1 Modelling the sorption behaviour of perfluoroalkyl carboxylates and

2 perfluoroalkane sulfonates in soils

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8 ABSTRACT

9 A simple parametric model was developed to predict the sorption of perfluoroalkyl

10 substances (PFASs) in soils. Initially, sorption and desorption solid-liquid distribution

11 coefficients (K_d and $K_{d,des}$ respectively) of eight PFASs (five perfluoroalkyl carboxylates,

12 PFCAs, and three perfluoroalkane sulfonates, PFSAs) in seven soils with organic carbon (OC)

13 content ranging from 1.6 to 41% were quantified using batch experiments. The information

14 obtained helped to fill the gaps in a literature-based database of K_d values of PFASs, which was

15 lacking data on soils with high OC content. The overall dataset finally comprised 435 entries.

16 Normalized sorption coefficients for the soil OC and mineral fraction contents (K_{OC} and K_{MIN}

17 respectively) were deduced for each PFAS by correlating the corresponding K_d values obtained

18 under a wide range of experimental conditions with the fraction of organic carbon (f_{OC}) of the

19 soils. Furthermore, the sorption mechanisms in each phase were shown to depend mainly on

20 PFAS chain length. The dependence of K_{OC} and K_{MIN} values on PFAS chain length defined the

21 basic equations to construct the model for predicting PFAS sorption, applicable to both PFCAs

22 and PFSAs with chain lengths ranging from 3 to 11 fluorinated carbons. The validation of the

23 proposed model confirmed its ability to predict the K_d of PFASs based only on the soil OC and

24 silt+clay contents and PFAS chain length. Therefore, it can be used in the first stages of a risk

25 assessment process aiming at estimating the potential mobility of PFASs in soils after a

26 contamination event.

27 **Keywords**: PFASs, soils, sorption, desorption, modelling, K_d

28

29 **Synopsis**

30 This study develops a new parametric model to predict the sorption of perfluoroalkyl substances

31 (PFASs) in soils.

1. Introduction

Perfluoroalkyl substances (PFASs), among them perfluoroalkyl carboxylates (PFCAs) and perfluoroalkane sulfonates (PFSAs), are anthropogenic organic pollutants with a fluorinated carbon chain attached to a functional group. These substances have been used for more than 50 years in a variety of applications including fire-fighting foams, inks, lubricants, and oil and water repellents for the leather, paper and textile industries (Prevedouros et al., 2006). Because they are widely used, highly toxic, and can bioaccumulate and persist in the environment, PFASs have garnered considerable scientific attention in recent years (Kannan, 2011). They have been found in environmental matrices such as soil, sediment, and biological samples, as well as in rain, freshwater, seawater, and groundwater (Prevedouros et al., 2006). Specifically, they have often been detected at levels of up to a few mg kg^{-1} in contaminated soils and at levels of up to several hundred µg L^{-1} in groundwater of contaminated sites (Brusseau et al., 2020; McGuire et al., 2014). Given these high concentrations, it is important to evaluate PFAS sorption in soils in order to develop sorption prediction models and to assess their mobility in the environment more accurately.

Several soil properties have been suggested to affect PFAS sorption in soils, including organic carbon (OC), silt and clay phases, pH and status of divalent metals. Higgins and Luthy (Higgins and Luthy, 2006) found that soil OC content was the main parameter affecting the sorption behaviour of PFASs in sediments, suggesting that most sorption occurred via hydrophobic interactions, although soil pH and the concentration of divalent cations might also play a role in the sorption process via electrostatic interactions. The presence of hydrophobic interactions in soils was further addressed by Milinovic et al. (Milinovic et al., 2015), and the effect of salinity and pH on sorption to sediments with OC < 1% has also been evaluated elsewhere (You et al., 2010). However, even though pH and ionic strength may play a role in the sorption process on mineral soils under controlled scenarios, these effects are minor

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compared to the effect of OC content. Moreover, studies exploring the sorption of PFASs on low OC soils (< 5%) have suggested that the mineral phase may have a positive influence on the sorption process (Knight et al., 2019; Martz et al., 2019). A literature review evaluating the role of soil and sediment properties in the sorption of PFASs concluded that OC alone could not satisfactorily account for the sorption of PFASs and suggested that other parameters, such as soil pH and clay content, should also be considered (Li et al., 2018). However, these conclusions were based on a data set that included mostly studies of soils or sediments with OC content < 10% and very few samples of soils with higher OC content which may be representative of environmental scenarios such as meadows, forest soil layers or peat soils. In addition, the sorption pattern was deduced from the widely-evaluated PFASs perfluorosulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), while only limited sorption data are available for other shorter or longer-chained PFASs in soils and sediments.

Among the models for predicting the sorption behaviour of PFASs currently in use, a mechanistic model was developed to predict the sorption of PFCAs, PFSAs, and linear alkylbenzenes in sediments with OC ranging from 0.6 to 9.7% via both electrostatic and hydrophobic interactions with the organic matter (Higgins and Luthy, 2007). The model was tested for its ability to predict the sorption parameters of PFCAs and PFSAs with 7–11 fluorinated carbons under specific experimental conditions. Moreover, Knight et al. (Knight et al., 2019) developed a model based on OC and soil silt and clay content, able to predict the sorption of PFOA under selected experimental conditions in soils with OC content ranging from 0.1–3.5%, thus excluding organic soils. Therefore, new experimental data for deriving PFAS sorption and desorption parameters in a diversity of soil types are required to improve current sorption models, making them less site-specific and covering a wide variety of PFASs, including the least commonly regulated species (especially short-chained PFASs) (Sima and Jaffé, 2021).

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82   In this study, we aim to construct a simple and global parametric model, based on a

83   small number of PFASs and easily-measurable physicochemical properties of soil, to predict

84   the sorption solid-liquid distribution coefficient (K_d) of any PFCAs and PFSAs with a number

85   of fluorinated carbon units between 3 and 11, and applicable to both mineral and organic soils.

