

14 Abstract

15 In the present work, laboratory column experiments were carried out to study the effect of pine bark
16 amendment (at doses of 0, 12, 48 and 96 Mg ha⁻¹) on the transport of three sulfonamide antibiotics
17 (sulfadiazine –SDZ-, sulfamethazine –SMT-, and sulfachloropyridazine –SCP-) through two crop soils. All
18 three sulfonamides showed high mobility in the unamend soils, with absence of retention in most cases.
19 However, some differences were detected regarding the degree of interactions between sulfonamides and
20 soils, being higher for soil 1, which was attributed to its higher organic carbon content. For both soils,
21 interactions with the antibiotics studied followed the sequence SDZ <SMT <SCP, indicating an increase as
22 a function of the hydrophobicity of sulfonamides. Pine bark amendment significantly increased the
23 retention of the three sulfonamides in both soils. Specifically, in the case of soil 1, the incorporation of the
24 highest dose of pine bark (96 Mg ha⁻¹) caused that retention increased from 0% to 70.3% for SDZ, from
25 2.7% to 71.3% for SMT, and from 0% to 85.4% for SMT. This effect of pine bark is mainly attributed to
26 its high organic carbon content (48.6%), including substances with potential to interact and retain
27 antibiotics, as well as to its acidic pH (4.5). Therefore, pine bark amendment would be an effective
28 alternative to reduce the transport of sulfonamides in soils and, thus, decrease risks of passing to other
29 environmental compartments, as well as harmful effects on the environment and public health.

30

31 **Keywords:** crop soils; pine bark; soil columns; sulfonamides; transport

32

33 1. Introduction

34 Antibiotics in the environment are considered of growing concern among emerging pollutants. These
35 molecules reach soil in most cases after being excreted by **livestock** and spread as fertilizers, as they are
36 highly used in veterinary medicine (Kemper, 2008; Milić et al., 2013; Conde-Cid et al., 2018). In fact,
37 sulfonamides are among the antibiotics most widely used in intensive livestock farming, which favors its
38 release into the environment through the application of organic amendments (Sarmah et al., 2006).
39 Regarding their environmental fate and evolution, some adsorption/desorption studies have been carried
40 out, indicating that sulfonamides are very mobile in soils (Leal et al., 2013; Srinivasan et al., 2014; Conde
41 -Cid et al., 2019a, 2019b). These results show that these molecules can be easily transported to subsurface
42 and ground waters, where they were also detected (Sun et al., 2017; Lei et al., 2019), entering the food
43 chain, thus being able to cause significant risks **for humans by development of microbial resistances, even**
44 **at low doses of antibiotics (Zhang et al., 2020)** and ecological health. Another way to study the dynamics
45 of sulfonamides in soils is to perform transport experiments by means of laboratory columns. Using this
46 methodology, Conde-Cid et al. (2019c) showed that soils with low organic matter content were the most
47 vulnerable to pollution due to sulfonamides.

48 In view of that, it could be desirable to have alternatives to increase the retention of these compounds in
49 soils, **which would reduce their transport to other environmental compartments, such as waterbodies, as**
50 **well as plant uptake, decreasing their bioavailability (Pikkemaat et al., 2016), also diminishing antibacterial**
51 **activity (Kümmerer, 2009), lowering risks of negative impacts on human and ecological health.** In this
52 sense, an interesting option could be based on the addition of low-cost bioadsorbent materials, such as pine
53 bark, and specifically bark from the abundant and widely used species *Pinus pinaster*. The natural

54 distribution of *Pinus pinaster* is wide in the western Mediterranean region and the Atlantic zone of
55 southwestern Europe. In Spain it covers more than one million hectares, of which half correspond to
56 reforestation (Ruano et al., 2009). In Galicia (NW of Spain) pine bark from *Pinus Pinaster* is generated at
57 a rate of approximately 350,000 Mg year⁻¹ (Jerez et al., 2009). It is a by-product that constitutes 10-22% of
58 the total volume of the wood, depending mainly on the size of the trees.

59 The use of pine bark as a bioadsorbent has different advantages, as it can be considered as an *in situ*
60 bioremediation technology, with minimal ecological damage, as well as a highly available low-cost
61 technology which facilitates recycling of a by-product, and also an easy to use technology, focusing on a
62 raw material without the need for any physicochemical pretreatment. Recent studies have highlighted the
63 potential of pine bark to adsorb metal cations, such as Pb²⁺, Cu²⁺, Zn²⁺, Cd²⁺, and Hg²⁺ (Gundogdu et al.,
64 2009; Cutillas-Barreiro et al., 2014; Fernández-Calviño et al., 2017). Its efficacy was also evidenced as
65 regards retention of organic molecules, such as trinitrotoluene (Nehrenhaim et al., 2011), or tetracycline
66 antibiotics (Conde-Cid, et al., 2019d). However, the effects of pine bark amendment on the retention and
67 transport of sulfonamide antibiotics has not been studied up to now.

