Mobility of ibuprofen, a persistent active drug, in soils irrigated with reclaimed water

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ABSTRACT

Ibuprofen is not completely removed in wastewater treatment plants, and consequently, it may enter the soil through irrigation with reclaimed water. Subsequently, due to the reversible adsorption which takes place in the soil, this emerging pollutant can become bioavailable for plants. The adsorption reversibility of this anti-inflammatory compound on four agricultural soils was quantified with adsorption-desorption experiments. The adsorption was found to be almost linear, with a minimum n_{ads} of 0.76 and a maximum of 1.08. In contrast, desorption was nonlinear, with a n_{des} which ranged from 0.84 to 2.75. The hysteresis index values were low, ranging from 0.42 to 0.66; hence the process takes place reversibly. In addition, ibuprofen was found to be moderately fixed in the soils studied, with organic carbon distribution coefficient (K_{OC}) values which ranged between 139.75 and 238.17 L/kg. Therefore, we conclude that this pollutant could be bioavailable for soil microorganisms or plants exposed to it and may reach groundwater by leaching.

Keywords: adsorption-desorption analgetic substance; pharmaceutical; Freundlich; Langmuir; linear isotherm models

Due to the water scarcity, increasing attention has been focused on the reuse of reclaimed urban wastewater for agricultural purposes since around 70% of freshwater is currently used for crop irrigation (Zimmerman et al. 2008). However, application of wastewater in agriculture may pose potential risks to the environment, as wastewater treatment plants have a limited capacity to remove organic chemicals (Bueno et al. 2012). Moreover, the application of sludge or fertilisers on agricultural soils represents another source of organic contamination in soils (Vácha et al. 2005, 2006).

Ibuprofen is one of the most widely consumed anti-inflammatory drugs in the world and reaches the environment because it is excreted in urine unchanged. It is one of the most frequently found drugs in environmental samples, and appears at the highest concentration levels (Bueno et al. 2012). The presence of this pollutant in the environment has been extensively studied, including an analysis of its presence in the food-chain, where it has already been detected (Calderón-Preciado et al. 2012). The persistence of ibuprofen implies that it may behave conservatively once reaching subsurface soils where anaerobic conditions may be prevalent. Furthermore, although this pollutant can be subject to microbial degradation in surface soil under aerobic conditions (Winker et al. 2010), both the poor adsorption and short residence times reported suggest that it may readily move downward (Lin and Gan 2011). Thus, groundwater contamination can take place, depending on soil properties such as organic matter content, clay content and pH (Xu et al. 2009). This transport of ibuprofen in soils is controlled by the adsorption-desorption equilibrium. Soil sorption parameters are often determined by conducting sorption isotherm experiments to estimate the soil's sorption capacity or retardation coefficients, which can then be used in transport modelling. The accuracy of

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the model's parameters will depend on whether the appropriate conceptual model was chosen (Bolster and Hornberger 2007).

Adsorption is an important mechanism for the removal of ibuprofen whenever it is present in soil (Karnjanapiboonwong et al. 2011). Previous research has shown that ibuprofen adsorption on soils is very low and generally less than that for other emerging contaminants (Dobor et al. 2012). Hence, any ibuprofen added to the soil through irrigation with reclaimed water is not completely removed, and can become bioavailable for organisms in the environment.

The aim of our research was to compare the three main models for describing ibuprofen adsorption by soils, and to estimate the mobility of this pollutant in four agricultural soils by analysing the results of adsorption and desorption assays and the desorption parameters obtained from these experiments. The importance of this study lies in the use of assessment of the mobility of this toxic compound as a tool for evaluation of the risk associated with its accumulation and dispersion in the environment.

MATERIAL AND METHODS

Experimental soils. The adsorption-desorption experiments were carried out on four surface samples of soil (0–30 cm), A, B, C and D, collected from an experimental plot in Carrión de los Céspedes, Seville, Spain. These soils were selected as a representative sample of the area of study, which is characterised as a land application system for use in future studies by the research group. The samples were dried naturally and sieved by passing them through a 2-mm sieve. The main physical and chemical properties were determined and are listed in Table 1.

