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Sorption behaviour of per- and polyfluoroalkyl substances (PFASs) in tropical soils

Danielle P. Oliver, Yasong Li, Ryan Orr, Paul Nelson, Mary Barnes, Michael J. McLaughlin, Rai S. Kookana

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Fluorine

Carbon

Oxygen

Sulphur

PFOS

Tropic of Cancer

Equator

Tropic of Capricorn
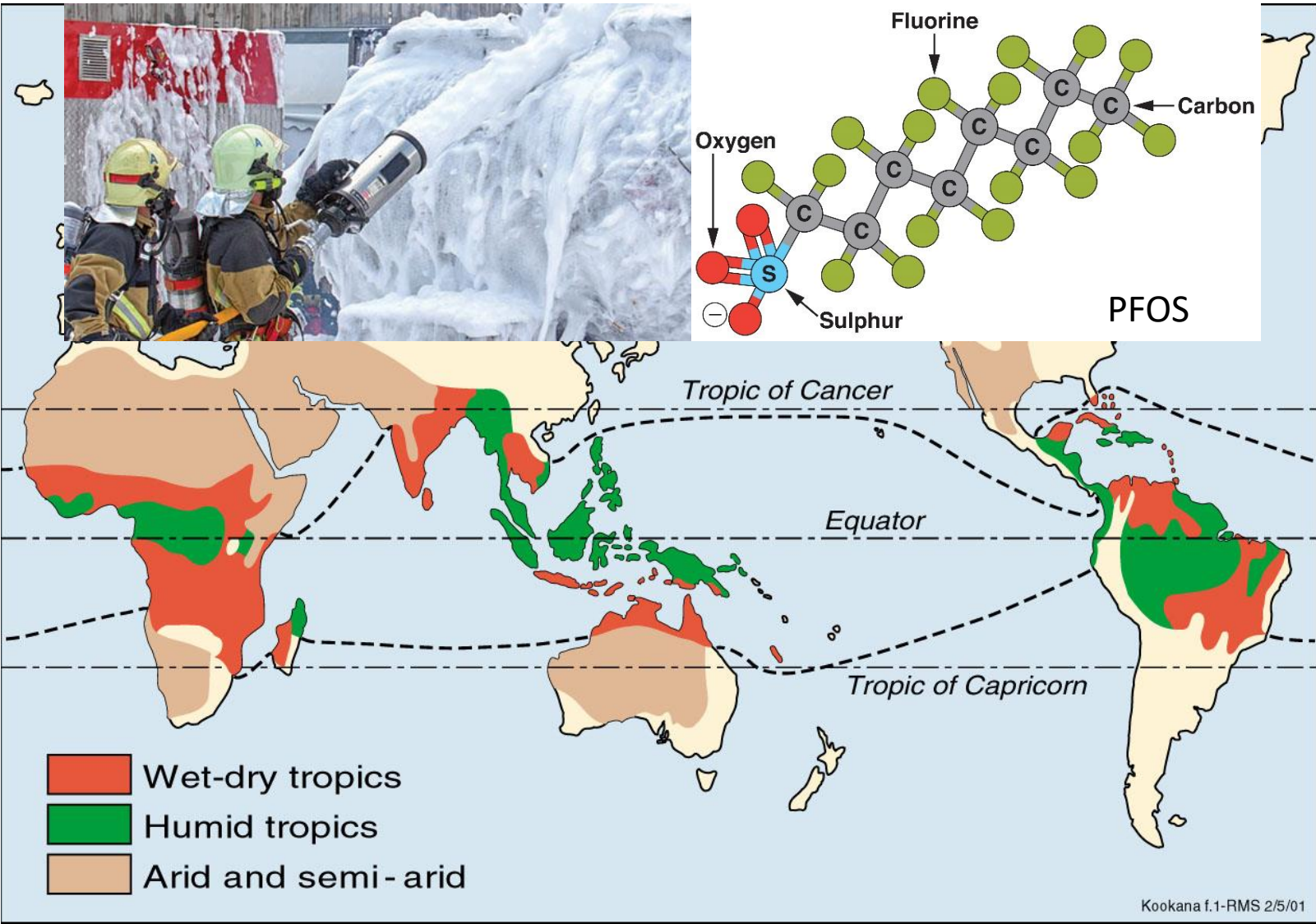
Wet-dry tropics
Humid tropics
Arid and semi-arid

Kookana f.1-RMS 2/5/01

1   Sorption behaviour of per- and polyfluoroalkyl substances (PFASs) in tropical soils.

2   Danielle P. Oliver,[a,*] Yasong Li[a,e], Ryan Orr[b], Paul Nelson[b], Mary Barnes[c], Michael J.

3   McLaughlin,[d] Rai S. Kookana,[a,d]

4   [a] CSIRO Land and Water, Locked Bag 2, Glen Osmond, 5064, South Australia, Australia

5   [b] College of Science and Engineering, James Cook University, Cairns, 4878, Qld, Australia

6   [c] Centre for Epidemiology and Biostatistics, Flinders University, Adelaide, SA 5001

7   [d] Soil Science, Waite Research Institute, University of Adelaide, Glen Osmond, 5064, South

8   Australia, Australia

9   *Corresponding author: E-mail address: Danni.Oliver@csiro.au

10

11   Email address of co-authors:

12   Yasong Li liyasong712@cags.ac.cn

13   Ryan Orr ryan.orr@jcu.edu.au

14   Paul Nelson paul.nelson@jcu.edu.au

15   Mary Barnes mary.barnes@flinders.edu.au

16   Michael McLaughlin Michael.mclaughin@adelaide.edu.au

17   Rai Kookana   rai.kookana@csiro.au

18   [e] Permanent address: Hebei and China Geological Survey Key Laboratory of Groundwater

19   Remediation, Institute of Hydrogeology and Environmental Geology, Chinese Academy of

20   Geological Sciences, Shijiazhuang, 050061, China

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22

23 **ABSTRACT**

24 The sorption behaviour of three perfluoroalkyl substances (PFASs), namely perfluorooctane

25 sulfonic acid (PFOS), perfluorooctanoic acid (PFOA) and perfluorohexane sulfonic acid

26 (PFHxS), was determined on 28 tropical soils. Tropical soils are often highly weathered,

27 richer in sesquioxides than temperate soils and may contain variable charge minerals. There

28 are little data on sorption of PFASs in tropical soils. The highest K_d values were found for

29 PFOS with mean values ranging from 0 to 31.6 L/kg. The K_d values for PFOA and PFHxS

30 ranged from 0 to 4.9 L/kg and from 0 to 5.6 L/kg, respectively. While these values are in the

31 range of literature sorption data, the average K_d values for PFOS and PFOA from the

32 literature were 3.7 times and 3.6 times higher, respectively, than those measured in this study.

33 Stepwise regression analysis did explain some of the variance, but with different explanatory

34 variables for the different PFASs. The main soil properties explaining sorption for PFOS and

35 PFOA were oxalate-extractable Al and pH, and for PFHxS was pH.

36

37 Summary finding:

38 The main soil properties explaining sorption for PFOS and PFOA to 28 tropical soils were

39 oxalate-extractable Al and pH, and for PFHxS was pH.

40

41

42 Keywords: PFOS, PFOA, PFHxS, sorption, tropical soils, weathered soils

43

1.   Introduction

44

45   Per- and polyfluoroalkyl substances (PFASs) are a unique class of organic chemicals in

46   that they have both a hydrophilic anionic functional head and a hydrophobic carbon chain.

