Immobilization mechanisms of heavy metals in contaminated soils with biochar amendments
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INTRODUCTION

Biochar* has emerged as a promising soil improver and carbon sink but its effects on trace elements in soils are still poorly known.

Recent studies[1][2][3] suggest different interaction mechanisms depending on element, biochar nature and environment. We confront here sorption studies with contaminated soil extraction to:

- Determine the main mechanisms involved in biochar effects on each metal
- Predict the long-term evolution of biochar influence on soil metal availability

* (valid product from biomass pyrolysis used as soil amendment)

MATERIALS & METHODS

Biochar: produced by Carbon Terra at ~450°C from woody biomass, sieved <2mm, untreated. High pH and buffering capacity, low CEC.

1) Sorption kinetics (Cd)

![Fig.1: Increase of adsorbed Cd quantity Q with time for two biochar particles sizes, modelled by Eqn 1: $Q(\text{mg/L}) = K_e C_0 a_0$](image)

- Slow reaction (equilibrium time > 1 day)
- Kinetics depend on particle size: Cd diffusion within biochar pores
- pH: rapid increase for 10 min after pH drop at pH 5 but no decrease within a week

⇒ Possible kinetic limitation by metal diffusion
⇒ Different sorption processes or reactions can successively occur, including $K_e$ exchange

2) Sorption / desorption isotherms (Cd, Zn, Pb)

![Fig.2: Biochar sorption isotherms fitted by Freundlich model](image)

- Cd, Zn: identical behavior
- Pb: much greater sorption
- Isotherms hysteresis: at least partial sorption irreversibility (10 to 20% for Cd and Zn but less than 3% for Pb)
- pH and carbonates decrease with increasing sorbed Pb
- Phosphates decrease with increasing sorbed Cd and Pb
- No evolution of Na, $K_e$ or Mg with increasing sorbed metal

⇒ Identical and partially reversible sorption for Zn and Cd, with possible surface complexation or precipitation
⇒ High and irreversible sorption of Pb, likely involving precipitation with carbonates or phosphates

3) Soil extraction (Cd, Zn, Pb)

![Fig.3: Relative metal availability (%) with biochar amendments compared to non-amended soils (100%)](image)

- Biochar effects linked with pH rise on acid soils
- Specific sorption still occurs for alkaline soil e.g. for Cd even without pH changes

RESULTS & DISCUSSION

![Table 1: Modification of soil available (compared to total) metal quantity (mg/gsoil) with 10% biochar amendments](image)

<table>
<thead>
<tr>
<th>Soil</th>
<th>Cd</th>
<th>Zn</th>
<th>Pb</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 0%</td>
<td>3.93 (17.4)</td>
<td>609 (1310)</td>
<td>1.20 (1170)</td>
<td>5.71</td>
</tr>
<tr>
<td>A 10%</td>
<td>&lt; 2.02</td>
<td>&lt; 246</td>
<td>&lt; 0.309</td>
<td>7.19</td>
</tr>
<tr>
<td>B 0%</td>
<td>0.158 (184)</td>
<td>3.08 (1749)</td>
<td>0.68 (1189)</td>
<td>7.63</td>
</tr>
<tr>
<td>B 10%</td>
<td>&lt; 0.125</td>
<td>&lt; 27.7</td>
<td>&lt; 0.066</td>
<td>7.76</td>
</tr>
</tbody>
</table>

Soils: contaminated (Cd, Zn, Pb) by smelters activity, with A: acid sandy-clayey loamy soil, B: limed silty-loamy-sandy soil

CONCLUSIONS

- Soil alkalisation can control biochar effects on metals but long-term influence is uncertain (surface complexation, e.g. with biochar aging?)
- Delay of effects can occur due to diffusion in small pores; irreversible sorption prevents rapid desorption risks if soil chemistry changes

PERSPECTIVES

- Soil biota and plants responses to biochar need also to be considered in order to predict long-term biochar effects on metal mobility and availability
- Column experiments will provide further information on sorption dynamics and on the importance of biochar labile fraction