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USING BIOCHAR FOR DECREASING THE MOBILITY OF 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.

Litterature^[1] suggests **different interaction mechanisms** depending on element, biochar nature and environment.

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

Cationic metals M^{2+} may be retained on the surface of biochar by various processes^[1]:

- **Electrostatic interactions** between M^{2+} and biochar surface
- **Cationic exchange** between M^{2+} and major cations
- **π -coordination** with electrons from C=C bounds of biochar
- **Surface complexation** with biochar functional groups
- **(Co)precipitation** with e.g. carbonate or phosphate

Indirect effects of biochars on soil metal mobility also exist, e.g. **an increased soil pH** affecting metal retention on soil particles^[2].

→ We compared here sorption studies with contaminated soil extractions in order to:

- Understand **how and where biochar can immobilize metals** at its surface
- Determine the **main mechanisms involved in metal immobilization in soils**
- Assess the **long-term influence** of biochar on **soil metal mobility**

MATERIALS:

METHODS:

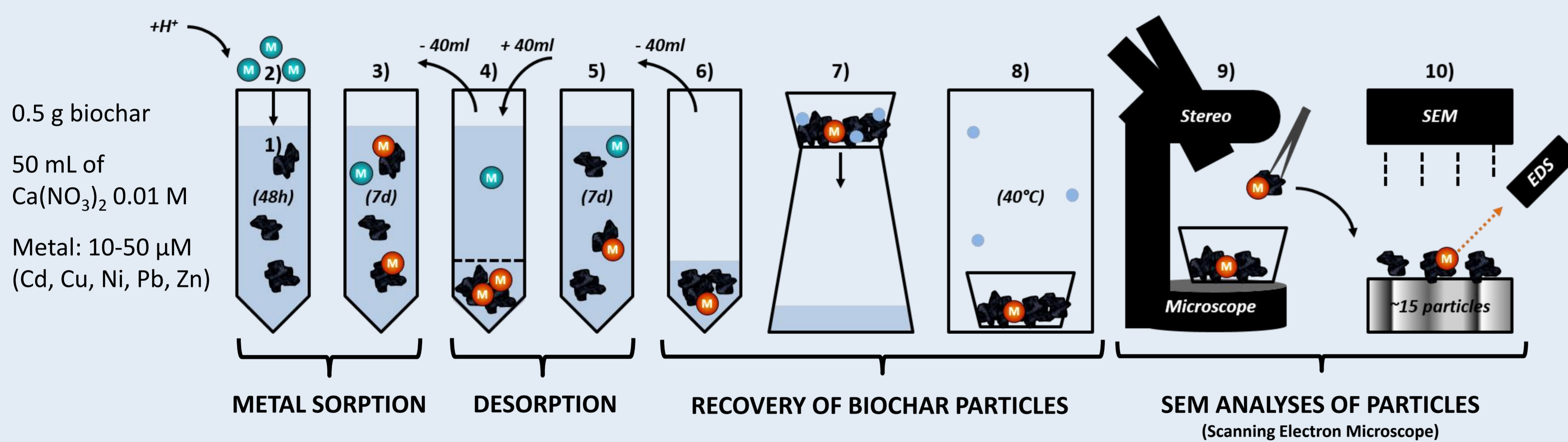
	Biochar	Soil A	Soil B	
pH	9.2	5.9	8.1	-
Cd	0.4 (0.3%)	17.6 (34%)	18.6 (1.3%)	mg kg ⁻¹
Pb	7.2 (-)	1120 (0.2%)	1080 (0.005%)	mg kg ⁻¹
Zn	112 (0.03%)	3170 (22%)	1380 (0.2%)	mg kg ⁻¹

1 biochar: produced at ~450°C from woody biomass, sieved to <2mm, untreated.