68 In view of that background, the main objective of this work is to determine the characteristics of retention
69 and transport processes for three sulfonamides (sulfadiazine –SDZ-, sulfamethazine -SMT-, and
70 sulfachloropiridazine –SCP-) in two crop soils, by means of laboratory columns, before and after amending
71 with different doses of pine bark (0, 12, 48 and 96 Mg ha⁻¹). As far as we know, this is the first time that it
72 is investigated, and the results could be useful to develop low-cost alternatives conducting to reduce
73 environmental risks associated to these antibiotics.

74

75 **2. Materials and methods**

76 **2.1. Soils and pine bark**

77 Soil samples were from A Limia (Ourense province, Galicia, Spain). A total of 20 subsamples, were taken,
78 corresponding to two surface horizons (0-20 cm depth) of soils dedicated to the cultivation of potatoes and
79 wheat in rotation. Then, each group of subsamples were combined to obtain two composite samples. Once
80 in the laboratory, they were air dried, sieved through a 2 mm mesh, and stored in polypropylene cans until
81 analysis.

82 The textural fractions and granulometric distribution were measured for sand (2-0.05 mm), silt (0.05-0.002),
83 and clay (<0.002 mm). The values of pH in water (pH_w) and in 0.1 M KCl (pH_{KCl}) were determined with
84 pHmeter (Crison 2001, Barcelona, Catalonia, Spain). Nitrogen (N) and organic carbon (OC) contents were
85 determined with a LECO CHN1000 equipment (LECO Co., St. Joseph, MI, USA). Exchangeable cations
86 (Ca_e, Mg_e, Na_e and K_e) were displaced with 0.2 M NH₄Cl following the method of Sumner and Miller
87 (1996), while 1 M KCl was used for exchangeable aluminum (Al_e) (Bertsch and Bloom, 1996). Divalent
88 and trivalent cations were measured by **atomic absorption spectrometry**, while Na_e and K_e were quantified
89 **by atomic emission spectrometry**, always using an AAnalyst 200 equipment (Perkin Elmer, Boston, MA,
90 USA). Phosphorus was determined based on the formation of a phosphomolibic complex in NaHCO₃
91 extracts (Olsen and Sommers, 1982). All determinations were made in triplicate.

92 Main physicochemical characteristics of both soils are shown in Table 1. These soils are acidic, with pH_w
93 close to 5, while pH_{KCl} was lower in both cases (around 4.5), indicating a predominance of negative charges

94 on soil colloids. Organic carbon content was higher for soil 1 (2.1%) than for soil 2 (1.1%). Regarding
95 texture, soil 1 had a slightly higher clay content, **resulting to be sandy clay loam, while Soil 2 was sandy**
96 **loam**. Soil 1 also had higher cation exchange capacity (**5.29 cmol_ckg⁻¹**) **as compared to soil 2 (4.25 cmol_ckg⁻**
97 **l⁻¹**).

98 Pine bark was a commercial product from Geolia (Madrid, Spain), previously characterized by Cutillas-
99 Barreiro et al. (2016). It had acid pH_w (4.5), and OC and N contents of 48.6% and 0.008%, respectively.
100 Regarding the composition of its organic matter, 47.9% was lignin, while glucan was 18.6%, and the sum
101 of xylan + galactan + arabinan + mannan + acetyl groups was 14.7% (Cutillas-Barreiro et al., 2016).

102

103 **2.2. Sulfonamide antibiotics used and methods for its quantification**

104 Three sulfonamide antibiotics were used: sulfadiazine (SDZ), 99.7% purity, sulfamethazine (SMT), 99.6%
105 purity, and sulfachloropyridazine (SCP), 99.7% purity, all three provided by Sigma-Aldrich (Barcelona,
106 Catalonia, Spain). Main characteristics of these three sulfonamides are presented in Table 2.

107 The quantification of the antibiotics was achieved using HPLC equipment (Dionex Corporation, Sunnyvale,
108 USA), with a P680 quaternary pump, an ASI-100 automatic sampler, a TCC-100 thermostated column
109 compartment, and an UVD170U **UV-visible** detector. Separations were performed on a Luna C18 column
110 (Phenomenex, Madrid, Spain) 150 mm long, 4.6 mm internal diameter, and 5 μm particle size, equipped
111 with a protective pre-column packed with the same material, being 4 mm length, 2 mm internal diameter,
112 and 5 μm particle size.

