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## Accepted Manuscript

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The role of surface charge and pH changes in tropical soils on sorption behaviour of per- and polyfluoroalkyl substances (PFASs).

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**ABSTRACT**

This study investigated the effect of surface charge on the sorption of perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA) and perfluorohexane sulfonic acid (PFHxS) onto 7 tropical soils as a function of pH. The net surface charge became less negative with decreasing pH (from 7.5 to 3.5) in all soils. The rate of change in net surface charge varied from -0.6 to -2.8 (cmol/kg)/pH unit. The effect on sorption behaviour of PFASs was variable among soils. For two soils, the average sorption increased 54- and 45-fold for PFOS, 33- and 9-fold for PFOA, and 39- and 400-fold for PFHxS, across the pH range 7.5 to 3.5. Sorption in another sandier soil showed negligible change with decreasing pH. Sorption in the other soils did not change significantly until the pH decreased to approximately 5.5. The soils with high contents of sesquioxides (Fe and Al oxides) showed the most marked increase in sorption with decreasing pH. This study demonstrated that in addition to hydrophobic interactions with OC and other processes, electrostatic interactions are also important in the sorption process for these chemicals in soils. In acidic, variably charged tropical soils there is the possibility that any PFOS, PFOA or PFHxS sorbed to the soils may become desorbed if management practises (e.g. liming) raised soil pH.

Keywords: PFOS, PFOA, tropical soils, weathered soils

## 1. Introduction

Per- and polyfluoroalkyl substances (PFASs) are a major environmental concern globally due to their widespread usage and persistence. They have found widespread applications in industry due to their unique chemistry of having both hydrophilic and hydrophobic (surfactant-like) properties (Krafft and Riess, 2015). Many of these PFASs are used in a wide range of applications such as the production of polymers, greases, stain protectants and lubricants. In addition, these chemicals are used extensively as foams for combating hydrocarbon fuel fires. However, concerns about these chemicals have been growing due to their long-term persistence in the environment, potential for bioaccumulation and toxicity to human and ecological health (Giesy and Kannan, 2001; Higgins et al., 2007; Pan and You, 2010).

PFAS chemicals have both a hydrophobic tail of varying C chain length and a hydrophilic head, which for the most commonly detected PFASs, consists of a carboxylic or sulfonate group. Du et al. (2014) have reviewed the sorption behaviour of PFASs on a range of materials and illustrated the importance of various types of interactions with the solid phase and sorption mechanism in soils and sediments. The review concluded that the electrostatic and hydrophobic interactions are likely to be the dominant mechanisms of sorption of PFASs. For non-ionisable organic pollutants organic carbon (OC) is the principal sorbent phase. However, due to their surfactant-like properties, PFASs would be expected to behave differently from traditional, non-ionisable organic pollutants (Villagrasa et al., 2006; Ding and Peijnenburg, 2013). Unlike most non-ionic organic compounds, OC alone is unlikely to be a good descriptor of their sorption behaviour in soils and sediments. Indeed, a recent review of the international literature of sorption data for PFASs in soils or sediments found weak relationships with OC or any other single soil property (e.g. pH, clay content or CEC) (Li et al., 2018). The commonly detected PFOS and PFOA are weakly acidic

chemicals and have pKa values  $<3$ . At the pH values in most soils the PFASs would exist as anions and electrostatic interaction with soil surfaces would be an important sorption mechanism.

