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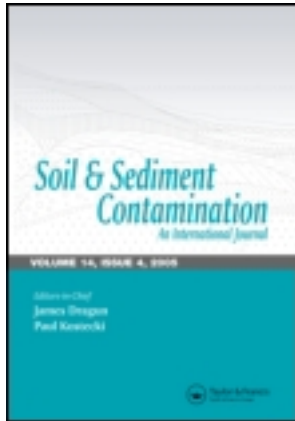
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Fate and Transport of Naproxen in a Sandy Aquifer Material: Saturated Column Studies and Model Evaluation

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Naproxen-C₁₄H₁₄O₃ is a nonsteroidal anti-inflammatory drug which has been found at detectable concentrations in wastewater, surface water, and groundwater. Naproxen is relatively hydrophilic and is in anionic form at pH between 6 and 8. In this study, column experiments were performed using an unconsolidated aquifer material from an area near Barcelona (Spain) to assess transport and reaction mechanisms of Naproxen in the aquifer matrix under different pore water fluxes. Results were evaluated using HYDRUS-1D, which was used to estimate transport parameters. Batch sorption isotherms for Naproxen conformed with the linear model with a sorption coefficient of 0.42 (cm³ g⁻¹), suggesting a low sorption affinity. Naproxen breakthrough curves (BTCs) measured in soil columns under steady-state, saturated water flow conditions displayed similar behavior, with no apparent hysteresis in sorption or dependence of retardation (R, 3.85–4.24) on pore water velocities. Soil sorption did not show any significant decrease for increasing flow rates, as observed from Naproxen recovery in the effluent. Sorption parameters estimated by the model suggest that Naproxen has a low sorption affinity to aquifer matrix. Most sorption of Naproxen occurred on the instantaneous sorption sites, with the kinetic sorption sites representing only about 10 to 40% of total sorption.

Keywords Naproxen, column sorption-desorption, transport parameters, aquifer media

Introduction

Since the early 1990s, the presence of pharmaceutical residues has been detected in aquatic environments (Daughton, 2004; Pal *et al.*, 2010; Tixier *et al.*, 2003) increasingly often. Although pharmaceuticals have been mainly detected in waters from sewage treatment plants and surface waters, widespread occurrence of a number of compounds in groundwater has been also observed. Their presence in groundwater can be attributed to different input pathways related to infiltration of non-treated or insufficiently treated water leaching from

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sanitary sewer infrastructures, water infiltration through spreading basins, etc. (e.g., Estévez *et al.*, 2012; Heberer *et al.*, 1997; Teijón *et al.*, 2010). A number of compounds are known to persist through the tertiary treatment process, with removal rates in wastewater treatment plants ranging from 3% to 90%, depending on the substance (Heberer, 2002; Lindqvist *et al.*, 2005). Many drugs behave in the solution as weak acids, weak bases, or sometimes as both (zwitterion), and are in dissociation equilibrium and ionized, depending on pH (Cairns, 2008). They may have a great mobility in groundwater media (Schaffer *et al.*, 2012). Among the most common acidic drugs found in aquatic media one can list Diclofenac, Gemfibrocil, Ibuprofen, Paracetamol, and Naproxen. The presence of Naproxen at detectable concentrations (between 35 ng L^{-1} and 3300 ng L^{-1}) in wastewater and surface waters has been documented by a number of authors (Calderón-Preciado *et al.*, 2011; Teijón *et al.*, 2010; Tixier *et al.*, 2003). Naproxen concentrations in Phaeozem and Leptosol soils in areas flood-irrigated with wastewater effluents were below 1 ng/g (Gibson *et al.*, 2010).

As the use of reclaimed water for managed (riverbank infiltration and soil aquifer treatment) or direct groundwater recharge is becoming a common practice for drinking water augmentation, increasing attention has been given by researchers to the interaction processes between drugs that exist as ionic species and porous media in order to prevent soil and groundwater contamination (Chefetz *et al.*, 2008; Drewes *et al.*, 2003; Durán-Alvarez *et al.*, 2012; Kreuzig *et al.*, 2003; Maeng *et al.*, 2011; Oppel *et al.*, 2004). Most of the research looking at the fate and transport of acidic pharmaceuticals, in particular at sorption and degradation processes, has been conducted using either batch experiments and/or undisturbed or repacked soil column experiments, covering a wide range of soils, different types of waters, porous media, and/or pH changes, to assess the leaching potential of pharmaceuticals to groundwater (Casey *et al.*, 2003; Das *et al.*, 2004; Drillia *et al.*, 2005; Scheytt *et al.*, 2004; 2006; Unold *et al.*, 2009; Yu *et al.*, 2008).

