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Esmeralda Estevez, Jose Manuel Hernandez-Moreno, Juan Ramon Fernandez-Vera, Maria Pino Palacios-Diaz

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IBUPROFEN ADSORPTION IN FOUR AGRICULTURAL VOLCANIC SOILS

Esmeralda Estevez[1], Jose Manuel Hernandez-Moreno[2], Juan Ramon Fernandez-Vera[3] and Maria Pino Palacios-Diaz[4]

1 Department of Physics, Universidad de Las Palmas de Gran Canaria, 35017 Las Palmas de Gran Canaria, Spain.
2 Department of Soil Science and Geology, Universidad de La Laguna, 38204 La Laguna, Spain.
3 Laboratorio Agroalimentario y Fitopatológico del Cabildo de Gran Canaria, 35413 Arucas, Spain.
4 Department of Animal Production, Universidad de Las Palmas de Gran Canaria, 35413 Arucas, Spain. +34928454353, mpalacios@dpat.ulpgc.es

ABSTRACT

Ibuprofen (IB) is a high environmental risk drug and one of the most frequently prescribed in human medicine. Recently, IB has been detected in Gran Canaria in reclaimed water for irrigation and in groundwater. Adsorption was studied in four volcanic soils from three islands of the Canarian Archipelago. Once the biodegradation process has been excluded from the experimental conditions, a batch method was applied using initial concentrations of 1-5-10-20-50-100-200 mgL^{-1} and two soil/water ratios (w/V): 1:5 (OECD, 2000) and 1:1. Non-linear and linearized Langmuir and Freundlich equations were well fitted. The wide IB range tested in our batch studies allowed us to measure experimental adsorption values close to the maximum adsorption capacity (S_{max}) as estimated by Langmuir, making it possible thereby to validate the use of the Langmuir equation when there is a burst of contamination at high concentration. The distribution coefficient (K_d), S_{max} and Retardation Factor (R_F) varied from 0.04 to 0.5 kgL^{-1}, 4-200 mgkg^{-1} and 1.2-1.9, respectively. The lowest S_{max} and K_d values were found for the 1:1 S/W ratio whereas most batch studies employ 1:5 S/W ratios, thus obtaining higher adsorption parameters than when considering field conditions (1:1). Despite the high anion retention of andic soils, similar K_d and R_F to those reported for other soils were obtained in 1:5, while high S_{max} was found. Our results demonstrate that IB adsorption in volcanic areas responds not only to the soil properties commonly cited in adsorption studies, but also depends on andic properties, sorbent concentration and Dissolved Organic Carbon, the higher values of which are related to the lower K_d and S_{max}. The low R_F and low detection frequency of the IB in groundwater suggests that a)reclaimed water irrigation is not the main source of IB, and b)the existence of some uncontrolled water disposal points in the zone.

Keywords: ibuprofen, adsorption, soil properties, Freundlich, Langmuir, volcanic soil.

1. Introduction

Ibuprofen, IB, ((RS)-2-[(4-2- methylpropyl)phenyl] propanoic acid, CAS number: 15687-27-1) is a non-steroidal anti-inflammatory drug (NSAID) and one of the "Essential Drugs" listed by the World Health Organization (http://www.who.int/medicines/publications/essentialmedicines/en/ index.html).

Its consumption in Spain increased from 0.39 in 1992 to 21.30 defined daily dose (DDD)/1000 habitants per day in 2006 (AEMPS, 2006). It was the second NSAID and the third active compound most consumed in terms of number of packs sold in 2009 (DGFPS, 2009).

Given the widespread occurrence of IB in aquatic environments, its potential for ecological impact has become a matter of growing concern (Christensen et al., 2009). IB has been proposed as a priority substance to be identified under the Water Frame Directive. However, the inclusion of IB was rejected in January 2012 due to lack of evidence of significant risks to aquatic environments (EC, 2012). In spite of this, IB in the water environment has been shown to affect reproduction in both vertebrates and invertebrates (Han et al., 2010; Hayashi et al., 2008), the growth of several bacterial and fungal species (Pomati et al., 2006), the genotoxic effects for fish (Ragugnetti et al., 2011) and cyto-genetic effects in freshwater bivalves (Parolini et al., 2011).

The entry routes of pharmaceutical compounds (PCs) into the environment are related with wastewater treatment plants (WWTPs), septic tanks, hospital effluents and animal excreta (Kümmerer, 2004; Daughton and Ternes, 1999). In Spain, IB is frequently detected in WWTP effluents (Martinez-Bueno et al., 2012) and at higher levels than expected (Ferrando-Climent et al, 2012). The environment concentration in sediments and soils is in g kg^{-1} and in surface water and groundwater is within a range from ng L^{-1} to µg L^{-1} (Lapworth et al., 2012; Hernando et al., 2006). This ubiquitous contaminant has been found at concentrations greater than 0.1 µg L^{-1} in Spanish aquifers (Cabeza et al., 2013; Jurado et al, 2012).A recent study carried out in Gran Canaria detected IB concentrations below 100 ng L^{-1} in reclaimed water employed to irrigate a golf course and 50 ng L^{-1} in groundwater corresponding to the subjacent aquifer (Estevez et al., 2012).

The main removal mechanisms for IB are biodegradation and sorption. There are several studies on IB biodegradation in batch experiments and real WWTPs (Borges et al., 2011; Caviglioli et al., 2002; Gagnon et al., 2008; Onesios et al., 2009; Quintana et al., 2005; Winkler et al., 2001). Zwiener et al. (2002) concluded that the IB transformation products (TPs) account for less than 10% of the initial concentration in their degradation experiments in both biofilm reactors (BFR) and batch experiments with activated sludge. Collado et al. (2012) pointed out the time-effect on the transformation rate of IB on its

TPs relative to IB input, which declines from 32% (after 24 h) to 3% (after 72 h). Highly mobile organic compounds have the potential to leach into groundwater, whereas strongly sorbing PCs can accumulate in top soil layers. Therefore, adsorption is a determining process in the environmental fate of organic chemicals in soils (Pignatello and Xing, 1995). The extent of adsorption is related to the physicochemical properties of contaminants and another factors such as the soil organic matter content (OM), surface adsorption to mineral constituents, ion exchange capacity, H-bonding, pH and complex formation with metal ions such us Ca, Mg, Fe and Al (Drillia et al., 2005; Karickhoff et al., 1979). Several studies have demonstrated the low sorption affinity of IB in soils (González-Naranjo et al, 2013; Lin and Gan, 2011; Xu et al., 2009).

Volcanic soils frequently present large amounts of short-range-ordered minerals (allophane, Fe and Al oxyhydroxides) and/or Al–humus complexes (Tejedor et al., 2009). These components determine a high reactivity due their large surface areas and bonding capacity for anions and cations. The phosphate retention is used as an index of this reactivity. These properties are defined as “andic”, whose higher expression is found in Andisols (Soil Survey Staff, 1999). A large macro- and mesoporosity, associated to a strong aggregation, is also common in andic soils, which favours the preferential flux of solutes. However, the amorphous components tend to crystallize with time (tens of thousands years) and the andic properties are increasingly lost. Soil management can also lead to a loss of the andic properties through a decrease of bulk density or the anion binding capacity; in consequence, the soil classification can easily shift to another soil Order (Tejedor el al., 2009). In the Soil Taxonomy System, andic properties (attenuated) appear at the Subgroup level of some soil Orders.

The aim of this paper is to determine the adsorption behaviour of IB in four volcanic soils from the Canary Islands under similar conditions to those used on agricultural farms. Another objective was to calculate adsorption parameters in extended concentration ranges. Furthermore, this work discusses exhaustively the regression methods and determines the best fit to the experimental equilibrium data by comparing the parameters provided by linear and non-linear models of the Langmuir and Freundlich isotherms.