86   First, sorption parameters of eight PFASs in seven soils with OC ranging from 1.6 to 41% were

87   determined to improve an overall database of K_d values of PFASs created with data from the

88   literature. Then, a parametric model was constructed based on the relationships between

89   normalized sorption coefficients (with respect to soil OC and mineral phase contents) and the

90   number of fluorinated carbons.

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92   **2. Materials and methods**

93   *2.1. Reagents and standards*

94   Milli-Q double deionized water (18.2 MΩ cm^{-1}) was obtained from a water purification

95   system (USF PureLaB Plus, Spain). High-performance liquid chromatography-grade

96   acetonitrile (≥99.9%), as well as extra-pure sodium azide (≥99.0%) and calcium chloride

97   dihydrate (99%), were supplied by Merck (Germany), and ammonium acetate (96%) was

98   supplied by Panreac (Spain). Analytical standards of perfluorobutanoic acid (PFBA) 98%,

99   perfluorohexanoic acid (PFHxA) 97%, perfluorooctanoic acid (PFOA) 96%, perfluorononanoic

100   acid (PFNA) 97%, perfluorododecanoic acid (PFDoA) 95%, and potassium perfluorohexane

101   sulfonate (PFHxS) 98% were supplied by Sigma-Aldrich (Germany). Tetrabutylammonium

102   perfluorobutane sulfonate (PFBS) 98% and tetrabutylammonium perfluorooctane sulfonate

103   (PFOS) 95% were supplied by Fluka (Austria). Isotope-labelled sodium perfluoro-1-[1,2,3,4,-

104   $^{13}C_4$]-octane sulfonate (MPFOS) and perfluoro-n-[1,2,3,4,-$^{13}C_4$]-octanoic acid (MPFOA), both

105   at concentrations of 50 μg mL^{-1} in methanol, were supplied by Wellington Laboratories

106   (Canada). Working solutions of 1,000 μg mL^{-1} containing the individual PFASs were prepared

107   in acetonitrile, whereas working solutions of MPFOS and MPFOA were prepared separately at

108   20 µg mL^{-1} in acetonitrile by diluting the commercial stock solutions. All solutions were stored

109   at -18°C in glass vials with polyethylene caps (Sigma-Aldrich, Germany).

110   The main physicochemical properties of all PFASs considered in this study, including

111   those not used in our experiments but incorporated in the database for our parametric model,

112   are summarized in Table S1. Based on the pK$_a$ values reported in Table S1, all selected PFASs

113   were expected to be in their anionic form under our experimental conditions. PFAS chain length

114   in this study was referred as the total number of fluorinated carbons in the alkyl chain (CF$_2$)

115   including the final –CF$_3$ moiety.

116

117   *2.2. Materials and characterization*

118   Seven field soil samples (topsoils; taken at 0–10 cm depth) with physicochemical

119   properties varying within a wide range were selected for our PFAS sorption and desorption

120   experiments (Table 1). The soil samples generally had an acidic pH ranging from 5.2 to 5.8 and

121   a CaCO$_3$ content below 3%, with the exception of the DELTA2 soil, which had a slightly basic

122   pH of 8.0 likely due to its higher CaCO$_3$ content. The OC content of the soil samples ranged

123   from 1.6 to 41%; four samples having an OC content above 25%. More information about the

124   soils and the physicochemical characterization procedures is provided elsewhere (Ramírez-

125   Guinart et al., 2017).

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127   *2.3. Sorption and desorption experiments*

128   To test the sorption behaviour of each PFAS in each soil, three grams of dried soil were

129   placed in 80-mL polypropylene (PP) centrifuge tubes with 30 mL of 0.01 mol L^{-1} CaCl$_2$ solution

130   containing 1 g L^{-1} of NaN$_3$ as a biodegradation inhibitor (OECD, 2000). The resulting

131   suspensions were end-over-end shaken at 60 rpm for 24 h, and then known volumes of

individual PFAS stock solutions were added to the suspensions. The initial spiked concentrations of each PFAS (Table S2) were selected to ensure that: i) the K_d value fell within the linear range of the sorption isotherm according to previous studies of PFAS sorption in soils performed by our research group (Milinovic et al., 2015); ii) the final sorbed concentrations were representative of concentrations that might be found in contaminated soils (Brusseau et al., 2020); iii) PFAS concentrations in the final liquid solution were below 70 µg L^{-1}, a value also representative of concentrations found in groundwater of PFAS-impacted sites (McGuire et al., 2014); and iv) the final concentration in the liquid solution led to reliable results after their analytical determination. After being spiked with a PFAS, tubes were shaken again at 60 rpm for 24 h to ensure that the equilibrium was reached in accordance with previous kinetic studies (Li et al., 2019; Mejia-Avendaño et al., 2020; Miao et al., 2017; Wei et al., 2017; Xiang et al., 2018; Zhi and Liu, 2018). Then, tubes were centrifuged for 30 min at 4 °C and 7,800 *g* (AJ2-HS, Beckman Coulter, USA) and supernatants were removed using a plastic syringe, filtered through 0.45 µm and stored in 50 mL glass vials at 4 °C until analysis. For the desorption experiments, soil residues from the sorption experiment were dried at 40°C and then tested using the same procedure as above, but without PFAS spiking, except for PFBA and PFBS that presented, in general, very low sorption levels. Shaking desorption time was 24 hours, in agreement with previous kinetic desorption experiments on soils and sediments with varying OC content (Miao et al., 2017; Zhi and Liu, 2018). In addition, preliminary studies revealed that PFAS sorption and desorption K_d values at 168 hours were statistically comparable to those found at 24 hours. The pH of the resulting supernatants from sorption and desorption experiments did not significantly differ (± 0.2) from the soil pH reported in Table 1.

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2.4. Quality control

All sorption and desorption batch experiments were performed in duplicate. The relative standard deviation between replicates was approximately 20% in the worst scenarios. Quality control of the analyses included blank soil samples that were tested using the same procedure described in 2.3, but without PFAS spiking, to test whether PFASs were present in the soil samples. In addition to this, aqueous control samples at PFAS concentrations representative of the tested concentration range were assayed to quantify PFAS losses during the experimental stages of the batch test.