113 More details regarding chromatographic analyses are: 50 μL was the injection volume; 1.5 mL min⁻¹ was
114 used as flow rate; for mobile phase, acetonitrile was used as phase A, while 0.01 M phosphoric acid was
115 used as phase B. The gradient used was as follows: 5% to 32% of phase A for 10.5 min; then, the initial
116 conditions were restored (from 32% to 5% of phase A) in 2 min, and maintained for 2.5 min. **The total time**
117 **for analysis was 15 min, with retention time of 5.3 min for SDZ, 7.6 min for SMT, and 10.3 min for SCP.**
118 **Wavelength for detection was 270 nm. Limits of detection (LOD) were 0.10, 0.07 and 0.06 μM for SDZ,**
119 **SMT and SCP, respectively, while limits of quantification (LOQ) were 0.33 μM for SDZ, 0.24 μM for**
120 **SMT and 0.20 μM for SCP. The linear range for the three compounds was 0-100 μM. All determinations**
121 **were made in triplicate.**

122

123 **2.3. Column experiments and modeling**

124 **2.3.1. Performance of column experiments**

125 **Previous to filling columns, samples of both soils (0.2 kg) were amended with three different doses of pine**
126 **bark**, obtaining 4 samples for each soil, which contained: 0 (Control), 12, 48 and 96 Mg of pine bark ha⁻¹.

127 The mixtures were kept on a rotary shaker for 72 hours and passed 10 times through a riffle splitter (Retsch,
128 Haan, Germany) in order to achieve homogenization.

129 Vertically oriented laboratory glass columns, **80 mm long and 25 mm internal diameter**, were used to carry
130 out the experiments. The bottom of the columns was connected to a peristaltic pump (Gilson Minipuls 3,
131 USA) using 1/16 inch PVC tubing. The pump was connected through a three-way valve to bottles with
132 distilled water, to a 10 mM Br⁻ solution, to 10 μM antibiotic solutions, and to a 0.005 M CaCl₂ solution.

133 The column outlet, at the top, was connected to a fraction collector (Gilson FC 203 B, USA), also using
134 1/16 inch PVC tubing.

135 Laboratory columns were filled with approximately 30 g of solid sample (soil or mixture soil/pine-bark).
136 Subsequently, a saturation phase was carried out by using distilled water at a flow of 1 mL h⁻¹ for three
137 days. Once saturated, the valve was turned to allow the entry of the Br⁻ solution (which acts as inert tracer),
138 with a flow of 3 mL h⁻¹ maintained for 8 hours. Next, the valve was rotated to allow the entry of the 0.005
139 M CaCl₂ solution for 48 hours, at the same flow of 3 mL h⁻¹, to elucidate the pattern of release for the inert
140 tracer (Br⁻). After that, the valve was turned again to allow the entry of the 10 μM solution for each
141 individual antibiotic separately (representing 2.5 mg L⁻¹ for SDZ, and 2.8 mg L⁻¹ for SMT and SCP), also
142 containing 0.005 M CaCl₂ as background electrolyte, at the same flow of 3 mL h⁻¹, for 8 hours. The
143 experiment ended by turning the valve again to allow the entry of the 0.005 M CaCl₂ solution, at the same
144 flow of 3 mL h⁻¹, for 48 hours, in order to make evident the release pattern of the antibiotic previously
145 retained. The entire transport experiment was carried out at room temperature (25 ± 2 °C).

146 After the transport experiments, each column was weighed to determine their pore volume capacity. All
147 outflow liquids from the experiments were collected using a fraction collector at 30 minute intervals (1.5
148 mL per sample) and stored at 4 °C until analysis. Br⁻ concentrations were quantified by using an automatic
149 segmented continuous flow injection analyzer (Bran-Luebbe AutoAnalyzer 3, Germany), by reaction with
150 chloramine-T and fluorescein. The values for pH were determined by using a glass micro-electrode (Crison
151 pH-Meter Basic 20, Spain) and the concentrations of each antibiotic were determined using HPLC-UV
152 equipment, as indicated above. All determinations were made in triplicate.

153

154 2.3.2. Modeling

155 Breakthrough curves were plotted using data from column experiments, where the evolution of the C/C₀
156 ratio (ratio between antibiotic concentration in the output solution, and antibiotic concentration in the input
157 solution) was represented. The moment analysis method (Valocchi, 1985; Stagnitti et al., 2000; Kamra et
158 al., 2001) was used to obtain a series of descriptive parameters for breakthrough curves.

