

The effect of clay mineralogy on the transport of bromide and nalidixic acid in water-saturated soil columns

K. Hanna¹, E. Clervil^{1,2}, M. Usman¹, E. Emmanuel², C. Ruby¹

¹Laboratoire de Physique Chimie et Microbiologie pour l'Environnement, LCPME, UMR 7564 CNRS
Université Henri Poincaré, 405, rue de Vandoeuvre, 54600 Villers-Lès-Nancy, France.

khalil.hanna@lcpme.cnrs-nancy.fr

²Laboratoire de Qualité de l'Eau et de l'Environnement, LAQUE, Université Quisqueya, BP 796, Port-au-Prince,
Haïti

Clays, organic matter and iron- and aluminum-oxides, are the most reactive solid constituents in soils and sediments, where they play a major role in the fate and transport of contaminants (Stumm, 1992). Interactions of nalidixic acid (quinolone antibiotic) with Fe and Al-oxides and clay-coated sand grains packed into columns were studied under both static batch and dynamic flow conditions. Three synthetic soils were used, SS0: 1wt% goethite (100-200 nm), 1wt% gibbsite (0.5-2 µm), 98wt% quartz sand (150-300 µm); SS1: 3wt% kaolinite, 1wt% goethite, 1wt% gibbsite, 95wt% quartz sand; and SS2: 3wt% bentonite, 1wt% goethite, 1wt% gibbsite, 95wt% quartz sand, in order to test the effect of clay on the non-reactive and reactive transport of species under saturated conditions. The breakthrough curves (BTC) of bromide used as a tracer non-reactive solute and nalidixic acid (NA) were determined at different water velocities (0.1- 0.4 cm/min).

Hydrodynamic properties of the various coated silica sands were different suggesting that the presence of clay can affect the spatial structure of the porous media. The bromide tracer breakthrough experiments at a flow rate of 1ml/min showed that kaolinite may cause an increase in dispersion coefficient of the medium, while preferential flow paths probably occurred when bentonite was present in the soil (Fig. 1a). Solute reactive transport experiments showed the breakthrough point and steepness of the BTC were dependent on both clay type and water velocity. The lack of local equilibrium in the column could explain the breakthrough behaviour of NA. The effect of nonequilibrium sorption can be tested by normalizing the solute breakthrough curve with its retardation factor and comparing the normalized solute BTC with the Br- tracer BTC. The assumption of local equilibrium can also be tested by estimating the Damköhler numbers which represent the ratio of hydrodynamic residence time to characteristic time for sorption of a compound in the column (Altfelder et al., 2001) All these results were consistent with that the solute BTC was affected by sorption kinetics.

On the other hand, the clay mineralogy seems to affect the mobility of NA in soil columns. The sorption isotherms determined under batch conditions showed that the sorption extent was dependent on both clay type and clay content. In particular, the presence of kaolinite can increase the retardation factor by about two-fold: $R \approx 6.4$ for the SS0-packed column, while $R \approx 11.0$ for the SS1 one at a flow

rate of 1 ml/min (Fig. 1b), and $R \approx 8.5$ for the SS0-packed column, while $R \approx 15.7$ for the SS1 one at 0.5 ml/min.

In contrast, the mobility of NA was found to be faster in SS2 column than for SS0 or SS1, suggesting that the presence of bentonite can modify the water flow paths and therefore reduce the accessibility of solute to the reactive phases in column. The consequences of these observations under flow conditions is that transport of such compounds in soils and sediments can be faster than expected based on batch experiments.

Finally, macroscopic sorption model implemented in HYDRUS-1D (Simunek et al., 1996) and surface complexation model incorporated in PHREEQC (Parkhurst and Appelo, 1999), coupled with the hydrodynamic parameters were used to describe the aqueous transport of NA as described in our previous work (Hanna et al., 2010). The modelling results showed that the multisurface modelling approach would be suitable to predict the reactive transport in soils and to a better understanding of the relationships between mobility and clay properties.

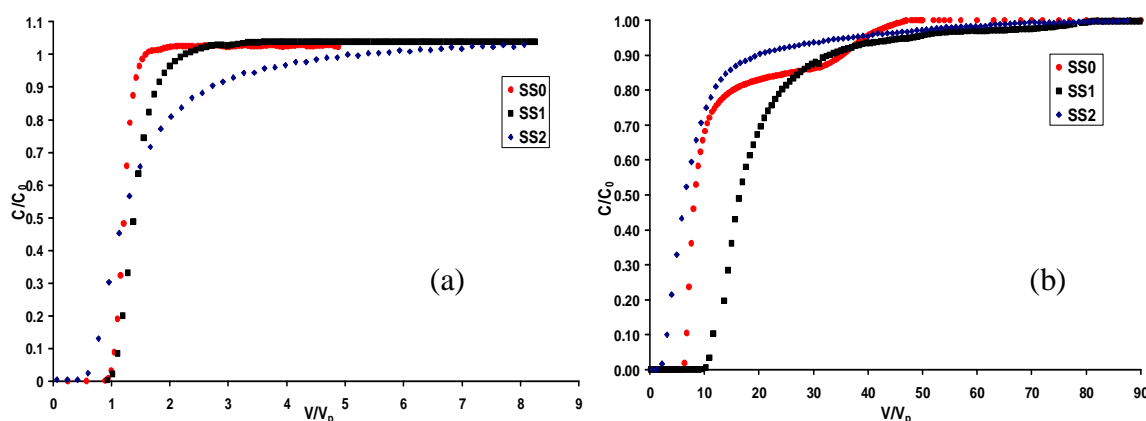


Fig. 1. Breakthrough curve of the non-reactive tracer (a) and of NA (b) for the three SS-packed columns. Flow rate = 1ml/min; $[Br^-] = 10$ mM; inflowing solution with $C_0 = 0.2$ mM of NA. $pH = 7 \pm 0.2$; $T = 20^\circ C$, 10 mM NaCl.

References

- Altfelder S, Streck T, Maraqa M G, Voice T C (2001) Nonequilibrium Sorption of Dimethylphthalate. Compatibility of Batch and Column Techniques. *Soil Science Society of America Journal* **65**, 102-111.
- Parkhurst D L and Appelo C A J, (1999) PHREEQC (version 2)-A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations.
- Simunek J, Sejna M, van Genuchten M Th (1996) The HYDRUS software package for simulating water flow and solute transport in two-dimensional variably saturated media. Version 1.0. IGWMC-TPS-53. Int. Ground Water Modeling Ctr., Colorado School of Mines.
- Stumm W (1992) Chemistry of the solid-water interface: processes at the mineral-water and particle-water interface in natural systems John Wiley & Sons, New York. 428 p.
- Hanna K, Rusch B, Lassabatere L, Hoffman A, Humbert B (2010) Reactive transport of gentisic acid in a hematite coated sand packed column: experimental and modeling study". *Geochimica and Cosmochimica Acta*, **74**, 3351-3366.