



Relevance of sorption in bio-reduction of amoxicillin taking place in forest and crop soils

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ABSTRACT

The fate of antibiotics reaching soils is a matter of concern, given its potential repercussions on public health and the environment. In this work, the potential bio-reduction of the antibiotic amoxicillin (AMX), affected by sorption and desorption, is studied for 17 soils with clearly different characteristics. To carry out these studies, batch-type tests were performed, adding increasing concentrations of AMX (0, 2.5, 5, 10, 20, 30, 40, and 50 $\mu\text{mol L}^{-1}$) to the soils. For the highest concentration added (50 $\mu\text{mol L}^{-1}$), the adsorption values for forest soils ranged from 90.97 to 102.54 $\mu\text{mol kg}^{-1}$ (74.21–82.41% of the amounts of antibiotic added), while the range was 69.96–94.87 $\mu\text{mol kg}^{-1}$ (68.31–92.56%) for maize soils, and 52.72–85.40 $\mu\text{mol kg}^{-1}$ (50.96–82.55%) for vineyard soils. When comparing the results for all soils, the highest adsorption corresponded to those more acidic and with high organic matter and non-crystalline minerals contents. The best adjustment to adsorption models corresponded to Freundlich's. AMX desorption was generally <10%; specifically, the maximum was 6.5% in forest soils, and 16.9% in agricultural soils. These results can be considered relevant since they cover agricultural and forest soils with a wide range of pH and organic matter contents, for an antibiotic that, reaching the environment as a contaminant, can pose a potential danger to human and environmental health.

1. Introduction

The environment is facing several threats, from climate change to air, water, and soil pollution. In recent times, a special attention is being paid to compounds called “emerging pollutants” (Taheran et al., 2018; Bilal et al., 2019), which include chemicals found in pharmaceuticals, personal care products, pesticides, industrial and household products, metals, surfactants, industrial additives and solvents. In some cases, these pollutants may cause severe damage on both the environment and human health (Petrisor, 2004). The current growth of the pharmaceutical industry increases the risk of spreading these compounds into the environment. Within pharmaceuticals, antibiotics, (which are increasingly used in medicine for the treatment of infectious diseases), become pollutants when spread into environmental compartments (Carvalho and Santos, 2016; Ezzariai et al., 2018). In fact, the number of studies that reveal the presence and effects of these compounds in soils, water and crops is increasing (Conde-Cid et al., 2018; Santás-Miguel et al.,

2020; Beltrán et al., 2021).

Among antibiotics, amoxicillin (AMX) is a broad-spectrum antimicrobial included in the penicillin group, from the β -lactam subclass, and one of the most widely used in human-medicine in the primary care setting. In Europe AMX supposed 40% of the total prescribed antibiotics in 2017 (Buckler et al., 2018), and worldwide its market value was at 4.4 billion \$ (Watson, 2018). The ample use of this antibiotic is due to, among other reasons, its effectiveness against a wide variety of gram-positive, and additionally some gram-negative bacteria, compared to penicillin (Sodhi et al., 2021). Due to its habitual use in medicine and the fact that between 80 and 90% of this antibiotic is excreted due to its poor absorption (Kidak and Doğan, 2018), its presence in the environment is considered an emerging problem, even though under the framework of OECD (European Centre for Disease Prevention and Control) tests, AMX did not present acute toxicity for denitrifying bacteria in soil, earthworms, and plants (Litskas et al., 2018). In fact, it can cause significant risks to human health, as well as environmental

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damage, such as the proliferation of antibiotics-resistant bacteria, eco-toxicity problems or their entry into the food chain.

Specifically, AMX is an antibiotic poorly absorbed in the intestine and, due to its low degradation into the body, it remains as an active compound in feces and urine (Andreozzi et al., 2005; Jara et al., 2007) and may end up being incorporated into wastewater, reaching Wastewater Treatment Plants (WWTP) (where available). In these plants, wastewater is subjected to purification processes that in most cases do not eliminate all of this and other antibiotics, while sludge can also accumulate these pollutants (Wang and Wang, 2016; Yang et al., 2016; Gogoi et al., 2018). In fact, Andreozzi et al. (2005) indicate that amoxicillin can appear in WWTP effluents in concentrations of up to 120 ng L^{-1} . As for sludge, they are frequently used as amendments in agricultural soils and in certain forested areas with pastoral exploitation, and despite the fact that in some countries it is mandatory that they undergo treatment for the elimination of pollutants before being incorporated into the soil, these treatments are not always totally effective in the case of antimicrobials. To note that the relatively high affinity of AMX to the sludge solid phase has been demonstrated in previous works (Andreozzi et al., 2004). Therefore, there is an obvious risk that, through the routes mentioned above, AMX and other antibiotics can reach the soil and be absorbed by plants from the soil solution (Rocha et al., 2021), entering the food chain, as shown by Azanu et al. (2016) for carrots and lettuce, with AMX levels between 14 and 45 ng g^{-1} being detected in those crops. In addition, AMX is an antibiotic highly used in veterinary (Binh et al., 2007; Yang et al., 2020a), with marked risks of entering soils and waterbodies when manures and slurries containing it are spread as fertilizers, as happens with other pollutants (Núñez-Delgado et al., 2002).