Naproxen- $\text{C}_{14}\text{H}_{14}\text{O}_3$ (Systematic IUPAC name: (+)-(S)-2-(6-methoxynaphthalen-2-yl) propanoic acid; CAS Number: 22204-53-1) belongs to the group of non-steroidal anti-inflammatory acidic drugs (NSAIDs) used increasingly worldwide to treat pain or inflammation in human beings. In its pure form, Naproxen exists as a powdered solid or crystalline powder, has a molecular weight of 230.26, an aqueous solubility of $159 \text{ (mg L}^{-1}\text{)}$ (www.chbr.noaa.gov/peiar/), a $\log K_{ow}$ of 3.18, $\text{p}K_a$ of 4.15 (Chefetz *et al.*, 2008; Tixier *et al.*, 2003), and half-life between 10 and 385 days (Araujo *et al.*, 2011). According to the $\log K_{ow}$, Naproxen is relatively hydrophilic and is dissociated in solutions at pH 6-8. The phototransformation process appears to be the main elimination process in the environment for this drug (Tixier *et al.*, 2003), with 6-O-desmethylnaproxen being its main metabolite (Selke *et al.*, 2010). Reported data from batch and column experiments with Naproxen show a high mobility of this compound in porous media with tap water and secondary treated wastewater (Chefetz *et al.*, 2008). Results from sorption experiments with various kinds of soils show a significant dependence of sorption on pH, with sorption and retardation being enhanced by a decreasing pH (Schaffer *et al.*, 2012). Sorption-desorption behavior in saturated porous media appears to also be conditioned by the ionic strength of the solution (Durán-Álvarez *et al.*, 2012). Hydrophilic interactions (cation exchange, hydrogen bonding, etc.) may greatly contribute to sorption and mobility of Naproxen in porous media, as demonstrated by Muller and Ramsburg (2011).

Although no acute-based environmental risk for aquatic organisms has been found, an enhanced phototoxicity of its transformation products has been observed for both acute and chronic exposure (Isidori *et al.*, 2005; Straub and Stewart, 2007).

In the Llobregat delta aquifer (in Spain), which is composed of unconsolidated materials, remedial measures were undertaken by directly injecting treated wastewater through wells into the aquifer to form up a hydraulic barrier (a pressure ridge along the coast) to control seawater intrusion (Cazurra, 2008). After a tertiary plus an additional treatment consisting of ultrafiltration, reverse osmosis, and UV disinfection, treated water was injected in the aquifer through four injection wells screened between 59–65 m below the ground surface. During the 2007–2010 sampling period, the average concentration of Naproxen detected in groundwater, due to its nearly constant input into the aquifer, was 170 ng L^{-1} , with a maximum of 263 ng L^{-1} (Cabeza *et al.*, 2012). Previous batch studies carried out by Teijón *et al.* (2013) with deep sandy aquifer material suggest that Naproxen has a low adsorption affinity to the aquifer material, with a measured value of the batch sorption coefficient (K_d) of $0.42 \text{ (cm}^3 \text{ g}^{-1})$. Naproxen adsorption-desorption showed a hysteretic behavior and adsorption affinity was not affected by changes of temperature. Under experimental conditions (i.e., pH 8.5), Naproxen is negatively charged (Cairns, 2008). Therefore, it has a low sorption affinity to negatively charged soil organic matter and clay minerals, while positively charged sites (e.g., Fe-Al-oxyhydroxides) are not present in the aquifer material. Consequently, Naproxen is highly mobile in the aquifer media and ionic interactions may represent important contributions to total sorption (Maeng *et al.*, 2011). Although sorption data on Naproxen from batch experiments are necessary for process understanding, miscible-displacement experiments may be more appropriate, since flowing conditions, even in the laboratory, may better represent dynamic, transient field conditions (Zhou *et al.*, 2010).

In this study, a set of adsorption-desorption, flow-through soil column experiments were performed at different flow velocities in a sandy material from the Llobregat deep aquifer using a miscible-displacement technique. The influence of different flow velocities on these processes has not been investigated and only limited information has been found on glyphosate sorption and transport mechanisms in columns of sandy soils under flowing conditions (Chefetz *et al.*, 2008). However, this information is important for the direct injection of treated wastewater into this aquifer.

The main goals of this work were to study and quantify the transport and reaction mechanisms of Naproxen in the Llobregat aquifer matrix material under different pore-water fluxes in column miscible displacement experiments, and to estimate transport parameters through numerical modeling. A two-site equilibrium/kinetic sorption model was often used to analyze observed breakthrough curves-BTCs (Brusseau *et al.*, 1992; Gamedainger *et al.*, 1990; van Genuchten and Wierenga, 1976). In this model, the sorption sites are divided into two parts, with sorption to one fraction of sorption sites governed by equilibrium, and to another fraction by first-order kinetics.

