Transport of naphthoic acids in metal-contaminated soil columns: Experimental study and modeling approach

K. Hanna[A], B. Bechet[B], L. Lassabatere[B], M. Usman[A], C. Ruby[A]

[A]Laboratoire de Chimie Physique et Microbiologie pour l'Environnement, LCPME, UMR 7564 CNRS-Université Henri Poincaré, 405, rue de Vandoeuvre, 54600 Villers-les-Nancy, France, Email khalil.hanna@lcpme.cnrs-nancy.fr
[B]Laboratoire Central des Ponts et Chaussées, Centre de NANTES - Division Eau et Environnement, Route de Bouaye BP4129, 44341 BOUGUENAIS, France

Abstract

Transport of two naphthoic acids (1-hydroxy-2-naphthoic acid (HNA) and 2-naphthoic acid (NA)) was studied in soil-packed columns. Firstly, the aqueous transport was described with surface complexation model incorporated in PHREEQC, implemented with the hydrodynamic parameters and by adjusting the sorption constants of solute breakthrough in column packed with an artificial soil. The experimental breakthrough curves of solutes in a metal contaminated soil were then determined and compared with those calculated using the sorption parameters derived from synthetic soil experiments. This modeling approach was used as tool to understand the mobility of HNA vs NA under convective-dispersive flow in contaminated soil. The effect of solute injection on the mobilisation of Pb, Zn and Cu from metal contaminated soil was also monitored. This study has important implications for the fate and transport of both carboxylated aromatic contaminants and heavy metals in mixed contaminated soils.

Key Words

PAH metabolites, metal, soil minerals, contaminated soil, modelling

Introduction

Soils contaminated by mixtures of heavy metals and Polycyclic Aromatic Hydrocarbons (PAHs) are frequently found in polluted industrial sites and along roads. Naphthoic acids are primary products of the biodegradation of PAHs composed of three rings such as phenanthrene and anthracene. They also are metabolic end-products in the biodegradation of the four-ring PAHs (Gibson, 1984). The environmental fate of PAH metabolites is prompted by their ubiquitous distribution and their potentially deleterious effects on human health. Naphtoic (NA) and hydroxynaphthoic (HNA) acids have been also identified as intermediates of PAH natural attenuation in soil studies (Gibson, 1984; Burgos et Pisutpaisal, 2006). These compounds may have distinctly different sorption affinities and reactivities toward environmental surfaces than their parent compounds (Parikh *et al*., 2004). Due to their higher mobility in porous media, the fate of naphthoic acids in the environment is of significant interest. Therefore, the potential risk of groundwater pollution associated with the transfer of these compounds should be considered through their interactions with main soil constituents. While there are numerous studies on the transport of low-molecular-weight organic acids, the mobility of these carboxylate compounds in soils has been scarcely explored. For such compounds, specific interactions with mineral surfaces may dominate their fate in soils (Hanna, 2007). In the present study, the mobility of two naphthoic acids (HNA and NA) was studied under column flow-through conditions in two soils: a lab-synthetic soil representative of natural soils and a contaminated roadside soil. The first objective was to develop a transfer model to simulate the breakthrough curves (BTC) of the naphthoic acids in the synthetic soil. Therefore, the model was applied to the roadside soil and discussed. The effect of naphthoic acids on the mobility of the main heavy metals from the contaminated soil was finally studied by measuring the metal aqueous concentrations in column eluates.

Methods

Preparation and characterization of soil samples

Synthetic Fe-Al-SiO_2 coating mineral was used as a model mineral soil due to abundance in the environment. In particular, ferrihydrite and gibbsite particles were deposited on quartz sand (Fontainebleau, France), with a grain size range of 150-300 µm. The final composition was 90% of sand, 4 % of ferrihydrite and 6% of gibbsite. The roadside soil was sampled along a major rural highway near Paris (France). An average representative sample of the soil was generated from the surface layer (0-2 cm). Experiments were carried out on the particle size fraction under 200 µm. Some mineralogical and physico-chemical parameters are summarized in Table 1 (Hanna *et al*., 2009). Cation exchange capacity (CEC) and heavy metal concentrations are reported in Table 2.

Table1. Characteristics of the contaminated soil

Parameter	
Natural pH_{H2O}	7.7
Organic carbon (%)	7.2
Clay (particles <2 μm) (%)	0.4
CaCO3 (%)	1.3
Quartz (%)	67
HAO (%)	2.2
HFO (%)	1.8
Soil particle density (g/cm3)	2.38
Specific area (m^2/g)	1.3

Table 2. Major elements and trace metals in contaminated soil.