When AMX reaches the soil, it can interact with some edaphic components and/or with active molecules contained in by-products present on the soil surface, allowing a variable degree of retention of the pollutant by means of sorption mechanisms (Kim et al., 2012; Mohammed et al., 2020; Pandey et al., 2021), as happens with other contaminants (Seco-Reigosa et al., 2013) and other antibiotics (Conde-Cid et al., 2019, 2020; Cela-Dablanca et al., 2021a). Analyses of sorption mechanisms are crucial for environmental risk assessments, and the European Medicine Agency has included the quantification of pharmaceuticals sorption into the guidelines for human medicinal products (EMA, 2006). The sorption, mobility and bioavailability of antibiotics will be mainly determined by the molecule's properties and soil physical-chemical characteristics, but also by meteorological factors. Several antibiotics, AMX among them, have been describe as highly mobile in soils and could therefore be rapidly transported to surface water (Kim et al., 2012).

Within the soil properties, soil organic matter favours the sorption of antibiotics to the soil particles since it provides negative charges and a high contact surface that can increase the sorption capacity, depending on the quantity and composition of this fraction (Thiele-Bruhn and Aust, 2004). On the other hand, soil pH can modify the charges of the antibiotics if, as for amoxicillin, they have zwitterion character. In forest soils, amoxicillin has been found to be more persistent than recently developed β -lactam antibiotics, even though the persistence was considered low ($t_{1/2}$ less than a day) (Braschi et al., 2013). The relatively high degree of sorption of AMX could be related to its zwitterion character, as happens with some fluoroquinolones and tetracyclines (Carrasquillo et al., 2008; ter Laak et al., 2006). In addition, Kim et al. (2012) found that the degree of AMX sorption was reduced onto two arable soils when decreasing pH and increasing soil organic matter content.

Also clearly interesting is the study of biodegradation of antibiotics (and specifically of AMX) present in environmental compartments as pollutants (Reis et al., 2020; Yang et al., 2020b), and the eventual effects of sorption processes on the availability of these antibiotics to be biodegraded (Wu et al., 2009; Wegst-Uhrich et al., 2014; Zhu et al., 2021).

Taking into account the previous background, this research aims to give new details on the retention of AMX in different agricultural and

forest soils, as well as on the influence of the physical-chemical properties of the soils on the fate of the antibiotic in that environment. Previous works have analysed the sorption mechanisms in a limited number of arable soils, but data regarding soils under different agricultural and forestry exploitations is missing. The authors of this work have no notice on equivalent research performed for this antibiotic and with this diversity of soils, while its importance is clear at the level of potential environmental and public health repercussions.

2. Materials and methods

2.1. Soil sampling

Seventeen soils were used in this study, sampling in a variety of geographic areas in Galicia (Northwest Spain), with some basic details presented in Table S1 (Supplementary Material).

These soils were within a set previously used, characterized and commented in Cela-Dablanca et al. (2021a). Among the 17 soils here used, 14 were from agricultural areas: 8 vine soils (4 in the province of Ourense, VO1 to VO4, and 4 in the province of Pontevedra, VP1 to VP4); meanwhile the other 6 agricultural soils were maize (corn) soils (M1 to M6). The other 3 soils were forest (F) soils from areas dominated by *Pinus* (FP), oak (*Q. robur*) (FR), or *Eucalyptus* (FE). The agricultural soils were managed by annual addition of WWTP sludge, during at least 3 consecutive years.

In each sampling zone, a composite sample was performed mixing ten sub-samples that were taken in surface (0–20 cm depth). Once at the laboratory, and previously to be stored for further study, all soil samples were dried (at $40 \text{ }^\circ\text{C}$) and sieved through a 2 mm mesh.

2.2. Soil analyses

The following physico-chemical characteristics were measured in all soil samples: pH (in H_2O), total C and N, clay and sand contents, effective cation exchange capacity, exchangeable Ca, Mg, Na, K and Al, non-crystalline Fe and Al contents, and Fe and Al bound to organic matter. The methods are detailed in the Supplementary Material, with Table S2 showing the results obtained.