The use of process-oriented, physically based models can constitute a tool for connecting the data generated at the two scales (batch and column). A successful application of a physically based mathematical model would allow estimation of congruent transport and reaction parameters controlling Naproxen fate and concentrations in porous media to assist with management strategies. Better knowledge of processes controlling Naproxen mobility, such as residence time and the rate of approach to equilibrium in aquifer media, can be used to assess the persistence of this pharmaceutical in soil and water environments, to evaluate if it presents a risk for groundwater quality and human health, and to minimize adverse impacts following its release. Improvements in the understanding of Naproxen's fate in the subsurface can lead to more accurate predictions of its behavior in aquifer formations composed of sedimentary unconsolidated materials, and additionally can provide the basis for better understanding of processes involved in the fate and transport of similar acidic drugs.

Materials and Methods

The methodological approach consisted of several steps. First, column miscible displacement experiments were carried out consisting of an initial application of a pulse of tracer into the water-saturated columns, followed by a continuous application of Naproxen. Second, effluent solution concentrations and breakthrough curves of tracer and Naproxen were analyzed using a processed-based numerical model and model transport parameters were estimated.

Aquifer Matrix Material

All experiments employed aquifer material directly sampled from the hydrostratigraphic unit of the delta aquifer from a depth of 59 to 65 m below the ground surface, where the direct wastewater injection occurs. The aquifer material was collected from three undisturbed soil cores obtained over the course of drilling three monitoring wells in the study area. The samples were thoroughly mixed before laboratory experiments and aquifer material was air-dried (at $21 \pm 1^\circ\text{C}$). Average soil texture over the sampled profile consisted of clay (0.04%), silt (2.9%), sand (29.6%), and gravel (67.4%). To characterize the porous material, the following soil parameters were obtained in the laboratory following ASTM (1993) standards: bulk density (ρ ; g cm^{-3}), volumetric water content/porosity (θ ; $\text{cm}^3\text{cm}^{-3}$), grain size distribution, and electric conductivity (EC ; $\mu\text{S cm}^{-1}$) at a ratio of 1:5. Soil pH was determined in deionized water at a soil solution ratio of 1:5. The organic matter content was measured using the Walkley and Black method (Walkley and Black, 1934). The Cation Exchange Capacity (CEC ; $\text{mmol}_c \text{kg}^{-1}$ of solid) and exchangeable cations were measured using ammonium/sodium acetate and the ammonium acetate method, respectively (Agronomy Society of America, 1965). For the clay fraction, the mineral content and the type of clays were obtained using X-ray diffraction (Brown and Brindley, 1980) on three samples; anorthoclase and quartz dominate the clay fraction and only the illite clay mineral is present. Basic textural characteristics and physico-chemical properties of the porous material are summarized in Table 1.

Chemicals

Column experiments were carried out with Naproxen ((S)-(+)-2-(6-Methoxy-2-naphthyl) propionic acid, 98%) and Pentafluorobenzoate acid (PFB, $\text{C}_7\text{HF}_5\text{O}_2$), used as a conservative tracer in the soil column experiments, provided by Aldrich (Steinheim, Germany). Working dilutions were prepared by an appropriate dilution of the stock solution shortly before its use. Solvents used in the Naproxen solution (methanol and acetonitrile) were HPLC-grade from Carlo Erba (Milan, Italy). Sodium hydroxide for the PFB solution preparation and calcium chloride for the electrolytic solution were obtained from Panreac (Barcelona, Spain). Reagent water was obtained from a MilliQ system (Millipore Iberica S.A., Barcelona, Spain).

Chemical Analyses

Chemical analyses of Naproxen residues in water samples were carried out using the Agilent 1200 series HPLC (Agilent, USA), equipped with a diode array detector. A Luna C18 column ($5 \mu\text{m}$, $150 \times 46 \text{ mm}$) and a C18 guard cartridge (Phenomenex, Torrance, CA, USA) were used. The mobile phase consisted of acetonitrile: 20 mM KH_2PO_4 solution

Table 1
Basic soil matrix characteristics (average of three samples)

Aquifer sample		Clay fraction			
Physico-chemical		RX Mineralogy (%)		Exchangeable cations (mmol _c kg ⁻¹)	
pH (1:5, in H ₂ O)	8.5 ± 0.5	Quartz	33.3 ± 8	Ca ²⁺	13.1 ± 1.3
CEC (mmol _c kg ⁻¹)	22.5 ± 0.4	Calcite	12.1 ± 1.4	Mg ²⁺	5.1 ± 0.5
EC (at 25°C, μS cm ⁻¹)	272 ± 10	Anorthoclase	34.3 ± 5.6	Na ⁺	3.2 ± 0.3
Organic Matter (%)	<0.6	Clinocllore	7.0 ± 0.9	K ⁺	1.1 ± 0.1
Bulk Density (g cm ⁻³)	2.1 ± 0.2	Illite	7.4 ± 0.6		
Porosity (cm ³ cm ⁻³)	0.20	Dolomite	5.6 ± 0.9		

