

SORPTION OF CATIONIC ORGANIC COMPOUNDS IN SOIL: DO CLAY MINERALS MATTER COMPARED TO ORGANIC MATTER?

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INTRODUCTION

Many pharmaceuticals, biocides, pesticides, surfactants and illicit drugs are positively charged at environmentally relevant conditions. Strong sorption to dissolved colloids and soil and sediment particles affect bioavailability and transport processes in contaminated environments and laboratory toxicity tests.

Ion-exchange controls sorption of cationic compounds in soils, at acidic sites in natural organic matter (NOM) and at negatively charged clay mineral surfaces [1-3]. Na^+ and Ca^{2+} affect ionic interactions between organic cation and ion-exchange site, while additional nonionic interactions can strengthen sorption.

To better understand which soil components dominate overall sorption, in this study we compared sorption affinities towards NOM and two clay minerals for a diverse set of >50 organic cations, including both simple and complex molecular structures.

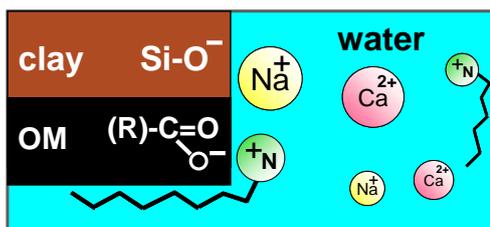


Fig 1. Cationic organic compounds compete with dissolved cations for ion-exchange sites on organic matter and clay surfaces in soil.

METHOD

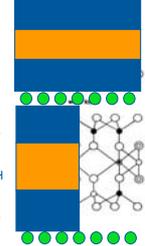
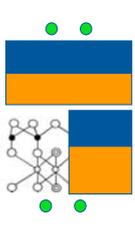
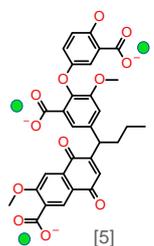
Pahokee peat (IHSS) is used as model soil NOM.

Kaolinite and illite are non-expandable clay minerals.

Pahokee peat (IHSS)
47% OC
CEC 2000 mmol/kg⁴

KAOLINITE (1:1)
30 m²/g
CEC 10 mmol/kg

ILLITE (2:1)
100 m²/g
CEC 200 mmol/kg



- Dynamic HPLC column method used to test sorption
- HPLC column packing: 3% sorbent, 97% inert SiC
- Eluents = 15 mM NaCl solution at pH 6
- Flow-rate (0.05 mL/min) ensures equilibrium
- Inject cations spiked in aqueous eluents via loop
- Retention time = sorption affinity
- Different concentrations injected = isotherms
- Freundlich isotherm fitted with fixed exponent
- Distribution coefficient ($\text{Log } K_d$) at 1 mmol/kg

CONCLUSIONS

Fig 2: • NOM: primary > analogue quaternary amines

• Clays: quaternary >> analogue primary amines

Fig 3: • Illite clay > kaolinite clay, following CEC difference ?

• Quaternary amines: clay can sorb – NOM (despite higher CEC !)

In natural soils, NOM is likely to dominate sorption, at least for primary to tertiary amines. For quats, (bare) clay may dominate sorption, e.g. in artificial soil - OECD guideline 207 (1984) = ASTM (1997) :

10% peat, 20% kaolin clay, 69% fine sand, 1% CaCO_3

Note: due to CaCO_3 in OECD soil, Ca^{2+} concentration is not well defined and this diminishes organic cation sorption affinity in an uncontrolled way!

RESULTS



■ NOM 15 mM Na ● NOM 15 mM Na
□ ILL 15 mM Na ○ ILL 15 mM Na

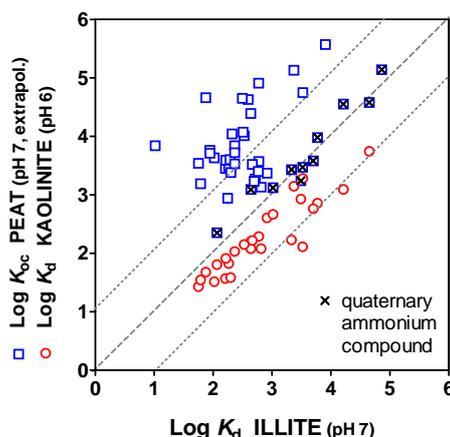
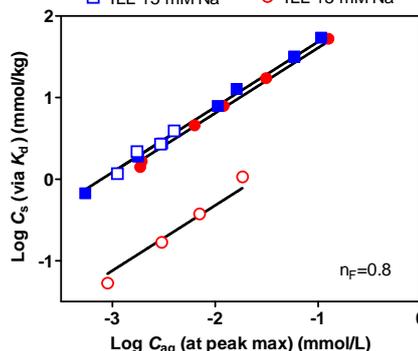


Fig 2. Colour images represent the estimated charge density surface for benzyltrimethyl ammonium (L) and benzylamine (R), in which: yellow: slightly negative, green: neutral, light blue: slightly positive, dark blue: strongly positive.

Sorption isotherm plotted from column data with either Pahokee peat (NOM) or illite clay (ILL), eluents of 100% water with 15 mM NaCl (pH6). Fitted lines are Freundlich curves with fixed nonlinearity exponent (n_F).

Fig 3. Sorption affinities of organic cations for illite clay plotted against either Pahokee peat or kaolinite clay, obtained in eluents of 100% water for 15mM NaCl (pH6-7). Data for Peat are extrapolated from 5mM CaCl_2 eluents, corrected for 1.2 log units higher sorption coefficient in NaCl (1.2 ± 0.13 for 8 compounds).

ACKNOWLEDGEMENTS

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