2 soils: contaminated by smelters activity, with similar properties except soil pH

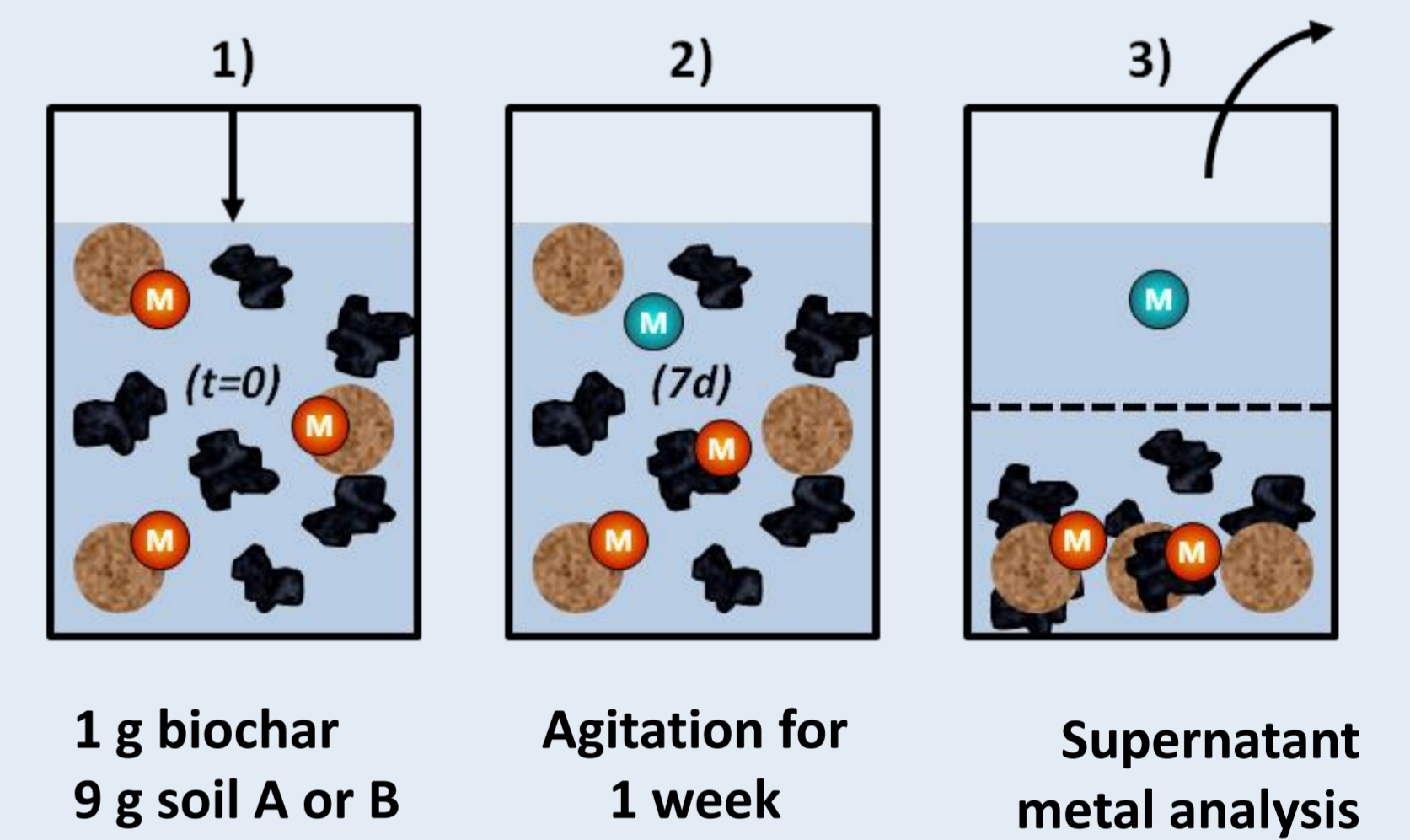
TOTAL CONTENT (CaCl₂ exchangeable fraction)