(50:50 isocratic) at a flow rate of 1 mL min⁻¹. A sample injection volume was 50 μL. UV detection was carried out at 225 nm. Retention time was 1.9 min at 20°C. The linearity of the method was evaluated in the range 0.5-500 μg L⁻¹ (regression coefficient, r² > 0.9999). A limit of detection and a limit of quantification, calculated on the ratio of signal to noise ratio of 3 and 10, respectively, were 0.1 and 0.3 μg L⁻¹. The continuous chemical analysis of PFB was carried out by a spectrophotometer (HP 8452, Waldbronn, Germany) with a diode array. Solid phase extraction was not applied for Naproxen determination, as matrix interferences were not observed.

Soil Column Experiments

For column experiments, two stainless-steel columns with lengths of 10 and 5 cm and diameters of 1.6 and 2 cm, respectively, were used. The column size selection was conditioned by the small amount of clay fraction sample available. The internal wall of columns was covered with a non-reactive material (Teflon) to provide a good contact of aquifer material with column wall with 25 μm filters at tubing connections to prevent sieving of particles. The column allowed experiments to be performed at a range of pressures between 0.1 and 25 MPa and did not interfere with the solute of interest (Lewis and Sjöström, 2010). The cylindrical steel columns were uniformly packed under vibration with air-dried soil and slowly saturated upward with the electrolyte solution (0.5 mM CaCl₂) at pH of aquifer media prior to the miscible experiments.

A peristaltic pump (Gilson[®]) was connected with Polytetrafluoroethylene (PTFE) tubing to the columns, and a 6-port stainless-steel valve (Omnifit[®]) was used to switch between different inflow solutions. Effluent solutions from the column were directed towards the spectrophotometer to allow continuous monitoring of the effluent solution concentrations or were collected in 2 mL aliquots using an automatic fraction collector (Gilson[®]) for the Naproxen chemical analysis.

A volume of 100 mL of Naproxen ($C_0 = 10 \mu\text{g L}^{-1}$) and a 100- μL pulse of PFB (25 mM) as a conservative tracer were prepared in the electrolyte solution. Four different soil columns and three flow rates of 0.06, 0.1, and 0.4 mL min^{-1} (error lower than $\pm 0.02 \text{ mL min}^{-1}$), which approximately correspond to average pore water velocities of 0.08, 0.19, and 0.7 cm min^{-1} , respectively, were used for the Naproxen adsorption-desorption (displacement) experiments. Due to technical problems (generation of air bubbles) during the small column experiment with the highest velocity (0.1 mL min^{-1}), obtained results had to be discarded and only results from three columns were considered. Different pore-water velocities were used to alter the residence time of pharmaceuticals in the column, and to evaluate their effect on the transport and fate of Naproxen in saturated porous media. A summary of the soil columns' principal characteristics and experiments is shown in Table 2.

The PFB tracer experiment was repeated three times for each column and average flow rate. The absence of dual peaks, early arrival, and long tailing in the PFB breakthrough curves were interpreted as indicative of the absence of preferential flow pathways. When a dual peak was observed, the column was discarded, repacked, and the tracer injection repeated. Tracer mass recoveries were 99%.

For the Naproxen experiments, 100 mL were injected into the water-saturated soil column. After the adsorption phase of the experiment, Naproxen was displaced from the column with the electrolyte solution until it could no longer be detected in the effluent ($C/C_0 \sim 0$) where C and C_0 are effluent and input concentrations, respectively. Naproxen mass recoveries were between 95 and 98.5% for all experiments.

Experimental methodology for soil columns thus involved four steps: (1) initial application of a pulse of 100 μL of the PFB tracer solution into the water-saturated columns to evaluate the packing of the soil column and to determine the pore volume of the column, dispersivity (λ), and the Peclet number (P); (2) subsequent displacement of PFB with the electrolyte solution at a constant flow rate; (3) continuous injection of Naproxen into the water-saturated soil column and analytical determination of Naproxen concentrations in the effluent; and (4) final displacement of Naproxen with the electrolyte solution. Finally, breakthrough curves (BTCs) were constructed from measured effluent concentrations.

Theory

Transport Model

The two-site equilibrium/kinetic sorption model with degradation (Brusseau *et al.*, 1992; Gamedainger *et al.*, 1990; van Genuchten and Wierenga, 1976) was selected. The two-site sorption model is a one-dimensional advective-dispersive transport model, which allows estimation of the rate parameters for non-equilibrium, irreversible sorption. The sorption sites are divided into two fractions, with sorption on one fraction of the sorption sites governed by equilibrium adsorption (S_1) and on another fraction by first-order kinetics (S_2). The sorption sites with instantaneous (or equilibrium, fast) sorption are usually referred to as "equilibrium sorption sites," while the sorption sites with kinetic sorption as "kinetic sorption sites." Note that both sorption sites are assumed to have the same sorption when equilibrium is also reached at the kinetic sorption sites, defined by the K_d distribution coefficient. This model is based on the idea of the heterogeneity of the soil solid phase, constituted by several different components (soil minerals, organic matter, oxides, etc.) that are likely to react with the solute at different rates and with different intensities. In the case of the PFB tracer, due to its conservative and non-reactive characteristics, an equilibrium model was used.