2. Material and methods

2.1. Chemicals

IB sodium salt (98% purity) was purchased from SIGMA-Aldrich® (Spain). Some characteristics of IB are included in Table 1. Acetonitrile and methanol (HPLC, gradient grade) orthophosphoric acid, calcium chloride dihydrate and sodium chloride were purchased from Panreac (Spain), and deionised water was prepared in a Milli-Q purification system (Millipore).

The stock standard solution of IB (1g L^{-1}) was prepared by dissolving 110 mg of the IB sodium dehydrated salt in 2 ml of methanol and thereafter in 100 ml of distilled water. The amount of methanol added to the batches was maintained at < 0.4% of the liquid volume to avoid co-solvent effects. Working solutions (1-5-10-20-40-50-100-200 mg L^{-1}) were prepared by diluting the stock solution with a 0.01 M equimolar solution of $CaCl_2$ and NaCl prepared in distilled water.

2.2. Soil Samples

Surface soils were collected over four locations on the Canary Islands (Figure S1). The first came from an irrigated field on the El Hierro island (EH) and can be classified as Torriarents (Soil Survey Staff, 1999) with andic properties (including volcanic glasses). Two soils were sampled in a golf course situated on the NE coast of Gran Canaria, and both have been irrigated with reclaimed water since 1976. One of these soil samples represented the original soil of the golf course area: GC1, and the other one was sampled in fairways covered with transported soils from the middlands of the NE of the island: GC2 (Estevez et al., 2010). Soil GC1 is a Torriarents (adjacent natural soils are vitritorrands) and the transported soil GC2 corresponds to an Ustalfs dominated zone. The fourth soil, FV, from Fuerteventura Island was sampled from a wastewater-irrigated field in the SE area of this arid island. This carbonate-rich soil can be classified as Torriarents. After collection, soil samples were stored at 4ºC until use. All the soils were air-dried, homogenised and sieved through 2-mm meshes for the laboratory analysis. The main physical and chemical soil characteristics are presented in Table 2.

2.3. Adsorption experiments

A preliminary biodegradation experiment using 1 mgL^{-1} of IB was performed. Batch tests were performed using sterilized and non-sterilized soils. For each subsample 10 g of soil were incubated with 10 ml or 50 ml of 1mgL^{-1} of IB to reach the 1:1 or 1:5 (w/V) soil/ solution ratios, respectively. The method for sterilization of soil was based on the incubation of soil samples in an autoclave at 121ºC and 1.1 atm for 45 min (Alef and Nannipieri, 1995). After 24h shaking, filtrated suspension was analyzed by HPLC-UV.

Adsorption of IB in the four soils was measured using the equilibrium batch method at room temperature (23 ± 2ºC) in triplicate, in 125 ml amber glass bottles with Teflon-lined caps. The adsorption experiment was conducted with initial IB aqueous concentrations of 1-5-10-20-40-50-100-200 mg L^{-1}.

Two soil/water ratios (w/V, kg dm^{-3}) were tested. The 1:5 ratio used in the OECD test guideline 106 (OECD, 2000) and, in order to better simulate the natural conditions in agricultural soils, a soil/water ratio of 1:1 S/W was also used.

Triplicates with (aliquots) of 10 g soil (dry weight equivalent) and 10 ml or 50 ml of IB working solutions were added to amber glass bottles to reach the 1:1 and 1:5 (w/V) soil/solution ratios, respectively. Bottles were shaken reciprocally on a horizontal plate shaker at 200 rpm for 24 h (Metafuge 1.0R, Heraeus Sepatech). Subsequently, the bottles were centrifuged at 2000 rpm for 10 min and the supernatant was filtered using luer syringes and Whatman 0.45 μm glass fibre microfilters (Fisher Scientific).

2.4. Analysis

The IB concentration was determined using High Performance Liquid Chromatography with a UV detector (HPLC-UV). The 844 UV/VIS detector (Compact IC Metrohm®, Switzerland) was set at 214 nm. Chromatographic separation was achieved using a ProntoSIL® 120-5-C18 column (AQ 140 x 4 mm and a 5 μm particle size). The mobile phase consisted of acetonitrile/water 40:60 adjusted at pH 2.5 by the addition of KOH with a flow of 2.17 ml min^{-1}. A multipoint standard calibration from 1 to 50 mg L^{-1} was performed and the IC Net 2.3 SR3 software (Metrhom®, Switzerland) was used for the quantification of IB.”

3. Theory and Calculations

3.1. Batch experiments

Many studies have demonstrated that the adsorption constant varies with different S/W (Chang and Wang, 2002; You et al., 1999; McDonald and Evangelou, 1997). OECD test guideline 106 (OECD, 2000) recommend a S/W of 1:5, which cannot represent the moisture regime of agricultural soils in semi-arid zones. Scheytt et al., (2005) mentioned that the 4:5 S/W better simulated the natural conditions in the unsaturated zone.

Most soil-water systems never reach their equilibrium state under field conditions (Rütters et al, 1999). Short-term transport and bioavailability of organic chemicals within soils are mainly governed by the initial rapid sorptive uptake (Beck and Jones, 1996). Besides, as daily frequency is the most widely used for drip irrigation, the 24-hour incubation period employed in the batch test represents agricultural conditions.

Our preliminary test demonstrated the inhibition of microbiological activity at high IB concentrations which neglects the effect of IB microbiological degradation. Non-significant differences were obtained between both treatments (fumigated and non-fumigated soils): 0.829 + 0.03; 0.827 + 0.04 mg L^{-1}, measured in the supernatant. This result coincides with that obtained by Xu et al. (2009). Also, Collado et al. (2012) demonstrated that the higher the IB concentration in their batch tests using wastewater sludge, the lower the K_{biol} value.

3.2. Adsorption models

The Langmuir isotherm model (Eq. 1) assumes monolayer adsorption on an energetically homogeneous surface, and a finite sorption capacity on the surface (Langmuir, 1916):

(1) $S = (S_{max}\ K_L\ Ce) / (1 + K_L\ Ce)$,

where S (mg kg^{-1}): adsorbed solute concentration, measured indirectly as the difference between the concentration at the beginning and the concentration in the solution after 24h stirring samples; S_{max} (mg kg^{-1}): maximum adsorption capacity of soil, Ce (mg L^{-1}): measured concentration of the solution after 24h stirring samples and K_L(mg L^{-1}): Langmuir-bonding strength coefficient.

The Freundlich equation (Eq. 2) can be theoretically derived by considering an exponential variation of the adsorption enthalpy with surface coverage:

(2) $S = K_F\ Ce^{1/n}$

where K_F ($mg^{1-n}\ L^n\ kg^{-1}$). Freundlich adsorption constant and n: Freundlich constant.

For non-linear determinations, a trial-and-error procedure can be used to determine the isotherm parameters. The Solver software (Bolster and Hornberger, 2007) add-in with Microsoft's spreadsheet Microsoft Excel can be utilised to obtain these parameters.

Linearization can be obtained from the adsorption data using the LMMpro software (Schulthess, 2008), which provides various equations (3 and 4). This method is a modification of the traditional normal least squares approach (Schulthess and Dey, 1996).

