

Effects and predictability of organic matter and Cu(II) and Zn(II) amendments on the sorption and transport of the sulfamethoxazole antibiotic in a silty-loam soil

Lorenzo Spadini (1), Jean M. F. Martins (1), Marie-Christine Morel (1,2), Aline Barbot (1), Emilie François (1), and Erwann Vince (1)

(1) University Grenoble-Alpes, IGE Geosciences Institute, Grenoble Cedex 9, France

(lorenzo.spadini@univ-grenoble-alpes.fr), (2) CNAM, Laboratoire d'analyses chimiques et bio analyses, Paris Cedex 3, France

Most antibiotics (ABs) are variable charge ligands, which possess metal complexing functional groups. They consequently bind to soil in various modes, e.g. pH-dependent complexation, ion exchange, hydrophobic interactions. This variability and the complexity of the soil make the prediction of AB sorption on soils a challenging task. Sulfamethoxazole (SMX) is a sulfonamide-class antibiotics. Its binding modes on a silty-loam soil were studied by combining batch and column experiments at varying organic matter (manure, percentage scale) amendment levels and at varying metal (Cu(II) and Zn(II)) contaminations. The site density of both soil and manure was equated to their proton sorption capacity between pH 4 to 10. That of manure (1.2 mmol/g) is 12 times higher than that of the 2% OM containing soil (0.1 mmol/g). In batch experiments the concentration of sorbed SMX ($0.003 \leq [\text{SMXads}] \leq 1 \mu\text{mol/g}$) increased with the site density equally in both soil and manure, and also equally in manure-amended soil. This shows that both substrates have a similar substrate-SMX sorption strength. This result combined to total organic carbon analysis suggests that both manure and soil OM have a high and similar reactivity toward SMX and that OM is the soil phase of dominant reactivity toward SMX. The effect of manure amendment on the sorption of SMX is predictable from single-phase experiments.

The sorption of SMX increased in copper- and zinc-contaminated soils. Quantitative speciation analysis of the SMX-soil-metal-pH system involving variable pH sorption experiments and a minimum number of adjustable constants were performed. The analysis indicates that metals form strong binding sites on the soil surface; SMX binds preferably as a ternary SMX-metal-soil complex. Overall, in batch experiments the effects of metals and OM additions on SMX sorption are quantitatively predictable.

In contrary the SMX reactive transport experiments in columns do not agree with this 'predictivity scenario'. On the reference soil the amount of sorbed SMX is slightly decreased compared to the predictions from batches. That expected result likely relates to a more difficult access of SMX to the sites of the soil present in the column in a compacted state. But unexpectedly, in the soil amended with manure the amount of sorbed SMX did not increase but decrease. Moreover, still contrary to batches, the contamination of the soil with metals does not increase the amount of sorbed SMX. These observations are probably due to a concentration effect of organic matter in the aggregated soil present in the columns. At increased concentrations such as existing in the column the OM from manure may completely imprison metals and close access to micropores thus decreasing dramatically the sites accessible to SMX sorption. Such effects appear plausible when considering the ductility of organic matter as highlighted from molecular dynamics calculations. The dispersion of the OM in dilute batch-like environments may limit such effects. All experiments were performed at a constant ionic strength. The combination of batch and column experiments appears to be a valuable frame for determining the predominant sorption modes of organic ligands on complex soil substrates.