1) Metal sorption isotherms and analysis of metal-loaded biochars



2) Soil extraction

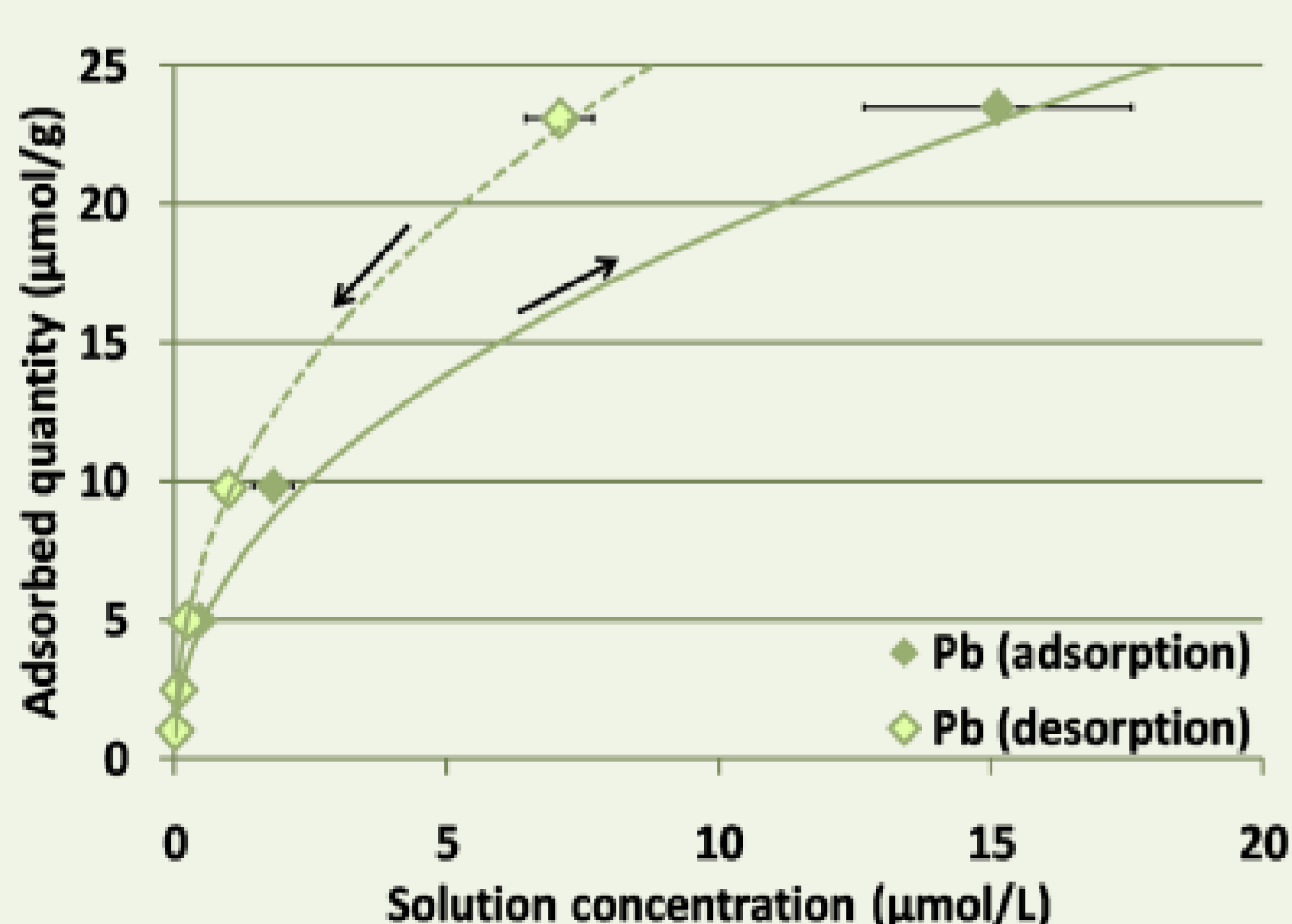
→ With 0% or 10% (w/w) biochar amendments



RESULTS & DISCUSSION

▪ Metals are **immobilized at the surface of biochar**, following the order: Pb>Cu>Cd>Zn>Ni^[3]