Langmuir (1918):

(3) $Ce / S = Ce / S_{max} + 1/ (K_L\ S_{max})$

Langmuir log-log:

(4) $\log(S/S_{max})/1 - (S/S_{max}) = \log Ce + \log K_L$

The linearized Freundlich equation in the logarithmic form is:

(5) $\log S = \log K_F + 1/n \log Ce$

3.3.- Data analysis

Adsorption data were fitted by different methods and a comparison of the non-linear (Langmuir and Freundlich) and linear methods was made. The non-linear equations were provided by Solver (Bolster and Hornberger, 2007). The non-linear methods by Solver provided the sum of the squared errors (SSE) values, the best-fit parameters and their standard errors and confidence intervals, and goodness-of-fit measures (Bolster, 2008). Also, the LMMpro (Schulthess and Dey, 1996) estimates the adsorption parameter considering Langmuir isotherm. The non-linear n-NLLS method by LMMpro stands for normal nonlinear least squares and provides η^{*2}, goodness of fit of a curve regression, which assumes that a normal minimum for the error terms corresponds to a better curve fit of the data collected (Schulthess and Dey, 1996). This regression method optimizes the parameters of the equation without converting the equation into another form or shape. The best fit is that equation that yields the smallest error. The error of each datum point is defined as the distance between the datum point and its nearest point (perpendicular to the tangent of the nearest point) on the parabolic curve. The linearized Langmuir equation (Langmuir, 1918) (3) and Langmuir log-log (4) were also provided by LMMpro.

The linear K_d distribution coefficient was determined from the slope obtained in the low range of the aqueous concentration, where adsorption isotherms (C_e vs S) are often linear (Yamamoto et al., 2009). In our experiment, K_d was calculated at the concentration range below 20 mg L^{-1}, where all the isotherms were linear.

Organic carbon-normalized adsorption coefficient (K_{oc}) was obtained by normalizing K_d in relation to the organic carbon content (f_{oc} = OC/100) according to:

(7) $K_{oc} = K_d/f_{oc}$.

The IB retardation factor, R_F, was calculated to estimate the potential of a substance to move downwards.

(8) $R_F = 1+(\rho_b/\theta) K_d$

where ρ_b: bulk density and θ: volumetric water content at saturation.

4. Results and discussion

The fitted results for the non-linear Langmuir and Freundlich equations 1 and 2 (1:1 and 1:5) provided by Solver and LMMpro are presented in Table 3. Good fittings were obtained when considering both the non-linear equations, except for in the case of the FV soil, although Sposito (1984) concluded that the Freundlich isotherm can only be applied to the data obtained at low Ce, whereas a wide range was used in our experiment (up to 200 mg L^{-1}). This paper also shows how the Freundlich isotherm is equivalent to the Langmuir isotherm where K_F is log normal distributed. In this sense, our K_F values provided for the volcanic soils offer contributions whereby to test this hypothesis in the future.

The adsorption parameters of linearized equations 3, 4 and 5 (1:1 and 1:5) are also presented in Table 3, along with the goodness of fits. Similar adsorption parameters were obtained using non-linear and linearized methods. In contrast, Kumar et al. (2005) obtained better equilibrium parameters with the non-linear method. Only one abnormally high value for S_{max} of EH 1:5 S/W estimated by n-NLLS method was obtained.

A high concentration range represents all the possibilities of the adsorption process in soils. In this sense, Yamamoto et al., (2009) tested from 20 to 100 µg L^{-1}, and assumed that the concentrations were higher than the environmentally relevant concentration in water. Other authors determined the IB concentrations as ranging from 57 to 857 µg L^{-1} in sediments (Scheytt et al., 2005), from 0.1 to 10 mg L^{-1} in soils irrigated with reclaimed water (Chefetz et al., 2008), from 0.5 to 10 mg L^{-1} in agricultural soils (Xu et al., 2009 and González-Naranjo et al., 2013), and from 1 to 50 mg L^{-1} in clay materials (Dordio et al., 2009) (Table 4). None of the aforementioned authors tested values close to saturation. In our experiment, the use of a concentration range up to 200 mg L^{-1} allowed us to measure values that came close to the maximum adsorption capacity. Our results validate the use of the Langmuir equation in high contaminant concentration discharge points.

Figure 1 depicts the adsorption isotherms for each soil and S/W. Only those soils with the most marked andic properties (EH) or the highest clay content (GC2) did not reach the saturation state, especially in the more diluted S/W. Yet the shape of the isotherms suggests that a multi-step adsorption process is likely for soils EH and GC1 at 1:5. A S_{max} value of 29 mg kg^{-1} obtained by Dordio et al, (2009), fell within the range of the values obtained in our study (4 to 81 mg kg^{-1}). Behera et al. (2012) studied IB adsorption as a function of the pH in activated carbon and soil minerals at much diluted S/W ratios (0.001 kg/1dm^3). The adsorption maxima decreased in the following order: Activated C > Montmorillonite > Kaolinite ~ Goethite. At pH values similar to those of our soil suspensions, the corresponding values were 10,000, 4,500 and 1,500 mg kg^{-1} (Table 4).

Our values for K_L are very low (Table 3) as compared to other studies, although the data available is scarce (Table 4). However, K_d shows similar values to those mentioned in the literature and it is orders of magnitude larger than the obtained K_L. The K_L parameter is related to the magnitude of the initial isotherm slope (Sposito, 1989), whereas in this work, K_d was determined by assuming a linear relationship of up to 20 mg L^{-1}. Thus, the curves behave in the same wave as S-curve isotherms characterised by an initially small slope that increases with adsorptive concentration (Sposito, 1989). According to Sposito (1989), this behaviour suggests that the affinity of the soil particles to the adsorbate is less than that of the aqueous solution to the adsorptive, for example as the result of the competition between the DOC and soil particles for an adsorptive. It is well known that the presence of DOC may reduce the adsorption of organic pollutants through stable DOC-pollutant interactions (Graber, 1997). In our case, where DOC concentrations are significant, IB-DOC interactions may explain the low initial IB adsorption observed. Once the IB concentration exceeds the sorbing capacity of DOC, an increase of IB adsorption on the soil particles may occur, as suggested by Sposito (1989) in the case of adsorption of Cu^{2+} by soil particles in the presence of DOC.

The soil/solution ratio greatly affected the adsorption rate, especially in soils EH and GC2. Both the S_{max} (Table 3) and K_d (Table 2) were higher for 1:5 than for 1:1 (Figure 2). Although this ratio effect has been contested in the literature, O'Connor and Connolly (1980) noted that certain chemicals strongly exhibited this effect whereas other chemicals were less affected. Di Toro (1985) also studied isotherms from a wide range of organic and inorganic sorbates and sorbents (soils, lake sediments, and inorganic particles) and observed that particle concentration affects the adsorption partition coefficient. Furthermore, the inverse relationship between the sorbent concentration and the partitioning coefficient has already been extensively reported by other authors (Chang and Wang, 2002; Di Toro, 1985; Grover and Hance, 1970). According to said authors, the effect of the soil water ratio on the extent of adsorption is related to the aggregation-disaggregation phenomena induced by the S/W, influencing the amount of surface that is available for adsorption. In this sense, the lower S_{max} and K_d obtained at 1:1 coincide with the higher DOC content (Table 2). Thus, lower IB adsorption in the 1:1 experiments may refer to the lower dispersion of soil aggregates, and higher DOC content. Despite the high S_{max} obtained for our soils, the experimental results reveal low adsorption coefficients. The K_d for both S/W (0.04 to 0.5, Table 2) was even lower than the 1.69 and 0.72 kg L^{-1}, obtained by Scheytt et al. (2005) and Yamamoto et al. (2009) using 4:5 and 1:5, respectively. In two agricultural soils using a 1:2 S/W, and in river sediments with different OC contents, Xu et al. (2009) and Dobor et al. (2012), respectively, obtained similar K_d to those given in the present study.