2.3. Experiments on adsorption and desorption

Batch-type experiments were used to carry out adsorption and desorption studies on the whole set of soil samples. The procedure was as that shown in Cela-Dablanca et al. (2021a), and it is included in Supplementary Material. Adsorption and desorption studies were performed using batch-type experiments, where 2 g of soil were mixed with 5 mL of solutions containing 2.5, 5, 10, 20, 30, 40, or $50 \text{ } \mu\text{mol L}^{-1}$ of AMX, as done in previously researches for the beta-lactam antibiotic cefuroxime (Cela-Dablanca et al., 2021b) and for various sulfonamide antibiotics (Conde-Cid et al., 2021).

2.4. Reagents and determination of AMX

Amoxicillin (with $\geq 95\%$ of purity) was provided by Sigma-Aldrich (Barcelona, Spain). Phosphoric acid (being 85% extra pure) and acetonitrile (with $\geq 99.9\%$ of purity) were from Fisher Scientific (Madrid, Spain), and Ca_2Cl (with purity of 95%) was from Panreac (Barcelona, Spain). MilliQ water (Millipore, Madrid, Spain) was used for preparing all solutions needed for HPLC quantification procedures.

HPLC analyses were performed as indicated in Cela-Dablanca et al. (2021a, 2021b), with details included in Supplementary Material. Also, Fig. S1 (Supplementary Material) shows some example chromatograms. Concentrations of the antibiotic added minus concentrations in the equilibrium solutions gave the amounts adsorbed. After adsorption, desorption experiments were carried out, thus informing on the eventual hysteresis of the process. The procedure consisted in adding 5 mL of

0.005 M CaCl₂ (with no antibiotic) to the soil materials derived from the adsorption phase, then repeating the process carried out for adsorption. All these procedures were performed in triplicate.

2.5. Modeling and statistics

Data from the adsorption experiments were fitted to various models: Linear, Langmuir, and Freundlich. More details are shown in Supplementary Material.

The software used for fitting models and for statistical analyses of Pearson correlations ($p < 0.05$) was SPSS 21.

3. Results and discussion

3.1. Soil characteristics

Table S2 (Supplementary Material) shows the physicochemical characteristics of the soils used. The soil pH ranged between 4.68 and 8.02, with the most acidic values corresponding to forest soils, and most of the agricultural soils being in the 5–6 range. The total C and N contents showed a high variability in the agricultural soils, with values ranging between 0.63–7.67% and 0.06–0.63%, respectively. The forest soils have the highest amount of total C (7.15–9.78%) and N (0.48–0.67%). Sand contents ranged between 43.42% and 69.35%, with the highest values generally corresponding to forest soils. The clay fraction ranged between 12.22% and 24.65%, with agricultural soils showing higher values. The effective cation exchange capacity (eCEC) values also showed a wide oscillation, between 5.94 and 42.81 cmol_c kg⁻¹, with Ca being the cation that dominated in most crop soils, while Al dominated in forest soils. The non-crystalline forms of Fe and Al also showed high variability. Specifically, total non-crystalline Fe (Fe_o) was between 1665 and 6990 mg kg⁻¹. Regarding Fe bound to organic matter (Fe_{pir}), the range went from 823 to 9239 mg kg⁻¹, while Al bound to organic matter (Al_{pir}) ranged from 1047 to 14,857 mg kg⁻¹, with generally higher values in forest soils and in those with more carbon and organic matter contents within agricultural soils.

Previous papers dealing with AMX adsorption onto soils are scarce, which makes somehow difficult to compare the characteristics of the soils here used with that corresponding to those included in other investigations with a coincident focus. Just as comparison, Jodeh et al. (2012) used a soil with pH 7.14 and organic carbon content 7.34% in a study on the leachate of pharmaceuticals (including amoxicillin) through soil columns. Kim et al. (2012) studied sorption characteristics of three antibiotics (including amoxicillin) in two different soil types (pH 5.64–8.13, and organic matter percentage 1.83–0.82, respectively), while Braschi et al. (2013) used two soils with pH 8.2–5.0 and total organic carbon 7.7–21.8 g kg⁻¹ (so 0.77–2.18 expressed as percentage values). As can be seen, these soils have values within the range of those corresponding to the current research.

3.2. Adsorption of AMX

AMX adsorption (which is expressed in μmol kg⁻¹, and in percentage), is represented as a function of the AMX concentration added in Table S3 (Supplementary Material). Specifically, Table S3 shows that the amount adsorbed increases as the added concentration is higher, while the total percentage adsorbed decreases in most cases. This is due to the fact that the adsorption sites in the soils become progressively saturated as higher concentrations of antibiotic are added.

The maximum values of AMX adsorption are in the range of 69.96–94.87 μmol kg⁻¹ in maize/corn soils, between 73.47 and 80.81 μmol kg⁻¹ in vine soils developed on granite, and between 90.97 and 102.54 μmol kg⁻¹ in forest soils. In vineyard soils on slate and schists, the adsorption values are in a wider range, oscillating between 43.41 and 85.40 μmol kg⁻¹ (Table S3).

