Quantification and modelling the mobility of trace metals in cultivated plots amended by composts of organic urban residues

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INTRODUCTION

Organic amendments from urban and livestock residues may increase the contents of certain trace metals in amended horizons after years. However, the evolution of the mobile metal fraction appears less predictable, depending on the variations of total contents but also on variations of retention factors such as pH and organic matter [1,2]. Our study aims to put in priority these influences through experimental data and modelling, based on a long-term field experiment equipped with fibreglass wick lysimeters

Field experimental site QualiAgro

QualiAgro is devoted to assessment of long-term effects of spreading urban composts on agrosystems typical of Paris Basin. Crossing 2 levels of inorganic N fertilization and 4 repetition blocks, the 5 modalities concern applications of:

• BIO, co-compost of the fermentable municipal residues collected separately and green waste (“biowaste compost”);
• GWS, co-compost of sewage sludge and green waste;
• MSW, compost of municipal solid waste, using a fermentative fraction sorted after MSW collection;
• FYM, farmyard manure as a reference amendment;
• CTRL, control without amendments.

Analyses of soil solutions collected in situ and modelling of transfers

Five plots, one for each modality, equipped for monitoring heat, water and solute transfers. The present study concerns waters collected with fibreglass wick samplers fixed on stainless steel plates of 25x25 cm kept against soil layers at 45 cm depth, during the period 2007-2010. Chemical analyses of these clear unfertilized waters include:

• pH, dissolved organic carbon (DOC), carbonate (performed at INRA-AgroParisTech, Grignon, FR);
• major cations and anions, trace elements (Cd, Cu, Zn here reported: Laboratoire d’Analyses des Solis INRA of Arras, FR).

MODELING. Hydrodynamic was simulated from physical data and models as in [3], without taking into account the samplers. For predicting metal concentrations, we tested several published “generalized Freundlich” equations [4]. We retained equations more in agreement with soil and average solution characteristics, and included them in Hydrus-1D. E.g., we simulated the fluxes of copper with Hydrus-1D completed by an equation of Tipping et al [2] predicting the Cu concentration from “reactive” soil Cu (EDTA extracted), soil OM content, pH and DOC.

MAIN RESULTS

Table 1: Selected properties of plough horizon amended in 2003 (10 years of organic amendment, except CTRL)

<table>
<thead>
<tr>
<th>Property</th>
<th>CTRL</th>
<th>GWS</th>
<th>MSW</th>
<th>FYM</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>2.44</td>
<td>4.00</td>
<td>3.67</td>
<td>3.56</td>
</tr>
<tr>
<td>EC</td>
<td>0.95</td>
<td>1.66</td>
<td>0.74</td>
<td>0.66</td>
</tr>
<tr>
<td>DOX</td>
<td>0.16</td>
<td>0.12</td>
<td>0.18</td>
<td>0.14</td>
</tr>
<tr>
<td>pH</td>
<td>7.80</td>
<td>7.08</td>
<td>7.28</td>
<td>7.48</td>
</tr>
<tr>
<td>Cu (mg/kg)</td>
<td>1.12</td>
<td>0.17</td>
<td>0.23</td>
<td>0.14</td>
</tr>
<tr>
<td>Zn (mg/kg)</td>
<td>0.21</td>
<td>0.11</td>
<td>0.23</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Other solutes (not shown): amendments increase concentrations of K, Mg, Na, NO3, SO4, Cl

Simple adsorption equilibrium models help to unravel and quantify the impact of organic amendments on trace metal mobility, through the negative or positive influences of increasing soil OM, increased DOC, affected pH, and “reactive” soil metal fractions. But they fail to simulate part of the data, e.g., the highest concentrations of Cu, probably due to insufficient evaluations of the nature and role of DOC, as well as of the “reactive” metal fraction. Kinetic phenomena could also generate variations of leachate composition, which should be addressed by particular functions of Hydrus-1D or of other reactive transfer models. Yet, the present simulations of fluxes with Hydrus-1D were partly consolidated by data obtained from interception plates at 45 cm, and help to quantify metal leaching toward deeper horizons and groundwater. They support that the risk of transfer would remain below 1 or 2 mg Cu/m²/year, and between 0.01 and 0.04 mg Cd/m²/year, to be compared to stocks of reactive metals in the plough horizons around 1800 mg Cu/m² and 50 mg Cd/m².