Chemicals. Ibuprofen ((*RS*)-2-(4-(2-methylpropyl)phenyl)propanoic acid) was purchased from the Sigma-Aldrich (Madrid, Spain).

Batch adsorption-desorption experiment. A stock solution of 1000 mg/L of ibuprofen was prepared by dissolving 100 mg of ibuprofen in 1 mL of methanol and adding deionised water to a final volume of 100 mL. The amount of methanol was less than 0.1% (v/v) to avoid co-solvent effects. Five grams of air-dried soil were each placed into a separate 60 mL amber glass bottle (it is worth noting that ibuprofen can bind to polypropylene) in triplicate and equilibrated with 25 mL of a solution containing 0, 0.5, 1, 2, 5 and 10 mg/L of ibuprofen, previously diluted in a background solution of calcium chloride and sodium chloride at a total concentration of 20 mmol/L. Three blank runs were also included, consisting of ibuprofen with no soil, in order to verify that no ibuprofen was adsorbed by glass. The experiments were carried out at 25°C. After shaking for 24 h on a horizontal shaker, the contents were centrifuged at 2000 rpm for 10 min. The supernatants were filtered through a 0.45-µm pore size filter and decanted into 100-mL glass bottles. Desorption was performed by replacing the supernatant with fresh background solution in a 60-mL amber glass bottle, after drying the soil. Then, the bottles were shaken for 24 h on a horizontal shaker, the contents were centrifuged at 2000 rpm for 10 min, and the supernatants were filtered through a 0.45-µm pore size filter and decanted into 100-mL glass bottles.

Ibuprofen concentration was determined using HPLC-UV (1200-Series, Agilent Technologies, California, USA) equipped with a Phenomenex C-18 column (15 cm × 4.60 mm, 5 µm), at a flow of

Table 1. Characteristics of soils used in the experiments

	Soil A	Soil B	Soil C	Soil D
pH	7.63	7.85	7.95	8.01
Electrical conductivity (dS/m)	0.20	0.20	0.24	0.14
$CaCO_3$ (%)	0.21	0.13	0.18	0.15
C_{ox} (%)	0.87	1.74	1.42	1.32
Sand (%)	42.50	47.50	45.00	37.50
Silt (%)	30.00	32.50	40.00	50.00
Clay (%)	27.50	20.00	15.00	12.50
Texture	Clay loam	Loam	Loam	Loam

2 mL/min of 37:63 acetonitrile:water (pH 2.5 by orthophosphoric acid) and detected by a UV absorbance detector (Kyoto, Japan) using 210 nm wavelengths and the retention time observed was 27 min.

Data analysis. A nonlinear regression was performed using the Solver Add-In function (Bolster and Hornberger 2007), obtaining the adsorption and desorption parameters of the Langmuir (1); Freundlich (2) and Linear isotherm (3) models and model efficiency, *E* (4):

$$c_{\mathrm{sorb}} = \frac{K_L c_{\mathrm{sorbmax}} c_{\mathrm{eq}}}{1 + K_L c_{\mathrm{eq}}} \qquad (1)$$

$$c_{\mathrm{sorb}} = K_F {c_{\mathrm{eq}}}^n \qquad (2)$$

$$c_{\mathrm{sorb}} = K_d c_{\mathrm{eq}} \qquad (3)$$

Where: c_{sorb} – sorbed concentration (mg/kg); c_{sorbmax} – maximum adsorption capacity of the soil (mg/kg); K_L (L/mg) and K_F [(mg/kg)/(mg/L)^n] – Langmuir and Freundlich adsorption and desorption coefficients; c_{eq} – equilibrium concentration (mg/L); n – linearity constant (dimensionless), and K_d – solid-water distribution coefficient (L/kg).