Results from the analyses of blank soil samples showed that no PFASs were present in the soils prior to the analysis. Regarding aqueous control samples, negligible losses for all the PFASs were observed, except for PFDoA (see section S1). Although some authors have reported sorption of PFOA on common laboratory equipment (Lath et al., 2019), our results agree with those reported in the literature for short- and mid-chained PFASs (Ahrens et al., 2011; Milinovic et al., 2015; Campos Pereira et al., 2018). However, for the long-chained PFDoA only 40% was recovered, and the results were corrected accordingly.

2.5. PFAS analysis by LC-MS/MS

To quantify the PFAS concentration resulting from the sorption and desorption experiments, 750 µL aliquots of the supernatants were transferred into a 2-mL chromatographic vial. 10 µL of either the MPFOS or MPFOA internal standard working solution and 240 µL of acetonitrile were then added into the vial to reach a final volume of 1 mL, and the PFASs were subsequently analysed via liquid chromatography with tandem mass spectrometry (LC-MS/MS). Details of the chromatographic methods can be found in Section S1 of the Supplementary Information.

178 *2.6. Quantification of sorption and desorption parameters*

179   The sorption solid-liquid distribution coefficient, K_d (L kg^{-1}), was calculated as the ratio

180   between the concentration of the target PFAS sorbed at the solid phase, C_s (ng g^{-1}), and the

181   concentration of the target PFAS in the aqueous phase at equilibrium, C_{eq} (ng mL^{-1}):

$$K_d = \frac{C_s}{C_{eq}} \tag{1}$$

182   C_{eq} values were directly determined by LC-MS/MS, whereas C_s was calculated using the

183   following equation:

$$C_s = \frac{(C_{in} - C_{eq}) \cdot V}{m} \tag{2}$$

184   where C_{in} (ng mL^{-1}) represents the initial concentration of PFAS in the suspension, V (mL) is

185   the total volume of contact solution, and m (g) refers to the dry mass of soil.

186   The sorption percentage (%S) was calculated as follows:

$$\% S = \frac{(C_{in} - C_{eq})}{C_{in}} \cdot 100 \tag{3}$$

187   As with K_d (Equation 1), the desorption solid-liquid distribution coefficient, $K_{d,des}$ (L

188   kg^{-1}), was calculated as follows:

$$K_{d,des} = \frac{C_{s,des}}{C_{eq,des}} \tag{4}$$

189   where $C_{s,des}$ (ng g^{-1}) and $C_{eq,des}$ (ng mL^{-1}) are PFAS concentrations in the solid and aqueous

190   phases, respectively, after the desorption experiments. $C_{eq,des}$ values were directly determined

191   by LC-MS/MS, whereas $C_{s,des}$ values were calculated as the difference between the initial PFAS

192   concentration in the solid residue resulting from the sorption experiments ($C_{in,des}$, ng g^{-1}) and

193   the PFAS desorbed with regard to the mass of soil, as follows:

$$C_{s,des} = C_{in,des} - \frac{C_{eq,des} \cdot V}{m} \tag{5}$$

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194    $C_{in,des}$ depends on C_s and the amount of PFAS present in the residual volume of solution (C_{eq} ·

195   V_{res}) that remained in the soil after the sorption experiment:

$$C_{in,des} = C_s + \frac{C_{eq} \cdot V_{res}}{m} \tag{6}$$

196

197   *2.7. Construction of the PFAS K_d datasets*

198   Two datasets including K_d values for PFASs in soils and analogous geological materials

199   (i.e., subsoils and sediments) were constructed using our own experimental data and additional

200   data from the literature. Our experimental dataset consisted of 56 entries, while the overall

201   dataset (which also included our experimental data) comprised 435 entries. K_d values from the

202   literature were only included in the data if they originated from batch experiments, given that

203   K_d values obtained from *in situ* experiments have been shown to be significantly higher due to

204   the non-equilibrium nature of natural systems (Li et al., 2018). Only studies in which a K_d value

205   could be confidently derived (i.e., linear isotherms with constant K_d; non-linear isotherms, but

206   with the reported K_d falling within the linear range of the isotherm; or K_d values calculated from

207   a low initial concentration, assuming that sorption saturation was not reached) were considered.

208   In addition, we only included data for PFCAs and PFSAs that contained from 3 to 11 fluorinated

209   carbons. Ancillary information about the soils, such as sand, silt, clay, and OC content, was

210   also included in both datasets.

211   Table S3 provides the references and information for the data used to build the overall

212   PFAS sorption dataset. Of the 222 samples obtained from these references, 167 were soils, 171

213   had an OC content less than 2%, and only 10 had an OC content greater than 10%. PFOS and

214   PFOA were the two PFASs with the highest number of entries, whereas limited data were

215   available in the literature for other PFASs, including PFDS, PFPeA and PFHpA.

3. Results and discussion

3.1. PFAS sorption and desorption patterns in soils

The sorption K_d values for each PFAS in each of the seven soils examined are summarized in Table 2, while sorption efficiencies expressed as percentages are summarized in Table S4. Buck and co-workers suggested a unified classification of PFASs into short- and long-chained groups (Buck et al., 2011). However, due to the differences in the log K_{OW} (see Table S1) and K_d values (see Table 2) for PFHxS and PFDoA as well as PFBA and PFOA, in this study we decided to adapt the PFAS definition by grouping the PFASs into short-, mid- and long-chained. We considered PFASs with ≤ 5 CF_2 (PFBA, PFBS, PFPeA, and PFHxA) to be short-chained, and PFASs with 6-9 CF_2 (PFHpA, PFHxS, PFOA, PFNA, PFOS, and PFDA) and > 9 CF_2 (PFUnA, PFDS, and PFDoA) to be mid- and long-chained respectively.

Short-chained PFASs (PFBA, PFBS and PFHxA) generally had K_d values below 7 L kg^{-1}, regardless of the soil characteristics or the PFAS functional group, indicating their low sorption affinity in soils and their potentially high mobility (Gellrich et al., 2012). On the other hand, mid-chained PFASs (PFHxS, PFOA, PFOS and PFNA) had higher K_d values ranging from 2–295 L kg^{-1} depending on the PFAS and the soil characteristics, indicating higher sorption affinity in the soils examined and therefore lower potential mobility. Sorption in low OC soils, as exemplified by the ALM soil, was significantly lower than in the rest of soils, and in general, K_d increased with OC content.