Biochar Pb sorption isotherms fitted by Freundlich model



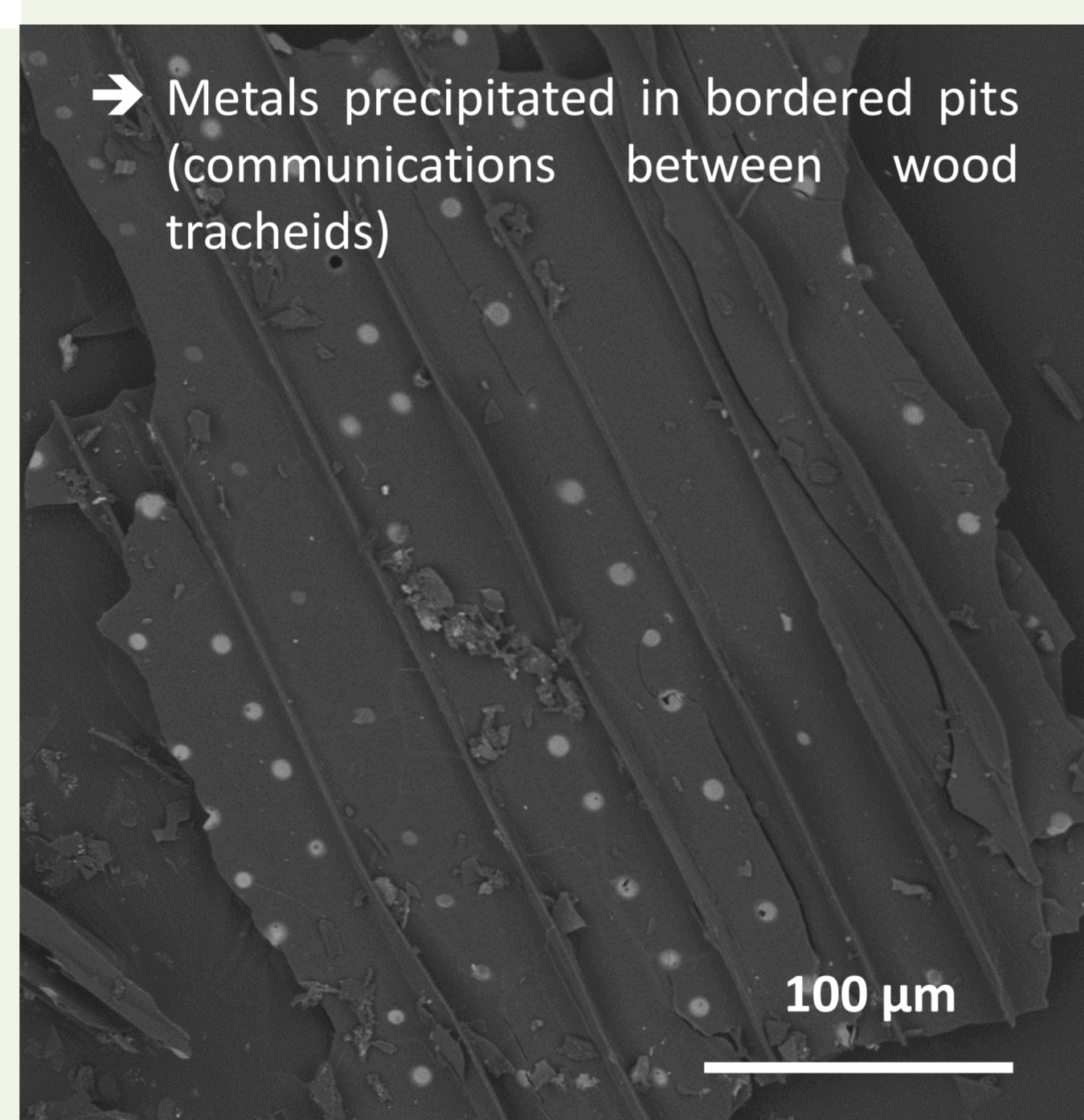
▪ Isotherms hysteresis:
→ **sorption is partially irreversible**

▪ No significant evolution of Na⁺, K⁺ or Mg²⁺ with increasing sorbed metal:
→ **cation exchange is limited**

