Behaviour of ciprofloxacin and Cu(II) in biosolid-amended soils

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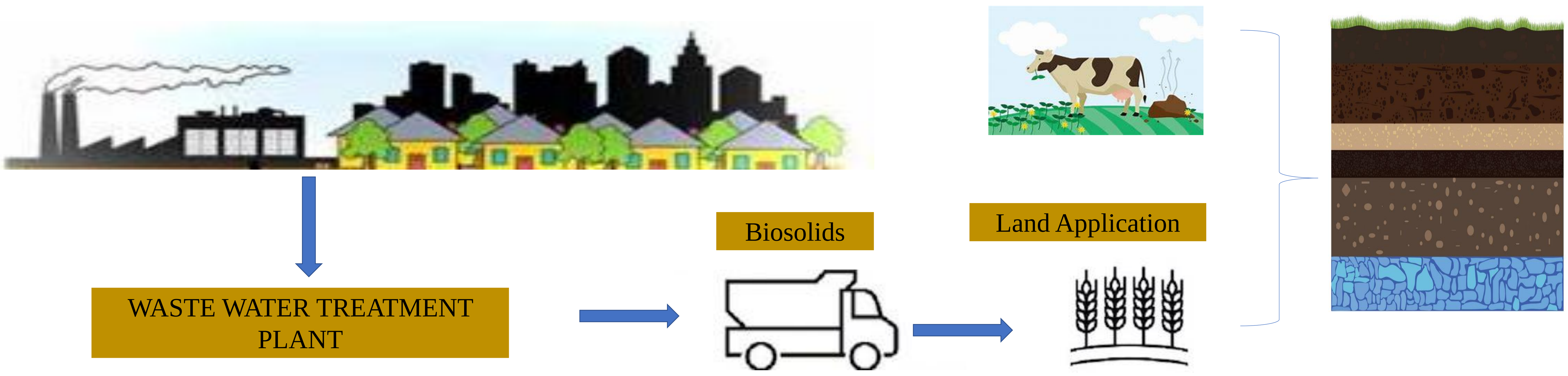
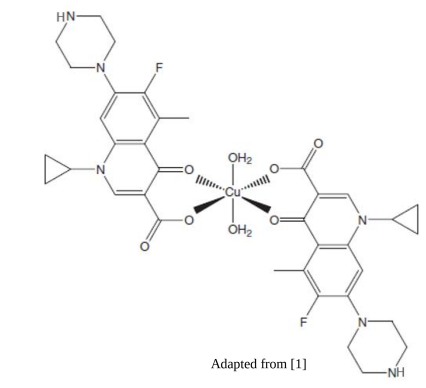
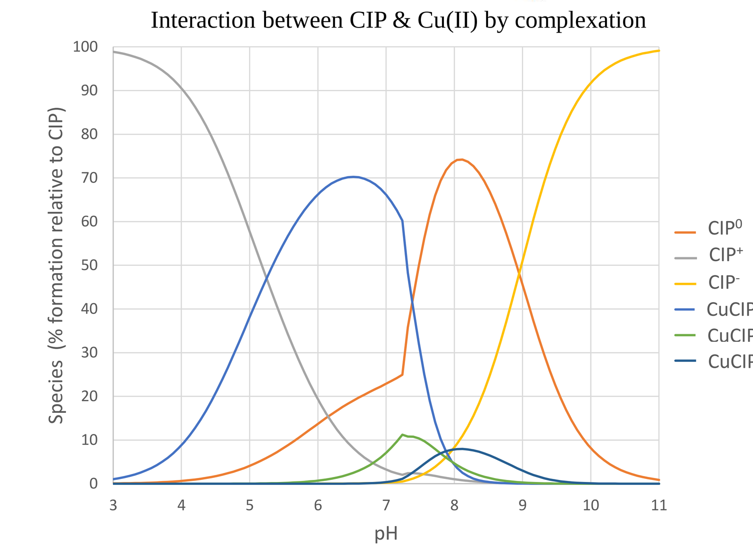




