated the effect of wastewater irrigation on the quality of soil organic matter and the amount of water extractable Cu and Cd. In a column experiment we tested if water treatment affects the leaching of both metals and dissolved organic carbon (DOC) out of soils that have been irrigated for more than 90 years with untreated wastewater.

The field study shows that long term irrigation increases the mineralizable carbon fraction and the DOC concentrations. The water extractable Cu and Cd concentrations also increase and correlate with DOC. In the column leachates the Cu concentrations also correlate with DOC, the Cd concentrations correlate with the sum of cations, chloride and DOC concentrations. Water treatment reduced Cd leaching, but it did have no substantial effect on Cu leaching.

Keywords Carbon mineralization; dissolved organic carbon; heavy metals; lixiviation; wastewater

Introduction

The sewage effluents from the metropolitan area of Mexico City have been used without previous treatment to irrigate agricultural land within the Mezquital valley since 1912. The area under irrigation has been growing continuously over time as the water discharge volumes increase. Today, 85,000 ha are irrigated and cultivated mainly with maize and alfalfa (Siebe and Cifuentes, 1995). This practice provides agriculture in this semiarid area with water and nutrients, and has increased the crop productivity significantly. It simultaneously solves the sewage treatment problem of Mexico City at a very low cost. Additionally, the local aquifer level has risen, so that nowadays the National Water Commission is considering this area as a drinking water source for Mexico City (Jiménez and Chávez, 1998).

However, a larger incidence of gastrointestinal diseases has been documented in the valley, particularly of helminth infections (Siebe and Cifuentes, 1995). Also soluble salts, tensioactive substances and heavy metals (Siebe, 1994) have increased their concentrations in the soils at irrigated sites. Therefore, national public health and water authorities are considering now to treat the effluents previous to their use in irrigation.

In soils irrigated during long periods of time, heavy metal concentrations have increased 3 to 6 fold above the local background concentrations (Siebe, 1994). Metals accumulate in the plough layer of the soils (0–30 cm) and are dominantly sorbed on the organic soil fraction. Siebe and Fischer (1996) found that total organic matter also increases with time at irrigated sites. This could suggest that heavy metals will remain relatively immobile. However, nothing is known about the quality of the accumulated organic matter. Carbon/nitrogen ratios of organic compounds in sewage effluents are narrow (4) as compared to agricultural soils (10–14), and also a larger proportion of them is soluble in water (Feigin et al., 1991). If the added organic matter mineralizes more easily, it might liberate...
the sorbed heavy metals into the soil solution, from where they could either be taken up by plants or leach and pollute the aquifer.

Mineralization of organic matter can increase when actual irrigation or soil management practices change. A greater frequency and depth of soil tillage enhances mineralization. Also water treatment diminishes the input of particulate and dissolved organic matter into the soils which in turn could cause an increase in soil organic matter mineralization as easily accessible energy and nutrient sources are removed by water treatment. Another factor that favors mineralization is an increase in air temperature. Global climate change can enhance microbial activities in the soil, which will lead to a larger mineralization of soil organic matter (Kirschbaum, 1995).

In this study we analyze if prolonged irrigation has affected soil organic matter quality and metal mobility in soils by comparing fields that have been irrigated during different periods of time. Additionally we test in a column experiment if water treatment changes the leaching of DOC and metals from soils that have been irrigated during more than 90 years with untreated wastewater.

**Materials and methods**

We sampled two different soil types (Leptosols and Vertisols) at sites that have been irrigated during 0, 16, 20, 35, 65 and 80 years with untreated sewage effluents. At each field we took 4 composite samples (of 16 subsamples each) from the upper 30 cm of the soils. These samples were air dried and sieved (< 2 mm). Carbon mineralization was determined by the Isermeyer method during 21 days (Schinner et al., 1993). Dissolved organic carbon was analyzed in soil:water extracts (1:2.5 wt/vol) and determined colorimetrically after wet oxidation with K$_2$Cr$_2$O$_7$ (Schlichting and Blume, 1966). In the same extracts water soluble copper and cadmium were determined by graphite furnace atomic absorption spectrometry (Perkin Elmer 3010) with Zeeman underground compensation.

Additionally we took 12 undisturbed soil columns (20 cm in diameter and from 0 to 20 cm depth) at a Vertisol and a Leptosol field irrigated for more than 90 years with untreated wastewater. In a greenhouse we set up a factorial experiment with 4 replicates, considering both soil types and 3 irrigation water qualities: (i) untreated waste water (UT) (ii) primary treated wastewater that passed through a storage period in a dam (PT) and tap water of Mexico City (TT). Table 1 shows general characteristics of the irrigation water.