47   Consequently, these chemicals exhibit surfactant-like properties (Krafft and Riess. 2015).

48   These chemicals have been used widely in industry due to these properties.   Industrial

49   applications include use as water repellents for numerous products such as paper and textiles,

50   and as lubricants, but these chemicals are most commonly known for their use in fire-fighting

51   foams (Krafft and Riess. 2015). While these chemicals have been produced and emitted into

52   the environment for over 50 years (Houde et al., 2011) concern has only recently arisen due

53   to the long-term persistence in the environment, potential for bioaccumulation, carcinogenic

54   toxicity and impacts on ecological health has resulted in these chemicals emerging as

55   contaminants of concern (Beach et al., 2006; Giesy and Kannan, 2001; Higgins et al., 2007;

56   Pan and You, 2010).   These highly fluorinated chemicals are extremely stable organic

57   compounds due to high electronegativity, low polarisability and high bond energies which is

58   discussed in greater details in the review by Du et al., 2014.

59   The surfactant-like properties of PFASs would suggest that these chemicals would

60   behave differently from traditional, non-ionisable organic pollutants (Villagrasa et al., 2006;

61   Ding and Peijnenburg, 2013). While strong relationships have been found between sorption

62   data and OC content for non-ionisable organic pollutants only weak relationships between

63   sorption data for PFASs and single soil properties (e.g. OC, pH, clay content or CEC) alone

64   were found in a recent review of international literature (Li et al., 2018). They found that both

65   organic and mineral phases in soil together with pH and clay should be taken into account for

66   accurate prediction of sorption of PFASs in soils and sediments. Generally, the published

67   literature on PFAS sorption has considered predominantly soils from temperate regions.

68   Tropical soils differ greatly from temperate soils in various aspects and this may affect

4

69 sorption behaviour. The mineralogy of tropical soils is dominated by kaolinite and

70 sesquioxides and as a result, tropical soils may have different charge characteristics than soils

71 from temperate regions. Highly weathered tropical soils usually have a low CEC and are

72 dominated by variable charge oxide minerals (Uehara and Gillman, 1981). Common soil

73 oxides usually have an iso-electric point between pH 7 and 9, so in the acid range (pH<6.5)

74 most soil oxides would be positively charged and may be present in sufficient quantities to

75 give the soil an appreciable anion exchange capacity (Taylor et al., 1993). These

76 characteristics may affect sorption behaviour of PFASs (Oliver et al., 2019). PFAS chemicals

77 are highly persistent and while certain countries have ceased production of some of these

78 chemicals they still persist in the environment and in order to manage and remediate

79 contaminated soils it is necessary to understand the fate and behaviour of these chemicals. To

80 our knowledge, this study is the first to consider the relationship between sorption of PFASs

81 and soil properties in tropical soils.

82 **2.   Materials and Methods**

83 *2.1   Soils*

84   The majority of soils in this study were collected from under banana plantations in

85 tropical Queensland. They were air-dried and sieved <2 mm. Selected physico-chemical

86 properties of the soils are given in Table 1. Soil characterisation involved measurements of

87 total carbon, total organic carbon, pH, electrical conductivity (EC), exchangeable cations,

88 cation exchange capacity (CEC), oxalate-extractable iron and aluminium, and total metal

89 concentrations. Details of the methodology for these soil measurements are given in the

90 Supporting Information.

91 *2.2   Batch Sorption*

92   The OECD 106 standard protocol for the adsorption – desorption of chemicals using a

93   batch equilibrium method (OECD/OCDE, 2000) was used for determining sorption

94   coefficients (K_d values). Sorption coefficients were determined for three commonly detected

95   PFASs, namely perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA) and

96   perfluorohexane sulfonic acid (PFHxS). Three replicates of each soil (1.5 g) were shaken for

97   24 h with 7 mL of 0.5 mM $CaCl_2$ (AnalaR®) (Higgins and Luthy, 2006) in a polypropylene

98   (PP) tube. The choice of container was based on our investigations on their suitability for

99   PFAS experimentation (Lath et al., 2019). An aliquot (0.5 mL) of a spiking solution was then

100   added to give a final concentration of 5 µg/L of PFOS, PFOA and PFHxS in 7.5 mL. Each

101   treatment was replicated four times. The spike was increased to 10 µg/L in 7.5 mL in those

102   soils that showed high sorption. To minimise cosolvent effects the methanol concentration

103   was <0.03%. After shaking for 24 h on an end-over-end shaker the samples were centrifuged

104   at 2012 g force for 20 min. A sample (125 µL) was taken, added to a PP insert in an LC vial

105   and 125 µL of methanol (Optima® LC/MS grade, Fisher Chemicals) was added. The spiking

106   concentration was used in the determination of sorption and was measured by analysis of a

107   spiked sample with no soil. The sorption coefficients (K_d) values were calculated as a ratio of

108   equilibrium solid to solution phase concentrations (OECD/OCDE, 2000). High performance

109   liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) was used for

110   analyses of PFOA, PFOS and PFHxS. Additional information about the sorption protocol,

111   and details of the operating conditions for the analyses by LC-MS/MS and QA/QC are given

112   in Supporting Information.

113   *2.3 Statistical analysis*

114   Statistical differences between log transformed average sorption coefficients and

115   relationships between sorption data and soil properties (both simple and multiple regressions)

116   were determined using Excel. To determine which soil properties were contributing to the

117 sorption of PFOA, PFOS and PFHxS, stepwise forward multiple regression was then

118 performed on the average K_d values and the soil properties for all 28 soils. The Akaike's

119 information criterion (AIC) was used to determine which predictors were included in each

120 model. Specifically, the 'stepAIC' function from the 'MASS" library in R (Venables and

121 Ripley, 2002) was used. To ensure the residuals were normally distributed a square root

122 transformation was performed on the sorption K_d values. The Shapiro-Wilk test of normality

123 was applied to the residuals to verify the success of square root transformation.

124 **3. Results and discussion**

125 *3.1 K_d values*

126   For all 28 soils the highest K_d values were found for PFOS with averages (n=3) ranging

127 from 0 to 31.6 L/kg. Generally, the sorption for PFOA and PFHxS was much weaker and K_d

128 values ranged from 0 to 4.9 L/kg and from 0 to 5.6 L/kg, respectively (Fig. 1; Supporting

129 Information, Table S1). The OECD protocol (OECD/OCDE, 2000) specifies a requirement

130 for >20% adsorption in the sorption test. Based on a maximum of 80% of the spiked amount

131 remaining in solution it was possible to calculate a minimum reliable K_d value according to

132 this protocol and this is indicated by the solid black line in Fig. 1. From Fig. 1 it can be seen

133 that sorption to these soils, particularly for PFHxS and PFOA, did not achieve this

134 requirement for nearly half of the soils. A review of all published PFAS K_d values in soils

135 and sediments found values ranged from 1.4 to 8684 L/kg for PFOS, from 0.12 to 1485 L/kg

136 for PFOA and from 0.37 to 976 L/kg for PFHxS (Li et al., 2018) (Fig. 2). However, when this

137 data collation was confined to only sorption values derived from laboratory studies, for

138 comparison with data in this study, the range was 1.4 to 224 L/kg for PFOS, 0.12 to 85 L/kg

139 for PFOA and 0.37 to 6.3 for PFHxS (Fig. 2). So the K_d values obtained with these tropical

140 soils are in agreement with other studies showing greater sorption of PFOS compared with

7

141   PFOA. However, the average K_d values from the literature were 3.7, 3.6 and 1.6 times

142   greater for PFOS (n=79), PFOA (n=34) and PFHxS (n=20), respectively, than those

143   determined for the tropical soils in this study.