Table 2
Physical and chemical parameters used in the Hydrus modeling analysis; confidence intervals are also shown

	Column experiment	1	2	3
Input parameters	Length, L (cm)	5	10	10
	Diameter, ϕ (cm)	2	1.6	1.6
	Water content, θ ($\text{cm}^3 \text{cm}^{-3}$)	0.25	0.27	0.27
	Pore volume, PV (cm^3)	3.9	5.4	5.4
	Bulk density, ρ (g cm^{-3})	1.93	1.83	1.83
	Pore water velocity, v (cm min^{-1})	0.08	0.19	0.7
	Estimated parameters	Dispersivity, λ (cm) †	1.1 ± 0.2	1.1 ± 0.2
K_d ($\text{cm}^3 \text{g}^{-1}$)		0.42	0.42	0.42
k_2 (min^{-1}) †		0.01 ± 0.0038	0.00075 ± 0.00028	0.00029 ± 0.0012
F †		0.6 ± 0.274	0.87 ± 0.03	0.63 ± 0.04
Peclet number, P †		4.54 ± 0.82	9.09 ± 1.65	9.09 ± 1.65
Dispersion coef. D ($\text{cm}^2 \text{min}^{-1}$) ⁺		0.091 ± 0.016	0.2035 ± 0.037	0.792 ± 0.14
R †		4.24	3.85	3.85
R_m †		2.94 ± 0.89	3.48 ± 0.085	2.79 ± 0.11
β †		0.69 ± 0.2	0.9 ± 0.022	0.72 ± 0.028
ω †		0.79 ± 0.53	0.016 ± 0.006	0.0043 ± 0.018
Recovery (%) ‡		96	95	98.5

F - fraction of instantaneous exchange sites; R - total retardation factor; R_m - mobile zone retardation factor; β - fraction of instantaneous retardation; ω - Damkohler number.

† estimated by Hydrus.

⁺ calculated from HYDRUS-estimated values.

‡ Naproxen mass recovered in the effluent compared to the mass input.

The governing equation for the two-site sorption model, with kinetic and equilibrium sorption sites, for steady-state flow in a homogeneous medium may be written as:

$$\left[1 + \frac{F\rho K_d}{\theta} \right] \frac{\partial C}{\partial t} + \frac{k_2\rho}{\theta} [(1-F)K_d C - S_2] = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \mu_l C - \frac{F\rho K_d \mu_{s_1} C}{\theta} \quad (1)$$

where F is the fraction of instantaneous exchange sites (type-1), $(1-F)$ is the fraction of sorption sites where the sorption is time-dependent (type-2), C is the volume-averaged solution concentration [M L^{-3}], θ is the volumetric water content [$\text{L}^3 \text{L}^{-3}$] (equal to porosity for saturated conditions), K_d is the sorbed/solution distribution coefficient [$\text{L}^3 \text{M}^{-1}$], ρ is the soil bulk density [M L^{-3}], k_2 represents a first-order kinetic rate coefficient [T^{-1}], x is

distance [L], t is time [T], D is the dispersion coefficient [$L^2 T^{-1}$], v is the pore-water velocity [$L T^{-1}$], S_2 is the volume-averaged sorbed concentration at the type-2 sites [$M M^{-1}$], and μ_l and μ_s are first-order decay coefficients for degradation in the liquid and sorbed phases, respectively [T^{-1}].

The previous equation can be expressed in the following non-dimensional form:

$$\beta R \frac{\partial C_1}{\partial T} = \frac{1}{P} \frac{\partial^2 C_1}{\partial X^2} - \frac{\partial C_1}{\partial X} - w(C_1 - C_2) - \xi C_1 \tag{2}$$

$$(1 - \beta) R \frac{\partial C_2}{\partial T} = w(C_1 - C_2) - \eta C_2 \tag{3}$$

where C_1 (C/C_0) and C_2 ($S_2/(1 - F)K_d C_0$) are the relative concentrations in the liquid phase and on type-2 sites, respectively, P (vL/D) is the Peclet number, which represents the relative contribution of the advective and dispersive fluxes to transport, R_m ($1 + (F\rho K_d)/\theta$) is the instantaneous retardation factor, R ($1 + (\rho K_d)/\theta$) is the retardation factor, which represents the effect of sorption on transport and indicates relative mobility of a particular solute, β (R_m/R) is the fraction of instantaneous retardation, ω ($[k_2(1 - \beta)RL]/v$) is the Damköhler number, which represents the ratio of hydrodynamic residence time to reaction time and thus the extent of nonequilibrium conditions, ξ ($(\theta\mu_l + F\rho K_d\mu_s)L/q$) and η ($[(1 - F)\rho K_d\mu_s L]/q$) correspond to the degradation terms in the equilibrium and kinetic phases, respectively, and L is the column length [L].