Soil constituents usually carry both positive and negative charges and can contain both permanent- and variable-charge surfaces. While the permanent-charges are fixed (Uehara and Gillman, 1980; Bolan et al., 1999; Qafoku et al., 2004) the variable charge in soils is developed through the dissociation of functional groups in OC and reactions (e.g. protonation/deprotonation) on mineral surfaces. Therefore, these charges vary with solution pH, ionic strength and reactions with anions and cations. The surface charge on soils would be expected to play a role in the sorption of these chemicals through electrostatic interactions. Recently, Ullberg (2015) modelled net charge of the surface of a Swedish Spodosol to assess the effect of pH and surface charge on sorption of PFASs and Campos Pereira et al. (2018), using the same soil, assessed sorption of a range of PFASs and net charge of soil organic matter. Ullberg (2015) generally found higher  $K_d$  values with decreasing negative surface charge for acidic PFASs but inconsistent results for three perfluoralkyl sulfonates. Campos Pereira et al. (2018) found decreased sorption with increasing modelled net negative charge on soil organic matter for most long-chained PFASs. However, the role of surface charge characteristics of soils or sediments in controlling sorption of PFASs to soils is currently poorly understood. Large areas of land globally have soils with dominantly variable charge, particularly under intensive weathering in subtropical and tropical regions or from volcanic ash parent materials (Qafoku et al., 2004). Currently, to our knowledge, there is no information in the literature on the interaction of PFASs with tropical soils having variable charge. The main objective of this study was to better understand the sorption behaviour of PFASs in tropical soils that have a variable charge. By adjusting the soil pH the net surface charge was expected to become less negative and sorption was expected to decrease since the

repulsion between the surface charge on the soil and the anionic head of the PFASs was expected to decrease.

## 1. Materials and Methods

### 2.1 Soils.

Soils from tropical Australia (Queensland) were used in the study. Soils were air-dried and sieved <2 mm prior to use. A range of physico-chemical properties of the soils are given in Table 1. The soils chosen for the study were selected to cover a range of soil properties that were considered important for sorption behaviour of PFAS chemicals, namely OC, pH, clay content, and iron and aluminium oxide content.

Total carbon was determined by high temperature combustion in an atmosphere of oxygen using a Leco TruMAC. Total OC was determined by correcting for inorganic carbon following a carbonate analysis (Sherrod et al., 2002; Rayment and Lyons, 2011a). Soil pH and electrical conductivity (EC) were determined using a 1:5 soil:water extract (Rayment and Lyons, 2011b, c and d). Exchangeable cations and cation exchange capacity (CEC) were determined using  $\text{NH}_4\text{Cl}$  solution at either pH 7.0 or pH 8.5 depending on soil pH (Rayment and Lyons, 2011e). Iron and aluminium oxide contents in soil were determined by an oxalate extraction (Rayment and Higginson, 1992). Clay mineralogy was determined by X-ray diffraction (XRD) analysis. The XRD results were normalised to 100%, and hence do not include estimates of unidentified or amorphous materials.

### 2.2 Batch Sorption

Three PFASs were chosen for this study, namely perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA) and perfluorohexane sulfonic acid (PFHxS). These are most commonly detected and regulated compounds, and these are either on the Stockholm



Convention list of persistent organic compounds (PFOS and PFHxS) or are under consideration (PFOA). Sorption coefficients of the three PFASs were determined using a modified version of the OECD 106 standard protocol for the adsorption – desorption of chemicals using a batch equilibrium method (OECD/OCDE, 2000). Briefly, soils (1.5 g) were weighed into polypropylene (PP) tubes and pre-equilibrated for 24 h with 7 mL of 0.5 mM CaCl<sub>2</sub> (AnalaR®) (Higgins and Luthy, 2006). The choice of containers were based on our investigations on their suitability (Lath et al., 2019). Next pH was measured using a smartCHEM-Lab™ pH meter and then adjusted with 1 M HCl (Scharlau) or 1 M NaOH (Univar). The pH was measured daily and further adjustments made until the desired pH was achieved, which took approximately one week. Then 0.5 mL of a spiking solution (10 µg/L for all samples except the most acidic samples which were spiked with 20 µg/L in 2% methanol) of a mixture of PFOS, PFOA and PFHxS was added to give a final volume of 7.5 mL (soil:solution ratio of 1:5) resulting in a final concentration of methanol <0.03%. The spiking solution was made from commercially available 1000 mg/L (PFOS and PFOA) or 500 mg/L (PFHxS) stock solution in 100% methanol (Cambridge Isotope Labs Inc., USA). The sorption solution was shaken for 24 h, centrifuged at 2012 x g force for 30 min and an aliquot (125 µL) was withdrawn and added to a PP insert in an liquid chromatography (LC) vial. Methanol (125 µL) (Optima® LC/MS grade, Fisher Chemicals) was then added to the insert (Higgins and Luthy, 2006) and the sample analysed by high performance liquid chromatography coupled with tandem mass spectrometry (LC-MS-MS); method details are provided below. In each batch the spiking concentration was measured as a spiked sample with no soil and this concentration was used as the pre-equilibration concentration in the determination of sorption. All samples from the sorption procedure were run in five replicates. Three replicates of blank soils (not spiked) were also measured to determine there were any PFASs present in the soils. The PFAS concentrations in the blank soils were