159 The first normalized moment (τ) indicates the average time for the output of the antibiotic, and was
160 calculated using the following equation:

$$161 \tau = \mu_1^{<n>} = M_1 / M_0$$

162 where M_0 and M_1 are the central moments 0 and 1, respectively, resulting from the integration of the general
163 expression of the breakthrough curve:

$$164 M_p = \int_0^{\infty} t^p f(t) dt$$

165 where p are values for each moment (0 for moment 0, 1 for the first moment, 2 for the second moment, and
166 so on).

167 Using the values of τ for the antibiotic and for the inert tracer (Br⁻), a relative retardation factor for the
168 antibiotic with respect to the solution was calculated, as follows:

$$169 R = \tau_p / \tau_{Br}$$

170 The second central moment (μ_2) indicates the variance of the curve, while the standard deviation of the
171 curve (σ) is given by its square root:

$$172 \sigma = \sqrt{\mu_2}$$

173 Dispersivity (λ) indicates the dispersion of the antibiotic inside the column (Schoen et al., 1999; Stagnitti
174 et al., 2000) and is given by the following expression (where L is the length of the column):

$$175 \lambda = (L/2) \cdot (\mu_2/\tau_2)$$

176 Finally, the third central moment (μ_3) indicates the asymmetry of the curve, and was used to calculate the
177 dimensionless skewness parameter (S):

$$178 S = \mu_3 / \mu_2^{3/2}$$

179

180 3. Results and discussion

181 3.1. Breakthrough curves for un-amended soils

182 Figure 1 shows breakthrough curves for the two crop soils and the three sulfonamides studied, as well as
183 for the inert tracer (Br^-). Maximum outlet concentration for Br^- was reached approximately after 2 pore
184 volumes (PV), with a C/C_0 value of 0.8 for soil 1 (Figure 1a, 1c and 1e) and 1.0 for soil 2 (Figure 1b, 1d
185 and 1f). Plots corresponding to un-amended soils (0 Mg of pine bark ha^{-1}) showed that breakthrough curves
186 of antibiotics suffered a slight displacement with respect to those of Br^- , reaching the maximum after 3-4
187 PV (Figure 1), which indicates the existence of interactions between sulfonamides and both soils. The
188 values of the transport parameters obtained from the modeling of the curves confirm this fact, as the
189 retardation factor (R) was always >1 (Table 3), evidencing the existence of a certain delay of the
190 sulfonamide antibiotics with respect to the inert tracer (Br^-). However, at the end of the experiment, after
191 the passage of 14 PV through the columns, there was practically absence of retention for all three antibiotics.
192 This fact suggests that there would be a high risk of leaching for these sulfonamides from soil to water
193 bodies in real field situations. This low retention of sulfonamides was previously reported for other soils
194 (Boxall et al., 2002; Figueroa-Diva et al., 2010; Leal et al., 2013; Srinivasan et al., 2014; Vieira et al., 2017;
195 Rath et al., 2019).

196 The values corresponding to percentage retention, retardation factor (R), and average time for outlet (τ) are
197 shown in Table 3. For SDZ and SCP, there was no retention (0%) in any of both soils when pine bark was
198 not added (Table 3), which indicates a very low affinity in both cases. For SDZ, R and τ showed similar
199 values for both soils, while they were higher for soil 1 in the case of SMT and SCP, indicating that these
200 two sulfonamides suffered more pronounced interaction with soil 1 than with soil 2. Taking into account
201 that both soils have very similar characteristics, with the exception of the OC content (2.1% in soil 1, and
202 1.1% in soil 2), it suggests that soils with higher organic matter content have higher retention potential for
203 sulfonamides. In fact, this is in accordance with what was previously observed by authors who studied the
204 adsorption and desorption of sulfonamides in soils of different characteristics (Thiele-Bruhn et al., 2004;
205 Laak et al., 2006; Lertpaitoonpan et al., 2009; Chu et al., 2013; Conde-Cid et al., 2019a, d). In addition, the
206 following sequence was found for interactions among sulfonamides and both soils: SDZ <SMT <SCP
207 (Figure 1), which is also in accordance with the values obtained for transport parameters. Specifically, the
208 values of the retardation factor (R), in the case of soil 1 were: 1.59 for SDZ, 2.12 for SMT, and 3.06 for
209 SCP, while the average time for outlet (τ) was 3.17 PV for SDZ, 4.23 PV for SMT and 6.12 PV for SCP
210 (Table 3). In the case of soil 2 the values of R and τ for soil 2 maintained the same sequence, always
211 increasing in the order SDZ <SMT <SCP (Table 3). However, the parameters λ and S followed an opposite
212 trend, showing the highest values for SDZ and the lowest for SCP (Table 3). The sequence in the degree of