Each column was irrigated with 552 mm of water in 6 events with 2 to 3 weeks intervals in between. Leachates were obtained applying a suction of –10 kPa (pF≈2) to the filter installed at the bottom of each column (PALL, cellulose acetate, pore size 5 µm, previously washed in 0.5% HCl and distilled water). In the total leachates at each event dissolved organic carbon (DOC, fraction < 5 _m) was determined using a TOC analyzer (UIC, Inc. Coulometrics CM 5120 and CM5012), Cu and Cd by ICP-MS (Quadrian, Thermo Jarrell Ash) and atomic absorption spectrometry using graphite furnace atomic absorption spectrometry (SpektrAA 200, Varian) with background correction by a Deuterium lamp. Chloride was determined by titration, Ca and Mg by atomic absorption and K and Na by flame emission spectrometry.

Additionally, during one irrigation event the leachates of 5 Vertisol columns (2 irrigated

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>E.C. dS m$^{-1}$</th>
<th>TOC mg L$^{-1}$</th>
<th>DOC mg L$^{-1}$</th>
<th>Total Cu µg L$^{-1}$</th>
<th>Total Cd µg L$^{-1}$</th>
<th>Cl$^-$ mmol L$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UT</td>
<td>7.86</td>
<td>1.57</td>
<td>132</td>
<td>30.5</td>
<td>109</td>
<td>2.1</td>
<td>4.7</td>
</tr>
<tr>
<td>PT</td>
<td>8.16</td>
<td>1.52</td>
<td>34</td>
<td>17.7</td>
<td>3</td>
<td>0.1</td>
<td>4.2</td>
</tr>
<tr>
<td>TT</td>
<td>7.23</td>
<td>0.44</td>
<td>5.5</td>
<td>4</td>
<td>45</td>
<td>0.1</td>
<td>1.4</td>
</tr>
</tbody>
</table>
with TT, 3 irrigated with UT) were sampled separately in 6 successive fractions. In each fraction we determined also the above mentioned parameters.

Finally, Cu and Cd species in leachate fractions were estimated using the geochemical model MINTEQA2 (Allison and Perdue, 1994) including the submodel for metal complexation by DOC with variable charge for the latter. DOC was assumed to have 50% carbon content and a molecular weight of 650 g. Equilibrium constants for metal complexation were taken form the MINTEQA2 database. Allison and Perdue (1994) reported that the value for total acidity included in MINTEQA2 is far too low for natural systems; for that reason we changed total acidity to be 6.3 µmol mg⁻¹ of humic acid based on data reported by Schnitzer (1977) for DOC of subtropical regions.

Results and discussion
Figure 1 shows the mean DOC concentrations in the soils as a function of irrigation time and soil type. A significant increase can be noticed with length of irrigation (p = 0.05); no significant differences occur between both soil types.

Figure 2 shows the amount of carbon mineralized during the 21 days incubation experiment from Leptosol and Vertisol samples irrigated for 16, 65 and 80 years and compared with never irrigated soils. As reported also by Friedel et al. (1998) for the study area, Leptosols mineralize more carbon than Vertisols. Carbon mineralization is larger in long term irrigated soils than in soils that have never been irrigated. For Leptosols, 0.9–1.6 g 100 g⁻¹ of the total organic C were mineralized in long-term irrigated samples, while 0.4–0.8 g 100 g⁻¹ were mineralized in Leptosol samples never irrigated.

These results show that long term wastewater irrigation alters the quality of soil organic matter, particularly in Leptosols. The added organic matter can be mineralized easier and there are more dissolved organic carbon compounds in the soils.

The water extractable Cu and Cd concentrations increase with irrigation time and correlate with the dissolved organic carbon concentrations in the soils (Figure 3). No differences exist between both soil types.

Table 2 shows the amounts of added and leached carbon from the soil columns during the column experiment. DOC concentrations are larger in Vertisol than in Leptosol leachates. The quantity of DOC leached from the columns decreases as water quality improves UT > PT > TT, and reflects the differences in C input.

The amount of C added by TT to the columns is small in comparison to the amount of C leached. This allows us to calculate the portion of carbon mineralized from the soil organic matter and leached as DOC which is larger for Leptosol (2.5 mg g⁻¹) than for Vertisol columns (2 mg g⁻¹). This agrees well with our results shown in Figure 2.

Figure 1  Mean dissolved organic carbon concentrations and standard error bars in Leptosol and Vertisol samples from 0–30 cm depth irrigated during different lengths of time
The C, Cu, Cd and sum of cations’ concentrations in leachate fractions of one column irrigated with UT and one column irrigated with TT are shown exemplarily in Figure 4, the other analyzed columns show the same trends (data not shown). DOC increases in the TT treatment from fraction 1 to 6, while columns irrigated with UT show larger DOC concentrations in the first fraction. This could be due to the simultaneous leaching of soil and wastewater DOC. We suppose that organic matter from UT (dissolved or particulate) moves through cracks in the Vertisol columns by preferential flow, since fraction 1 was turbid, while the other fractions were not.

Results on Cu, Cd and the sum of cations shown in Figure 4 will be discussed later in this section.