In general, the adsorption maxima appeared to be influenced by the clay content, amorphous materials and OM (Figure 2). As observed, and contrary to what may be expected, higher clay contents were not always related to higher S_{max} and K_d. The lowest S_{max} and K_d observed in FV coincided with the soil with the highest pH and EC, the lowest OM and a large calcium carbonate content (Table 2). The two soils with the highest adsorption parameters and carbonate –free were the soil with the highest clay and OM contents (CG2) and the soil with the most pronounced andic properties (EH). Although the EH soil has a lower OM than the GC soils (Figure 2), it nevertheless presented higher S_{max} and K_d.

Despite the high anion retention of andic soils, similar K_d, K_F and R_F to those reported for other soils (Table 4) were obtained. The influence of amorphous materials was more evident in the 1/1 soil/water ratio. The effect of the soil/water ratio was noteworthy in the case of GC2 which was a clayish soil. The reduced adsorption capacity of the GC1 soil can be attributed to the effect of $CaCO_3$. This is a secondary carbonate formed under arid climate and pervading the soil matrix, acting as a cementing agent that reduces the specific surface of the andic soil.

As already mentioned, OM is an important adsorbing component in soils. Figure 3 shows the relationship between the K_d and OM, and includes the results of Yamamoto et al. (2009) and Xu et al. (2009). The K_{oc} (3.29 and 2.89) calculated by the two correlation equations using only the octanol/water partition coefficient, K_{ow}, (Karickhoff et al., 1979: $\log K_{oc} = \log K_{ow} - 0.21$ and Sontheimer et al., 1983: $\log K_{oc} = 0.807 \log K_{ow} + 0.068$ respectively) do not match our experimental data (1.0-1.5), when using eq (7). This divergence was also obtained in the case given in Scheytt et al. (2005) whose findings indicate that an estimation of partitioning coefficients cannot be based on K_{ow} alone, and that the ionic character plays an important role in IB adsorption. The reason for this may be due to the fact that the carboxyl moieties (–COOH) in the IB are completely dissociated and negatively charged ions in the pH range of our experiments (6.7 - 8.1). In this sense, adsorption mechanisms (such as electrochemical affinity), in addition to hydrophobic interaction, also play important roles in adsorption to sediment/soil (Yamamoto, 2009).

As wastewater is an environmental entry route of IB, the presence of DOC, which increases pharmaceuticals solubility, slightly lowers the amount of IB adsorbed (Dordio et al., 2009). Furthermore, Lin and Gan, (2011) found a negligible adsorption for IB. This fact implies high mobility in soil, hence a potential risk for groundwater contamination when treated wastewater is used for irrigation purposes when the IB is not eliminated in the water treatment process. Xu et al. (2009) indicated the high potential of IB to move downwards with percolated water, as shown by the low R_F (3-13). Our low R_F values (Table 2), influenced by the low ρ_b and the high porosity characteristics of andic soils, indicate that IB has a high leaching potential in the soils studied. Despite IB being a highly consumed drug, and as our results show, the low intensity of its retention in our soils, IB was not frequently detected by Estevez et al. (2012) in either reclaimed water (used to irrigate GC1 and GC2) or groundwater at 250 m below the surface. This suggests that irrigation is not the main source of IB and the existence of uncontrolled discharge points.

5. Conclusions

Similar adsorption parameters were obtained using either linear or non-linear methods. Langmuir and Freundlich models provide good fitting. Our K_F values provided for volcanic soils will offer valuable contributions to future experiments to check whether K_F is log normally distributed and if so, whether the Freudlich and Langmuir equations will be equivalently effective in describing the adsorption process in these soils.

The experimental determination of values close to S_{max} is a validation of the use of the Langmuir equation when there is accidental contamination at high concentrations. The approach of evaluating the adsorption through the linear partition coefficient, $K_{d,}$ overestimated the extent of the adsorption at low sorbate concentrations as compared to the Langmuir model. The effect of the soil/water ratio was more remarkable in soils with the highest contents of amorphous materials or clay. Considering that the proposed ratio S/W 1:1 better simulates agricultural soil conditions than the OCDE batch protocols (1:5 ratio), our results provide valuable data to input into the hydrological model simulations used in environmental risk assessment.

This work corroborates the typical dependence of the OM content on the adsorption process, and the importance of the ionic character in IB adsorption. Despite the high anionic retention capacity described for andic soils, similar K_d and R_F but higher S_{max}, were obtained as compared to other soils mentioned in the literature. Our results demonstrate that IB adsorption in volcanic areas responds not only to the soil properties commonly cited in adsorption studies (and routinely determined in agronomic laboratories) but also depends on the presence of andic soil properties, sorbent concentration and DOC, the last of which is inversely proportional to K_d and S_{max}.

The low R_F and low detection frequency of IB in groundwater (mentioned in other studies in Gran Canaria where a secondary effluent was used over a long period) suggest that reclaimed water irrigation is not the main source of IB. In spite of this, IB is detected in groundwater, suggesting the existence of uncontrolled water disposal points in the zone.

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References

Agencia Española de Medicamentos y Productos Sanitarios (AEMPS). Utilización de Antiinflamatorios No Esteroideos (AINE) en España. Ministerio de Sanidad y Consumo, Gobierno de España; 2006.

Alef K, Nannipieri P. Methods in applied soil microbiology and biochemistry. London: Academic Press; 1995.

Beck AJ, Jones KC. The effects of particle size, organic matter content, crop residues and dissolved organic matter on the sorption kinetics of atrazine and isoproturon by clay soil. Chemosphere 1996; 32: 2345-2358.

Behera S, Oh S, Park H. Sorptive removal of ibuprofen from water using selected soil minerals and activated carbon. Int J Environ Sci Technol 2012; 9: 85-94.

Blakemore LC, Searle PL and Daly BK. Methods for chemical analysys of soils. Lower Hutt, NZ: CSIRO Soil Bureau, Department of Scientific and Industrial Research; 1981.

Bolster CH. Revisiting a statistical shortcoming when fitting the Langmuir model to sorption data. J Environ Qual 2008; 37: 1986-1992.

Bolster CH, Hornberger GM. On the Use of Linearized Langmuir Equations. Soil Sci Soc Am J 2007; 71: 1796-1806.

Borges KB, de Oliveira ARM, Barth T, Jabor VAP, Pupo MT, Bonato PS. LC–MS–MS determination of ibuprofen, 2-hydroxyibuprofen enantiomers, and carboxyibuprofen stereoisomers for application in biotransformation studies employing endophytic fungi. Anal Bioanal Chem 2011; 399: 915-925.

Cabeza Y, Candela L, Ronen D, Teijon G. Monitoring the occurrence of emerging contaminants in treated wastewater and groundwater between 2008 and 2010. The Baix Llobregat (Barcelona, Spain). J Hazar Mater 2012; 239– 240: 32– 39.

Caviglioli G, Valeria P, Brunella P, Sergio C, Attilia A, Gaetano B. Identification of degradation products of Ibuprofen arising from oxidative and thermal treatments. J Pharm Biomed Anal 2002; 30: 499-509.

Collado N, Buttiglieri G, Ferrando-Climent L, Rodriguez-Mozaz S, Barceló D, Comas J, et al. Removal of ibuprofen and its transformation products: Experimental and simulation studies. Sci Total Environ 2012; 433: 296-301.

Chang TW, Wang MK. Assessment of sorbent/water ratio effect on adsorption using dimensional analysis and batch experiments. Chemosphere 2002; 48: 419-426.

Chefetz B, Mualem T, Ben-Ari J. Sorption and mobility of pharmaceutical compounds in soil irrigated with reclaimed wastewater. Chemosphere 2008; 73: 1335-1343.