213 affinity for soils observed for the three sulfonamides (SDZ <SMT <SCP) is in accordance with that obtained
214 by Leal et al. (2013) in Brazilian soils, that was: SDZ <sulfamethoxazole <SMT <SCP <sulfathiazole.
215 Similarly, Rath et al. (2019) obtained the sequence SDZ <SMT <sulfadimethoxin <SCP <sulfaquinoxaline
216 in other Brazilian soils. Thiele-Bruhn et al. (2004) studied the adsorption of five sulfonamides in different
217 soils in Germany, and obtained the sequence <SDZ <sulfadimethoxin <SMT <sulfapyridine. This different
218 adsorption behavior observed for SDZ, SMT and SCP suggests that the substituent at the base of the
219 structure of the sulfonamide molecule has an important influence on the interactions of these compounds
220 with soils.

221

222 3.2. Retention mechanisms

223 It should be taken into account that sulfonamides are amphoteric compounds, which causes that depending
224 on the pH of the medium they can exist in cationic, neutral and/or anionic form. In the present work the
225 experiments took place at an approximate pH of 5. At this pH value, both SDZ and SMT are almost entirely
226 neutral (94.9% for SDZ, and 99.6% for SMT) while, in the case of SCP, 26% of the species are in anionic
227 form (and 74% as neutral). In view of that, it could be expected that SCP would have lesser degree of
228 interaction with soils than SDZ and SMT, due to the repulsion between the anionic species of SCP and the
229 surfaces of various soil components, which have a predominance of negative charges at this pH value (pH
230 around 5). However, the results obtained clearly indicate that SCP has higher affinity for soils than SDZ
231 and SMT, so that the predominance of one or other species (cationic, zwitterionic and/or anionic) does not
232 explain the different behavior for interaction/retention observed for these three sulfonamides. In fact, this
233 is in accordance with that previously reported by Leal et al. (2013), who also found no relation between
234 adsorption to soils of different sulfonamides and the values of their acid dissociation constants (pK_a).
235 However, there is another property of the molecules that is also dependent on the substituent at the base of
236 the structure of the sulfonamides, called hydrophobicity, which could aid to give further explanation. In
237 this way, it is needed to take into account the value of the octanol-water partition coefficient (K_{OW}), which
238 describes the propensity of the molecules to dissolve in a nonpolar medium. Specifically, at pH 5.0, values
239 of $\log K_{OW}$ are -0.14 for SDZ, 0.27 for SMT, and 0.69 for SCP (Carda-Broch and Berthod, 2004). This
240 trend (or sequence) of values for $\log K_{OW}$ is consistent with that of the interaction of the three sulfonamides
241 with soils (SDZ <SMT <SCP), suggesting that this interaction is largely influenced by the hydrophobicity
242 of the antibiotics, implicating higher interaction with soils when the hydrophobic of the molecule of
243 antibiotic is also higher (that is, higher $\log K_{OW}$ value). In fact, this is in accordance with data previously
244 reported by others authors (Figuroa-Diva et al., 2010; Leal et al., 2013). In view of that, taking into account
245 that the affinity of sulfonamides for soils is mainly influenced by the degree of hydrophobicity of the
246 antibiotic, and by the organic matter content of the soil, it could be inferred that hydrophobic partition
247 (related to the value of the hydrophobicity partition coefficient) can be the main mechanism that determines
248 the interaction of these compounds with soils, with organic matter acting as a non-polar phase, which is
249 in accordance with what was previously reported by Srinivasan et al. (2014), and by Rath et al. (2019).

250

251 3.3. Breakthrough curves for pine-bark-amended soils

252 Figure 1 also shows as very relevant fact that the incorporation of pine bark to the soils favored the retention
253 of the three sulfonamides. Specifically, maximum concentrations shifted to higher PV values, and when
254 high doses of pine bark were added the curves become flattened, which indicates a very strong retention of
255 sulfonamides. This occurs for all three antibiotics and for both soils. This effect of the pine bark amendment
256 can also be observed depending on the values of the descriptive parameters obtained from the modeling of
257 the curves (R and τ), which resulted markedly increased with the incorporation of pine bark to soils. In the
258 case of soil 1, with the highest dose of pine bark (96 Mg ha^{-1}), R values increased from 1.59 to 3.48 for
259 SDZ, from 2.12 to 4.80 for SMT and from 3.06 to 5.24 for SCP, while in the case of soil 2 increased from
260 1.60 to 3.45 for SDZ, from 1.64 to 4.10 for SMT, and from 2.56 to 6.72 for SCP (Table 3). The values of τ
261 follow the same trend, increasing (in the case of soil 1), from 3.17 to 7.77 PV for SDZ, from 4.23 to 10.71
262 PV for SMT, and from 6.12 to 11.68 PV for SCP, while for soil 2 they went from 3.20 to 7.10 PV for SDZ,
263 from 3.30 to 8.45 PV for SMT, and from 5.13 to 13.84 PV for SCP.