Metals (mg/kg)	
Pb	2580±150
Zn	720±30
Cu	200±20
Cationic exchange capacity (meq/100 g)	
Total	16
Calcium	11.2
Sodium	3.96
Magnesium	0.60
Potassium	0.14

Column experiments

Solid materials were dry packed into glass chromatographic columns with 5 cm in diameter. The porous bed had a length of 20 ± 0.5 cm and a dry mass of 433 ±3 g. After packing to a uniform bulk density (1.10 ±0.01g.cm^{-3} for the roadside soil and 1.73±0.1g.cm^{-3} for the synthetic material), the columns were wetted upward with a background electrolyte solution (NaCl, 8.10^{-2} mol.L^{-1}) at a constant flow rate (3 ml.min^{-1}). Bromide tracer experiments (8.10^{-2} mol.L^{-1} in a pulse mode) were performed to identify the flow characteristics through the columns. Bromide concentrations were measured by ionic chromatography and BTC analyzed by using the method of moments and the model MIM (LTHE, Grenoble). The pore volume of soil column is V_p = 118 ± 2 mL for the roadside soil and 92 ±2 mL for the synthetic soil. Different synthetic soil columns sets were then fed with HNA (0.25 mmol.L^{-1}) and NA (0.25 mmol.L^{-1}) solutions at pH 6.6 ± 0.1 in a continuous mode at a constant flow rate (3 ml min^{-1}, Darcy velocity (q) = 0.15 cm min^{-1}). Roadside soil columns were also submitted to similar injection experiments. High Performance Liquid Chromatography (HPLC) was used to measure HNA and NA concentrations used in column eluates. Then, the trace element release from the contaminated soil was studied through the injection of HNA / NA mixture at the same flow rate and the HNA / NA transfer was characterized by UV-Vis online detection (wavelength = 254 nm). Dissolved iron and metal concentrations in the collected fractions were measured by ICP-AES. As the collected volumes were dedicated to metal analyses and the absorbance increases were observed at the same time as for single component injections, the variations of absorbance were related to naphthoic acids transfer without further HPLC analyses.

Modeling approach

The MINTEQA thermodynamic database incorporated in PHREEQC-2 formed the core to which surface complexation parameters were added. Modeling was based on the assumption that only one single type of reactive site exists on each mineral sorbent. Various physical and chemical properties of the solid adsorbent material are required before surface complexation modeling can be applied to experimental adsorption data: (i) the number of binding sites (mol of sites/ m^2 of pore volume); (ii) the specific area of adsorbent material (m^2/g) and (iii) the mass of reactive material (g/L). Surface characteristics parameters for quartz, for hydrous ferric oxide HFO and for HAO (including specific surface area, surface site density, and surface acidity constants for iron oxide) were taken from published data (Dzombak and Morel, 1990). Binding sites ≡SOH, which is responsible for all surface complexation reactions, can accept and release hydrogen ions and take part in complexation reactions with anions. The surface sites were denoted by ≡SiOH for quartz, by ≡FeOH for iron oxides and by ≡AlOH for aluminium oxides. In this study, a 1:1 stoechiometry (mononuclear surface complexes) was postulated in accord with the SCM approach developed for organic anion adsorption.

Results

The transport experiments were firstly conducted in column packed with synthetic soil. The breakthrough curves of NA and HNA were modeled with PHREEQC by fitting the surface sorption constants. One surface reaction was assumed with each of the main sorbent phases of synthetic soil (SiO_2, HFO and HAO). The corresponding surface complexation constants adjusted using SCM incorporated in PHREEQC2 are: log K_{int} = 0.05, log K_{int} = 1.1 and log K_{int} = 3.2 for ≡SiHL, ≡AlHL and ≡FeHL surfaces complexes (HNA as HL^-), and log K_{int} = 0.02, log K_{int} = 0.4 and log K_{int} = 1.5 for ≡SiL, ≡AlL and ≡FeL surfaces complexes (NA as L^-). The breakthrough curves of NA and HNA through the column packed with the roadside contaminated soil are shown in Figure 1. For NA, the point of breakthrough was at 4 V/V_p, while for HNA, breakthrough started at about 17 V/V_p and then completed at about 30 V/V_p.

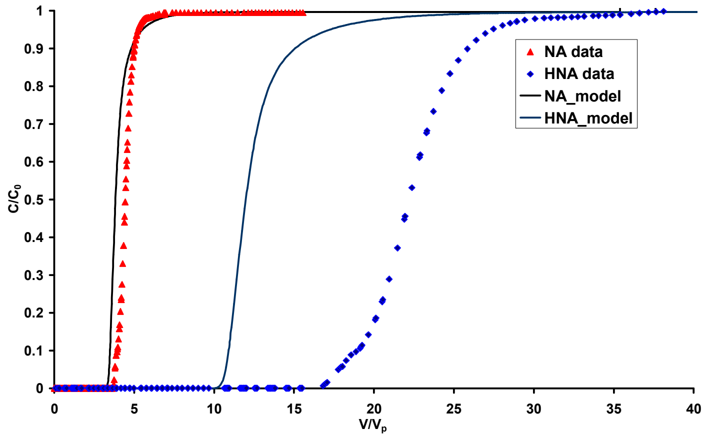

Figure 1. Experimental (symbols) and calculated (lines) breakthrough curves of HNA and NA for the roadside soil column (relative aqueous concentration of solute against the number of pore volumes (V/V_p)). Inflowing solution with $C_0 = 0.25$ mmol.L^{-1}, pH= 6.6 ± 0.1; T=20°C.