144   PFOS and PFOA both have an 8-carbon chain length but differ in the functional head

145   (Supporting Information, Table S2). Other studies have found stronger sorption of

146   perfluorinated sulfonates in comparison with perfluorinated carboxylates with the same

147   perfluorocarbon chain length (Supporting Information, Table S2) to soils (Higgins and Luthy,

148   2006; Milinovic et al., 2015), clay particles (Jeon et al., 20011) and to mineral phases (Zhao

149   et al., 2014). Sorption of PFASs to soils and sediments would be expected to involve several

150   interactions due to the dual hydrophobic and hydrophilic properties of these chemicals (Du et

151   al., 2014; Krafft and Riess, 2015). These interactions have been outlined in detail by Sao et

152   al. (2011) and include the hydrophobic interaction between hydrophobic surface constituents

153   on soils and sediments and the perfluorocarbon chain, electrostatic interaction between the

154   anionic functional head and positively charged sites on the sorbent; and repulsion between

155   the adjacent PFAS molecules. Differences between sorption behaviour of perfluorinated

156   sulfonates compared with carboxylates with the same carbon chain length has been attributed

157   to the smaller carboxylic head in the PFOA molecule than that of the sulfonate head in PFOS.

158   The decreased size of the carboxylic functional group in PFOA results in less hydrophobicity

159   of PFOA compared with PFOS. This is further demonstrated by the water solubility for

160   PFOS which is considerably lower than that for PFOA (Supporting Information, Table S2),

161   suggesting that hydrophobic interactions were important for PFOS in these soils for

162   controlling sorption behaviour. By comparison, PFHxS and PFOS have the same sulfonate

163   functional head but PFHxS has a shorter carbon chain length (6 carbon) compared with PFOS

164   which decreases the hydrophobicity of the chemical and consequently its sorption. However,

165   the sorption process for these chemicals does not rely solely upon hydrophobic interactions

166 and recent studies have highlighted the contribution of electrostatic interaction with soils(Du

167 et al., 2014, Li et al., 2018, Knight et al., 2019).

168 *3.2 Relationship between K_d values and single soil properties*

169   Generally, for non-polar organic chemicals sorption behaviour has been explained

170 predominantly by the soil organic carbon content. The pKa values for these three PFASs

171 (Supporting Information, Table S2) indicate that at the pH values of these tropical soils (5.5

172 to 7.8) (Table 1), PFOS, PFOA and PFHxS would exist as negatively ionised compounds

173 (Krafft and Riess, 2011). Generally, temperate soils carry a net negative charge. Highly

174 weathered tropical soils usually are dominated by variable charge oxide minerals (Uehara and

175 Gillman, 1981). Solution pH and ionic strength can affect the dissociation of functional

176 groups on Al and Fe oxides which can change the surface charge on tropical soils containing

177 these sesquioxides, and these changes in surface charge would be expected to affect

178 electrostatic interaction with negatively ionised compounds. Soils that contain appreciable

179 amounts of oxides can give the soil a significant anion exchange capacity under acidic pH

180 conditions (Taylor et al., 1983; Qafoku et al., 2004). This would suggest that in addition to

181 partitioning into the carbon fraction of soils sorption of PFASs would also involve

182 electrostatic interactions with charged surfaces on the organic and mineral phases (Higgins

183 and Luthy, 2006, Du et al., 2014). It was hypothesised that there may be a relationship

184 between the sorption values for these three PFASs and the oxide content of these soils.

185 Consequently, the role of a range of soil properties (as single and then multiple combinations)

186 on sorption in these soils was assessed. The relationship between K_d values (n=28) for PFOS

187 and oxalate-extractable Al was significant ($P<0.05$) (Fig. 3) albeit with a low R^2 value (0.155)

188 (Table 2) but the relationship was strongly influenced by one soil (soil 18, 4.8% OC) and

189 removal of this data point resulted in the relationship becoming not significant. This

190 relationship between sorption values and oxalate-extractable Al was not found for PFOA and

9

191   PFHxS. The relationship between K_d values and soil pH was significant only for PFHxS

192   sorption values but again the R^2 value was low (0.176) (Table 2; Fig. 4c). There were no

193   significant relationships between K_d values for any of the three chemicals and any other

194   single soil property (OC, clay, sand, EC, CEC, oxalate-extractable Al, Mn or Fe, total Al, Mn

195   or Fe) (Supporting Information Figs. S1-S13). Strong correlations between sorption of

196   PFASs and OC content of soils or sediments has been found by others (Higgins and Luthy,

197   2006; You et al., 2010; Guelfo and Higgins, 2013), which may be expected due to the

198   interaction between the perfluorocarbon chain and hydrophobic constituents on the sorbent

199   surface. However, in this study no significant relationship was found between K_d values for

200   all three chemicals and OC. The OC content of the soils in this study ranged from 0.5 to 4.8

201   % while the %OC of the soils from the literature studies used for the PFOS sorption

202   measurements (n=79) ranged from 0 to 16%. Even when the literature sorption values were

203   restricted to sites with OC content <5%, to match the soils in this study, the average sorption

204   values from the literature were 3.1 and 1.8 times higher for PFOS (n=76) and PFOA (n=31),

205   respectively, compared with those determined in this study. Further, the median K_d values of

206   the restricted literature dataset (OC<5%) were 3.5 and 2.3 times higher for PFOS and PFOA,

207   respectively, compared with those K_d values determined for tropical soils in this study. So

208   differences in the OC content between soils in this study and those from the literature

209   collation do not explain the differences in the average sorption measurements. One difficulty

210   with comparing this dataset with literature data is that many studies in the literature have not

211   reported pH. Of the 12 and 7 studies, respectively, for PFOS and PFOA sorption with OC

212   content <5%, only 4 recorded pH and the range was 2.5 to 8.5 with a median of 7.3.

213

214   The relationship between sorption coefficients of PFASs and OC in the literature has

215   been variable. While some have found strong relationships (Higgins and Luthy, 2006; You et

216 al., 2010; Guelfo and Higgins, 2013), others did not (Ahrens et al., 2011; Li et al., 2018). In

217 some studies, removal of a single value resulted in the relationship becoming statistically

218 non-significant (Higgins and Luthy, 2006; Millinovic et al., 2015). Soil pH may be an

219 important factor affecting PFAs sorption and this is examined further in the next section.

220   This suggests that the sorption of these PFAS chemicals involved more than one phase

221 within these soils and could not be explained by any single soil property. Results of forward

222 stepwise regression of sorption coefficients and soil properties are given in Table 3. For

223 sorption of PFOA and PFHxS, pH was a significant soil property explaining sorption and for

224 PFOS oxalate-extractable Al was the most significant property with the inclusion of pH

225 slightly improving the model. Generally, no additional information with regard the sorption

226 of the PFASs to these soils could be determined by the forward stepwise regression than was

227 found by the simple regression. Li et al. (2019) recently considered sorption of PFASs to six

228 soils and the role of a range of soil properties. They found the key soil properties affecting

229 sorption of PFASs were protein, iron oxides and anion exchange capacity. They found the

230 contributions of OC, aluminium oxides and fulvic acid to sorption were analyte-dependent.