The selection of the two-site sorption model was based on the sorption-desorption characteristics of Naproxen breakthrough curves that demonstrated features common for non-equilibrium processes. On the other hand, a physical non-equilibrium model was not used because of the almost symmetrical and sigmoidal shape of PFB breakthrough curves that did not show such features.

The initial and boundary conditions for the two-site sorption transport model can be written as follows:

$$\text{Initial conditions : } C(x, t) = S_1(x, t) = S_2(x, t) = 0; 0 \leq x < L, t = 0 \tag{4}$$

$$\text{Boundary conditions : } \frac{\partial C}{\partial x}(x, t) = 0; x = L; t > 0 \tag{5}$$

$$\left(-D \frac{\partial C}{\partial x} + vC\right) \Big|_{x=0} = \begin{cases} vC_0 & 0 < t < t_0 \\ 0 & t \geq t_0 \end{cases} \tag{6}$$

The numerical code HYDRUS-1D (Šimůnek *et al.*, 2008) was used to analyze the PFB tracer and Naproxen BTCs results from soil column experiments. Input parameters for curve fitting were column physical characteristics, pore water velocity, and effluent data from column experiments. The distribution coefficient, K_d , the degradation constants, μ , and the retardation factor, R , for Naproxen were independently estimated from batch sorption experiments (Teijon *et al.*, 2013). The model additionally requires the estimation of dispersivity, λ ($= D/v$), the fraction of instantaneous sorption sites, F , and the first-order kinetic sorption rate coefficient, k_2 .

Parameters Estimation

The inverse routine directly implemented in HYDRUS-1D was used to obtain the best-fit model solutions to measured BTCs and to estimate transport and reaction parameters and their confidence intervals. Values of λ were determined by fitting an equilibrium model to

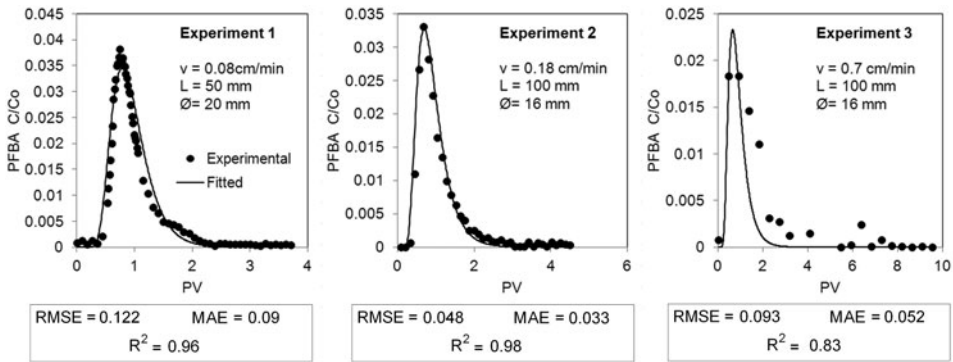


Figure 1. Experimental and modeled PFB breakthrough curves for three column experiments (L is the length of the column, ϕ is the column diameter, v is the pore-water velocity, and PV is the pore volume).

the PFB breakthrough curves and P and D were estimated from Eqs. (2) and (3). Parameters F and k_2 were determined by fitting a non-equilibrium model to the Naproxen breakthrough curves. Dimensionless variables and parameters reported in this study (such as the Peclet number, retardation factors, and parameters β and ω) were additionally calculated from the non-dimensional form of the transport equation (i.e., Eqs. (2) and (3)).

Results and Discussion

Column Experiments: Breakthrough Curves

The relative PFB and Naproxen concentrations in the effluent solution (C/C_0) versus the number of leached pore volumes (PV) are shown in Figures 1 and 2, respectively. All PFB breakthrough curves displayed only very small deviations from symmetrical shape and sigmoidal form, which suggests the absence of the physical non-equilibrium behavior. The center of the plume mass breaks through when approximately one pore volume is