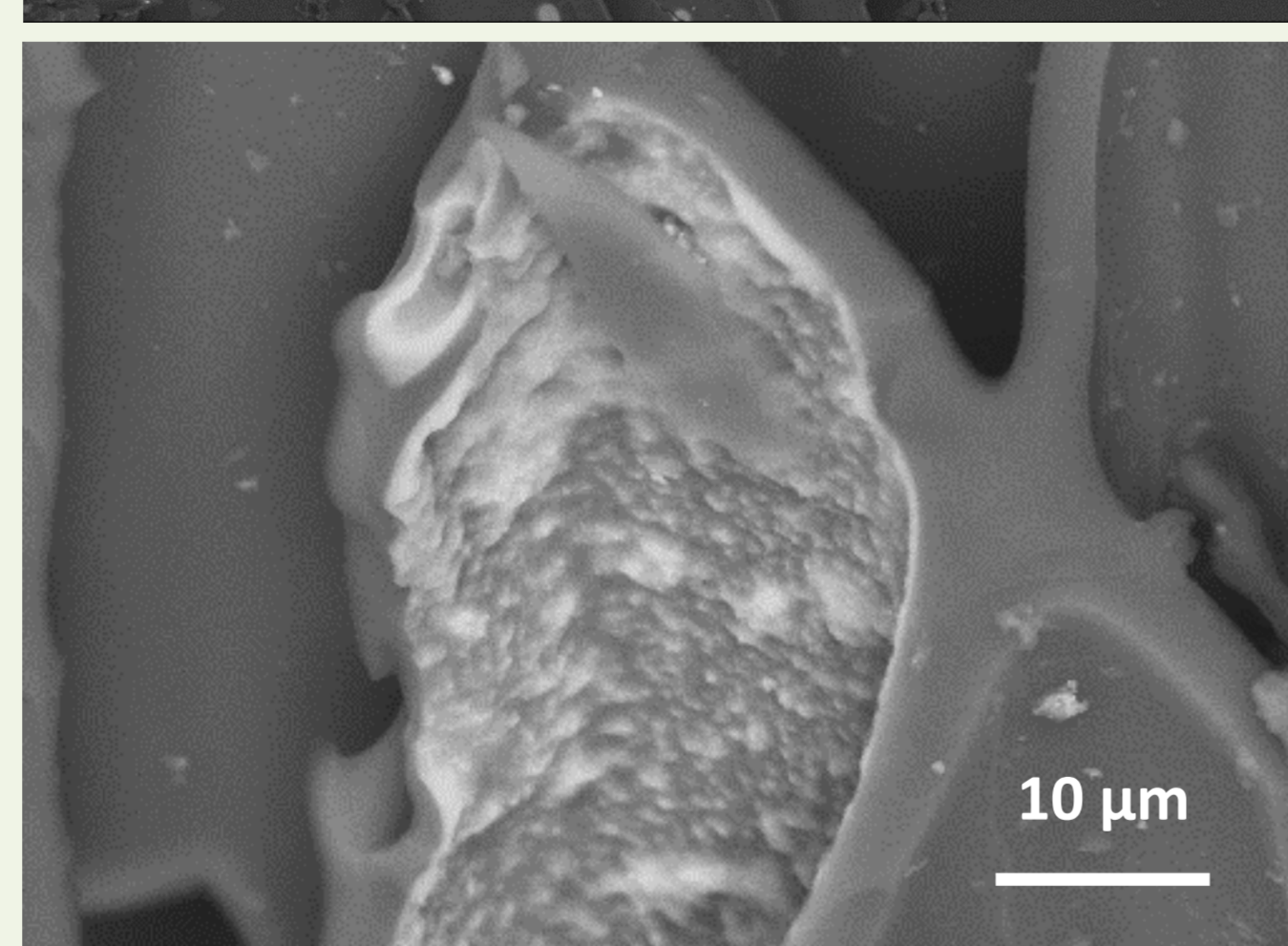
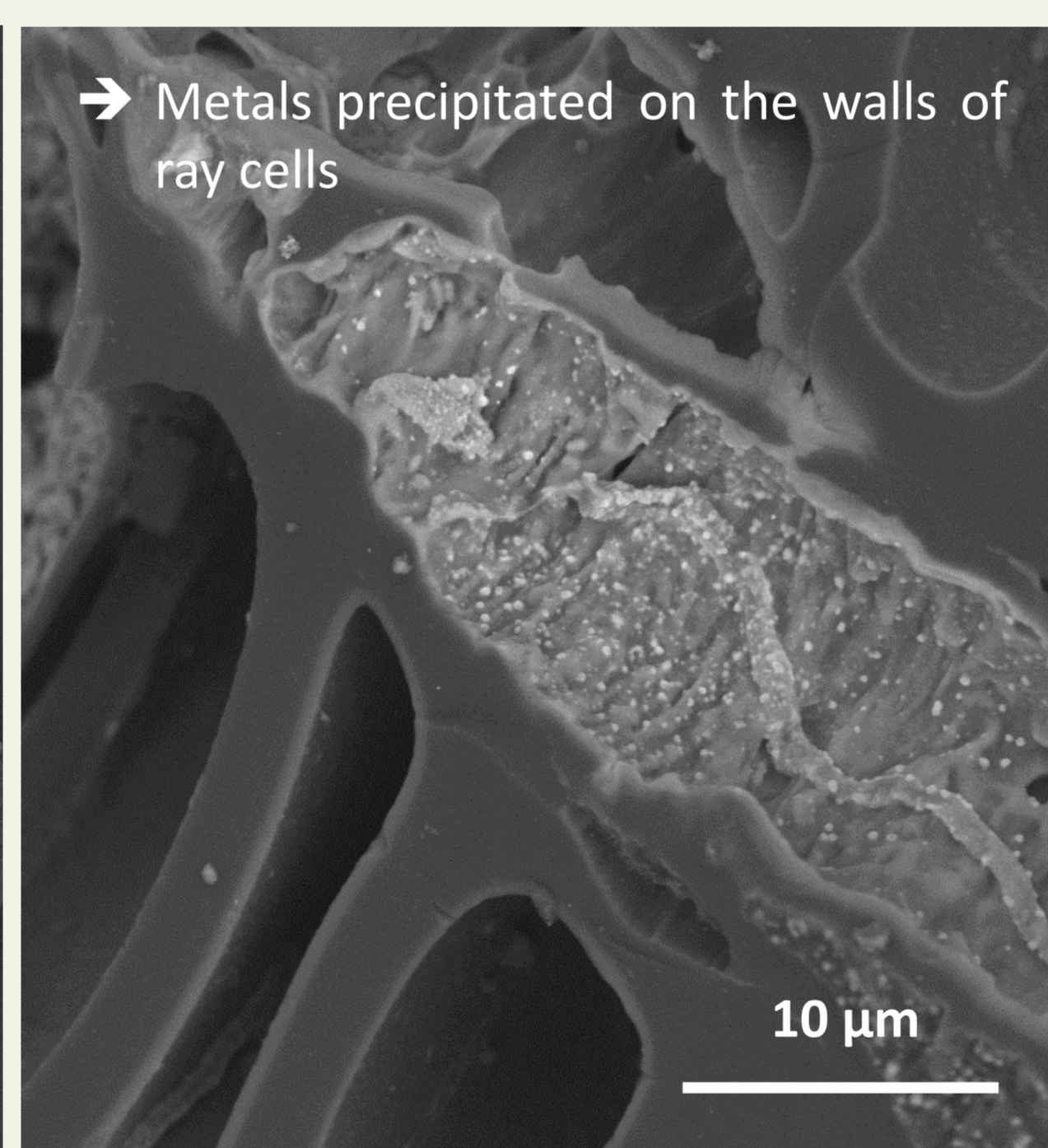
▪ pH and carbonates ↓ when sorbed Pb ↑:
→ **precipitation of metals with carbonates**