231 Common soil oxides usually have an iso-electric point between pH 7 and 9, so in the acid

232 range (pH<6.5) most soil oxides would be positively charged and may be present in sufficient

233 quantities to give the soil an appreciable anion exchange capacity (Taylor et al., 1993). The

234 surface of both Al and Fe oxides would be positively charged so their involvement in

235 sorption would be through electrostatic interaction (Gao and Chorover, 2012). While the net

236 surface charge was not measured for all 28 soils studied the net surface charge was

237 determined for a subset (7) of these soils. At the natural pH of these seven soils the net

238 surface charge ranged from -3.2 cmol/kg for soil 3 (pH 7.23 and OC 0.6%) to -21.2 cmol/kg

239 for soil 4 (pH 7.65 and OC 1.8%) (Oliver et al., 2019). The study on the subset of soils

240 showed that at the natural pH of these soils sorption was insensitive to pH and generally

241   sorption only increased when the pH was decreased to <5.5. However, in soils that had high

242   oxalate-extractable Al and/or Fe content sorption of PFOS, PFOA and PFHxS was found to

243   increase linearly with decreasing pH (Oliver et al., 2019). This would suggest that at the

244   natural pH of these tropical soils the variable charge oxide minerals are not influencing the

245   sorption behaviour of these PFAS chemicals. These soils were collected predominantly from

246   banana plantations and it is possible that the addition of phosphate fertiliser may have

247   increased the net negative charge on these soils, due to binding of the phosphate anion to the

248   positively charged sites (Uehara and Gillman, 1981), compared to tropical soils not under

249   agriculture. In addition, the anionic functional group of PFASs could bond with surface

250   hydroxyl groups on the Al and Fe oxides (Gao and Chorover, 2012).

251   **4.   Conclusions**

252   Sorption of PFOS and PFOA to these tropical soils was generally weaker than is

253   reported in the literature for temperate soils. The average K_d values for PFOS and PFOA

254   from the literature were 3.7 times and 3.6 times higher, respectively, compared with the

255   average values obtained in this study with 28 tropical soils. Tropical soils are usually in areas

256   of high and intense rainfall and generally tend to have good soil structure with high

257   permeability. So the combination of low sorption and high permeability of these soils would

258   suggest that there is greater likelihood of leaching of PFASs from these soils. No single soil

259   property (e.g. OC, clay, pH etc.) could explain the sorption behaviour of PFOS, PFOA or

260   PFHxS to any great extent. Some of the variance in the sorption of PFOS was explained by

261   oxalate-extractable Al but the relationship was strongly influenced by one soil (soil 18, 4.8%

262   OC) and removal of this data point resulted in the relationship becoming not significant. The

263   relationship between K_d values and soil pH was significant only for PFHxS sorption values

264   but the amount of variance explained was low ($R^2 = 0.176$). Stepwise regression analysis did

265   explain some of the variance in sorption but with different explanatory variables for the three

266   PFAS chemicals studied. The main soil properties explaining sorption for PFOS and PFOA

267   was oxalate-extractable Al and pH, and for PFHxS was pH.

268

269   **Declarations of interest:**

270   The authors declare no competing interests.

271

282

283   **Appendix A. Supplementary data**

284   Supplementary data to this article can be found online at

285   This includes details of:

286   Methods for soil characterisation

287   Batch sorption protocol

288   Analytical methodology for analysis of PFOA, PFOS and PFHxS

289

290   Regressions between average K_d values for PFOS, PFOA and PFHxS with single soil

291   properties.

292   Table S1. Average K_d values for 28 soils studied.

293   Table S2. Selected properties of PFOS, PFOA and PFHxS.

294   Fig. S1- S13. Relationship between average K_d values for 28 soils studied for PFOS,

295   PFOA and PFHxS with various soil properties.

296

297 **References**

298 Ahrens, L., Yeung, L.W.Y., Taniyasu, S., Lam, P.K.S., Yamashita, N., 2011. Partitioning of

299   perfluorooctanoate (PFOA), perfluorooctane sulfonate (PFOS) and perfluorooctane

300   sulphonamide (PFOSA) between water and sediment. Chemosphere 85, 731-737.

301 Beach, S.A., Newsted, J.L., Coady, K., Giesy, J.P., 2006. Ecotoxicological evaluation of

302   perfluorooctanesulfonate (PFOS). Rev. of Environ. Contam. Tox. 186, 133-174.

303 Brooke, D., Footitt, A., Nwaogu, T.A., 2004. Environmental risk evaluation report:

304   Perfluorooctanesulphonate (PFOS). U.K. Environment Agency.

305 http://chm.pops.int/Portals/0/docs/from_old_website/documents/meetings/poprc/submissions/

306   Comments_2006/sia/pfos.uk.risk.eval.report.2004.pdf (accessed February 2019).

307 CSIRO 2018. The Australian Soil Classification.

308 http://www.clw.csiro.au/aclep/asc_re_on_line/soilkey.htm (accessed September 2018).

309 Deng, S., Niu, L., Bei, Y., Wang, B., Huang, J., Yu, G., 2013. Adsorption of perfluorinated

310   compounds on aminated rice husk prepared by atom transfer radical polymerization.

311   Chemosphere 91, 124-130. doi: 10.1016/j.chemosphere.2012.11.015.

312 Ding, G., Peijnenburg, W.J.G.M., 2013. Physicochemical properties and aquatic toxicity of

313   poly- and perfluorinated compounds. Crit. Rev. Env. Sci. Tec. 43, 598-678.

314 Du, Z., Deng, S., Bei, Y., Huang, Q., Wang, B., Huang, J., Yu, G., 2014. Adsorption

315   behaviour and mechanism of perfluorinated compounds on various adsorbents – A

316   review. J. Haz. Mat. 274, 443-454.

317 Gao, X., Chorover, J., 2012. Adsorption of perfluorooctanoic acid and

318   perfluorooctanesulfonic acid to iron oxide surfaces as studied by flow-through ATR-

319   FTIR spectroscopy. Environ. Chem. 9, 148-157.

320 Giesy, J.P., Kannan, K., 2001. Global distribution of perfluorooctane sulfonate in wildlife.

321   Environ. Sci. Technol. 35, 1339-1342.

322 Guelfo, J.L., Higgins, C.P., 2013. Subsurface transport potential of perfluoroalkyl acids at

323   aqueous film-forming foam (AFFF)-impacted sites. Environ. Sci. Technol. 47, 4164-

324   4171.

325 Higgins, C.P., Luthy, R.G., 2006. Sorption of perfluorinated surfactants on sediments.

326   Environ. Sci. Technol. 40, 7251-7256.

327 Higgins, C.P., McLeod. P.B., MacManus-Spencer, L.A., Luthy, R.G., 2007. Bioaccumulation

328   of perfluorochemicals in sediments by the aquatic oligochaete Lumbriculus variegatus.

329   Environ. Sci. Technol. 41, 4600-4606. DOI: 10.1021/es062792o

330 Houde, M., De Silva, A.O., Muir, D.C.G., Letcher, R.J., 2011. Monitoring of perfluorinated

331   compounds in aquatic biota: An updated review. Environ. Sci. Technol. 45, 7962-7973.

332 Jeon, J., Kannan, K., Lim, B.J., An, K.G., Kim, S.D., 2011. Effects of salinity and organic

333   matter on the partitioning of perfluoroalkyl acid (PFAS) to clay particles. J. Environ.

334   Monitor. 13, 1803-1810.

335 Knight, E.R., Janik, L.J., Navarro, D.A., Kookana, R.S., McLaughlin, M.J. 2019. Predicting

336   partitioning of radiolabelled C-14-PFOA in a range of soils using diffuse reflectance

337   infrared spectroscopy. Sci. Tot. Environ. 686, 505-513.

338   Krafft, M.P., Riess, J.G., 2015. Selected physicochemical aspects of poly- and

339   perfluoroalkylated substances relevant to performance, environment and sustainability-

340   part one. Chemosphere 129, 4-19.