AMX adsorption percentages are generally high, even for the

maximum concentration of antibiotic added (50 μmol L⁻¹), with AMX adsorption values ranging between 61 and 93% in crop soils with maize/corn, between 87 and 99% in vineyard soils on granite, between 72 and 95% in vineyard soils on slate and schists, and between 74 and 82% in forest soils (Table S3).

The adsorption of antibiotics onto soils is dependent on the characteristics of these molecules (polarity, hydrophobicity, and molecular structure) and on soil characteristics (organic matter, pH, clays, and non-crystalline minerals) (Zhi et al., 2019). When comparing for the different soils AMX adsorption, some clear differences are observed. Specifically, when the maximum concentration of AMX (50 μmol L⁻¹) is applied, the maximum adsorption percentages correspond to one maize soil (M2, with 92.6%), and to one vineyard soil (VP3, with 82.5%), as well to the three forest soils (82.4, 81.8, and 74.2%, for FP, FE, and FR, respectively). These soils have in common a pH ≤ 5.5, organic matter content higher than 4.5%, and a sum of Fe and Al extracted with oxalate (which estimates low crystallinity minerals) above 15,000 mg kg⁻¹.

Putra et al. (2009) found that AMX adsorption on carbon and bentonite is strongly affected by pH. Githinji et al. (2011) reported a decrease in AMX adsorption as the pH of the adsorbent increased from 3.5 to 8.5, while other studies described a decrease in the maximum adsorption for pH > 5 when the adsorbent was peel shell pistachio (Mohammed et al., 2020) or activated charcoal (Shahrouzi et al., 2019). At very acidic pH values (<5.0), the amine groups of the antibiotic can become protonated, acquiring a positive charge, while at less acidic and basic pH the carboxyl groups are deprotonated, creating negative charges (see the molecular structure of AMX in Fig. S1, Supplementary Material).

Within a certain pH range, antibiotics can behave as a zwitterion, showing negative and positive charges at the same time. In the case of AMX, the compound has three pK_a values and its molecular charge suffers modifications depending on the pH, due to the presence of different functional groups, such as carboxyl (with pK_{a1} = 2.68), amino (pK_{a2} = 7.49) and phenolic (pK_{a3} = 9.63) (Homsirikamol et al., 2016). At pH < pK_{a1}, the positive charge of the amino group confers a charge on the molecule that is also positive, while at pH values between pK_{a1} and pK_{a2} the molecule behaves as a zwitterion with deprotonated carboxyl groups and protonated amino groups. On the other hand, at pH between pK_{a2} and pK_{a3} deprotonated carboxyl and amine groups are predominant, and, finally, at pH > pK_{a3} phenolic groups are also deprotonated (Pezoti et al., 2016). Soils with clearly acidic pH (specifically, pH < 5), may have a negative charge on clays with a permanent charge, and a positive charge on components of variable charge (1:1 clays, organic matter, non-crystalline components), while at pH > 5, negative charges will generally predominate, rising as the pH increases.

For the soils used in the present work, two clear pH ranges can be differentiated: a) pH < 5 in forest soils, and b) pH between 5 and 6.5 in most agricultural soils (with the exception of a corn soil that reaches a value of 8 and a vineyard soil that has pH = 7.27). Most of the pH of these soils lie between the pK_{a1} and pK_{a2} of AMX, values for which the antibiotic behaves like a zwitterion. A variety of mechanisms could be involved in the adsorption processes of AMX in the soil, including electrostatic interactions, cationic bridges and H bonds (Anastopoulos et al., 2020). In the forest soils of the present study, which have pH < 5, electrostatic interactions can occur between the positively charged variable charge components of the soil (organic matter and non-crystalline components, very abundant in these soils) with the deprotonated carboxyl groups of AMX, and interactions between negatively charged soil components (2:1 clays) with the protonated amine groups of the antibiotic. With pH values between 5 and 6.5, soils will preferentially present a negative charge, which can interact with the protonated amine groups of AMX. However, at pH > 6 negative charges will predominate in soils and antibiotics, favoring adsorption through a cationic bridge. In addition, adsorption decreases with rising pH due to the increase of OH⁻ ions in the solution, ions that can compete with the COO⁻ groups of the antibiotic for the adsorption sites in the soil

(Shahrouzi et al., 2019).

In the present work, the soils with the highest AMX adsorption have $\text{pH} < 5.5$ and high organic matter and non-crystalline minerals contents (Table S2, Supplementary Material), which at these pH values will have a positive charge, so adsorption would occur preferentially between the deprotonated carboxyl groups of AMX and the positive charges of these variable charge components of the soil.