$$E = 1 - \frac{\sum_{i=1}^{N} w_i (c_{\mathrm{sorb}i} - c_{\mathrm{sorbmod}i})^2}{\sum_{i=1}^{N} (w_i c_{\mathrm{sorb}i} - c_{\mathrm{sorbwavg}})^2} \qquad (4)$$

Where: N – number of observations; w_i – i^{th} weighting factor ($w_i = 1/(c_{\mathrm{sorb}})^2$); c_{sorb_i} – i^{th} measured value of the dependent variable; c_{sorbmod_i} – i^{th} model-predicted value of the dependent variable, and $c_{\mathrm{sorb}_{\mathrm{wavg}}}$ – weighted mean of the measured values.

The apparent adsorption-desorption hysteresis was quantified for each of the isotherms using the hysteresis index (dimensionless) *H* (5), defined by Huang et al. (1998):

$$H = \frac{(c_{\mathrm{desorb}})_{\mathrm{avg}}}{(c_{\mathrm{sorb}})_{\mathrm{avg}}} \qquad (5)$$

Where: $(c_{\mathrm{desorb}})_{\mathrm{avg}}$ and $(c_{\mathrm{sorb}})_{\mathrm{avg}}$ – mean values of the desorbed and adsorbed concentrations for all points of the isotherm experiment, respectively. The organic carbon distribution coefficient, K_{OC} (6) was calculated from K_d and the organic carbon fraction (f_{OC}) of the soil, as shown in the following equation, expressed in L/kg (Schwarzenbach et al. 2003):

$$K_{\mathrm{OC}} = \frac{K_d}{f_{\mathrm{OC}}} \qquad (6)$$

RESULTS AND DISCUSSION

The control assays performed showed that degradation processes did not take place and the glass did not adsorb ibuprofen during the experiment, so we can conclude that the experimental concentrations used were conserved during the assay. We also obtained the chromatogram corresponding to the soil solution with the background solution, and no interference was observed, since no peak appeared for ibuprofen retention time under the chromatographic conditions used.

Adsorption. The adsorption isotherms of ibuprofen are depicted in Figure 1, and Table 2 summarises the fitting parameters of ibuprofen adsorption using the nonlinear Freundlich and Langmuir equations with the aid of the Solver Add-In function, and Linear isotherms. To compare the fit of our experimental data to these equations, we studied model efficiency, E, as described by Trakal et al. (2011), who also compared models for describing adsorption processes on soils. The results can be seen in Table 2. The values for E ranged from 0.430 to 0.986, from –3.036 to 0.999 and from –0.285 to 0.999 for the Freundlich, Langmuir and Linear isotherm models, respectively. According to these results, the model that gives the best fit to describe ibuprofen adsorption by soils is the Freundlich model because it obtained efficiency values closest to 1. This model is the most widely used for describing ibuprofen adsorption by soils (Dordio et al. 2009). The values lower than 1 obtained for the Langmuir and Linear isotherm models indicate that a better prediction would be obtained by taking the average of all the measured values, rather than by using either model alone. Although the Langmuir model does not completely explain the phenomenon, it was observed that the soil with the highest value of maximum adsorption, 76.6, corresponded to soil B, which was also the soil with the highest value of organic matter content, 3.51%, whereas soil C, with the lowest value of maximum adsorption, 38.2, was the soil with the lowest clay content, 15.0%. These results are to be expected because both organic matter and clay content are usually directly related to adsorption of contaminants in soils (Xu et al. 2010), although other studies have reported that clay content does not play a major role (Lin and Gan 2011). It can be seen from the Freundlich adsorption parameters that adsorption was low, as indicated by the Freundlich constant, $K_{F\mathrm{ads}}$, with values between 1.05 and 2.26, similar to reported data for adsorption of ibuprofen on sediments (Styszko et al. 2010). The results for n_{ads}, from 0.76 to 1.08, indicated that the processes were almost linear, in agreement with the results obtained for a soil with similar properties (Xu et al. 2009).