The sorption K_d values for the mid-chained PFHxS, PFOA and PFOS in this study were comparable to previously reported values (Higgins and Luthy, 2006; Oliver et al., 2020) and were higher than the corresponding short-chain PFASs, indicating that sorption was favoured by greater PFAS hydrophobicity. Despite having the same CF_2, PFOS had higher K_d values than PFNA, suggesting an influence of the hydrophilic functional group with a slightly higher sorption affinity of the sulfonate group than the carboxylate group. These differences between

241 sorption affinity for PFOS and PFNA have also been described elsewhere (Enevoldsen and

242 Juhler, 2010; Higgins and Luthy, 2006) and confirm that PFCAs have a higher mobility than

243 PFSAs (Sepulvado et al., 2011). The long-chained PFAS, PFDoA, had the highest K_d values

244 among the PFASs tested, with a high K_d even for the low OC ALM soil, indicating a very low

245 mobility of these PFASs in soils.

246   The reversibility of the sorption process was also evaluated. The $K_{d,des}$ values obtained

247 are reported in Table S5 and were higher than the corresponding K_d values for sorption. The

248 hysteresis coefficient, calculated as the ratio between $K_{d,des}$ and K_d, was therefore larger than

249 one in all cases. These results indicate the irreversibility of PFAS sorption and are agreement

250 with previous studies (Enevoldsen and Juhler, 2010; Miao et al., 2017). Because desorption

251 data were scarce in the literature and only available for a few PFASs all subsequent analyses

252 focus solely on sorption data.

253

254 *3.2. Correlation of sorption and desorption parameters with soil OC*

255   Given the importance of soil OC content for PFAS sorption and desorption parameters,

256 especially for mid- and long-chained PFASs, the sorption K_d values reported in Table 2 were

257 further examined for their dependence on the fraction of OC (f_{OC}), expressed as kg of OC per

258 kg of soil. We additionally examined the relative contribution of OC and mineral binding sites

259 to the overall sorption. Specifically, iron, aluminium and titanium oxides have all been reported

260 to be able to interact with PFASs and to participate in PFAS sorption (Lu et al., 2016). Although

261 a preliminary overview of our results showed that K_d values were correlated with extracted

262 amorphous Fe content, this correlation might be attributed to the correlation between extracted

263 Fe and soil OC ($r^2 = 0.81$) (data derived from Table 1). This conclusion agrees with previous

264 studies which observed no correlation between K_d and Fe content in soils where OC was the

265 primary driver of PFAS sorption (Higgins and Luthy, 2006; Miao et al., 2017).

266   The OC-normalized sorption coefficient (K_{OC}, L kg OC^{-1}) is defined as the ratio between

267   K_d and the soil f_{OC} (OECD, 2000).

$$K_{OC} = \frac{K_d}{f_{OC}} \qquad (7)$$

268   Equation 7 considers that the sorption is driven entirely by soil OC; it may therefore

269   overestimate K_{OC} if the soil mineral fraction plays a role in the sorption of the target compound,

270   a situation that several authors have pointed out for PFASs in mineral soils (Knight et al., 2019;

271   Li et al., 2018; Wang et al., 2021). Thus, a constant term has to be added in equation 7 referring

272   to the sorption contribution of non-OC soil fractions, which may be attributed to the soil mineral

273   fraction ($K_{d,MIN}$, L kg^{-1}) (Milinovic et al., 2015; Sorengard et al., 2019):

$$K_d = K_{OC}\ f_{OC} + K_{d,MIN} \qquad (8)$$

274    $K_{d,MIN}$ can be quantified by extrapolating the correlation to $f_{OC} = 0$. In this scenario,

275   sorption is driven entirely by the mineral fraction and thus $K_{d,MIN}$ could be directly considered

276   as the normalized sorption coefficient referring to the mineral phase (K_{MIN}, L kg mineral^{-1}). The

277   K_{OC} and K_{MIN} values obtained for each PFAS after applying Equation 8 using both the overall

278   dataset and our own are summarized in Table 3. To our knowledge, although other authors have

279   attempted to calculate different mineral-normalized sorption coefficients (Sorengard et al.,

280   2019; Wang et al., 2021), this is the first time that mineral-normalized sorption coefficients

281   values have been calculated from data assembled from the literature. Significant correlations

282   for each PFAS ($p < 0.05$) were obtained between K_d and f_{OC} for both datasets. Derived K_{MIN}

283   values of PFASs were much lower than the respective K_{OC} values, indicating that PFASs have

284   a higher sorption affinity to the OC sites present in the soil. The application of Equation 8 to

285   the overall dataset allowed us to derive K_{OC} and K_{MIN} for PFASs not included in our

286   experiments, such as PFPeA, PFHpA, PFDA, PFUnA, and PFDS. Since the K_d values of the

287   overall dataset were obtained under a wide range of experimental conditions, the K_{OC} and K_{MIN}

288   values derived were affected by the intrinsic variability of the literature data. However, K_{MIN}

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289 values derived from the overall dataset can be considered more representative than those

290 derived from ours, as the overall dataset contained a higher number of soils with low OC.