3.3. Modeling adsorption

Adsorption curves for the 17 soils studied are shown in Fig. 1, where the amounts of AMX adsorbed are plotted versus its equilibrium concentrations. Data on adsorption (as a function of the AMX concentration added), are shown in Table S3 (Supplementary Material) expressed as amount and percentages. The fitted curves are non-linear for most of the soil samples, and the adsorption of the antibiotic rises with the increase in concentration, and remains constant after the equilibrium. The adsorption capacity differs according to the type of soil.

Table 1 also shows the fitting of adsorption parameters for three models (Freundlich, Langmuir, and Linear) assessed. Taking into account the coefficient of determination (R^2) values and the errors associated, AMX adsorption would show a better fit to the Freundlich model in most soils (only M2 does not adjust to this model). Even though the R^2 values for the Langmuir model are not low (>0.72) the errors associated are too high to allow the adjustment. The Linear model has smaller errors than the Langmuir model, but the coefficients of determination are the lowest of the three models. In 94% of the samples that fit the Freundlich model, the R^2 values are higher than 0.89. Other authors also obtained a better fit for this antibiotic with the Freundlich model (with R^2 values > 0.8), while with the Langmuir model the R^2 values were < 0.4 (Kim et al., 2012).

A better adjustment to the Freundlich's model, is indicative of clear increase of the amount adsorbed as a function of the growth of the concentration of the adsorbate present in solution (this when the concentrations of that adsorbate are low), while, at high concentrations, the amount adsorbed trends to a constant value (Proctor and Toro-Vazquez, 1996). This model assumes heterogeneity in the energy of the surface sites and that there is no specified limit for maximum adsorption. A good fit to the Langmuir model would indicate that the adsorption is in a monolayer (Foo and Hameed, 2010), with a finite number of identical and specific adsorption sites, so that the amount adsorbed increases until reaching a limit value, corresponding to the coating of the surface by one layer, being the maximum predictable adsorption. Contrary to our results, other authors found that amoxicillin sorption fits the Sips model, which suggests, like the Langmuir model, that sorption of AMX occurs predominantly by chemisorption in a monolayer (Espina de Franco et al., 2017).

The values of the distribution coefficient (K_d) in the Linear model are smaller for the maize and forest soil samples than for the vineyard soils (Table 1), and are lower than those obtained in previous studies for cefuroxime (Cela-Dablanca et al., 2021a, 2021b) and for tetracyclines (Conde-Cid et al., 2019), but higher than those obtained for sulfonamides (Conde-Cid et al., 2020). This would indicate that the interactions involved in the adsorption of AMX onto these soils are stronger than those of sulfonamides, but weaker than those of tetracyclines and cefuroxime. When K_d values were statistically analysed, a significant and positive correlation was found with the Freundlich's K_F ($r = 0.597$, $p < 0.01$), and with the Langmuir's K_L ($r = 0.495$, $p < 0.05$) (data not shown).

The values of the Freundlich affinity coefficient (K_F), associated with the relative adsorption capacity, are (similarly to K_d) smaller for the maize and forest soil samples and higher for the vineyard soils, especially for the soils over granite (VP) (Table 1). The K_F coefficient is related to the adsorption capacity and the values obtained are generally lower than those obtained in previous studies for cefuroxime (Cela-Dablanca et al., 2021a, 2021b) and for tetracyclines (Conde-Cid et al.,

