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▶ **To cite this version:**

Frédéric Rees, Marie-Odile Simonnot, Jean-Louis Morel. Immobilization mechanisms of heavy metals in contaminated soils with biochar amendments. 4th International Congress EUROSOIL 2012, Jul 2012, Bari, Italy. 2012. hal-02803642

HAL Id: hal-02803642
https://hal.inrae.fr/hal-02803642

Submitted on 5 Jun 2020

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BIOCHAR IMMOBILIZATION MECHANISMS OF HEAVY METALS IN CONTAMINATED SOILS

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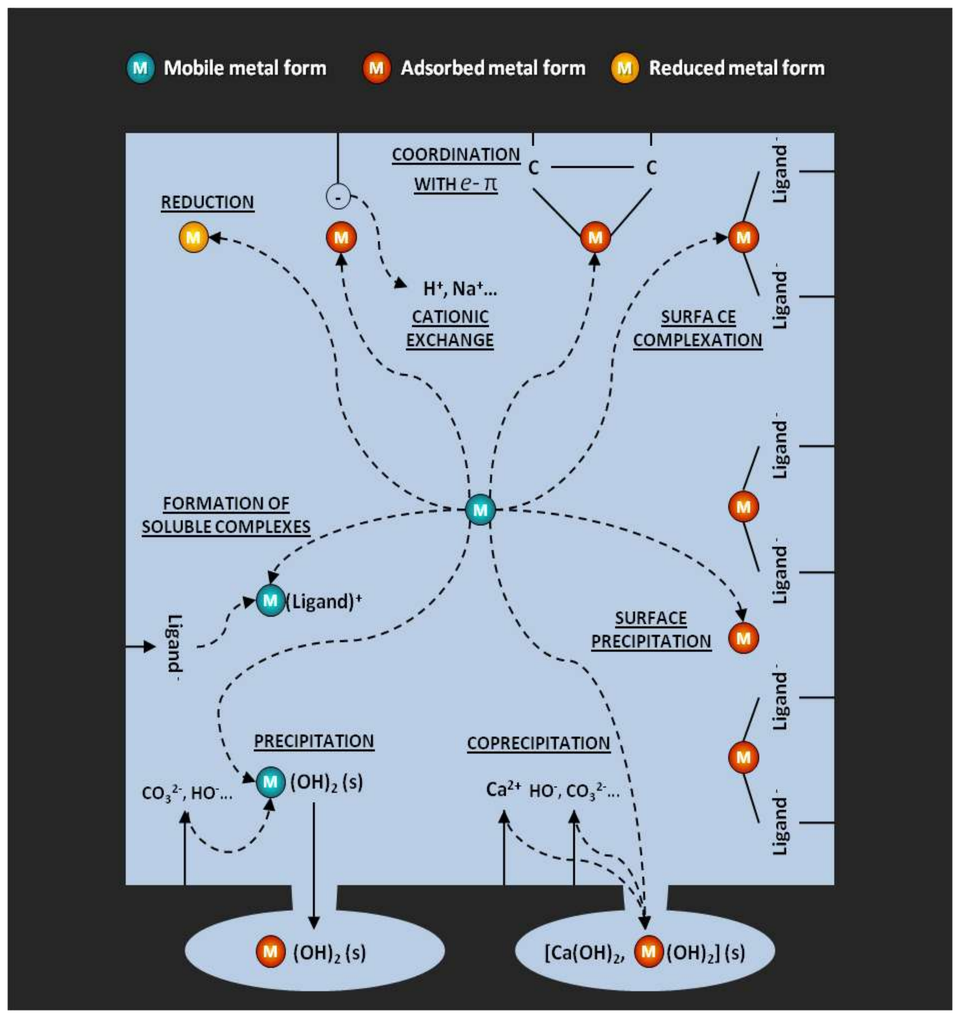
INTRODUCTION

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**

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



BIOCHAR-METALS INTERACTIONS …

DIRECT INTERACTIONS

- **Electrostatic interactions** between M^{2+} and negatively charged biochar surface
- **Cationic exchange** between M^{2+} and H^+ or major cations from biochar surface
- **π-coordination** between M^{2+} and electrons from C=C bounds on biochar surface
- **Surface complexation / precipitation** with biochar functional groups (*e.g.* C-O type)
- **Reduction** from M^{II} to M^0 in specific cases

INDIRECT INTERACTIONS

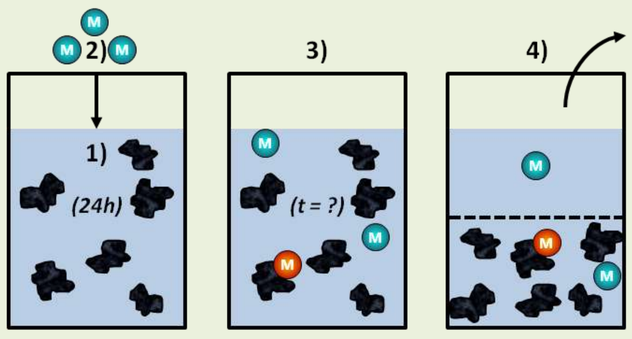
- **(Co)precipitation** with compounds generated by biochar (*e.g.* HO^-, CO_3^{2-}) or **formation of soluble complexes**
- **Influence on plants and soil biota** indirectly affecting soil metal mobility