291 The K_{OC} values of PFASs we obtained were lower than K_{OC} values calculated solely

292 based on equation 7 reported elsewhere (Enevoldsen and Juhler, 2010; Guelfo and Higgins,

293 2013; McLachlan et al., 2019) but comparable to reported K_{OC} derived by considering sorption

294 at mineral sites as well (Higgins and Luthy, 2006; Milinovic et al., 2015). Direct comparisons

295 with previously reported K_{MIN} values were not possible. However, K_d data of PFASs are

296 available for pure mineral phases, such as phyllosilicate minerals, which can serve as analogues

297 for soils with $f_{OC} = 0$. The overall K_d in these materials therefore equals $K_{d,MIN}$ and,

298 consequently, K_{MIN}. For the mid-chained PFOS and PFOA, two of the most frequently studied

299 PFAS, the K_{MIN} values that we derived from the overall dataset were 9.4 and 3.3 respectively.

300 These values are similar to the range of K_d values (2.6 – 14 L kg^{-1} for PFOS and 0.5 - 2.3 L kg^{-1}

301 for PFOA) obtained on pure phyllosilicate minerals such as kaolinite and montmorillonite

302 (Jeon et al., 2011; Johnson et al., 2007; Xiao et al., 2011), two clay minerals which are often

303 present in soils. Furthermore, K_{MIN} values for PFOS were higher than for PFNA, in agreement

304 with previous observations (Xiao et al., 2011). Besides, K_{MIN} values for PFASs with ≤ 5 CF_2

305 were lower than 1; this is consistent with the hypothesis that sorption of short-chained PFASs

306 is not thermodynamically favourable under systems with low ionic strength (1 - 10 mM) (Xiao

307 et al., 2011), which are the most common scenarios of the experiments used to construct the

308 overall database.

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309   *3.3. Correlation of K_{OC} and K_{MIN} with PFAS physicochemical properties*

310   As shown in Table S1, the hydrophobicity of the PFASs, expressed as log K_{OW},

311   increased linearly with each fluorinated carbon added to the alkyl chain (log K_{OW} = 0.71 ($\pm$

312   0.08) $\times$ number of CF_2, r^2 = 0.97, p < 0.001, n = 13). Due to this strong correlation, the effect

313   of PFAS properties on K_{OC} and K_{MIN} can reasonably be evaluated based on either the number

314   of CF_2 or log K_{OW}. In principle, K_{OW} values better differentiate PFASs that have the same

315   number of CF_2 but different functional groups, such as PFOS and PFNA, but log K_{OW} values

316   vary significantly in the literature. Therefore, correlations were performed using the number of

317   CF_2, an easily available parameter that is descriptive of PFASs.

318   As shown in Figure 1, the K_{OC} and K_{MIN} values derived from both our experimental and

319   literature-assembled datasets were logarithmically correlated with the number of CF_2 of the

320   PFASs reported in Table S1. The correlations were significant, and both the slope and the y-

321   intercept were comparable between datasets. Equations 9 and 10 show the relationships

322   between the number of fluorinated carbons and each of K_{OC} and K_{MIN} derived from the overall

323   dataset:

$$\log K_{OC} = 0.41\ (\pm 0.04) \times \text{number of } CF_2 - 0.70\ (\pm 0.30) \qquad (r^2 = 0.98;\ p < 0.001) \quad (9)$$

$$\log K_{MIN} = 0.32\ (\pm 0.08) \times \text{number of } CF_2 - 1.70\ (\pm 0.60) \qquad (r^2 = 0.89;\ p < 0.001) \quad (10)$$

324   The high quality of these correlations allowed us to derive predicted K_{OC} and K_{MIN}

325   values for PFASs for which only the number of CF_2 units were available. In agreement with

326   previous findings (Milinovic et al., 2015), K_{OC} values increased with higher PFAS

327   hydrophobicity, which strongly suggested that sorption to OC was mainly driven by

328   hydrophobic interactions. Humic substances, which are the main organic compounds present in

329   the soil organic phase, often possess hydrophilic moieties that can also interact with PFASs

330   through mechanisms such as hydrogen bonding or divalent cation bridging (Du et al., 2014).

331   However, experiments testing the sorption of PFASs on humic acids extracted from soils have

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shown that these hydrophilic contributions are not predominant, thus confirming that hydrophobic interactions are the main sorption mechanism (Xiang et al., 2018; Zhao et al., 2014).

K_{MIN} values also increased with increasing PFAS chain length, a finding that is comparable to the K_d increase reported for the C_7–C_{10} PFAS series on kaolinite clay (Xiao et al., 2011). The interaction between the negatively charged kaolinite surface and the negatively charged PFAS could be explained by the presence of divalent cations either acting as an intermediate bridge in electrostatic interactions (Du et al., 2014), which may explain the positive effects of the presence of calcium on the K_d of PFASs (Higgins and Luthy, 2006), or inhibiting the negative repulsions within the electrical double layer of the mineral surface (Xiao et al., 2011). Moreover, recent computational studies have identified the hydrophobic patches of montmorillonite clay as the primary adsorption domains and the stabilization of adsorption enthalpy in the presence of cations (Willemsen and Bourg, 2021). Nevertheless, further mechanistic insights between negatively charged PFASs and different clay minerals are still required. Overall, these results suggest that both sorption of the PFASs in the mineral and organic phases of the soil become more favourable as the PFAS chain length increases. However, the ratio between K_{OC} and K_{MIN} values also increased with increasing PFAS chain length, indicating that long-chained PFASs have a higher affinity for the organic phases than mid- and short-chained PFASs.

3.4. Development and validation of a PFAS sorption model in soils

To develop a parametric model to predict the sorption of PFCAs and PFSAs in soils based only on the number of CF_2 of PFASs and on a few physicochemical properties of the soil, we used the correlations presented in Equations 9 and 10 as descriptors of the sorption on the OC and mineral pool sites respectively. Based on a multiple regression analysis, Li et al.

16

357 concluded that soil OC, clay content, and pH all have a significant effect on the K_d of PFASs

358 (Li et al., 2018). Similarly, Knight et al. found that OC and the mineral silt and clay fractions

359 contributed significantly to the sorption of PFOA in a large number of mineral soils (Knight et

360 al., 2019). The silt and clay fractions have also been reported to have a positive effect on the K_d

361 of PFOS, PFOA and PFHxS in sediments (Oliver et al., 2020), and a study of PFOA sorption

362 on various soil size fractions confirmed that K_d decreases along the sequence: clay > fine silt >

363 coarse silt > fine sand > coarse sand (Xiang et al., 2018). Indeed, Wang and co-workers derived

364 silt+clay normalized sorption coefficients using a three-compartment distribution model to

365 account for the contribution of the mineral fraction to the overall K_d (Wang et al., 2021).