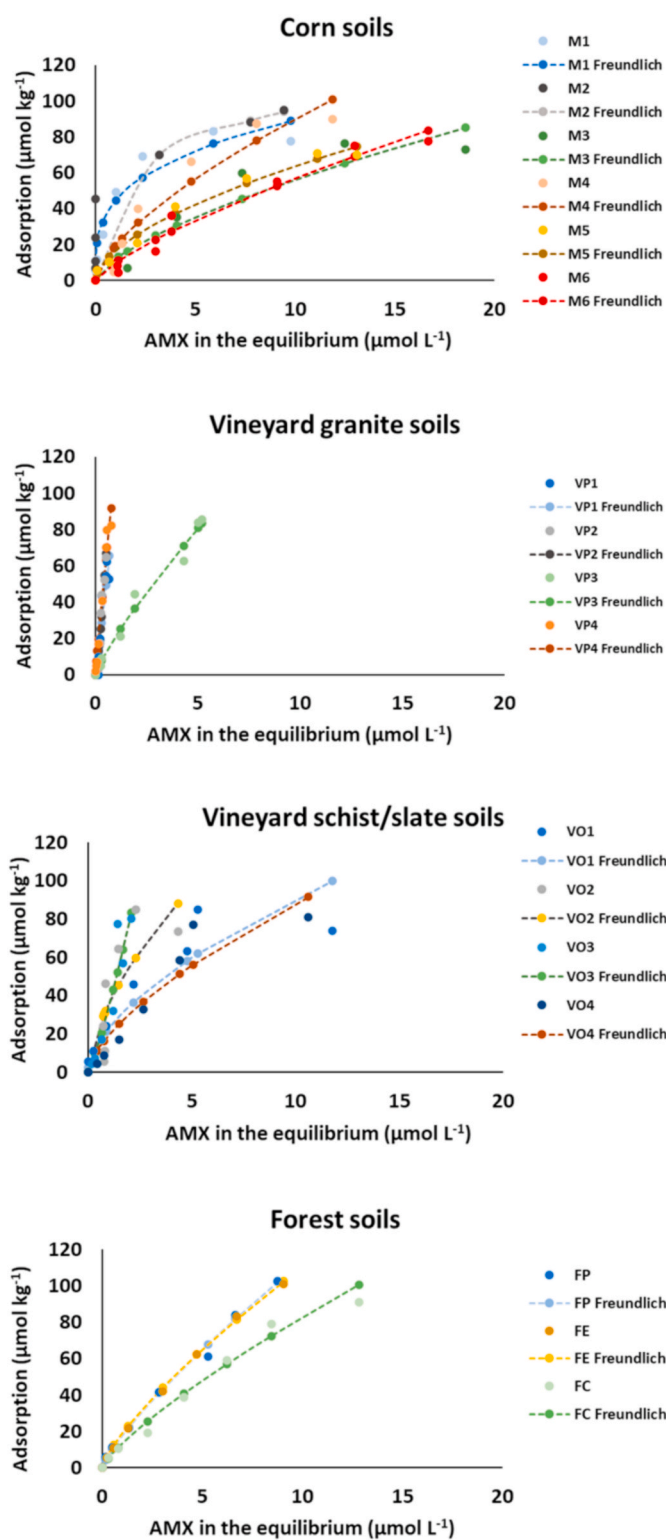


Fig. 1. Adsorption curves for AMX onto the various types of soils studied. Dash lines show the Freundlich isotherm for each soil sample.

2019), but much higher than those obtained for sulfonamides (Conde-Cid et al., 2020). Compared with a study where natural phosphates from the soil mineral phase were analysed (Bouyarmene et al., 2015) the K_F coefficients for AMX are much higher in the soils used in the current research. When performing a statistical analysis, K_F shows a significant and positive correlation with the K content ($r = 0.712$, $p < 0.01$), with q_m ($r = 0.600$, $p < 0.01$), with the Freundlich's n parameter ($r = 0.482$, p

Table 1

Fitting of adsorption results to the parameters of the Freundlich, Langmuir and Linear models. K_F ($L^n \mu\text{mol}^{1-n} \text{kg}^{-1}$); n (dimensionless); K_L ($L \mu\text{mol}^{-1}$); q_m ($\mu\text{mol kg}^{-1}$); K_d ($L \text{kg}^{-1}$). -: error values too high for fitting.

Soil	Freundlich					Langmuir					Linear		
	K_F	Error	n	Error	R^2	K_L	Error	q_m	Error	R^2	K_d	Error	R^2
M1	44.17	4.64	0.306	0.06	0.94	1.24	0.22	89.53	3.94	0.99	10.72	2.30	0.37
M2	-	-	-	-	-	-	-	112.70	48.88	0.72	11.27	3.79	0.78
M3	11.81	4.22	0.68	0.14	0.90	0.07	0.04	140.85	40.68	0.94	5.06	0.57	0.81
M4	19.17	4.63	0.67	0.11	0.93	0.12	0.05	161.81	34.49	0.96	9.30	0.95	0.84
M5	16.51	2.04	0.59	0.05	0.99	0.13	0.03	115.37	10.94	0.99	6.28	0.49	0.90
M6	9.82	2.42	0.76	0.10	0.97	0.05	0.02	180.07	50.51	0.98	5.34	0.34	0.94
VO1	22.85	2.45	0.60	0.06	0.98	0.21	0.03	125.68	9.15	0.99	10.35	0.83	0.89
VO2	35.47	8.76	0.62	0.23	0.68	0.34	0.32	144.26	78.10	0.72	23.55	4.22	0.53
VO3	34.18	6.48	1.20	0.32	0.89	-	-	-	-	-	37.5	3.37	0.88
VO4	19.29	5.08	0.66	0.14	0.90	0.13	0.07	150.203	43.32	0.94	9.68	1.15	0.79
VP1	99.53	20.66	1.09	0.28	0.84	-	-	-	-	-	93.63	0.67	0.48
VP2	150.34	34.64	1.33	0.25	0.90	-	-	-	-	-	3.49	0.26	0.91
VP3	21.03	3.11	0.83	0.10	0.98	0.08	0.06	293.44	165.57	0.98	16.37	0.68	0.97
VP4	116.05	9.89	0.93	0.13	0.97	-	-	-	-	-	120.34	5.63	0.97
FP	17.74	1.70	0.81	0.05	0.99	-	-	-	-	-	12.27	0.41	0.98
FE	18.81	0.57	0.77	0.02	1.00	0.06	0.01	278.39	34.52	1.00	12.07	0.45	0.98
FR	13.44	1.89	0.79	0.07	0.99	0.05	0.02	269.63	67.59	0.99	8.49	0.38	0.97

< 0.05), and with K_d ($r = 0.597$, $p < 0.05$) (data not shown).