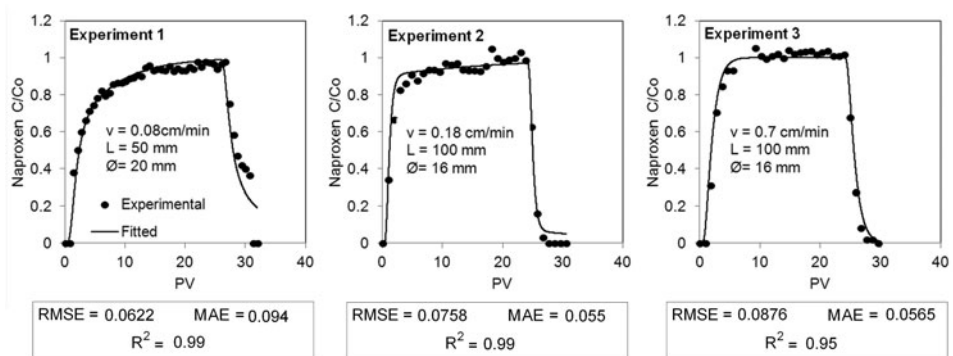


Figure 2. Experimental and modeled Naproxen breakthrough curves for three column experiments (L is the length of the column, ϕ is the column diameter, v is the pore-water velocity, and PV is the pore volume).

displaced (Figure 1). However, such small asymmetry was anticipated due to the small size of the columns. Inverse modeling with a two-region transport model with mobile and immobile waters (van Genuchten and Wierenga, 1976) tended to produce zero immobile water contents, which helped us to reject the hypothesis of physical non-equilibrium with mobile and immobile regions. Although BTCs may have been slightly affected by boundary problems related to a relatively short length of our laboratory columns, it can be concluded that PFB behaved as a conservative tracer and was not subject to physical non-equilibrium conditions (i.e., immobile regions).

Experimental BTCs for Naproxen showed a similar behavior at different pore water velocities, with no apparent hysteresis and dependence of instantaneous retardation (R_m) on pore water velocity (Figure 2, Table 2). The low partition coefficient (K_d) determined for Naproxen in our batch study (Teijón *et al.*, 2013) will thus result in a relatively early breakthrough. BTCs displayed only a limited retardation ($R_m \sim 3$) and soil sorption did not show any significant decrease for increasing flow rates as observed from Naproxen recovery. Interestingly, at lower velocities (i.e., 0.08 and 0.18 cm min⁻¹), relative breakthrough concentrations increased to only about 0.95 after the displacement of 20 PV, while at the highest velocity (i.e., 0.7 cm min⁻¹), this value was attained after only about 10 PV. The gradual increase of relative concentrations behind the concentration front (referred to in the literature as tailing), which was observed for the two lower flow rates, reflects the kinetic sorption at the type-2 sorption sites. On the other hand, the flow rate in the column with the highest pore water velocity was such that the kinetic sorption process was no longer visible in the breakthrough curve, which did not display similar tailing as BTCs for lower flow rates. At high flow rates, the residence time of Naproxen in the column was too short for the effects of the kinetic sorption process to be visible in the BTC.

No data involving column displacement experiment has been found in the literature for Naproxen. However, under water-saturated conditions of sand column experiments (Mersmann *et al.*, 2002; Scheyt *et al.*, 2004) and for the acidic drug Diclofenac, which has similar physico-chemical characteristics as Naproxen, similar breakthrough curves, displaying minimal degradation and retardation ($R = 2.6-2$) were observed. In their experiments, medium sand aquifer sediment (with no clay) with a higher organic matter content, groundwater, and velocities higher than the values applied in our experiment were used.

BTCs Modeling and Model Parameters

Comparisons between the experimental and calculated BTCs for several displacement experiments and goodness-of-fit results are shown in Figures 1 and 2. Correspondence between simulated and observed data was guided by visual inspection and statistical measures. The low values of the RMSE (root mean square error) and MAE (mean absolute error) and the high value (>95%) of R^2 (coefficient of determination) confirmed that the model was able to successfully simulate experimental data.

Parameters fitted to the experimental Naproxen breakthrough curves are summarized in Table 2. Relatively narrow confidence intervals were obtained for optimized parameters. In order to improve uniqueness of optimized parameters, it is often recommended to limit the number of optimized parameters and to determine the majority of them by independent measurements. For example, the distribution coefficient K_d can be determined by conducting laboratory batch experiments, the dispersion coefficient D by fitting the tracer BTCs using an equilibrium transport model. Then, only the fraction of sorption sites with instantaneous sorption F and the sorption kinetic rate k_2 need to be curve-fitted against the BTCs of Naproxen.

Optimized values of F , the fraction of instantaneous sorption sites, show that most sorption occurs on the instantaneous sorption sites; estimated F values suggest that the fraction of equilibrium sites is between 60 and 90%. For the long column experiments ($L = 10$ cm), the F parameter shows the expected trend of having more instantaneous sorption sites for the smaller flux than for the larger one. Since for slower fluxes the solute residence time in the column is larger, it is expected that more adsorption sites will reach equilibrium than for faster fluxes. Although the F value for the short column with the low water flux was similar to that for the long column with the highest velocity (0.7 cm min^{-1}), estimation errors are much larger than those for the other columns.