264 Retention percentages increased in both soils as a function of the dose of pine bark (Table 3). For SDZ, in
265 soil 1 retention values went from 0.0% (un-amended soil) to 70.3% (amended soil with 96 Mg ha^{-1} of pine
266 bark). Similar scores were obtained for soil 2, where retention increased from 0.0% (un-amended) to 80.4%
267 (soil amended with 96 Mg ha^{-1} of pine bark) (Table 3). SMT had a similar behavior, but retention
268 percentages after the addition of 96 Mg ha^{-1} of pine bark was slightly lower, reaching 71.3% and 58.8% for
269 soil 1 and soil 2, respectively (Table 3). The highest retention rates were found for SCP, going for soil 1
270 from 0.0% (un-amended) to 85.4% (amended with 96 Mg ha^{-1} of pine bark), and going from 0% to 99.6%
271 for soil 2 (Table 3). These results are better than those obtained amending with biochar (Vithanage et al.,
272 2014; Liu et al., 2017), or with pig manure (Wang et al., 2015).

273 This effect of pine bark on the retention and transport of sulfonamides is mainly due to the fact that it has
274 a high content of organic matter compared to soils, bearing in mind that organic matter is the main
275 constituent of soils that determines retention of sulfonamides. In addition, it should be noted that pine bark
276 has an acidic pH (4.5), lower than that of soils, and, at acidic pH values, as pH decreases, the proportion of
277 positively charged antibiotic species increases, favoring the interaction of sulfonamides with soils, which
278 have a predominance of negative charges at these pH values. This is in accordance with that previously
279 reported by various authors (Białk-Bielińska et al., 2012; Park and Huwe, 2016; Liu et al., 2017; Conde-
280 Cid et al., 2019c), who found that a decrease in pH resulted in an increase in the adsorption of sulfonamides
281 in all cases.

282 Although no previous papers focused on studying the effect of pine bark on the transport of sulfonamides
283 in soils by using laboratory column experiments, some authors used other amendments which also clearly
284 reduced the mobility of sulfonamides, such as a wheat straw biochar (Liu et al., 2015), and a biochar
285 obtained from invasive plants (Ahmad et al., 2014). Likewise, it has also been observed that pig farm
286 residues can delay the transport of sulfonamides in soils (Zhou et al., 2016), as well as liquid cow manures
287 (Strauss et al., 2011). However, these manures can contain sulfonamides in their composition, as well as
288 other pollutants, and if applied to soils for years they could be a source of water pollution (Spielmeyer et
289 al., 2017).

290

291 **4. Conclusions**

292 The three sulfonamide antibiotics here studied showed very low retention in crop soils, with subsequent
293 high risk of being transported to surface and ground waters, as well as of entering the food chain and cause
294 significant damage to human and environmental health. All three sulfonamides showed higher interaction
295 with soil 1, which was attributed to its higher organic matter content. The retention sequence SDZ <SMT
296 <SCP detected for the antibiotics indicates that those with the highest hydrophobicity were the most
297 retained. In view of that, is clearly relevant the importance of hydrophobic partition in the retention of these
298 compounds in soils, with organic matter acting as a non-polar phase. Pine bark amendment significantly
299 increased the retention of all three sulfonamides in the crop soils studied; **specifically, retention percentages**
300 **increased for all three sulfonamides and both soils from 0% (un-amended) to values between 59-100%**
301 **(amending with pine bark at 96 Mg ha⁻¹). These values show the potential of pine bark** to decrease the
302 transport of these compounds to surface and ground waters, preventing their entry into the chain food, thus
303 reducing risks for human and ecological health.
304

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314

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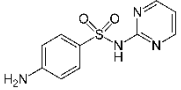
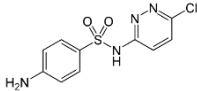
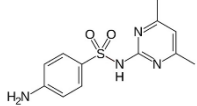
466 **Table 1.** Main physicochemical characteristics of the soils studied. pH_w: pH in water; pH_{KCl}: pH in 0.1 M
 467 potassium chloride; OC: organic carbon; N: total nitrogen; Ca_e: exchangeable calcium; Mg_e: exchangeable
 468 magnesium; Na_e: exchangeable sodium; K_e: exchangeable potassium; Al_e: exchangeable aluminum; eCEC:
 469 effective cation exchange capacity. Average values of 3 replicates, with coefficients of variation always
 470 <5%