366   Preliminary attempts to model the K_d values of PFASs in soils based only on CF_2 and

367 OC led to an underestimation of K_d values in mineral soils, thus highlighting that the mineral

368 contribution needed to be considered in the modelling. Therefore, the K_d of PFASs was further

369 modelled from a separate contribution of the organic and mineral phases ($K_{d,ORG}$ and $K_{d,MIN}$

370 respectively), regardless of the f_{OC} value:

$$K_d = K_{OC}\, f_{OC} + K_{MIN}\, f_{MIN} \tag{11}$$

371   Where f_{MIN} is the mineral fraction, expressed as kg of mineral per kg of soil. According

372 to the above discussion, the mineral phases mainly responsible for PFAS sorption are silt and

373 clay. Then, f_{MIN} should be limited to the silt+clay fraction, f_{S+C}, expressed as kg of silt+clay per

374 kg of soil, and the K_{MIN} values reported in Table 3 could be considered as silt+clay normalized

375 sorption coefficients (L kg silt+clay^{-1}), leading to the following model based on OC, CF_2 and

376 silt+clay content:

$$K_d = K_{OC}\, f_{OC} + K_{MIN}\, f_{S+C} = 10^{(0.41\ \text{number of CF}_2 - 0.70)}\, f_{OC} + 10^{(0.32\ \text{number of CF}_2 - 1.70)}\, f_{S+C} \tag{12}$$

377   We tested the predictive ability of this model using only the entries from our datasets

378 that contained data for both soil OC and textural fractions. The predictive accuracy for the

379 model was quite satisfactory both for our experimental data and for the overall dataset (see

17

380 Figure 2a and 2b). The model's RMSE and RPD values (calculated according to Section S2)

381 indicated that its quality was acceptable. The model's predictive ability increased if the K_{OC}

382 and K_{MIN} values for each PFAS, reported in Table 3, were used in the model rather than the

383 K_{OC} and K_{MIN} values predicted from the correlations with the number of CF_2 (log $K_{d,model}$ =

384 0.92 ($\pm$ 0.05) $\times$ log $K_{d,exp}$, r^2 = 0.78, p < 0.001, n = 353). In that case, RMSE and RPD values

385 were 0.37 and 1.94, respectively. However, this model cannot be applied to PFASs for which

386 no K_{OC} and K_{MIN} data are available. Although the inclusion of other soil properties (e.g., the

387 status of divalent metal ions, pH, or metal oxide content) could be examined to further improve

388 the established prediction model, this would also increase the model's complexity without

389 enhancing its range of applications. Nevertheless, according to the RPD values derived from

390 the predictions of the overall dataset, we warn against the use of the model for attempting to

391 derive very accurate K_d values of PFASs in soils. In Figure 2b some scattering of the data is

392 observed for scenarios with low sorption, likely attributable to the weak interaction between

393 PFAS and the solid phase, in addition to the intrinsic variability due to the use of literature-

394 assembled data. The model, instead, may be capable of predicting approximate K_d values for

395 categorizing scenarios with very low (K_d < 10 L kg^{-1}), medium (K_d of 10 - 1000 L kg^{-1}), and

396 high (K_d > 1,000 L kg^{-1}) sorption. According to the associated risk, intervention actions and/or

397 more accurate site-specific K_d values could be deduced from further *in-situ* studies. Besides, it

398 is unclear at present how the model would behave with regard to the prediction of PFAS species

399 other than PFCAs and PFSAs with a number of fluorinated carbons between 3 and 11.

400   For the external validation of our proposed model, we used the Kennard and Stone

401 method (Kennard and Stone, 1969) to select two-thirds of the data from the overall dataset as a

402 calibration set for training the model, while the remaining one-third of the data was used as a

403 representative validation set. K_{OC} and K_{MIN} values were first recalculated for the calibration set

404 data according to Equation 8, and the correlations between each parameter and CF_2 were

405 similarly recalculated. Both the resulting slopes and intercepts of the K_{OC} and K_{MIN} correlations

406 with CF_2 were statistically comparable to Equations 9 and 10, demonstrating that the model

407 obtained from the calibration data was equivalent to the model obtained from the full data set.

408 We then used the model from the calibration data to predict K_d for the validation data set,

409 leading to an accurate prediction (log $K_{d,model}$ = 0.9 ($\pm$ 0.1) × log $K_{d,exp}$; r^2 = 0.76, p < 0.001, n

410 = 121).

411   Although OC sites have a higher affinity for PFAS sorption than silt+clay sites (that is,

412 K_{OC} is higher than K_{MIN}), the relative amount of OC and mineral sites also influences the total

413 K_d of a given PFAS in a given soil. Thus, mineral sites may govern PFAS sorption in mineral

414 soils with low OC, especially in the case of short and mid-chained PFASs. We therefore used

415 our well-established prediction model to quantify the actual distribution of PFASs among OC

416 and silt+clay sites. The proportional contribution of mineral sites, which we quantified as the

417 percentage of $K_{d,MIN}$ with respect to the overall K_d (% $K_{d,MIN}$), was calculated using the K_d

418 values predicted from the overall dataset. We specifically evaluated % $K_{d,MIN}$ for PFBS, PFOA,

419 PFOS and PFDoA, which served as representatives of short-, mid-, and long-chained PFASs.

420 Results were grouped by soil classes defined by their OC content, as shown in Table 4. Sorption

421 at OC sites was predominant (% $K_{d,MIN}$ ≤ 3) for all the PFASs in soils with OC > 10%. In soils

422 with a lower OC content, especially < 2%, the contribution of mineral sites (% $K_{d,MIN}$) varied

423 significantly with the soil and PFAS properties, as the % $K_{d,MIN}$ values depended on the

424 silt+clay content (higher % $K_{d,MIN}$ for higher silt+clay content). Thus, % $K_{d,MIN}$ increased with

425 the silt+clay content, especially for the soils with OC < 2% and the short-chained PFASs.

426 Despite this relatively higher PFAS affinity for mineral sites in low OC soils, we note that low

427 OC soils had generally low overall K_d values of PFASs, indicating that in these soils PFAS

428 contamination might present a higher environmental risk.