Freundlich's n values are related to the heterogeneity of the adsorbent's active sites (Foo and Hameed, 2010). In the soil samples object of this study, n values are, in most cases, lower than 1, coinciding with that obtained by Githinji et al. (2011), which would indicate that the adsorption is non-linear. When n is between 0 and 1, it is indicative of adsorption taking place in a heterogeneous matrix, with the highest energy sites being the first to be occupied. The closer to zero is n , the more heterogeneous the adsorption surface will be, with adsorption being predominantly of chemical type (Foo and Hameed, 2010; Kong et al., 2012). When n is above 1 (just in three or our vineyard samples), it would indicate a deviation from the Freundlich model, which could be caused by irreversible reactions, such as precipitation (Elbana et al., 2018), or cooperative adsorption processes taking place (Foo and Hameed, 2010).

3.4. Desorption of AMX

Fig. 2 represents the sorption and desorption of AMX (in percentage), from the different soils as a function of the concentration of added antibiotic. Numerical values are presented in Tables S3 and S4 (Supplementary Material). Desorption amounts increase with higher concentrations of antibiotic added (Table S4, supplementary material), although the trend is not clear when expressed as percentage desorption (Fig. 2). When comparing desorption values among the set of soils, some differences are observed. Specifically, when the highest concentration of AMX is added, forest soils are those with the lowest desorption (with a maximum = $6.51 \mu\text{mol kg}^{-1}$), followed by granite vineyard soils (maximum = $9.72 \mu\text{mol kg}^{-1}$) and those on slate and schists (maximum = $13.21 \mu\text{mol kg}^{-1}$), and the maximum desorption values corresponding to maize (corn) soils ($18.49 \mu\text{mol kg}^{-1}$) (Table S4, Supplementary Material). The fact that forest soils present less desorption than agricultural soils indicates that those having lower pH and higher organic matter and non-crystalline minerals contents (Table S2, supplementary material) adsorb antibiotics with enhanced retention intensity.

Desorbed AMX is generally less than 10%, in all samples in the case of forest soils, results that were also obtained in these same soils for the desorption of cefuroxime (Cela-Dablanca et al., 2021a, 2021b). These desorption values are higher than those found in previous studies for tetracyclines (Conde-Cid et al., 2019), but they are notably lower than those found for sulfonamides, which reached up to 50% (Conde-Cid et al., 2020). For other antibiotics that present higher sorption under basic pH soil conditions, like the macrolide tylosin, higher desorption levels in forest vs. crop soils have been described (Jeong et al., 2012).

The results obtained in the present study for AMX desorption indicate that, in most cases, the adsorption process is not easily reversible.

3.5. Environmental significance

A wide variety of antibiotics end up in agricultural soils coming from different sources. In the case of amoxicillin the origin can be animal or human, since it is used both in veterinary and human medicine. Antibiotics reach the soils through the repetitive use as fertilizers of WWTP sludge or slurry from animal farms. If the soil sorption intensity is weak, antibiotics get released/leached into surface run-off or groundwater (Díaz-Cruz et al., 2003). Soils can act as a filter, by adsorbing and accumulating antibiotics in the soil particles and avoiding/reducing contamination of water courses, if the sorption mechanisms and their intensities are strong. Protection of water from contamination with antimicrobials is recognized by FAO as the first step to reduce their impact on the environment (FAO, 2018).

It is relevant that even for the same antibiotic the adsorption mechanisms differ among different types of soils (Wang and Wang, 2015). The capacity of soil to sorb amoxicillin has been proved, but in a reduced number of soil types. For the analysis of the sorption mechanisms, the isotherm modeling is of key relevance. Sorption on amoxicillin is complex due to the zwitterion character of the molecule at the most common range of soil pH. This study shows that the amoxicillin sorption-desorption processes depend on soil characteristics such as pH and soil organic matter. The positive impact of low soil pH values on antibiotic sorption mechanisms has been described for other antibiotics, like sulfonamides (Park and Huwe, 2016) or trimethoprim (Zhang et al., 2014). Our research findings are significant for soils subjected to antibiotic pollution. The fact that forest soils show less desorption than agricultural soils, that are usually more exposed to these pollutants, should be considered when the risk of antibiotic contamination is assessed, both for soils and water courses. The development of agroforestry cropping strategies could be interesting because the forest area would act as a buffer mitigating antibiotic loss from agroecosystems (Chu et al., 2010). The results in the present study help to understand the dynamics of amoxicillin in different soil types.