341   Lath, S., Knight, E.R., Navarro, D.A., Kookana, R.S., McLaughlin, M.J., 2019. Sorption of

342   PFOA onto different laboratory materials: Filter membranes and centrifuge tubes.

343   Chemosphere 222, 671-678.

344   Li, F., Fanf, X., Zhou, Z., Liao, X., Zou, J., Yuan, B and Sun, W., 2019. Adsorption of

345   perfluorinated acids onto soils: Kinectics, isotherms, and influences of soil properties.

346   Sci. Total Environ. 649, 504-514.

347   Li, Y., Oliver, D., Kookana, R., 2018. A critical analysis of published data to discern the role

348   of soil and sediment properties in determining sorption of per and polyfluoroalkyl

349   substances (PFAS). Sci. Total Environ. 628-629, 110-120.

350   Milinovic, J., Lacorte, S., Vidal, M., Rigol, A., 2015. Sorption behaviour of perfluoroalkyl

351   substances in soils. Sci. Total Environ. 511, 63-71.

352   OECD/OCDE (2000) OECD Text No. 106: Adsorption – Desorption using a batch

353   equilibrium method.

354   http://www.oecd-ilibrary.org/environment/test-no-106-adsorption-desorption-using-a-batch-

355   equilibrium-method_9789264069602-en (accessed July 2019).

356   Oliver, D.P., Li, Y., Orr, R., Nelson, P., Barnes, M., McLaughlin, M.J., Kookana, R.S., 2019.

357   The role of surface charge and pH changes in tropical soils on sorption behaviour of

358   per- and polyfluoroalkyl substances (PFASs). Sci. Total Environ. 673, 197-206.

359   Pan, G., You, C., 2010. Sediment-water distribution of perfluorooctane sulfonate (PFOS) in

360   Yangtze River Estuary. Environ. Pollut. 158, 1363-1367.

361   Prevedouros, K., Cousins, I.T., Buck, R.C., Korzeniowski, S.H., 2006. Sources, fate and

362   transport of perfluorocarboxylates. Environ. Sci. Technol. 40, 32-44

363   Rayment, G.E., Higginson, F.R., 1992. Oxalate-extractable Fe, Al and Mn (method 13A1),

364   in: Rayment, G.E., Higginson, F.R. (Eds.), Australian Laboratory Handbook of Soil and

365   Water Chemical Methods. Inkata Press, Melbourne, Australia, pp. 70-73.

366   Rayment, G.E., Lyons, D.J., 2011a. Carbonates by pressure change - transducer (method

367   19B2), in: Rayment, G.E., Lyons, D.J. (Eds.), Soil Chemical Methods -

368   Australasia. CSIRO Publishing, Melbourne, Australia, pp. 420-422.

369   Rayment, G.E., Lyons, D.J., 2011b. pH of 1:5 soil/water suspension (method 4A1), in:

370   Rayment, G.E., Lyons, D.J. (Eds.), Soil Chemical Methods - Australasia. CSIRO

371   Publishing, Melbourne, Australia, pp. 8-39.

372   Rayment, G.E., Lyons, D.J., 2011c. pH of 1:5 soil/0.01M calcium chloride extract –

373   following method 4A1 (method 4B4), in: Rayment, G.E., Lyons, D.J. (Eds.), Soil

374   Chemical Methods - Australasia. CSIRO Publishing, Melbourne, Australia, pp. 41.

375   Rayment, G.E., Lyons, D.J., 2011d. Electrical conductivity (EC) of 1:5 soil/ water extract

376   (method 3A1), in: Rayment, G.E., Lyons, D.J. (Eds.), Soil Chemical Methods -

377   Australasia. CSIRO Publishing, Melbourne, Australia, pp. 20-22.

378   Rayment, G.E., Lyons, D.J., 2011e. Exchangeable bases and CEC (method 15D2), in:

379   Rayment, G.E., Lyons, D.J. (Eds.), Soil Chemical Methods - Australasia. CSIRO

380   Publishing, Melbourne, Australia, pp.318-321.

381   Rayment, G.E., Lyons, D.J., 2011f. Pseudo-total elements of soils and sediments (method

382   17C1), in: Rayment, G.E., Lyons, D.J. (Eds.), Soil Chemical Methods -

383   Australasia. CSIRO Publishing, Melbourne, Australia, pp.381-382.

18

384   Sherrod, L.A., Dunn, G., Peterson, G.A., Kolberg, R.L., 2002. Inorganic carbon analysis by

385   modified pressure-calcimeter method. Soil Sci. Soc. Am. J. 66, 299-305.

386   Taylor, R.M., McKenzie, R.M., Fordham, A.W., Gillman, G.P., 1993. Oxide minerals, in:

387   CSIRO Division of Soils (Eds.), Soils: an Australian viewpoint, Division of Soils,

388   CSIRO Publishing, Melbourne, Australia, pp. 309-334.

389   Uehara, G., Gillman, G., 1981. The mineralogy, chemistry and physics of tropical soils with

390   variable charge clays. Westview Press, Boulder, Colorado USA. 170pp.

391   USEPA, 2002. Revised draft hazard assessment of perfluorooctanoic acid and its salts.

392   http://www.ewg.org/files/EPA_PFOA_110402.pdf. (accessed February 2019).

393   Venables, W. N., Ripley, B. D., 2002. Modern Applied Statistics with S. Fourth Edition.

394   Springer, New York. ISBN 0-387-95457-0

395   Villagrasa, M., López, D.A.M., Barceló, D., 2006. Environmental analysis of fluorinated

396   alkyl substances by liquid chromatography-(tandem) mass spectrometry: a review.

397   Anal. Bioanal. Chem. 386, 953-972.

398   Wells, G., Prest, H., Russ IV. C.W., 2011. Signal noise, and detection limits in mass

399   spectrometry. Agilent Technical Note.

400   https://www.agilent.com/cs/library/technicaloverviews/Public/5990-7651EN.pdf (accessed

401   July 2019)

402   Xiao, F., Zhang, X., Penn, L., Gulliver, J.S., Simcik, M.F., 2011. Effects of monovalent

403   cations of the competitive adsorption of perfluoroalkyl acids by kaolinite: experimental

404   studies and modelling. Environ. Sci. Technol. 45, 10028-10035.

405   You, C., Jia, C., Pan, G., 2010. Effect of salinity and sediment characteristics on the sorption

406   and desorption of perfluorooctane sulfonate at sediment-water interface. Environ.

407   Pollut. 158, 1343-1347.

408   Zhao, L., Bian, J., Zhang, Y., Zhu, L., Liu, Z., 2014. Comparison of the sorption behaviours

409   and mecanisms of perfluorosulfonates and perfluorocarboxylic acids on three kinds of

410   clay minerals. Chemosphere 114, 51-58.

Table 1. Selected chemical properties of the soils used in sorption experiments. All soils were collected 10-25cm except Go and Ko (0-10cm).