4. Conclusions

The results of the present study confirm that the overall sorption behaviour of PFASs in soils of varying OC content can be estimated by modelling the relative sorption at OC and mineral sites. Specifically, the model presented is able to predict, with acceptable accuracy, scenarios from very low to high sorption of target PFCAs and PFSAs (with a total number of fluorinated carbons ranging from 3 to 11), based on only a few physicochemical properties of the soil (OC and silt+clay content) and the number of fluorinated carbons of the target PFAS. This information may be relevant for an early evaluation of contamination events. Although soil OC content is the main parameter governing PFAS sorption, the relative contribution of the sorption at mineral sites can be significant when short-chained PFASs are sorbed in soils with low OC and high silt+clay content. However, the associated K_d of PFASs for these scenarios are very low, and therefore a high related PFAS mobility is expected.

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580

Supplementary material

Modelling the sorption behaviour of perfluoroalkyl carboxylates and perfluoroalkane sulfonates in soils

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Table S1. Main physicochemical properties of target PFASs.

Name	PFAS acronym	Chemical form	CAS number	Molecular Weight (g/mol)	Number of CF_2	log K_{ow}	pK_a
Perfluorobutanoic acid	PFBA	$C_4HF_7O_2$	375-22-4	214.0	3	2.3 [a]	0.4 [a]
Perfluorobutane sulfonic acid	PFBS	$C_4HF_9O_3S$	375-73-5	300.1	4	2.7 [a]	0.14 [a]
Perfluoropentanoic acid	PFPeA	$C_5HF_9O_2$	2706-90-3	264.1	4	2.9 [c]	n.a.
Perfluorohexanoic acid	PFHxA	$C_6HF_{11}O_2$	307-24-4	314.1	5	3.1 [a]	-0.16 [a]
Perfluoroheptanoic acid	PFHpA	$C_7HF_{13}O_2$	375-85-9	364.1	6	3.8 [b]	n.a.
Perfluorohexane sulfonic acid	PFHxS	$C_6HF_{13}O_3S$	355-46-4	400.1	6	4.3 [a]	0.14 [a]
Perfluorooctanoic acid	PFOA	$C_8HF_{15}O_2$	335-67-1	414.1	7	4.6 [a, b]	-0.2 [a]
Perfluorononanoic acid	PFNA	$C_9HF_{17}O_2$	375-95-1	464.1	8	5.5 [b]	n.a.
Perfluorooctane sulfonic acid	PFOS	$C_8HF_{17}O_3S$	1763-23-1	500.1	8	5.3 [a, b]	-3.27 [a]
Perfluorodecanoic acid	PFDA	$C_{10}HF_{19}O_2$	335-76-2	514.1	9	6.4 [b]	n.a.
Perfluoroundecanoic acid	PFUnA	$C_{11}HF_{21}O_2$	2058-94-8	564.1	10	7.4 [b]	n.a.
Perfluorodecane sulfonic acid	PFDS	$C_{10}HF_{21}O_3S$	335-77-3	600.1	10	6.4 [c]	n.a.
Perfluorododecanoic acid	PFDoA	$C_{12}HF_{23}O_2$	307-55-1	614.1	11	8.1 [c]	n.a.

n.a. = not available; [a] Deng et al., 2012; [b] Kelly et al., 2009; [c] Pubchem database

Table S2. Initial concentrations of spiked PFASs (ng mL^{-1}) in each soil for the sorption experiments.

Soil	PFBA	PFBS	PFHxA	PFHxS	PFOA	PFNA	PFOS	PFDoA
ALM	30	30	35	50	50	60	170	330
DELTA2	30	30	35	50	50	170	170	500
OVI01	30	30	35	50	50	170	170	500
UIAR	30	50	50	140	150	570	670	1000
BRA	30	50	50	140	150	570	670	1000
DUBLIN	30	50	50	140	150	570	670	1000
KOM	30	50	50	140	150	570	670	1000

Section S1. PFAS determination in the supernatants by LC-MS/MS.

PFASs concentrations in the supernatants were analysed by HPLC equipped with an auto-sampler (Agilent 1100 Wellplate) thermostatized at 10 ºC and a pump and solvent system (Agilent 1100 LC). A Luna C_{18} (2)-HST reverse phase column (2.5 µm, 100 x 2.00 mm, Phenomenex) thermostatized at 45ºC was used for the chromatographic separation. The chromatographic separation conditions were adapted from (Gómez-Canela et al., 2012) and briefly consisted in an injection volume of 10 µL (full loop) with a mobile phase A composed of 10 mmol L^{-1} ammonium acetate and a mobile phase B composed of acetonitrile. The flow rate was set at 300 µL min^{-1} while the elution gradient was set at 75% A during one minute and then reached until 85% B during 5 minutes. After, mobile phase reach 100% B during the next 30 seconds and this percentage was set during 30 seconds more until decrease at 25% B during the next minute. This elution grade of 25 % B was held during the next 7 minutes to condition the column for the next analysis.

Detection was performed using a triple quadrupole mass spectrometer (API3000 Perkin-Elmer Sciex Instruments) provided with a ionization chamber (Turblon Spray[TM]) located at 10 mm from the analyser and working in the negative mode, ESI(-). The most significant m/z transition of each PFAS was used for quantification while the second one was used for confirmation. The dwell time for each transition was established at 30 ms, and the software used for the determination was Absciex Analyst. Experimental parameters of the mass spectrometer were set as:

PFAS	Transition (m/z)	Declustering Potential (V)	Focusing Potential (V)	Collision Energy (V)
PFBA	213 > 169	-17	-91	-18
PFHxA	313 > 269, 119	-20	-104	-21
PFOA	413 > 369, 169	-23	-122	-20
PFNA	463 > 419, 169	-27	-123	-21
PFDoA	613 > 569, 319	-32	-110	-24
PFBS	299 > 80, 99	-40	-121	-45
PFHxS	399 > 80, 119	-43	-133	-58
PFOS	499 > 80, 130	-44	-131	-68
MPFOA	417 > 372, 172	-23	-122	-20
MPFOS	503 > 80, 99	-44	-131	-68

Quantification was performed using 1/x weighted calibration curves using calibration standards of 0; 0.5; 2; 5; 10; 20; 50; 100 and 200 ng mL^{-1} for each PFAS, together with the inner standards MPFOS and MPFOA. The Pearson coefficients of the resulting calibration lines were up to 0.999. The limit of detection (LOD) and the limit of quantification (LOQ) were determined as a signal-to-noise ratio set at 1:3 and 1:10 respectively, and were similar to other LODs and LOQs reported elsewhere (Habibullah-Al-Mamun et al., 2016; Liu et al., 2015). Repeatability was determined after ten analysis at a concentration of 20 ng mL^{-1}.