MATERIALS & METHODS

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

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

1) Sorption kinetics (Cd)

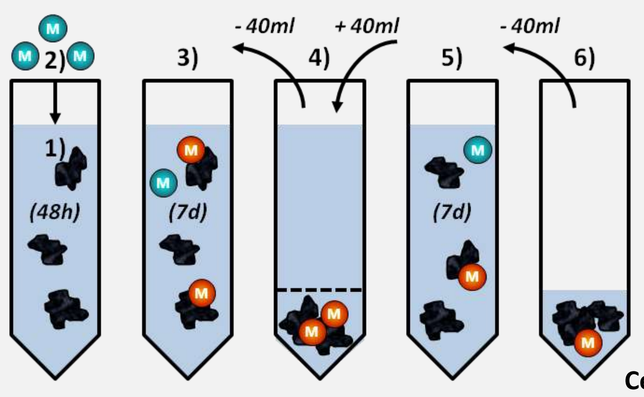


1g biochar
99mL water
1mL $Cd(NO_3)_2$

Agitation for
1min - 7 days

Soluble metal concentration analysis

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



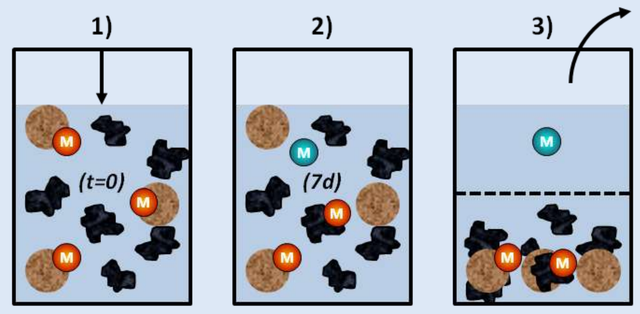
0.5g biochar
49.5mL $Ca(NO_3)_2$ 0.01M
0.5mL $M(NO_3)_2$ 1-50mM

Centrifugation, Replacement of 40ml

Centrifugation, Metal in supernatant analysis

3) Soil extraction (Cd, Zn, Pb)

With 0% or 10% (w/w) biochar amendments



1g biochar
9g soil A or B
100mL $Ca(NO_3)_2$

Agitation for 1 week

Decantation Supernatant metal analysis

RESULTS & DISCUSSION

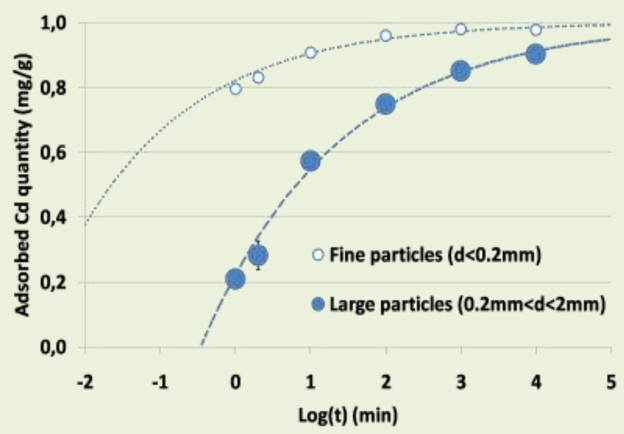
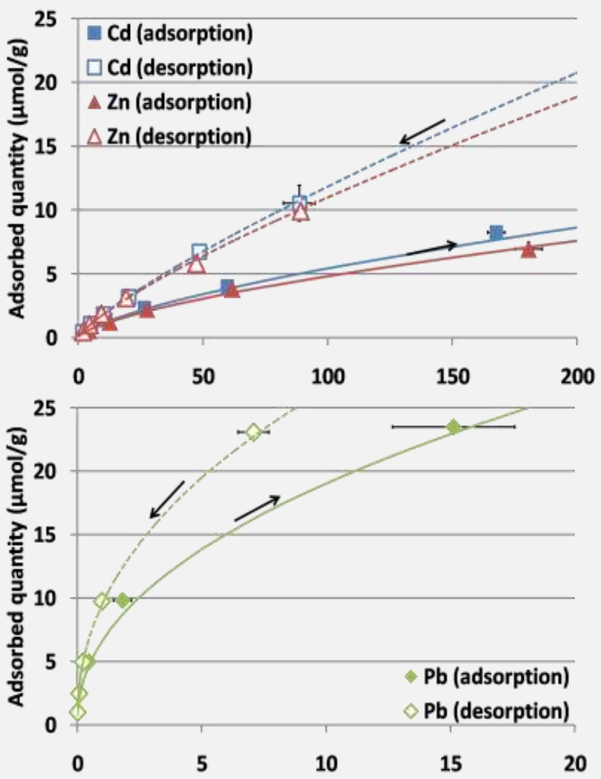