significantly less than the instrument detection limit. After centrifuging a separate aliquot was taken for measuring EC and pH. The sorption coefficients ( $K_d$ ) values were calculated in the standard manner (OECD/OCDE, 2000).

### *2.3 Determination of surface charge on soils.*

The method for determining total surface charge after pH adjustment was taken from Gillman (1984). Initially the soils (2 g) were weighed in duplicate and 20 mL 0.1 M  $\text{CaCl}_2$  added and shaken on end-over-end shaker for 2 h. Samples were then centrifuged at 2012.4 x g for 15 mins and the supernatant was discarded. An aliquot (20 mL) of 0.002 M  $\text{CaCl}_2$  was then added, samples were shaken for 30 min on end-over-end shaker, centrifuged and the supernatant was discarded. This was repeated three times but on the third washing adjustment of pH commenced using 1 M HCl or 1 M NaOH. The adjustment of pH continued over a week with samples being returned to the end-over-end shaker after addition of alkali or acid until the required pH was achieved. The sample was then centrifuged at 2012.4 x g for 15 mins and the supernatant was analysed for cations and chloride ( $\text{Cl}^-$ ). The samples were then weighed to determine the residual 0.002 M  $\text{CaCl}_2$  remaining in the sample and then 20 mL 1 M  $\text{NH}_4\text{NO}_3$  was added. The samples were shaken for 2 h, centrifuged and the supernatant was analysed for cations and  $\text{Cl}^-$  ions. Cations were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES). The sample was nebulised into the plasma of an iCAP6500 Radial spectrophotometer (Thermo Scientific, England) (APHA/AWWA/WEF, 2012a) and  $\text{Cl}^-$  was measured colorimetrically (APHA/AWWA/WEF, 2012b).

The net charge at each measured pH was calculated by:

Net charge = - [(sum of cations) -  $\text{Cl}^-$ ] (after correction of  $\text{Ca}^{2+}$  +  $\text{Cl}^-$  from residual 0.002M  $\text{CaCl}_2$  after the third washing] (cmol+/kg) (Gillman, 1984).

#### 2.4 Analysis of PFOA, PFOS and PFHxS.

All samples were analysed for PFOA, PFOS and PFHxS using LC/MS-MS. Calibrations standards and samples (10  $\mu$ L) in 50% 0.5 mM CaCl<sub>2</sub>:50% methanol were injected onto a Thermo Dionex UltiMate 3000 HPLC system with a Phenomenex Hypersil Gold PFP 100 x 2.1 mm column. The flow rate was set at 0.25 mL/min. The mobile phase was 5 mM ammonium acetate (A) and methanol (B). The mobile phase started at 95% A:5% B, changing to 5% A:95% B over 5 mins; holding at this ratio until 7 mins; reverting back to 95% A:5% B until 8 min; and continuing in this ratio until 13 mins. The column temperature was maintained at 30 °C. Detection of the chemicals was determined using a Finnigan TSQ Quantum Discovery MAX triple-quadrupole mass spectrometer operating in electrospray negative ionization mode. The ion spray voltage was 30 V, 56 V and 46 V for PFOA, PFOS and PFHxS, respectively. Ions were monitored with a multiple reaction monitoring mode and the MS/MS monitored parent and product ions *m/z* for quantification were 412.9, 169.00, 369.10 for PFOA; 498.8, 80.17 and 98.73 for PFOS and 399, 79.97 and 98.98 for PFHxS. Quantification was performed using a five point external standard calibration curve of 1, 2, 3, 4 and 5  $\mu$ g/L. The instrument detection limit was 0.3ppb for PFHxS, 0.8ppb for PFOA and 2.1 ppb for PFOS (Wells et al., 2011).