Soil code	Soil Order[a]	TC[b]	OC[c]	CEC[d]	Clay <0.002 mm	Silt 0.002-0.05 mm	Sand 0.05-2 mm	pH$_w$[e]	pH$_{Ca}$[f]	EC (1:5)[g]	Oxalate-extractable Al	Oxalate-extractable Fe	Oxalate-extractable Mn
		%	%	cmol+/kg	%	%	%			dS/m	mg/kg	mg/kg	mg/kg
1	Red Ferrosol	1.9	1.8	10.00	45	12	43	7.0	6.6	0.21	2580	4170	1360
2	Red Ferrosol	2.1	2.1	9.54	41	23	36	7.1	6.6	0.14	3750	6060	1150
3	Red Kandosol	0.6	0.6	2.83	7	1	91	6.9	6.3	0.07	185	466	361
4	Red Ferrosol	1.8	1.8	27.69	52	21	27	7.9	7.3	0.37	2400	7870	977
5	Red Dermosol	1.5	1.5	7.18	48	13	40	6.9	6.3	0.13	2570	4120	955
6	Grey Dermosol	0.9	0.9	3.64	30	22	48	5.7	5.1	0.10	929	2350	75
7	Redoxic Hydrosol/ Brown Dermosol	0.9	0.9	5.83	22	11	66	7.0	6.4	0.08	2060	2260	110
8	Orthic Tenosol	1.1	1.1	10.86	25	21	54	7.4	6.8	0.13	1850	4410	491
9	Redoxic Hydrosol	1.6	1.6	15.69	24	16	60	7.6	7.1	0.21	1470	3370	1170
10	Red Ferrosol	1.6	1.6	15.20	56	0	44	6.1	5.6	0.27	3730	8500	1560
11	Yellow Dermosol	1.7	1.7	7.61	44	23	34	6.2	5.4	0.06	2650	2720	125
12	Brown Dermosol	1.3	1.3	12.72	28	19	54	7.2	6.7	0.13	2150	3450	787
13	Red	1.6	1.6	5.24	32	12	55	6.9	6.2	0.09	1630	2710	209

	Kandosol												
14	Red Ferrosol	1.2	1.2	17.75	56	7	36	7.8	7.0	0.23	1790	3220	1020
15	Red Ferrosol	1.6	1.5	10.81	29	4	67	7.8	7.2	0.15	2080	2430	459
16	Red Kandosol	1.0	1.0	14.74	31	9	60	7.7	7.1	0.22	1610	1820	399
17	Redoxic Hydrosol	1.6	1.6	5.42	46	16	38	5.8	5.0	0.09	2370	3660	75
18	-	4.8	4.8	17.30	13	24	49	5.9	5.0	0.06	19400	4320	135
19	Red Kandosol	0.8	0.8	4.34	21	5	74	6.5	5.8	0.10	655	1580	405
20		1.0	1.0	16.30	58	15	21	5.3	5.5	0.07	2720	2910	912
21	Red Kandosol	3.5	3.5	9.98	22	8	70	6.5	5.7	0.10	5720	2260	50
22	Grey Ferrosol	1.1	1.1	19.12	52	13	35	7.5	7.0	0.21	2460	3780	1340
23	Red Dermosol /Red Kandosol	1.3	1.3	7.10	24	16	60	7.2	6.5	0.09	1530	2030	595
24	Red Kandosol	1.3	1.3	7.54	22	11	67	7.2	6.6	0.11	2070	1820	772
25	Brown Dermosol	0.9	0.9	6.17	26	15	59	6.4	5.8	0.10	1680	2560	474
26	Brown Ferrosol	1.3	1.3	12.67	43	7	49	7.0	6.5	0.26	1420	3270	1020
27	Red Ferrosol	2.0	2.0	6.82	47	29	24	5.6	5.0	0.12	4150	10400	1140
28	Brown Kandosol	1.8	1.8	20.41	52	6	42	7.4	6.9	0.29	1480	4200	578

[a] CSIRO (2018); [b] Total carbon; [c] Organic carbon; [d] Cation exchange capacity; [e] 1:5 water measurement; [f] 1:5 0.1M $CaCl_2$ measurement;

[g] Electrical conductivity 1:5 water measurement;

Table 2. Regression analysis of log transformed average sorption coefficient (n=3 for each soil) and single soil parameters.

Soil property	n	PFOS		PFOA		PFHxS	
		R^2	Significance	R^2	Significance	R^2	Significance
OC[a]	28	0.114	0.078 NS	0.015	0.538 NS	0.001	0.853 NS
pH[b]	28	0.061	0.205 NS	0.099	0.104 NS	0.176	0.026 *
Clay (<2μm) %	28	0.002	0.814 NS	0.005	0.722 NS	0.003	0.774 NS
CEC[c]	28	0.020	0.478 NS	0.009	0.641 NS	0.020	0.472 NS
Oxalate Al[d]	28	0.155	0.038 *	0.029	0.383 NS	0.009	0.628 NS
Oxalate Fe[e]	28	0.002	0.830 NS	0.000	0.927 NS	0.002	0.814 NS
Oxalate Mn[f]	28	0.020	0.473 NS	0.016	0.524 NS	0.036	0.333 NS

[a] OC=organic carbon (%), [b] pH 1:5 water; [c] CEC=cation exchange capacity (cmol+/kg),

[d] oxalate-extractable Al, [e] oxalate-extractable Fe, [f] oxalate-extractable Mn

NS – statistically non-significant (P> 0.05); * P<0.05

Table 3. Results from stepwise regression analysis of sorption coefficient and all soil properties based on average K_d values (n=3 for each soil).

	PFOS				PFOA				PFHxS			
	Estimate	Upper 95% CI[a]	Lower 95% CI	P value	Estimate	Upper 95% CI	Lower 95% CI	P value	Estimate	Upper 95% CI	Lower 95% CI	P value
Intercept	-2.87	-7.68	1.94	0.253	-2.71	-5.82	0.40	0.100	-2.74	-5.30	-0.19	0.045
Oxalate Al[b]	0.20	0.08	0.31	0.002	0.06	-0.01	0.13	0.126				
pH	0.69	-0.01	1.39	0.065	0.53	0.08	0.99	0.029	0.54	0.16	0.92	0.010
P value for equation	0.005				0.053				0.010			
Adjusted R^2 for equation	0.294				0.147				0.202			