In a first approach, the acid transport was modeled with PHREEQC, implemented with the hydrodynamic parameters defined by the Br^- tracer breakthrough experiment and the adjusted sorption constants derived from naphthoic acids breakthrough experiment in synthetic soil-packed column. The agreement between the experimental breakthrough curve of NA and that calculated using the sorption parameters derived from previous experiments is relatively good (solid lines in Fig. 1). The predicted breakthrough however underestimated HNA sorption in the column system by a factor of about 3 (Figure 1). The implementation of kinetic limitations did not improve the prediction of experimental HNA elution, which seems to indicate that the kinetics may be not the cause of such discrepancy. The best fit of experimental breakthrough curves of NA in the roadside contaminated soil with sorption parameters derived from synthetic soil, led us to believe that NA may interact preferentially with polar soil mineral surfaces such as HFO and HAO. In contrast, the underpredictions observed for HNA possibly relates to sorbent fractions which are not considered in the modeling approach of breakthrough experiment of synthetic soil (e.g. organic matter fractions). Therefore, 1-Hydroxy-2-naphthoic acid can sorb to the soil mineral surfaces but also to organic matter via hydrophobic interactions. This indicated that HNA may have specific retention on soil surfaces, which dominate its mobility through soil column. The model predictions were based on model parameters derived in the laboratory for well-characterized sorbents, while the conditions met in natural and heterogeneous soils may be very different from these model systems. Moreover, the lack of local geochemical equilibrium in the column could describe the inability of the model simulation to describe outflow concentrations.

In addition, the mobilization of metals through roadside soil packed column upon HNA and NA mixture transport was monitored (Fig. 2). A slight increase of metals was observed after the elution of two pore volumes, in relation with an increase of optical density, but no significant breakthrough of mobilized metal from soil was observed as the absorbance increases at V/Vp =15. The first front could be attributed to NA breakthrough and the second one to HNA elution, the retardation factor between the two compounds being close to 5, as shown in Figure 1.

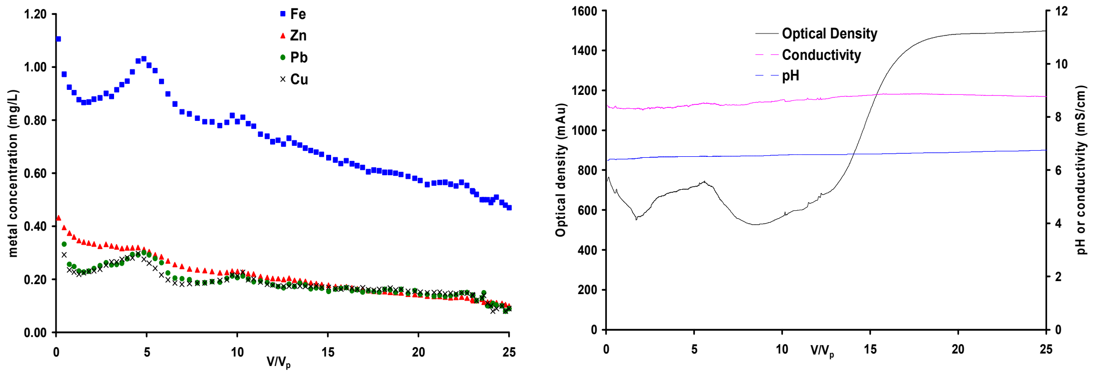

Figure 2. Experimental metal breakthrough curves (Fe, Pb, Zn and Cu) and pH, conductivity and optical density (254 nm) of the leachates from roadside contaminated soil upon injection of HNA and NA mixture.

The pH of the leachates increased slightly and then stabilized between 6.7 and 6.8. The eluted mass of trace metals, Fe, Zn, Pb and Cu remains very low by comparison with the initial content. The leaching of metal upon HNA/NA sorption is low relative to that mobilized using acetic acid (pH5) or EDTA (pH7) (Delmas *et al.*, 2002; Hanna *et al.*, 2009). This difference in metal leaching could be due to the stronger molecular chelation of EDTA towards cationic metals.

Conclusion

The multisurface modeling approach would be able to predict the transfer of organic ligands from contaminated soils and to a better understanding of the relationships between leaching and oxides surfaces properties in contaminated soils. The retention of NA in dynamic conditions (columns) could be successfully predicted through coupling aqueous transport (convection and dispersion) and retention parameters derived from synthetic soil experiment. The underpredictions observed for HNA possibly relates to sorbent fractions which are not considered in the present modeling approach (e.g. organic matter fractions). Due to its chemical structure, HNA has distinctly different sorption process toward environmental reactive surfaces than NA. In addition, the mobilization of metals through soil packed column upon HNA and NA mixture transport was found to be very low and less than that observed when weak acid solution such as acetic acid was injected. Further study is required to include a model for other important soil fractions such as soil organic matter into multisurface modeling approach.

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