Christensen AM, Markussen B, Baun A, Halling-Sørensen B. Probabilistic environmental risk characterization of pharmaceuticals in sewage treatment plant discharges. Chemosphere 2009; 77: 351-358.

Collier K J. Spectrophotometric determination of dissolved organic carbon in some South Island streams and rivers (Note). New Zeal J Mar Freshwat Res 1987, 21: 349-351.

Daughton CG, Ternes TA. Pharmaceuticals and personal care products in the environment: Agents of subtle change? Environ Health Perspect 1999; 107: 907.

Di Toro DM. A particle interaction model of reversible organic chemical sorption. Chemosphere 1985; 14: 1503-1538.

Dirección General de Farmacia y Productos Sanitarios (DGFPS). Principios activos de mayor consumo en el Sistema Nacional de Salud en 2008. Ministerio de Sanidad. Información Terapéutica del Sistema Nacional de Salud. Volumen 33; 2009.

Dobor J, Varga M, Záray G. Biofilm controlled sorption of selected acidic drugs on river sediments characterized by different organic carbon content. Chemosphere 2012; 87: 105-110.

Dordio AV, Estêvão Candeias AJ, Pinto AP, Teixeira da Costa C, Palace Carvalho AJ. Preliminary media screening for application in the removal of clofibric acid, carbamazepine and ibuprofen by SSF-constructed wetlands. Ecol Eng 2009; 35: 290-302.

Drillia P, Stamatelatou K, Lyberatos G. Fate and mobility of pharmaceuticals in solid matrices. Chemosphere 2005; 60: 1034-1044.

González-Naranjo V, Boltes K, Biel M. Mobility of ibuprofen, a persistent active drug, in soils irrigated with reclaimed water. Plant Soil Environ 2013; 59(2): 68-73.

Graetz DA and NairVD. Phosphorous sorption isotherm determination. In: Pierzynski GM, editor. Methods of phosphorus analysis for soils, sediments, residuals and water. Manhattan: North Carolina State University; 2000. p. 35–38.

Estevez E, Cabrera MC, Fernandez-Vera JR, Hernandez-Moreno JM, Mendoza-Grimon V, Palacios-Diaz MP. Twenty-five years using reclaimed water to irrigate a golf course in Gran Canaria. Span J Agric Res 2010; 8(S2), S95-S101.

Estevez E, Cabrera MC, Molina-Díaz A, Robles-Molina J, Palacios-Díaz MP. Screening of emerging contaminants and priority substances (2008/105/EC) in reclaimed water for irrigation and groundwater in a volcanic aquifer (Gran Canaria, Canary Islands, Spain). Sci Total Environ 2012; 433: 538-546.

European Commission (EC). Report from the Commission to the European parliament and the Council on the outcome of the review of Annex X to Directive 2000/60/EC of the European Parliament and of the Council on priority substances in the field of water policy; 2012.

Ferrando-Climent L, Collado N, Buttiglieri G, Gros M, Rodriguez-Roda I, Rodriguez-Mozaz S, et al. Comprehensive study of ibuprofen and its metabolites in activated sludge batch experiments and aquatic environment. Sci Total Environ 2012; 438: 404-413.

Gagnon C, Lajeunesse A, Zamorano M, Brebbia C, Kungolos A, Popov V, et al. Persistence and fate of highly soluble pharmaceutical products in various types of municipal wastewater treatment plants. Waste management and the environment IV. International Conference on Waste Management and the Environment, Granada, Spain, 2008. WIT Press, 2008, pp. 799-807.

Graber ER. Effect of irrigation with secondary sewage effluent on the transport of soil-borne pesticides. In: Rosen D, Tel-Or E, Hadar Y, Chen Y, editors. Modern Agriculture and the Environment. Dordrecht: Kluwer Academic Publisheres; 1997. p. 317–322.

Grover R, Hance RJ. Effect of Ratio of Soil to Water on Adsorption of Linuron and Atrazine. Soil Science 1970; 109: 136-138.

Han S, Choi K, Kim J, Ji K, Kim S, Ahn B, et al. Endocrine disruption and consequences of chronic exposure to ibuprofen in Japanese medaka (Oryzias latipes) and freshwater cladocerans Daphnia magna and Moina macrocopa. Aquat Toxicol 2010; 98(3):256-64.

Hayashi Y, Heckmann L-H, Callaghan A, Sibly R. Reproduction recovery of the crustacean Daphnia magna after chronic exposure to ibuprofen. Ecotoxicology 2008; 17: 246-251.

Hernando MD, Mezcua M, Fernández-Alba AR, Barceló D. Environmental risk assessment of pharmaceutical residues in wastewater effluents, surface waters and sediments. Talanta 2006; 69: 334-342.

Jurado A, Vàzquez-Suñé E, Carrera J, López de Alda M, Pujades E, Barceló D. Emerging organic contaminants in groundwater in Spain: A review of sources, recent occurrence and fate in a European context. Sci Total Environ 440: 82–94.

Karickhoff SW, Brown DS, Scott TA. Sorption of hydrophobic pollutants on natural sediments. Water Res 1979; 13: 241-248.

Kumar KV, Sivanesan S. Prediction of optimum sorption isotherm: Comparison of linear and non-linear method. J Hazar Mater 2005; 126: 198-201.

Kümmerer K. Pharmaceuticals In The Environment: Sources, Fate, Effects and Risks. London: Springer; 2004.

Langmuir I. The constitution and fundamental properties of solids and liquids I. Part I Solids. J Am Chem Soc 1916; 38: 2221-2295.

Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum. . J Am Chem Soc 1918; 40: 1361-1403.

Lapworth DJ, Baran N, Stuart ME, Ward RS. Emerging organic contaminants in groundwater: A review of sources, fate and occurrence. Environ Pollut 2012; 163: 287-303.

Lin K, Gan J. Sorption and degradation of wastewater-associated non-steroidal anti-inflammatory drugs and antibiotics in soils. Chemosphere 2011; 83: 240-246.

Martinez Bueno MJ, Gomez MJ, Herrera S, Hernando MD, Agüera A, Fernández-Alba AR. Occurrence and persistence of organic emerging contaminants and priority pollutants in five sewage treatment plants of Spain: Two years pilot survey monitoring. Environ Pollut 2012; 164: 267-273.

McDonald LM, Evangelou VP. Optimal Solid-to-Solution Ratios for Organic Chemical Sorption Experiments. Soil Sci Soc Am J 1997; 61: 1655-1659.

Meylan WM, Howard PH, Boethling RS. Improved method for estimating water solubility from octanol water partition coefficient. Environ Toxicol Chem 1996; 15: 100–106.

Mestre AS, Pures J, Nogueira JMF, Parra JB, Carvalho AP, Ania CO. Waste-derived activated carbons for removal of ibuprofen from solution: Role of surface chemistry and pore structure. Bioresour Technol 2009; 100: 1720-1726.

Neely WB, Blau GE. Environmental Exposure from Chemicals. 2nd ed. Boca Raton, FL: CRC Press; 1985.

O'Connor DJ, Connolly JP. The effect of concentration of adsorbing solids on the partition coefficient. Water Res 1980; 14: 1517-1523.

Organisation for Economic Co-operation and Development. OECD guideline for testing of chemicals 106: adsorption - desorption using a batch equilibrium method. Paris: OECD Publishing; 2000.

Onesios KM, Jim TY, Bouwer EJ. Biodegradation and removal of pharmaceuticals and personal care products in treatment systems: a review. Biodegradation 2009; 20: 441-466.

Parolini M, Binelli A, Provini A. Chronic effects induced by ibuprofen on the freshwater bivalve Dreissena polymorpha. Ecotox Environ Safe 2011; 74: 1586-1594.