[a] CI = confidence interval; [b] oxalate-extractable Al
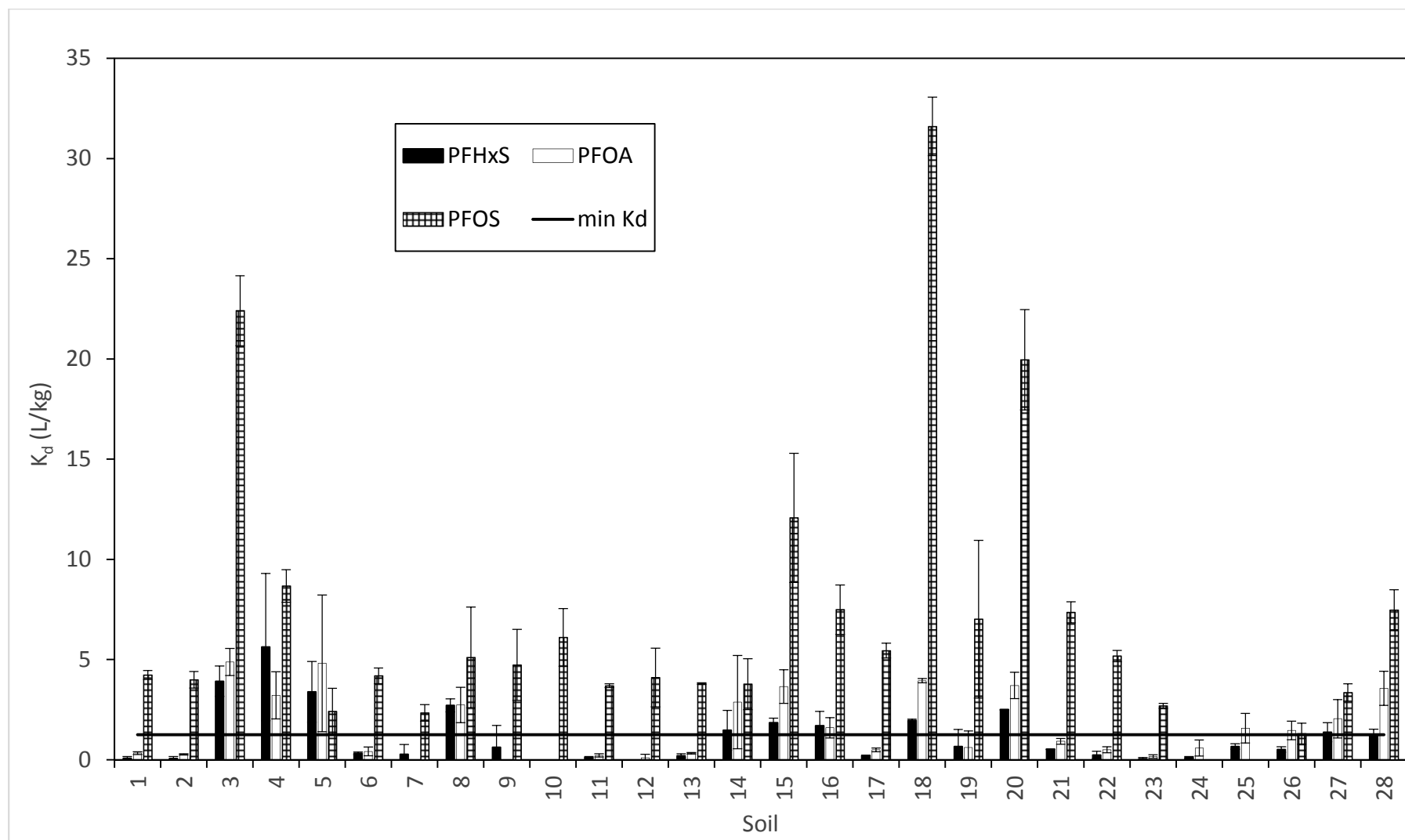
Fig. 1. Average ($\pm$ std dev) (n=3) K_d values (L/kg) for PFHxS, PFOA and PFOS for soils studied. The solid line indicates the minimum K_d required to meet the OECD (2000) requirement that a minimum of 20% of the chemical be sorbed for an accurate determination of K_d value.
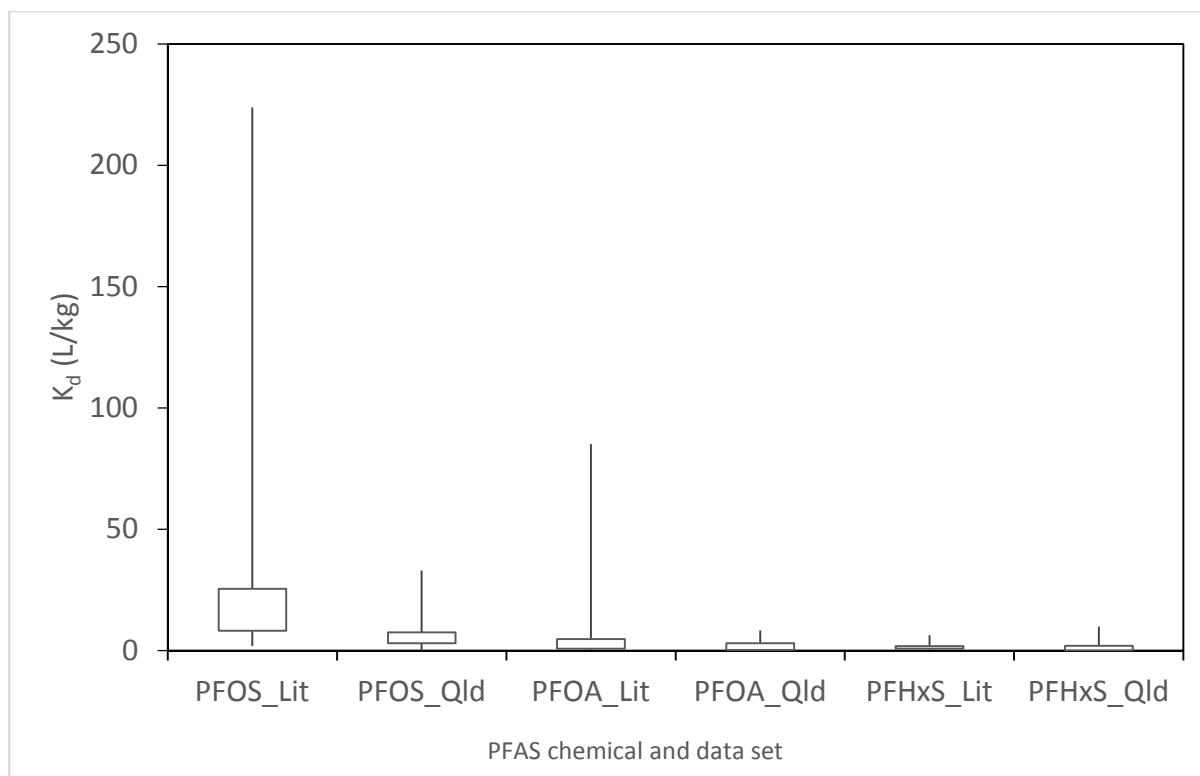
Fig. 2. Box plot of K_d values from this study (designated _Qld) and from literature values (designated _Lit) for PFOS, PFOA and PFHxS. The literature values for PFOS and PFOA are only from laboratory measurements for direct comparison with data from this study. The literature values for PFHxS are from field and laboratory measurements because of limited data (n=20) for PFHxS.
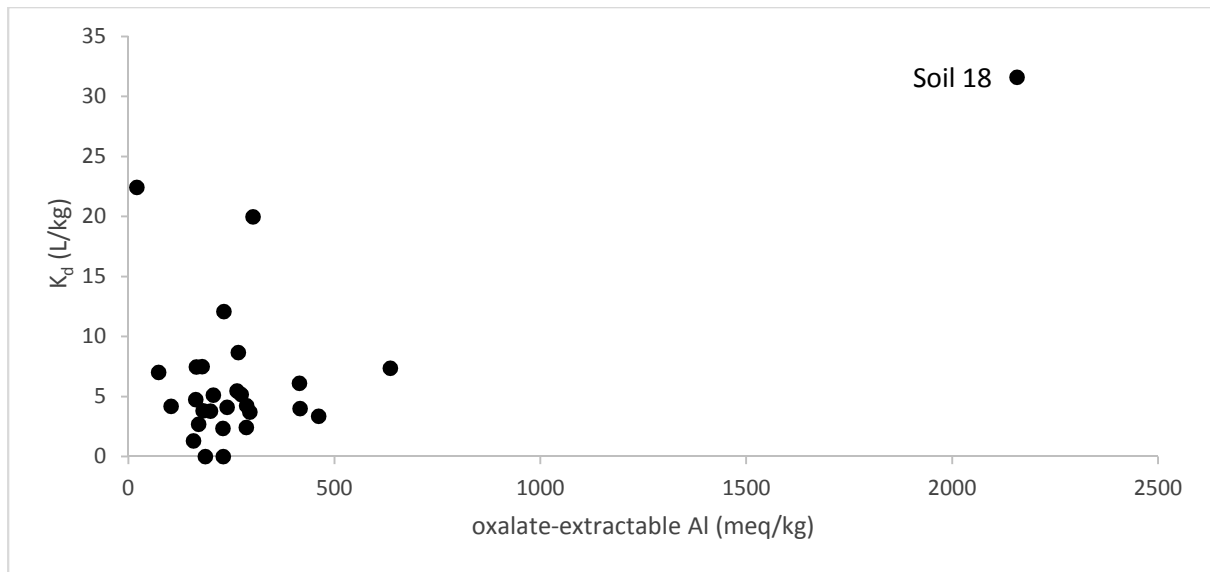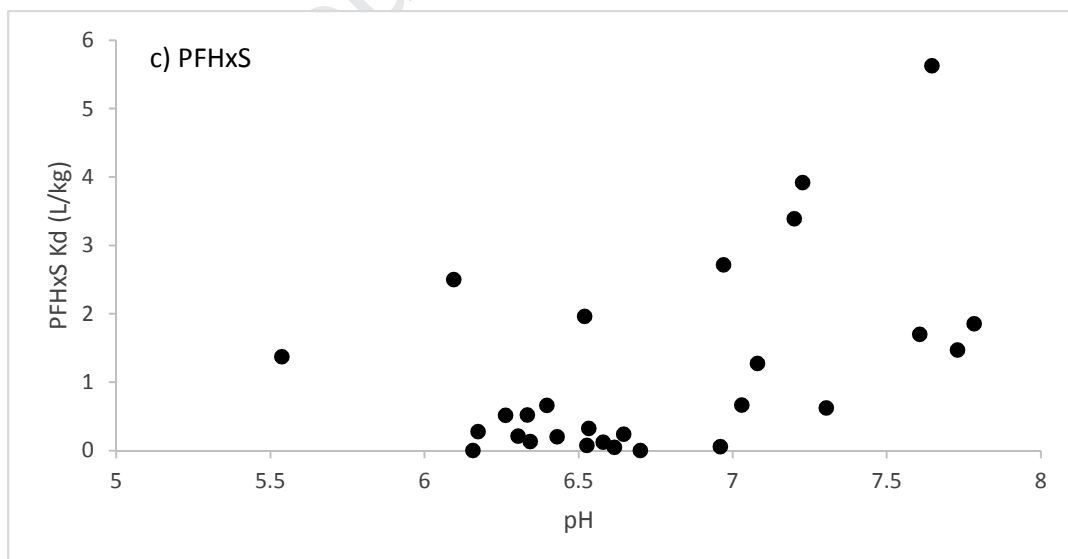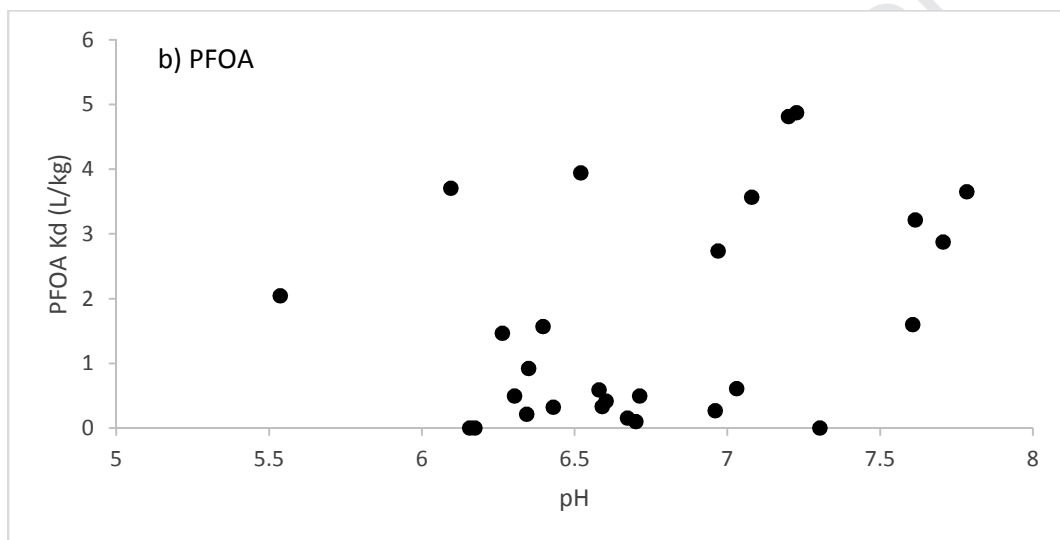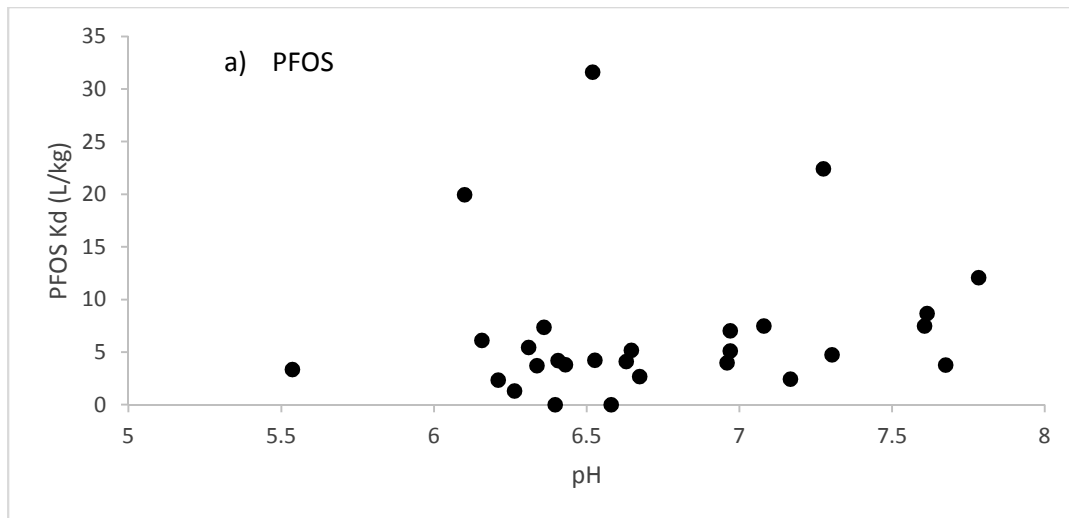
Fig. 3. Relationship between average K_d values for PFOS and oxalate-extractable Al. Soil 18 is indicated on the figure and removal of this data point resulted in the relationship being not significant.