4. Conclusions

In the present study, the soils showing the highest amoxicillin (AMX) adsorption capacities are those with both the most acidic pH (<5.5) and high organic matter and low-crystallinity minerals contents, these characteristics corresponding to all forest soils and two crop soils. This

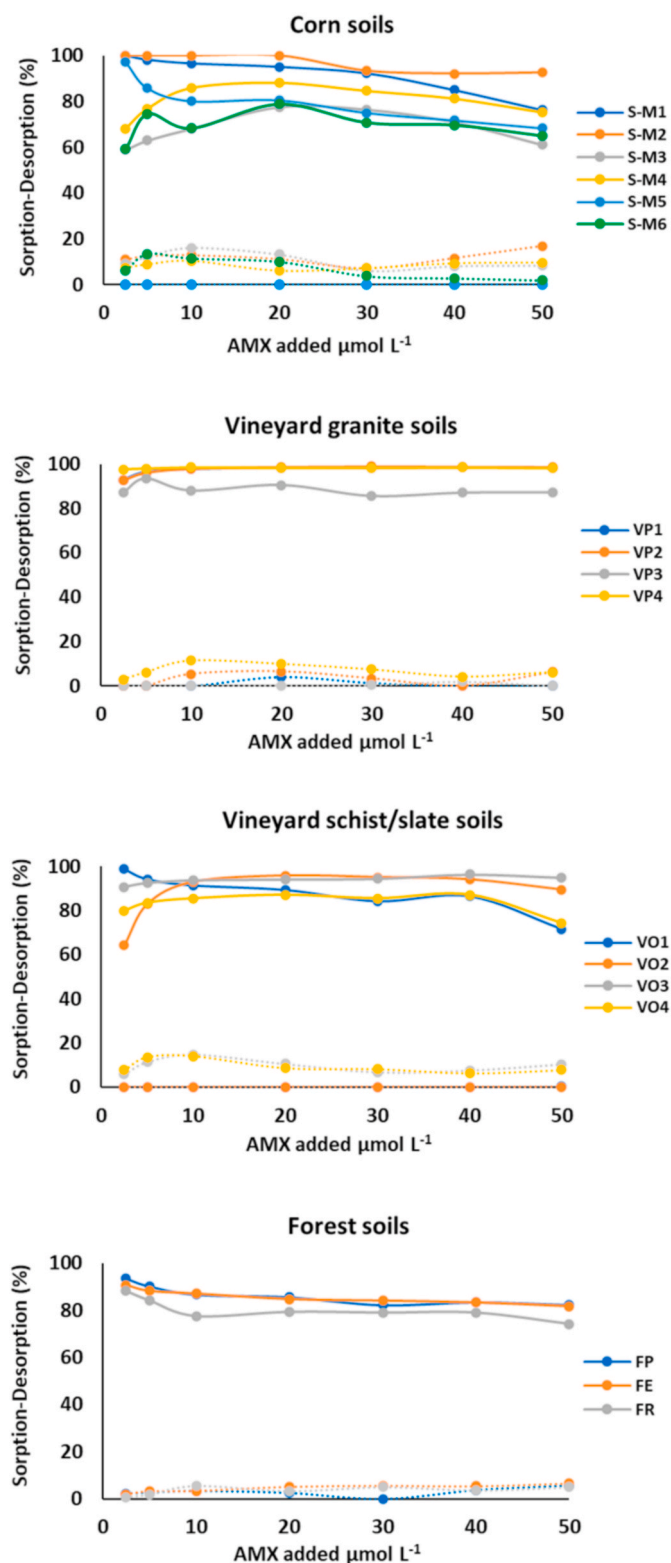


Fig. 2. Sorption and desorption (%) of each soil. Solid lines = Sorption; Dash lines = Desorption.

would indicate that adsorption occurs preferentially by interactions between the deprotonated carboxyl groups of AMX and the positive charges of these variable charge components of the soil. The Freundlich's model is the one that best explains the adsorption of AMX onto these soils, with n values suggesting the dominance of heterogeneous adsorption sites. AMX desorption is generally less than 10%, indicating a

certain irreversibility of the adsorption process. Desorption is clearly lower in forest soils compared to agricultural soils, which would indicate a greater adsorbent-sorbate binding force in soils with more acidic pH and with higher organic matter and non-crystalline minerals contents. The results obtained in this work can be considered relevant regarding the evaluation of the risks associated to the incorporation of AMX into soils, in terms of its retention potential and probabilities of mobilization towards water bodies or entry into the food chain.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envres.2022.112753>.

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