Pignatello JJ, Xing B. Mechanisms of Slow Sorption of Organic Chemicals to Natural Particles. Environ Sci Technol 1995; 30: 1-11.

Pomati F, Castiglioni S, Zuccato E, Fanelli R, Vigetti D, Rossetti C, et al. Effects of a Complex Mixture of Therapeutic Drugs at Environmental Levels on Human Embryonic Cells. Environ Sci Technol 2006; 40: 2442-2447.

Quintana JB, Weiss S, Reemtsma T. Pathways and metabolites of microbial degradation of selected acidic pharmaceutical and their occurrence in municipal wastewater treated by a membrane bioreactor. Water Res 2005; 39: 2654-2664.

Rafols C, Roses M, Bosch E. A comparison between different approaches to estimate the aqueous pKa of several non-steroidal anti-inflammatory drugs. Anal Chim Acta 1997; 338: 127–134.

Ragugnetti M, Adams M, Guimarães AB, Sponchiado G, Vasconcelos E, Oliveira C. Ibuprofen Genotoxicity in Aquatic Environment: An Experimental Model Using Oreochromis niloticus. Water Air Soil Pollut 2011; 218: 361-364.

Rütters H, Höllrigl-Rosta A, Kreuzig R, Bahadir M. Sorption behavior of prochloraz in different soils. J Agric Food Chem 1999; 47: 1242-1246.

Scheytt T, Mersmann P, Lindstädt R, Heberer T. Determination of sorption coefficients of pharmaceutically active substances carbamazepine, diclofenac, and ibuprofen, in sandy sediments. Chemosphere 2005; 60: 245-253.

Schulthess CP, Dey DK. Estimation of Langmuir Constants using Linear and Nonlinear least squares regression analyses. Soil Sci Soc Am J 1996; 60: 433-442.

Schulthess CP. Langmuir software and Michaelis-Menten software (for Windows, copyright 2007 - 2008): Estimates the Langmuir parameters using linear and nonlinear methods. LMMpro (version 1.06) Copyright © 2007, 2008 by C.P. Schulthess. 2008.

Soil Survey Staff. Soil survey laboratory methods manual. Soil Survey Investigations Rep. 42. Ver. 3. National Soil Survey Center, Lincoln, NE. 1996.

Soil Survey Staff. Soil Taxonomy: A Basic System of Soil Classification for Making and Interpreting Soil Surveys. Soil Conservation Service, U.S. Department of Agriculture, Washington DC, USA. 1999.

Sontheimer H, Cornel P, Seym M. Untersuchungen zur Sorption von aliphatischen Chlorkohlenwasserstoffen durch Böden aus Grundwasserleitern (Investigations on the sorption of aliphatic chlorinated organic compounds in soils from aquifers). Karlsruhe: Veröffentlichungen des Bereichs und des Lehrstuhls für Wasserchemie der Universität Karlsruhe; 1983.

Sposito G. The surface chemistry of soils. New York: Oxford Univ Press; 1984.

Sposito G. The chemistry of soils. New York: Oxford Univ Press; 1989.

Stuer-Lauridsen F, Birkved M, Hansen LP, Holten Lützhøft HC, Halling-Sørensen B. Environmental risk assessment of human pharmaceuticals in Denmark after normal therapeutic use. Chemosphere 2000; 40:783–793.

Tejedor M, Jiménez C, Armas-Espinel S, Hernández-Moreno JM. Classification of Anthropogenic Soils with Andic Properties. Soil Sci Soc Am J 2009; 73: 170-175.

Winkler M, Lawrence JR, Neu TR. Selective degradation of ibuprofen and clofibric acid in two model river biofilm systems. Water Res 2001; 35: 3197-3205.

Xu J, Wu L, Chang AC. Degradation and adsorption of selected pharmaceuticals and personal care products (PPCPs) in agricultural soils. Chemosphere 2009; 77: 1299-1305.

Yalkowsky SH, Dannenfelser RM. Aquasol Database of Aqueous Solubility Version 5. College of Pharmacy, University of Arizona, Tucson, AZ. 1992.

Yamamoto H, Nakamura Y, Moriguchi S, Nakamura Y, Honda Y, Tamura I, et al. Persistence and partitioning of eight selected pharmaceuticals in the aquatic environment: Laboratory photolysis, biodegradation, and sorption experiments. Water Res 2009; 43: 351-362.

You S-J, Yin Y, Allen HE. Partitioning of organic matter in soils: effects of pH and water/soil ratio. Sci Total Environ 1999; 227: 155-160.

Zwiener C, Seeger S, Glauner T, Frimmel F. Metabolites from the biodegradation of pharmaceutical residues of ibuprofen in biofilm reactors and batch experiments. Analytical and Bioanalytical Chemistry 2002; 372: 569-575.

FIGURE CAPTIONS

Fig. 1. Langmuir isotherms for the four soils (EH, GC1, GC2 and FV) and the two soil/water ratios 1:1 and 1:5, obtained using LMMpro software.

Fig. 2. K_d (L kg^{-1}) and S_{max} (mg kg^{-1}) vs $Al_o + ½ Fe_o$, soil organic matter (OM, %) and clay (%), for each soil sample (EH, FV, GC1 and GC2) and both S/W ratios (1:1 and 1:5).

Fig. 3. Relationship for IB between K_d and soil organic matter content (OM) of soils in this study and other studies (Yamamoto et al., 2009; Xu et al., 2009).

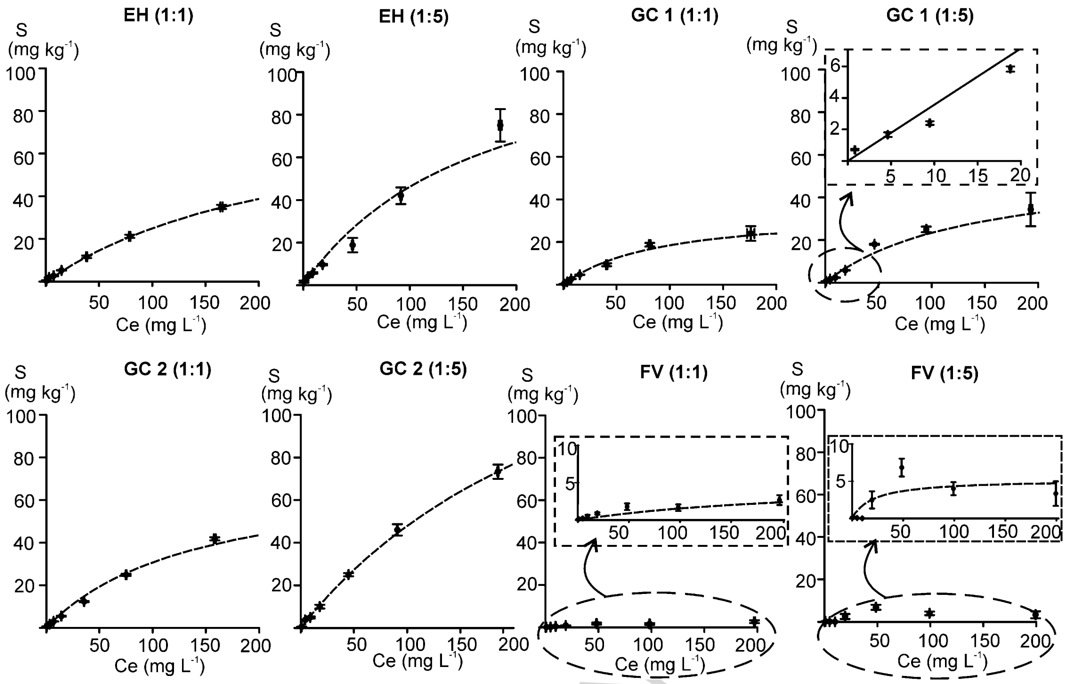
EH (1:1)
EH (1:5)
GC 1 (1:1)
GC 1 (1:5)
GC 2 (1:1)
GC 2 (1:5)
FV (1:1)
FV (1:5)
S (mg kg-1)
Ce (mg L-1)
0
20
40
60
80
100
50
100
150
200
2
4
6
5
10
15
20