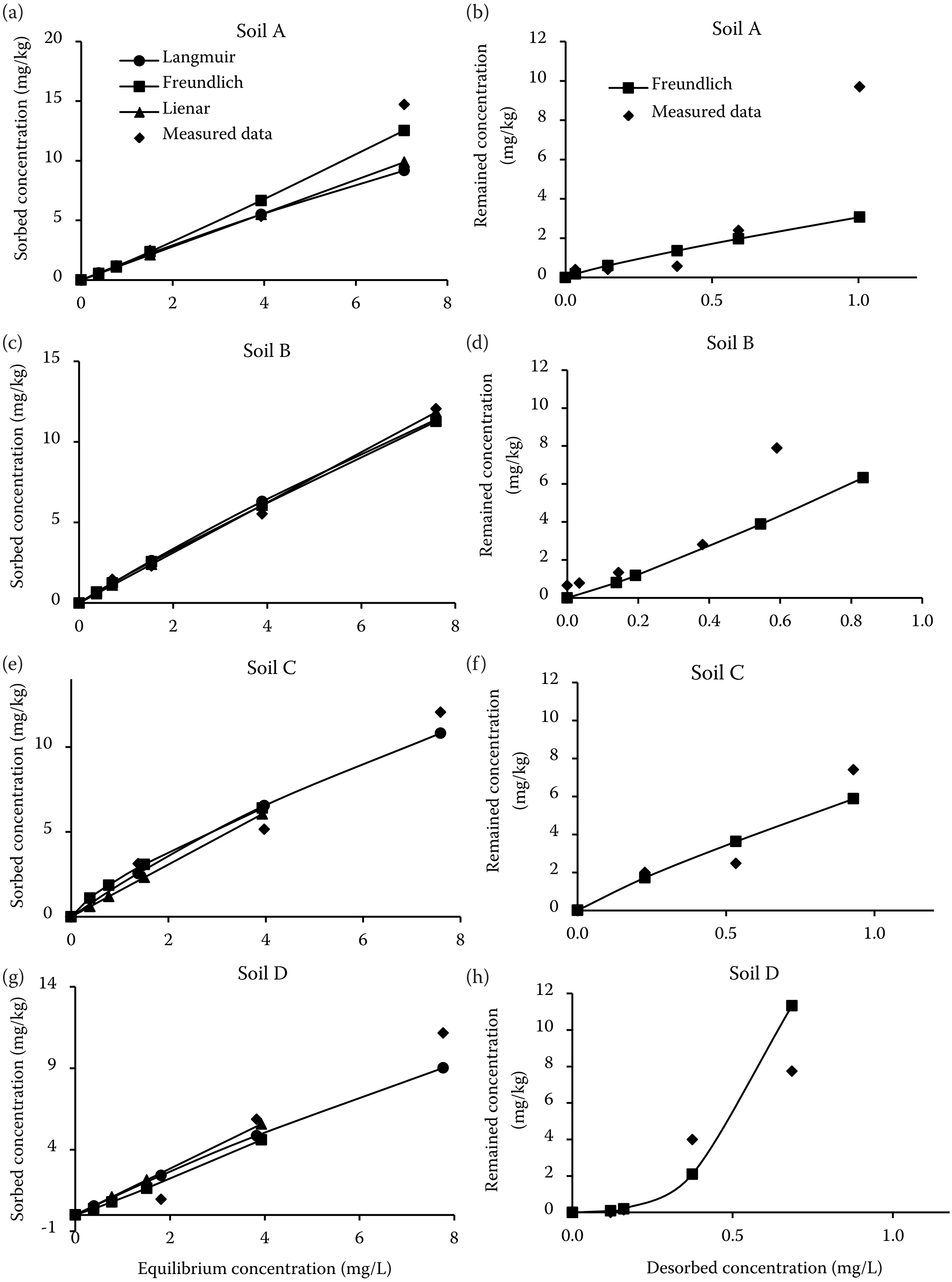

Figure 1. Adsorption isotherms for ibuprofen fitted at Langmuir, Freundlich and Linear models for soil A (a); soil B (b); soil C (c) and soil D (d), and desorption isotherms for ibuprofen fitted at Freundlich model for soil A (e); soil B (f); soil C (g), and soil D (h)