Parameter	Soil 1	Soil 2
pH _w	5.0	5.1
pH _{KCl}	4.4	4.5
OC (%)	2.1	1.1
N (%)	0.20	0.11
Sand (%)	61	67
Silt (%)	16	14
Clay (%)	23	19
Ca _e (cmol _(c) kg ⁻¹)	2.48	2.17
Mg _e (cmol _(c) kg ⁻¹)	0.51	0.99
Na _e (cmol _(c) kg ⁻¹)	0.29	0.23
K _e (cmol _(c) kg ⁻¹)	1.25	0.64
Al _e (cmol _(c) kg ⁻¹)	0.76	0.22
eCEC (cmol _(c) kg ⁻¹)	5.29	4.25
P _{Olsen} (mg kg ⁻¹)	191	116

471

472

473 **Table 2.** Main physicochemical characteristics of the three sulfonamide antibiotics studied

Common name	Chemical structure	Chemical formula	Molecular weight (g mol ⁻¹)	Log K _{ow} ¹	pK _a ²	Water solubility (mg L ⁻¹) ¹
Sulfadiazine		C ₁₀ H ₁₀ N ₄ O ₂ S	250.3	-0.09	2.10 - 6.28	77
Sulfachloropyridazine		C ₁₀ H ₉ ClN ₄ O ₂ S	284.7	0.31	1.87 - 5.45	35
Sulfamethazine		C ₁₂ H ₁₄ N ₄ O ₂ S	278.3	0.89	2.07 - 7.49	1500

474 ¹ Chen et al. (2015); ² Babic et al. (2007)