▪ SEM observations confirm that **metals (Pb, Cd, Zn) concentrate in carbonate phases:**

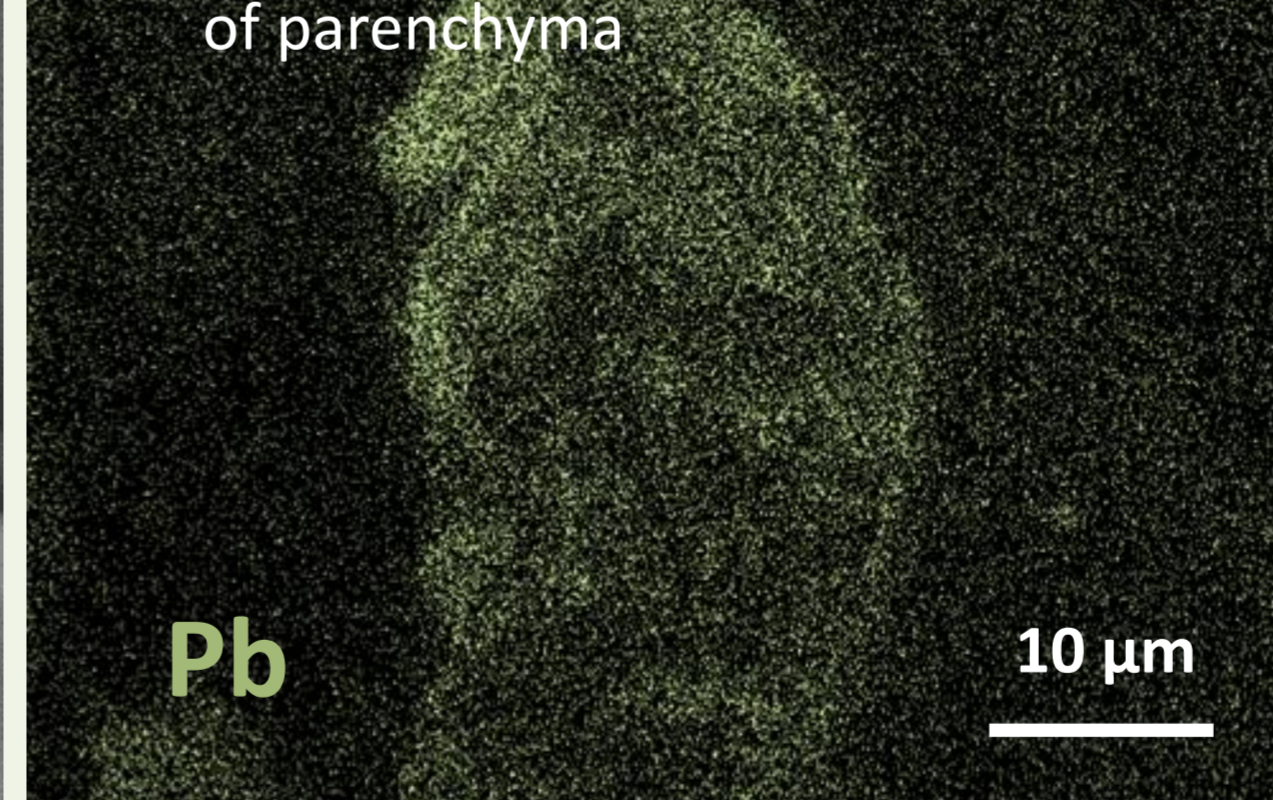
→ Metals precipitated in bordered pits (communications between wood tracheids)



→ Metals precipitated on the walls of ray cells



→ Pb precipitated on the walls of parenchyma



▪ The presence of biochar in both soils leads to^[3]:

→ **Soil A: pH ↑**; metal extractability strongly ↓
→ **Soil B: no pH change**; Cd extractability ↓ but no significant effects for Zn or Pb

pH and equilibrium concentration of metal measured in soil extracts

Soil	C _{eq} (μmol/L)	Zn	Cd	Pb	pH (-)
		Control	1072	3.56	0.62
Soil A	Biochar	369	1.73	0.16	6.9
Soil B	Control	6.3	0.19	0.04	7.2
	Biochar	4.1	0.13	0.03	7.4

▪ The amount of immobilized metals in soils is different from the maximal amounts of metals sorbed on biochar assessed from sorption isotherms.