The quality figures of the method were:

PFAS	Repeatability at 20 ng mL^{-1} (%RSD)	LOD (ng L^{-1})	LOQ (ng L^{-1})	Pearson coefficient of calibration curves	Recovery of controls (%)
PFBA	4	0.10	0.30	0.999	> 98
PFHxA	5	0.04	0.10	0.991	> 98
PFOA	3	0.02	0.08	0.997	> 95
PFNA	4	0.01	0.05	0.998	> 95
PFDoA	4	0.01	0.04	0.995	40
PFBS	5	0.03	0.10	0.997	> 98
PFHxS	5	0.03	0.10	0.998	> 98
PFOS	5	0.06	0.20	0.999	> 95

Table S3. List of references including information about which PFASs were used to construct the dataset of PFAS sorption parameters.

Reference	Number of samples (total entries)	OC range (%)	PFBA	PFBS	PFPeA	PFHxA	PFHpA	PFHxS	PFOA	PFNA	PFOS	PFDA	PFUnA	PFDS	PFDoA
Hong Chen et al., 2012	5 (5)	0.42 – 1.43									X				
Mejia-Avendaño et al., 2020	5 (15)	1.7 – 7.3							X		X	X			
Chen et al., 2013	5 (10)	0.52 – 16							X		X				
Enevoldsen & Juhler, 2010	2 (12)	0.42 – 1.0		X			X		X	X	X	X			
Guelfo & Higgins, 2013	3 (30)	0.8 – 4.5	X	X	X	X	X	X	X	X	X	X	X		
Higgins & Luthy, 2006	5 (24)	0.56 – 9.66							X	X	X	X	X	X	
Higgins & Luthy, 2007	1 (1)	4.34													X
Internal report, 3M, 2000	4 (4)	1.3 – 2.8									X				
Internal report, Dupont, 2003	4 (4)	0.8 – 5.76							X						
Jeon et al., 2011	3 (6)	0.21 – 0.55							X		X				
Johnson et al., 2007	1 (1)	2.5									X				
Milinovic et al., 2015	2 (6)	0.2 – 3.9		X					X		X				
Knight et al., 2019	100 (100)	0.1 – 3.5							X						
You et al., 2010	15 (15)	0.16 – 1.49									X				
Kwadijk et al., 2013	1 (1)	2.6									X				
Martz et al., 2019	5 (5)	0.05 – 11.7							X						
Miao et al., 2017	10 (10)	0.52 – 5.76							X						
Ahrens et al., 2011	3 (5)	0.03 – 1.6							X		X				
Oliver, et al., 2020	19 (57)	0.1 – 11						X	X		X				
Wei et al., 2017	6 (6)	0.87 – 2.71									X				
Gredelj et al., 2020	1 (9)	1.43	X	X	X	X	X		X	X	X	X			
Pan et al., 2009	1 (1)	0.75									X				
Hong Chen et al., 2009	1 (1)	0.91									X				
Brusseau et al., 2019	2 (2)	0.10 – 0.38									X				
Xiao et al., 2019	5 (5)	0.10 – 5.3							X						
Huiting Chen et al., 2016	1 (5)	2.52						X	X	X	X	X			
McLachlan et al., 2019	2 (24)	0.40 – 0.93	X	X	X	X	X	X	X	X	X	X	X		X
Aly et al., 2019	1 (6)	1.44		X			X	X	X	X	X				
Campos Pereira et al., 2018	1 (6)	45	X	X	X	X	X		X						
Xiang et al., 2018	1 (1)	0.69							X						
Zhi & Liu, 2018	1 (2)	47							X		X				
This study	7 (56)	1.6 – 41	X	X		X		X	X	X	X				X

Table S4. Sorption percentages (%S) resulting from the batch experiments.

Soil	PFBA (3)	PFBS (4)	PFHxA (5)	PFHxS (6)	PFOA (7)	PFNA (8)	PFOS (8)	PFDoA (11)
ALM	5.2	5.7	23	19	21	52	76	98
DELTA2	8.2	14	20	29	28	78	88	98
OVI01	3.2	12	11	35	42	80	92	99
UIAR	8.3	13	21	64	72	91	94	> 99
BRA	11	23	35	63	73	92	95	> 99
DUBLIN	15	41	34	68	79	92	97	> 99
KOM	11	23	39	64	79	93	95	> 99

Table S5. Desorption $K_{d,des}$ (L kg^{-1}) values derived from the batch experiments.

Soil	PFHxA (5)	PFHxS (6)	PFOA (7)	PFNA (8)	PFOS (8)	PFDoA (11)
ALM	N.Q.	4.4	18	35	43	761
DELTA2	N.Q.	16	11	43	83	6591
OVI01	9.1	7.7	12	57	107	7117
UIAR	25	18	38	177	437	9376
BRA	29	29	41	226	560	12705
DUBLIN	32	41	61	262	760	13148
KOM	23	37	48	297	749	17888

N.Q.: Not quantifiable

Section S2. Evaluation of the predictive accuracy of the model

To evaluate the predictive accuracy of the model, the root square mean error (RMSE) and the residual predictive deviation (RPD) were calculated as:

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^{n} (m_i - p_i)^2}{N}}$$

where m are the measured values, p are the predicted values, i is the entry being tested and N is the total number of entries included in the model. The RPD was calculated as:

$$\text{RPD} = \frac{\text{SD}}{\text{RMSE}}$$

where SD is the standard deviation of the original data. RPD values indicate the quality of the model: RPD values < 1.5 are considered poor; RPD values from 1.5 to 2.0 are acceptable; RPD values between 2.0 and 3.0 are good; and RPD values > 3.0 are excellent (Knight et al., 2019).

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