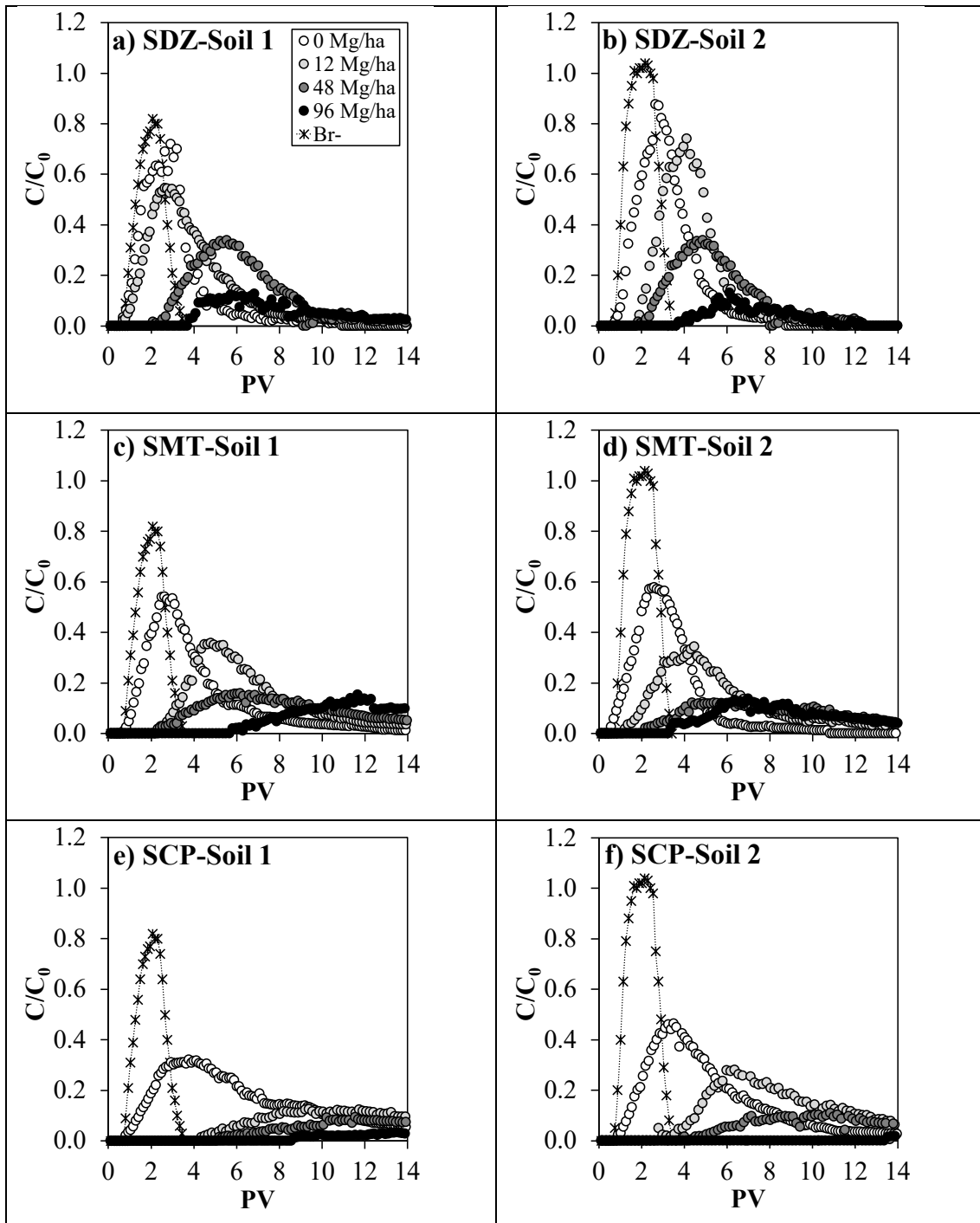
475

476 **Table 3.** Sulfonamides retention (% and $\mu\text{mol kg}^{-1}$) and transport parameters derived from column
 477 experiments. Average values of 3 replicates, with coefficients of variation always <5%; τ : average time for
 478 outlet (breakthrough time); R : retardation factor, compared to Br^- ; σ : standard deviation for the curve; λ :
 479 dispersivity; S : skewness; PV: number of pore volumes; SDZ: sulfadiazine; SMT: sulfamethazine; SCP:
 480 sulfachloropyridazine; PB: pine bark

SDZ	PB dosage (Mg ha^{-1})	% retained	Amount retained ($\mu\text{mol kg}^{-1}$)	τ (PV)	R	σ (PV)	λ (cm)	S
Soil 1	0	0.00	0.0	3.17	1.59	1.81	0.81	2.13
	12	17.9	1.2	3.88	1.94	1.90	0.60	1.18
	48	37.1	2.8	6.20	2.80	2.20	0.32	1.11
	96	70.3	5.5	7.77	3.48	2.61	0.28	0.62
Soil 2	0	0.0	0.0	3.20	1.60	1.32	0.42	1.19
	12	17.9	1.3	4.45	1.92	1.62	0.33	1.81
	48	31.9	1.9	5.73	2.74	2.35	0.42	0.55
	96	80.4	5.5	7.10	3.45	1.78	0.16	0.49
SMT	PB dosage (Mg ha^{-1})	% retained	Amount retained ($\mu\text{mol kg}^{-1}$)	τ (PV)	R	σ (PV)	λ (cm)	S
Soil 1	0	2.7	0.2	4.23	2.12	2.57	0.92	1.53
	12	28.4	1.8	6.60	3.32	2.55	0.37	0.96
	48	48.0	2.9	7.87	3.56	2.86	0.33	0.28
	96	71.3	4.5	10.71	4.80	2.03	0.09	-0.32
Soil 2	0	8.3	0.7	3.30	1.64	1.62	0.61	1.71
	12	34.4	2.2	5.76	2.49	2.88	0.62	1.04
	48	58.2	3.6	7.86	3.76	3.01	0.37	0.22
	96	58.8	3.8	8.45	4.10	2.66	0.24	0.18
SCP	PB dosage (Mg ha^{-1})	% retained	Amount retained ($\mu\text{mol kg}^{-1}$)	τ (PV)	R	σ (PV)	λ (cm)	S
Soil 1	0	0.0	0.0	6.12	3.06	3.22	0.69	0.63
	12	68.0	4.6	9.94	4.99	2.47	0.15	-0.18
	48	61.4	4.2	10.60	4.79	2.26	0.11	-0.41
	96	85.4	6.1	11.68	5.24	1.58	0.05	-0.22
Soil 2	0	0.0	0.0	5.13	2.56	2.71	0.70	1.11
	12	47.4	3.2	8.26	3.56	2.66	0.26	0.35
	48	75.3	4.6	9.65	4.62	2.42	0.16	-0.10
	96	99.6	7.7	13.84	6.72	0.19	0.00	-0.14

481

482



483 **Figure 1.** Breakthrough curves from laboratory column experiments. **SDZ:** Sulfadiazine; **SMT:**
 484 **Sulfamethazine;** **SCP:** Sulfachloropyridazine; C/C_0 : Ratio between outlet and inlet concentrations. PV:
 485 number of pore volumes.

486