Immobilized quantities of metal in the presence of biochar, predicted from sorption isotherms and actually observed

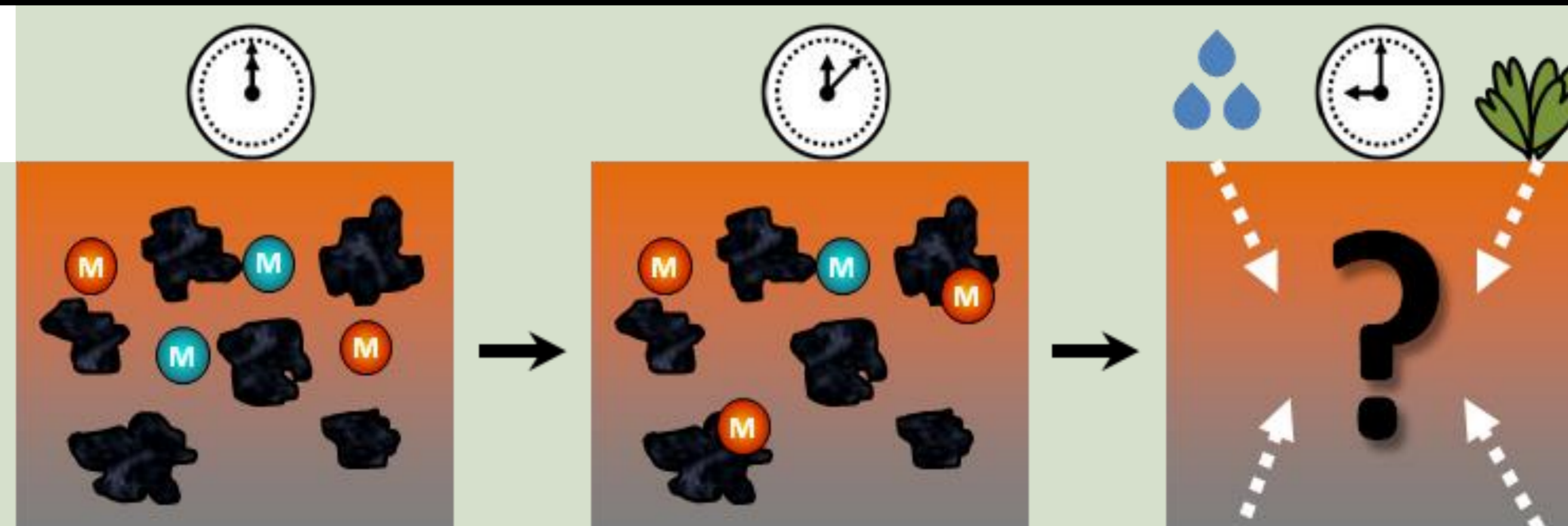
Soil	Q _{ads} (μmol/g)	Zn	Cd	Pb
		Predicted	0.83	0.27
Soil A	Observed	56	0.15	0.04
Soil B	Predicted	0.25	0.030	0.494
	Observed	0.16	0.004	0.000

→ **Indirect effect of biochar by increased soil pH** explains the effects on soil metals mobility better than sorption on biochar

CONCLUSIONS

▪ Biochar amendments in soils can decrease soil metal mobility by:

- 1) **Direct effects** by sorption at biochar's surface, e.g. by **precipitation of metals with carbonates**
- 2) **Indirect effects** on soil metal retention, by **soil pH increase**.



PERSPECTIVES

- **Different feedstocks and pyrolysis conditions** could affect biochars ability to sorb metals (e.g. with various pH and carbonate content)
- **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.

[1] Beesley et al. (2011.) A review of biochars potential role in the remediation, revegetation and restoration of contaminated soils. *Environmental Pollution*

[2] Houben et al. (2013) Mobility, bioavailability and pH-dependent leaching of cadmium, zinc and lead in a contaminated soil amended with biochar. *Chemosphere*

[3] Rees et al. (2014) Short-term effects of biochar on soil heavy metal mobility are controlled by intra-particle diffusion and soil pH increase. *European Journal of Soil Science*