Interaction between CIP & Cu(II) by complexation



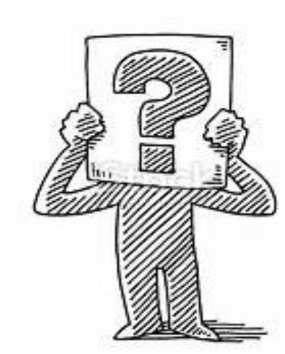
- Fluoroquinolones are synthetic antibiotics (AB) which are detected in biosolids, manure and wastewater treatment plant (WWTP) effluents, and thus widely encountered in the environment especially in soils and water *via* amendments and/or irrigation.
- To assess the transfer risk of these pharmaceuticals and predict their fate, a better insight is needed about their retention/release behaviour at the soil/water interface, which is governed by their sorption.
- Metallic trace elements (MTE) which are naturally present in soils or originate from industrial wastes and various agricultural treatments, can significantly modify the antibiotics sorption/retention properties since they are likely to interact together by complexation [1-2] .

Objectives

In this study we focused on one fluoroquinolone, ciprofloxacin (CIP), widely used in human medicine, and one MTE, Cu(II), present in soils and biosolids. Their retention was studied on two soils of different composition and physico-chemical properties using the batch technique. The same experiments were carried out onto biosolid-amended soils in order to study the impact of the amendment on the contaminant behaviour. Finally, similar experiments were conducted for bi-adsorbate systems (CIP and Cu(II)) in order to study the influence of CIP and Cu(II) co-presence on their respective retention/mobility in soils and amended-soils.

How does biosolid application modify AB and MTE retention and transfer in soils?

Can the mobility of AB and MTE in amended-soils be related to soils and biosolids composition/properties?



How does the presence of metals influence the mobility of antibiotics in soils and amended-soils, and *vice versa*?

What are the most and least risky conditions for AB and MTE transfer in soils?

Studied systems

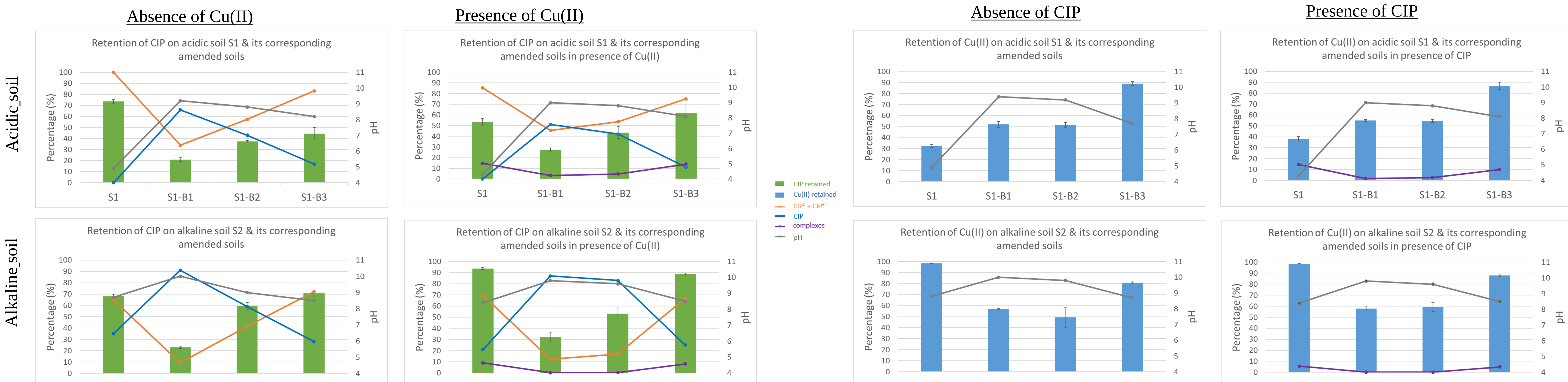
- Two soils, acidic (S1) and alkaline (S2), of different composition were studied.
- Three biosolid samples (B1: fresh biosolid, B2: one-month aged biosolid, and B3: two-months aged biosolid) were provided by a WWTP for a population equivalent of 200,000 inhabitants (France).