Fig.1: Increase of adsorbed Cd quantity Q with time for two biochar particles sizes, modelized by $Q(t) = Q_{max} - K.t^{-n}$

- Slow reaction (equilibrium time ≥ 1 day)
- Kinetics depend on particles size: limitation by Cd diffusion within biochar pores?
- pH: rapid increase for 10 min after pH drop at t=0 but new decrease within a week

⇒ Possible kinetic limitation by metal diffusion
⇒ Different sorption processes or reactions can successively occur, including H^+ exchange

Fig.2: Biochar sorption isotherms fitted by Freundlich model



- Cd, Zn: identical behavior
- Pb : much greater sorption
- Isotherms hysteresis: at least partial sorption irreversibility (10 to 20% desorption 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^+ or Mg^{2+} 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

Table1: Modification of soil available (compared to total) **metal quantity (mg/kg_{soil}) with 10% biochar amendments**

Soils	Cd	Zn	Pb	pH
A 0%	3.91 (17,.6)	609 (3170)	1.20 (1120)	5.71
A 10%	**↘ 2.02**	**↘ 246**	**↘ 0.309**	**↗ 7.19**
B 0%	0.158 (18.6)	3.08 (1780)	0.068 (1080)	7.63
B 10%	**↘ 0.125**	**→2,77**	**→ 0.066**	**→ 7.76**

- ***Soil A:*** considerable pH increase, decrease of availability for all 3 elements in the order Cd<Zn<Pb
- ***Soil B:*** no pH change; 20% decrease of Cd availability but no significant effects for Zn or Pb

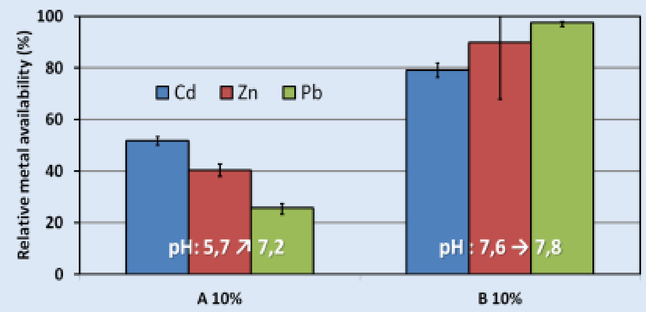
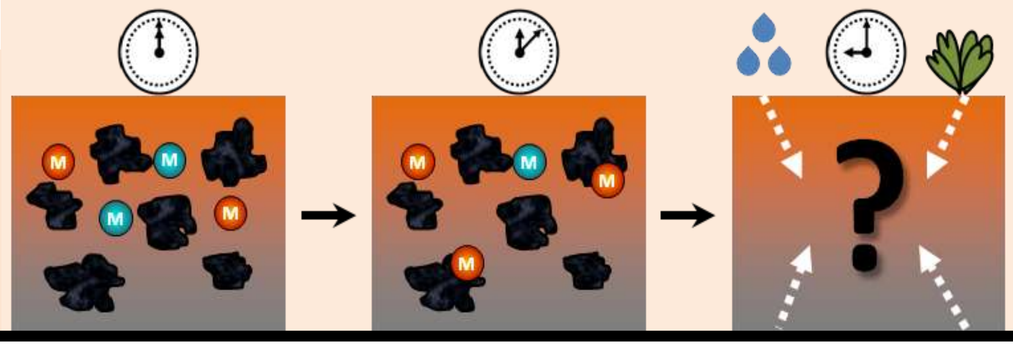


Fig.3: Relative metal availability (%) with biochar amendments compared to non-amended soils (100%)

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

CONCLUSIONS

- **Soil alkalinisation** 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**

[1]Beesley L., Moreno-Jiménez E., Gomez-Eyles J.L. « Effects of biochar and greenwaste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil ». *Environmental Pollution*. 2010. Vol. 158

[2]Uchimiya M., Lima I.M., Thomas Klasson K., Chang S., Wartelle L.H., Rodgers J. E. « Immobilization of heavy metal ions (CuII, CdII, NiII, and PbII) by broiler litter-derived biochars in water and soil ». *Journal of Agricultural and Food Chemistry*. 2010. Vol. 58

[3]Cao X., Ma L., Gao B., Harris W. « Dairy-Manure Derived Biochar Effectively Sorbs Lead and Atrazine ». *Environmental Science & Technology*. 2009, Vol. 43

This work belongs to the research program LORVER and has been funded by Lorraine Region and FEDER program.

EUROSOIL 2012