Fig. 1

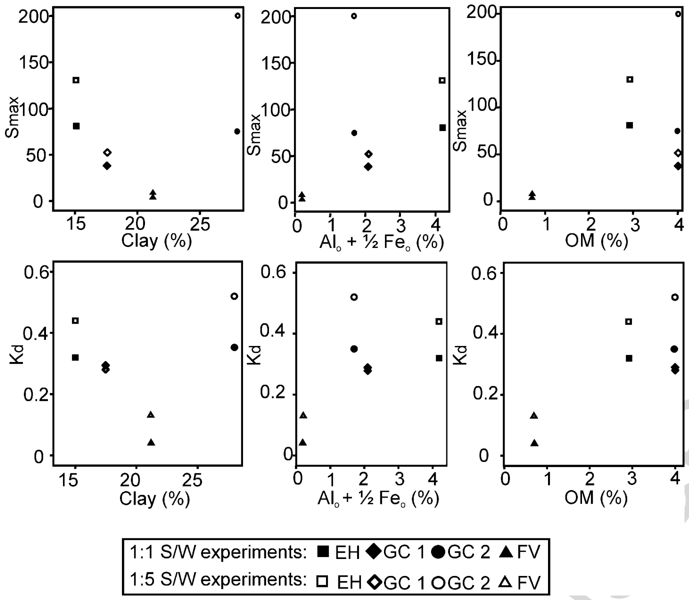
Smax
0
50
100
150
200
15
20
25
Clay (%)
0
1
2
3
4
Al$_o$ + ½ Fe$_o$ (%)
OM (%)
Kd
0
0.2
0.4
0.6
1:1 S/W experiments: ■ EH ◆ GC 1 ● GC 2 ▲ FV
1:5 S/W experiments: □ EH ◇ GC 1 ○ GC 2 △ FV

Fig. 2

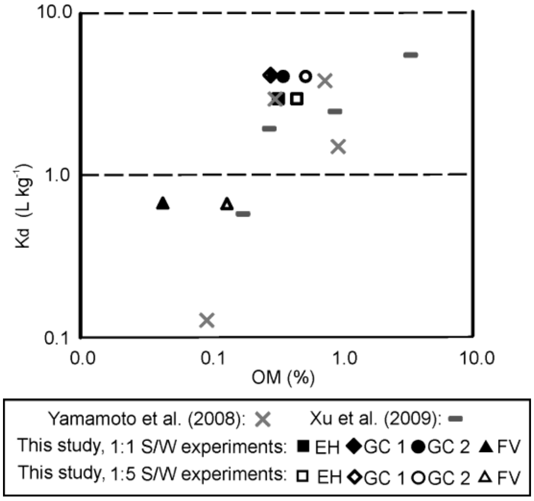
10.0
1.0
0.1
Kd (L kg-1)
0.0
0.1
1.0
10.0
OM (%)
Yamamoto et al. (2008): ×
Xu et al. (2009): ▬
This study, 1:1 S/W experiments: ■ EH ◆GC 1 ●GC 2 ▲FV
This study, 1:5 S/W experiments: □ EH ◇GC 1 ○GC 2 △FV

Fig. 3

Table 1

Properties of Ibuprofen (IB):

PROPERTIES	
Melting point (ºC)	76
pKa Disociation constant$_a$	4.91
Chemical formula	$C_{13}H_{18}0_2$
Water solubility of IB (mg/L)$_b$	21
Water solubility of IB sodium salt: $C_{13}H_{17}$ $Na0_2$ (mg/L)$_c$	100,000
Vapor pressure (Pa)$_d$	2.47E^{-02}
Henry`sLaw constant (atm m^3/mole)$_e$	1.50E^{-07}
log Kow$_f$	3.5

a: Rafols et al. (1997); b: Yalkowsky and Dannenfelser (1992); c: http://www.sigmaaldrich.com, d: Neely and Blau (1985); e: Melyan and Howard (1996); f: Stuer-Lauridsen et al. (2000).

Table 2

Physico chemical characteristics of the soils studied and K_d (L kg^{-1}) values obtained from the liner section of the isotherms (i.e. initial concentration: 1-20 mg L^{-1}), retardation factor ($R_F = 1 + K_d (\rho_b / \theta)$) and log K_{oc}, where $K_{oc} = K_d / f_{oc}$

	EH	**GC1**	**GC2**	**FV**
^{1}Soil pH	7.9	8.5	8.1	8.7
^{2}Soil EC (mS cm^{-1})	0.17	0.33	0.23	0.73
^{3}OM (%)	2.91	4.03	3.97	0.67
^{4}Exchangeable K^{+} (me 100g^{-1})	2.7	4.0	2.9	1.6
^{4}Exchangeable Ca^{+2} (me 100g^{-1})	15.4	23.1	15.8	13.6
^{4}Exchangeable Mg^{+2} (me 100g^{-1})	6.7	7.9	8.5	5.3
^{4}Exchangeable Na^{+} (me 100g^{-1})	3.9	4.3	2.5	10.1
^{5}P (mg kg^{-1})	26.0	62.0	149.5	5.0
^{6}N (%)	0.2	0.2	0.3	0.1
$^{7}Al_o$ + ½ Fe_o (%)	4.2	2.1	1.7	0.2
^{8}P retention (%)	81.8	41.5	44.8	-
$^{9}CaCO_3$(%)	n.d.	2.2	n.d.	10.6
^{10}Clay (%)	14.9	17.5	28.0	21.2
^{10}Silt (%)	28	28	31	34
^{10}Sand (%)	57	54	41	45
^{11}Texture	sandy loam	sandy loam	clay loam	loam
CEC (me 100g^{-1})	28.7	39.2	29.7	30.7
^{12}DOC 1:1 S/W (g m^{-3})	4.7	19.5	13.7	18.4
^{12}DOC 1:5 S/W (g m^{-3})	3.2	8.0	7.5	5.2
ρ_b (kg L^{-1})	1.03	1.09	1.3	1.41
Θ (m^3 m^{-3})	0.48	0.45	n.a.	0.34
K_d 1:1 S/W (L kg^{-1}) (r^2)	0.32 (0.94)	0.29 (0.99)	0.35 (0.99)	0.04 (0.66)
K_d 1:5 S/W (L kg^{-1}) (r^2)	0.44 (0.95)	0.28 (0.96)	0.52 (0.92)	0.13 (0.44)
R_F 1:1 S/W	1.7	1.7	n.a.	1.2
R_F 1:5 S/W	1.9	1.7	n.a.	1.5
Log K_{oc} 1:1 S/W	1.28	1.10	1.18	1.04
Log K_{oc} 1:5 S/W	1.42	1.08	1.35	1.52

1: Soil pH measured in a 1:2.5 soil/water suspension; 2: Soil Electrical Conductivity (EC) measured in saturation extracts 1:5 S/W; 3: Calculated OM =OC x 1.724. 3 and 6: Organic Carbon (OC) and Total N were determined by dry combustion (1340ºC) oxidation with acid potassium dichromate; 4: Exchangeable cations were extracted with buffered neutral 1 mol L^{-1} NH_4OAc or NaOAc (Soil Survey Laboratory Staff, 1996); 5: Available P estimated using the Olsen method; 7: Oxalate-extractable Al and Fe, determined according to Blakemore et al. (1981); 8: Phosphorus retention was determined by batch equilibrium method in which soil was shaken with P solutions of 1gL^{-1} (Graetz and Nair, 2000); 9: Calcium carbonate content was determined by reaction with acid in calcimeter; 10: Granulometric analysis was performed by hydrometer method; 11: U. S. Department of Agriculture Classification; 12: Dissolved Organic Carbon (DOC) (Collier, 1987) of the solutions corresponding to both S/W used in the batch experiments. N.d.: non detectable and n.a.: non available data.