DISCUSSION and CONCLUSIONS

Simple adsorption equilibrium models help to unravel and quantify the impact of organic amendments on trace metal mobility, through the negative or positive influences of increasing soil OM, increased DOC, affected pH, and “reactive” soil metal fractions. But they fail to simulate part of the data, e.g., the highest concentrations of Cu, probably due to insufficient evaluations of the nature and role of DOC, as well as of the “reactive” metal fraction. Kinetic phenomena could also generate variations of leachate composition, which should be addressed by particular functions of Hydrus-1D or of other reactive transfer models. Yet, the present simulations of fluxes with Hydrus-1D were partly consolidated by data obtained from interception plates at 45 cm, and help to quantify metal leaching toward deeper horizons and groundwater. They support that the risk of transfer would remain below 1 or 2 mg Cu/m²/year, and between 0.01 and 0.04 mg Cd/m²/year, to be compared to stocks of reactive metals in the plough horizons around 1800 mg Cu/m² and 50 mg Cd/m².

ACKNOWLEDGEMENTS and REFERENCES

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Water fluxes estimated from collected volumes by wick lysimeters at 45 cm depth and simulated by Hydrus-1D

Figure 4. Comparison between these experimental data (symbols) and simulated drainage under 45 cm (continuous line) – case of GWS plot.

Figure 5: Simulated drainages at different depths in the same plot.

Other plots showed similar simulations, close to experimental data at 45 cm, with slightly higher recorded volumes in the CTRL plot (not shown).

Simulated fluxes of trace metals and comparison with experimental data (drainage period 2007-2008)

Comparison of fluxes calculated from volumes and concentrations of solutions collected by lysimeters (symbols in Figures) with simulated metal transfer fluxes at 45 cm depth, during the period 2007-2010.

Table 2. Treatments ranked for pH or solute concentration (non parametric paired tests over 2007-2010)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>pH</th>
<th>Cu (µg/L)</th>
<th>Zn (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTRL</td>
<td>7.61</td>
<td>1.10</td>
<td>0.21</td>
</tr>
<tr>
<td>GWS</td>
<td>7.08</td>
<td>1.20</td>
<td>0.22</td>
</tr>
<tr>
<td>MSW</td>
<td>7.28</td>
<td>1.18</td>
<td>0.23</td>
</tr>
<tr>
<td>FYM</td>
<td>7.48</td>
<td>1.23</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Other solutes (not shown): amendments increase concentrations of Cu, K, Mg, Na, NO3, SO4, Cl

Figure 6-7: Flux of Cu at 45 cm depth in plots GWS and CTRL; simulations very close to experimental (similar results with FYM and CTRL).

Figure 9: Flux of Cd at 45 cm depth in plots GWS and CTRL; simulations underestimate the mobility of Cu

Table 3. Summary of soil-solution equilibrium modelling

<table>
<thead>
<tr>
<th>Substance</th>
<th>Equation used</th>
<th>Value of parameters</th>
<th>Comparison with measured data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>Tipping’s equation</td>
<td>1.3×10^-6 mg/L</td>
<td>More satisfactory for 4 plots among 5; but not for the highest values, mainly found in plot MSW</td>
</tr>
<tr>
<td>Zn</td>
<td>No satisfactory equation found in literature</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For predicting metal concentrations, we tested several published “generalized Freundlich” equations

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A simpler equation [5] predicts the order of magnitude, but not all differences between treatments. A fuller model involving organic matter (OM) and pH, but not pH alone, would be needed for accurate predictions.

Figure 3 (example). Cu concentrations in leachates of the 5 plots during 3 years (Dec.2007-June 2010) compared with predictions from regression equation of Tipping et al (2003), using their unmodified coefficients of soil variables OM, pH, “reactive Cu” (estimated by EDTA), and DOC. The equation: Modelling rather satisfactory for 4 plots among 5; but not for the highest values, mainly found in plot MSW

Figure 10: Flux of Cd (example of GWS)