The ω value, the Damköhler number for the same column length ($L = 10$ cm), varies inversely with velocity; smaller ω values correspond to the fastest velocities. Sorption non-equilibrium effects, as indicated by $\omega < 1$, are similar at different velocities, decreasing for faster velocities. However, the existence of non-equilibrium sorption sites does not influence the retardation factor, R , and has no effect on the mean solute velocity. It was observed that the first-order rate constant, k_2 , is dependent on water flux and, apparently, also the column length. The value of k_2 decreases as pore water increases, and the highest values were obtained for the short column. This result is unexpected, since only the sites with the slowest sorption rates are included into the class of kinetic sites for lower fluxes, while for larger fluxes a broader range of sites is included into this class of sorption sites.

Naproxen adsorption-desorption in the aquifer matrix proved to be process-dependent on pore water velocities and on the residence time of the soil solution in the soil column. Most sorption of Naproxen occurred on instantaneous sorption sites, with the kinetic sorption sites representing only about 10 to 40% of total sorption. The lower the pore water velocity, the longer the contact time between the Naproxen soil solution and soil particles, and the more extensive the exchange phenomena.

Taking into account the half-life reported in the literature (~ 364 days in darkness; Araujo *et al.*, 2011) and the duration of our laboratory experiments (less than two days for the slowest velocity), it was expected that degradation would play only a minor role in our experiments and could be neglected; i.e., μ_l and μ_s were assumed to be zero. Naproxen degradation is in this case unlikely to occur during the time scale of the column experiments, and abiotic processes (such as chemical immobilization) are likely responsible for any mass loss (mass recovery is between 95 and 98.5%, as reported in Table 2).

Chemical mechanisms responsible for the mass loss that need to be considered when simulating the experimental data should be related with the nature of Naproxen sorption processes. Under the experimental conditions, Naproxen predominantly exists in anionic form and is therefore negatively charged, presenting a low adsorption affinity to the soil organic matter and clay minerals (Schaffer *et al.*, 2012). This is consistent with other results presented in the literature for sandy soils with a low organic matter content (Chefetz *et al.*, 2008), Ottawa sand (Muller and Ramsburg, 2011), and similar experimental conditions (Durán-Álvarez *et al.*, 2012). Mechanisms governing sorption of ionizable and ionic pollutants are similar to those occurring for inorganic contaminants (precipitation, cation exchange, cation bridging at clay surfaces, surface complexation, chemical immobilization, hydrogen bonding, etc.). A detailed analysis of reaction pathways and mechanisms of sorption reactions requires further investigation.

Conclusions

Detailed examination of experimental and modeling results leads to some important conclusions about mechanisms involved in Naproxen adsorption-desorption. Although Naproxen

adsorption in the aquifer material is predominantly an instantaneous process, there is some evidence that soil sorption decreased at increasing flow rates, corresponding to increasing non-equilibrium effects. Average pore water velocities in our column experiments were not slow enough to provide sufficient solute residence time for the attainment of near-equilibrium conditions.

No significant differences were observed between the retardation factors optimized for the column experiments and those evaluated from batch equilibrium tests. Having the distribution coefficient from batch experiments allowed us to limit to three the number of optimized parameters related to dispersion (dispersivity λ) and kinetics of the sorption process (fraction of instantaneous sorption sites F , and first-order kinetic sorption rate coefficient k_2), thus avoiding over-parameterization. This confirms the fact that batch equilibration studies are an important technique for estimating the input equilibrium parameters for kinetic transport models.

The selected two-site sorption transport model has been able to successfully simulate Naproxen breakthrough curves for laboratory column experiments under saturated conditions. In this particular case, the model assumed a porous medium that was homogeneous in terms of physical, chemical, and biological processes, which can be acceptable for such small-scale laboratory studies. Obviously, this assumption is not likely to be true for almost any real-world, large-scale, field applications (Candela *et al.*, 2010; Oppel *et al.*, 2004). Yet, given the conditions typically present in the deep-aquifer, coarse-textured, sandy materials, which are highly permeable and contain low organic matter and clay contents, the principal mechanisms affecting Naproxen transport through the vadose and groundwater zones may include, in addition to chemical non-equilibrium, physical non-equilibrium as well.

At the field scale, when reclaimed wastewater is applied at the soil surface via irrigation, preferential flow pathways and soil heterogeneity will be of decisive importance for the transport of the contaminant through the vadose zone (Gibson *et al.*, 2010). Transport behavior under such conditions may deviate from saturated conditions (Scheytt *et al.*, 2006).

Our results may also contribute to better understanding of the fate of similar acidic compounds, which also enter aquifer materials via direct aquifer recharge and storage.

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