Table 3

Adsorption and statistical parameters for Langmuir (K_L: L kg^{-1} and S_{max}: mg kg^{-1}) and Freundlich ($K_{F:}$ L kg^{-1} and n) models obtained using non linear and linear methods.

	Non linear methods (*solver* add-in with Microsoft's spreadsheet. Microsoft Excel)																			
	Langmuir										Freundlich									
	1:1					1:5					1:1					1:5				
Soil	E	SSE	AIC	K_L	S_{max}	E	SSE	AIC	K_L	S_{max}	E	SSE	AIC	K_F	n	E	SSE	AIC	K_F	n
EH	0.99	15	2	0.005	81	0.92	1.046	89	0.006	130	0.99	21	8	0.6	0.8	0.93	997	89	1.7	0.7
GC1	0.93	107	41	0.010	38	0.88	426	71	0.010	52	0.91	149	49	0.7	0.7	0.85	550	76	0.7	0.8
GC2	0.99	53	27	0.007	75	0.99	184	53	0.003	200	0.99	36	19	0.9	0.7	0.98	309	64	0.7	0.9
FV	0.69	6.7	-16	0.01	4	0.30	11	42	0.01	8	0.65	8	-14	0.1	0.6	0.10	140	47	0.1	0.8

E (Efficiency), SSE (Sum of Squared Errors), AIC (Akaike Information Criterion).

	Langmuir (LMMpro software)											
	Non linear Langmuir (n-NLLS method)						Linearized Langmuir (Langmuir, 1918)					
	1:1			1:5			1:1			1:5		
Soil	η^{*2}	K_L	S_{max}	η^{*2}	K_L	S_{max}	η^2	K_L	S_{max}	η^2	K_L	S_{max}
EH	0.99	0.004	85	0.96	0.001	372	0.99	0.004	85	0.92	0.006	124
GC1	0.93	0.009	39	0.96	0.014	39	0.93	0.011	34	0.94	0.010	45
GC2	0.997	0.004	113	0.99	0.003	189	0.99	0.007	74	0.99	0.003	194
FV	0.71	0.0193	3	0.45	0.04	4	0.58	0.004	5	n.a	n.a	n.a

η^{*2}: goodness of fit of a curve regression, which assumes that a normal minimum for the error terms corresponds to a better curve fit of the data collected, η^2: goodness of fit of a curve, which assumes that a vertical minimum for the error terms corresponds to a better curve fit of the data collected, n.a.: non admissible results obtained by using LMMpro software. n-NLLS: normal-nonlinear least squares method (Schulthess,C.P. and Dey, D.K., 1996).

	Linearized methods Log-Log													
	Langmuir Log-Log (LMMpro software)								Freundlich Log-Log					
	1:1				1:5				1:1			1:5		
Soil	R^2	η^2	K_L	S_{max}	R^2	η^2	K_L	S_{max}	R^2	K_F	n	R^2	K_F	n
EH	0.92	0.99	0.007	64	0.84	0.92	0.006	145	0.91	0.6	1.2	0.93	1.6	1.5
GC1	0.98	0.93	0.008	46	0.94	0.94	0.008	52	0.99	0.5	1.3	0.96	0.6	1.3
GC2	0.94	0.98	0.008	72	0.99	0.99	0.003	196	0.99	0.9	1.3	0.98	0.7	1.1
FV	0.62	0.49	0.05	8	n.a	n.a	n.a	n.a	0.68	0.1	1.5	0.46	0.03	1.1

R^2: goodness of fit of the line, η^2: goodness of fit of a curve, which assumes that a vertical minimum for the error terms corresponds to a better curve fit of the data collected, n.a.: non admissible results obtained by using LMMpro software.

Table 4

Experimental conditions (Ci: mg L^{-1}), and adsorption parameters (Kd: L kg^{-1}, log K_{oc}, K_L: L kg^{-1}, S_{max}: mg kg^{-1}, K_F: mg^{1-n} L^n kg^{-1} and R_F) obtained in this study and other references.

References	Exp.conditions	K_d	Log K_{oc}	K_L and S_{max}	K_F	R_F
This study	- Sorbent: 4agric.volcanic soils - Ci= 1 - 200 - S/W: 1:1, 1:5	EH: 0.32-0.44 GC1: 0.29- 0.28 GC2: 0.35-0.52 FV: 0.04-0.13	1.28 – 1.42 1.10 – 1.08 1.18– 1.35 1.04 – 1.52	K_L: 0.001-0.07 Smax: 1 – 260	0.6 – 1.7 0.7 – 0.5 0.9 – 0.7	1.2-1.9
González-Naranjo et al., 2013	- Sorbent: 4agricultural soils - Ci= 0.5 - 10 - S/W: 1:5	Bad fit 1.40-1.56	2 - 2.3	Bad fit K_L: 0.02 – 0.2 Smax: 5.3 – 76.6	Good fit 1 – 2.2	
Behera et al, 2012	-Sorbent (pH: 7): Soil minerals and activated carbon -Ci = 60 -S/W: 1:100			Smax: Kaolinite: 1500 Montmorillonite: 4500 Geothite: 1500 AC: 10000		
Dobor et al, 2012	-Sorbent (pH 3-12) : 2 river sediments Ci : 4 10^{-7} M -S/W: 1:5	0.1-0.4				
Lin and Gan., 2011	-Sorbent: 2 soils -Ci = 0.002-0.04 -S/W : 1:5	1.08- 1.14				
Dordio et al., 2009	-Sorbent: 3 cork -Ci= 1 - 50 -S/W: 1:0.8, 1:1.25			Bad fit K_L: 0.18 Smax: 29	Good fit 0.004	
Yamamoto et al., 2009	-Sorbent (pH 7): 3 river sediments, 1 model soil -Ci =0.02 – 0.1 S/W: 1:5	0.09, 0.3, 0.9 0.7	2.08, 1.97, 1.25 1.5			
Xu et al., 2009	-Sorbent: agricultural soils -Ci = 0.5-10 -S/W: 1:2	Clay - OM 42% -2.5%: 0.17 18% - 5.5%: 0.45	0.86 - 2.33		0.27-3.42	3-13
Mestre et al., 2009	-Sorbent (2-11): 6 carbon adsorbents -Ci = 20 -120 -S/W: 1:6, 1:3			Smax: 430400 - 145200	0.02 -0.12	
Scheytt et al., 2005	-Sorbent (4.6,): 2 sandy sediments -Ci= 0.05 – 0.857 -S/W : 1 :5, 4:5	Low OC 1.69	2.1		0.0008	
Kümmerer, 2004	Pharmaceuticals	0.2 - 6000				

HIGHLIGHTS

Ibuprofen adsorption at 1-200 mgL^{-1} in four volcanic soils, at 1:1 and 1:5 S/W ratios
Non-linear and linearized Langmuir and Freundlich equations were well fitted
1:1 S/W better simulates field conditions and provides lower parameters than 1:5
Similar K_d , R_F, and higher S_{max} in andic soils comparing to literature
IB adsorption is related to S/W, DOC and soil properties, including andic ones