Table 2. Sorption and desorption parameters of ibuprofen in the four soils used in the experiment

Soil	Adsorption									Desorption		
	Langmuir			Freundlich			Linear			Freundlich		
	$c_{sorbmax}$	K_L	E	n	K_F	E	K_d	E	K_{OC}	n	K_F	H
A	59.2	0.026	0.999	1.08	1.52	0.840	1.40	0.999	173.21	0.84	3.66	0.52
B	76.6	0.023	0.996	0.93	1.71	0.986	1.56	0.998	217.92	1.15	7.80	0.43
C	38.2	0.052	–3.036	0.76	2.26	0.790	1.54	–0.285	238.17	0.87	6.26	0.42
D	5.3	0.264	0.982	1.07	1.05	0.430	1.42	0.950	139.75	2.79	32.56	0.66

$c_{sorbmax}$ – maximum adsorption capacity; K_L – Langmuir adsorption coefficient; E – model efficiency; n – linearity constant; K_F – Freundlich adsorption and desorption coefficient; K_d – solid-water distribution coefficient; K_{OC} – organic carbon distribution coefficient; H – hysteresis index

The solid-water distribution coefficients (Table 2), K_d, were very similar for the four soils, ranging from 1.40 to 1.56 L/kg. The values obtained, above 1, indicate that adsorption increased as equilibrium concentrations increased, and thus there were differences between the K_d and the Freundlich constants, because of the nonlinearity of the isotherms. This was probably due to a higher affinity to water than to the soil when the solute concentrations were low. The values for this parameter were higher than those reported by Lin and Gan (2011), who found values close to 1 for K_d for ibuprofen adsorption on two soils. They are also similar to the values obtained by Radjenović et al. (2009) for primary and secondary sludges, but more than 100 times lower than the data reported by Hörsing et al. (2011) in their study of drug sorption on sludges. The K_{OC} values for the four soils were moderate (Table 2), ranging from 139.75 to 238.17 L/kg, similar to results obtained for sandy sediments (Scheytt et al. 2005) and higher than the results reported for soils (Xu et al. 2009). These values indicate that ibuprofen is moderately fixed in the soil.

Desorption. The desorption isotherms of ibuprofen are shown in Figure 1. For the soils A and B, the last points of the measured data are higher than those predicted by the Freundlich model, which demonstrates that the desorption is overestimated by this model for these concentrations. For this phenomenon (the results are presented in Table 2) higher values for the Freundlich constants, K_{Fdes}, were obtained (3.66–32.56), showing a stronger retention of ibuprofen on soil particles in desorption processes than in adsorption processes. The desorption process was nonlinear, as indicated by n_{des} values, which ranged from 0.84 to 2.79, suggesting differential distribution of adsorption site energies, as Soukup et al. (2004) found for isoxaflutole sorption on soils. The low hysteresis index, H, values, which ranged from 0.42 to 0.66, indicated that ibuprofen adsorption in soils was reversible and that hysteresis occurred during desorption. Therefore, ibuprofen might be leached through the soil profile and contaminate groundwater, or become bioavailable for organisms.

In conclusion, the adsorption-desorption processes for ibuprofen were studied in four agricultural soils. The results showed that the Freundlich model is better than the Langmuir and Linear isotherm models for describing ibuprofen adsorption by soils, and thus the adsorption-desorption phenomenon can be explained by using this model. The parameters obtained from the desorption experiments revealed that adsorption was stronger in the desorption process than that observed in adsorption processes. Ibuprofen in the studied soils was found to be moderately fixed in the soil, and the almost linear adsorption took place reversibly, with low hysteresis index values. These results demonstrate that the pollutant might be bioavailable for plants and microorganisms exposed to it, and may reach groundwater by leaching.

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