	S1	S2	B1	B2	B3
clay (%)	1.0	13.1	33.8	35.0	40.7
silt (%)	6.7	21.4	42.8	24.5	39.1
sand (%)	92.3	65.4	23.5	40.5	20.1
carbonate (%)	0.0	26.2	6.6	8.1	11.2
pH	6.5	8.3	11.2	10.8	8.6
OM (%)	1.1	3.9	45.4	40.7	44.7
CEC (cmol+/kg)	3.4	9.5	14.7	8.7	13.5

Results & Discussion

CIP — Absence of Cu(II) / Presence of Cu(II)

Cu(II) — Absence of CIP / Presence of CIP



CIP

Application of fresh biosolid ⇒ ↗ soil pH ⇒ changing CIP speciation ⇒ ↗ CIP^- more mobile in soils

CIP retention in soils ↗ ⇒ CIP mobility ↘ when (CIP^0+CIP^+) ↗ and CIP^- ↘

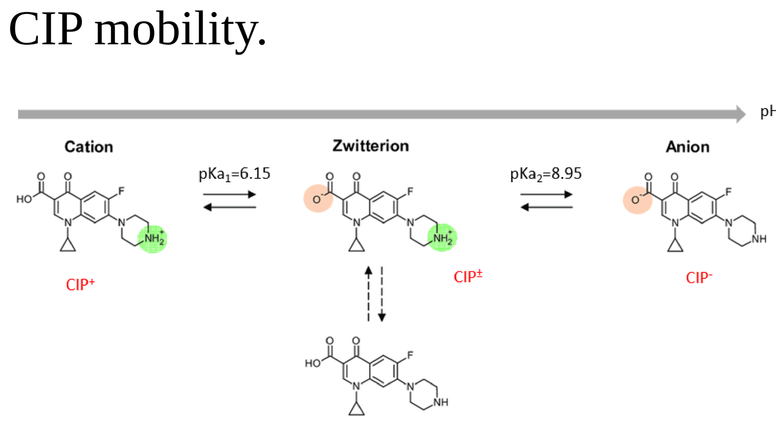
- CIP retention ↘ ⇒ CIP mobility in soils ↗ when fresh biosolid is added.
- Biosolid aging ↘ pH of amended soils ⇒ biosolid aging limits CIP mobility.

- In presence of Cu(II), a part of CIP forms complexes with Cu^{2+}

↳ CIP mobility ↗ in the non-amended acidic soil (S1)

↳ CIP mobility ↘ in the non-amended alkaline soil (S2)

↳ CIP mobility ↘ in both amended soils



Cu(II)

- Biosolid application ⇒ ↗ Cu(II) retention, ↘ Cu(II) mobility — in the acidic soil (S1)

⇒ ↘ Cu(II) retention, ↗ Cu(II) mobility — in the alkaline soil (S2)

- Biosolid aging ⇒ ↘ Cu(II) mobility in both amended soils.
- These behaviours seem due to pH change upon biosolid addition:
↗ pH ⇒ ↗ retention except for pH > 8 where mobility ↗ (role of DOC brought by biosolid?)
- No significant effect of CIP except for S1 & S2-B3 due to complexation between CIP and Cu(II).

Conclusions & outlooks

- It is recommended to age biosolid on the storage platform before application to limit CIP and Cu(II) mobility in soils.
- More acidic and alkaline soils are currently studied to confirm these observations and investigate the role of soil composition and properties on CIP and Cu(II) retention in amended-soils.
- Comparative analysis of contaminant transfer from various organic waste sources will be conducted to evaluate the potential risks associated with their use in agriculture and to devise appropriate management strategies.

[1] Ftouni, H., Sayen, S., Boudesocque, S., Dechamps-Olivier, I., Guillon, E., 2012. Structural study of the copper(II)–enrofloxacin metallo-antibiotic. Inorganica Chimica Acta 382, 186–190.
[2] Khurana, P., Pulicharla, R., Kaur Brar, S., 2021. Antibiotic-metal complexes in wastewaters: fate and treatment trajectory. Environ. Int. 157, 106863.