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2

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Fig. 4. Relationship between average K_d values and pH measured at the end of the sorption experiments for a) PFOS, b) PFOA and c) PFHxS.

Sorption behaviour of per- and polyfluoroalkyl substances (PFASs) in tropical soils.

Danielle P. Oliver,[a,*] Yasong Li[a,e], Ryan Orr[b], Paul Nelson[b], Mary Barnes[c], Michael J.

McLaughlin,[d] Rai S. Kookana,[a,d]

HIGHLIGHTS

- Sorption values for PFOS, PFOA and PFHxS were determined for 28 tropical soils.
- PFOS sorption values were approximately 3.7 times lower than mean literature values
- PFOA sorption values were approximately 3.6 times lower than mean literature values
- Sorption of PFOA and PFOS was explained by pH and oxalate-extractable Al.

AUTHOR CONTRIBUTION STATEMENT

Sorption behaviour of per- and polyfluoroalkyl substances (PFASs) in tropical soils.

Danielle P. Oliver,[a,*] Yasong Li[a,e], Ryan Orr[b], Paul Nelson[b], Mary Barnes[c], Michael J. McLaughlin,[d] Rai S. Kookana,[a,d]

Danielle P. Oliver

Developed experimental design, performed experiments, wrote first draft of manuscript and revised manuscript

Yasong Li

Performed experiments, prepared data including tables and figures for manuscript

Ryan Orr

Reviewed drafts of the manuscript

Paul Nelson

Reviewed drafts of the manuscript

Mary Barnes

Performed statistical analyses

Michael McLaughlin

Assisted in development of experiments and reviewed drafts of manuscript

Rai Kookana

Assisted in development of experiments and reviewed drafts of manuscript

Declaration of interests

☒ 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Declaration of interest: none.