The amount of Cu leached (Figure 5) is larger in Vertisol than in Leptosol columns. Differences between irrigation water qualities are small; the only statistically significant ones are those between UT and PT in Leptosol columns (p < 0.05).

Although clear differences exist in the amount of Cu entering the columns with the different irrigation water qualities, differences in Cu leaching between the treatments are very
small. For that reason we conclude that most part of the leached Cu originates from the soil and not from irrigation water. This is confirmed by the fact that the amount of Cu added with the PT irrigation water represents only 7 or 15% of the amount of Cu leached for Vertisol and Leptosol columns, respectively. This means that Cu leaching from long-term wastewater irrigated soils in the Mezquital Valley will not be reduced in short time periods by reducing Cu input; soils present a “memory effect”.

The amount of Cu leached correlates with DOC (Figure 6) as it has been shown also for soil water extracts above (Figure 3). This agrees well with many literature reports which stress the importance of DOC for Cu mobility (Zhu and Alva, 1993; Kalbitz and Wennrich, 1998; Christensen et al., 1999). Linear regression equations in Figure 6 show a statistically significant steeper slope for Vertisol columns in comparison with Leptosol ones (Students t-test, p<0.05). This could be due to different DOC metal complexation characteristics which may change from one soil type to another (Schnitzer, 1977). Contrarily, Esteves da Silva (2002) did not find differences in metal complexation characteristics between fulvic acids from soil and those from composted sewage sludge. However, these characteristics depend largely on pH, the ratio of metal to DOC and ionic strength. For that reason complexation characteristics for DOC from soils of the Mezquital Valley should be studied in more detail.

In the case of TT, Cu and DOC also correlate in leachate fractions during one irrigation event (Figure 4), while this is not the case for the UT treatment. In the latter, this could be due to simultaneous leaching of UT-DOC with soil DOC as mentioned before.

Cu speciation with MINTEQA2 (Table 3) indicates the importance of Cu-DOC and
CuCO₃ (aq) complexes in column leachates. Concentrations of all main species increase from fraction 1 to 6, being the increase for Cu-DOC more pronounced than for the others.

The amount of Cd leached is largest in UT, followed by PT and least in TT (Figure 5). Differences between UT and PT reflect differences in Cd input, the smaller amount of Cd leached in columns irrigated with TT could be due to lower concentrations of bivalent cations or Cl in comparison with UT and PT. Bivalent cations could exchange Cd adsorbed to soil particle surfaces, Cl is known to form complexes with Cd increasing thus its mobility (Aussendorf and Deschauer, 1993; Wang et al., 1997). Correlations are significant ($p < 0.05$) for Cd and the sum of cations on the one hand (Vertisol: $r = 0.45$, Leptosol: $r = 0.46$) and Cd and Cl on the other hand (Vertisol: $r = 0.59$, Leptosol: $r = 0.56$). Cadmium is known to form also complexes with DOC (Datta et al., 2001) although, according to literature reports, this seems to play a minor role for Cd mobility (König et al., 1986; Aussendorf and Deschauer, 1993; Camobreco et al., 1996). In our experiment Cd and DOC show a significant correlation only for Leptosol leachates ($r = 0.5$).

Differences in Cd leaching between soil types are significant ($p < 0.05$) indicating that at least part of the Cd comes from the soil. Generally, Cd concentrations are low in column leachates; diminishing Cd input by changing irrigation water would lead to an even further decrease in Cd leaching.

Differences between UT and TT in leachate fractions during one irrigation event (Figure 4) show also a clear positive dependence of Cd concentrations from the sum of cations and Cl (data for the latter not shown), the correlation of Cd and DOC is poor and restricted to fractions 4 to 6.

Cadmium speciation by MINTEQA2 (Table 4) indicates the importance of free Cd⁺² and Cd-DOC complexes. Summarizing the above mentioned, we find an influence of the sum of cations, Cl and DOC on Cd leaching in our experiment.

**Conclusions**

Long term irrigation with untreated wastewater increases the mineralizable carbon fraction, especially in Leptosols, and the DOC concentrations in soils. The water extractable heavy metal concentrations also increase with irrigation time and correlate well with DOC.
A change in irrigation water quality did not increase Cu and Cd mobility in long-term wastewater irrigated soils during the experimental period of 6 months. On the contrary, Cd leaching was diminished and Cu showed little dependence on water quality.

Acknowledgements

The authors thank the Eiselen-Stiftung, Ulm and the Dirección General de Apoyo al Personal Académico, UNAM, for funding, Daniel Mendoza for his help in water and leachate sample analysis, and Mr. Lizzy from the University of Hohenheim for his help in designing and constructing the columns for the experiment. Dr. Ofelia Morton and Elizabeth Hernández from the LUGIS, Instituto de Geofísica, UNAM, did the ICP-MS analysis of the leachates and Georgina Mendez form the Instituto de Ecología, UNAM helped with the DOC analysis in leachate samples.

References