#### 2.5 QA/QC

All glassware was rinsed with methanol (Optima® LC/MS grade, Fisher Chemicals) before use in any procedure. In every batch, 5 replicates of blanks (0.5 mM CaCl<sub>2</sub> only with no soil and no spike), that had been included through the sorption procedure, were also run with every batch. Also 2 replicates of blank 0.5 mM CaCl<sub>2</sub> and methanol (Optima® LC/MS grade, Fisher Chemicals) solutions that had not been through the sorption procedure were included in each analytical batch. Also standards were repeated every 10<sup>th</sup> sample throughout

the batch and the complete calibration standard set was repeated at the end of analytical batch to ensure linearity and repeatability throughout the analysis.

### *2.6 Determination of cations in solution with pH changes*

The effect of pH changes on the cations entering solution, either through dissolution of the mineral fraction or from exchangeable cations on the soil surface, was quantified across a pH range similar to that for the sorption studies. The same protocol was followed as outlined for the sorption studies with pH adjustment but after one week a 6 mL aliquot was taken, filtered through 0.45  $\mu\text{m}$  filter and analysed on a Perkin Elmer Avio 200 inductively coupled plasma optical emission spectrometer (ICP-OES) for  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Al}^{3+}$ ,  $\text{Mn}^{2+}$ , total P,  $\text{Fe}^{2+}$  and total S (APHA/AWWA/WEF, 2012a). Blank samples of 0.5 mM  $\text{CaCl}_2$  were also included in triplicate. The data was converted from mg/L to meq/g for each polyvalent cation. The average  $\text{Ca}^{2+}$  (meq/g) in the blank samples was subtracted from the  $\text{Ca}^{2+}$  and then the sum of polyvalent cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Fe}^{2+}$ ) was determined. The other cations were < detection limit in the blanks. After one week pH and EC were also measured on the solution after removal of the aliquot.

### *2.7 Statistical analysis.*

Linear regressions and bent-stick relationships were fitted to the net charge data and the sorption data using the Solver tool in Excel. The segmented function of the segmented R package was used to determine breakpoints for segmented (bent stick) regression. A segmented (or broken-line) relationship is defined by the slope parameters and the breakpoints where the linear relation changes. In our  $K_d$  versus pH case just one breakpoint was estimated. The segmented function implements the bootstrap restarting algorithm described in Wood (2001). The bootstrap restarting is expected to escape the local optima of the

objective function when the segmented relationship is flat and the log likelihood can have multiple local optima. The objective function to be minimised is the log likelihood.

Stepwise regression was then performed using R (version 3.5.1) (R Core Team, 2018) script on a subset of sorption data that increased with decreasing pH. This subset was: all Go and Gu data, no Cb data (because of negligible change in  $K_d$  values across the pH range studied), Ly data only for pH values  $\leq 6$ , Bg and Vi data only for pH values  $\leq 5.5$ , Bl data only for pH values  $\leq 6.5$ . Akaike Information Criterion (AIC) was used as the stopping criteria for the stepwise regressions and both directions (forwards and backwards) were searched for the pool of candidate variables in the stepwise selection.

### 3. Results and Discussion

#### 3.1 Sorption across all soils at natural pH

The sorption affinity of all three chemicals for soils at their natural pH, was in the order PFOS>PFOA>PFHxS. The average  $K_d$  values ranged from 0 – 5.1 L/kg for PFHxS, from 0 – 10.7 L/kg for PFOA and 0 – 38.4 L/kg for PFOS. For all three chemicals the lowest average  $K_d$  value was found in soil Bg. The three highest average  $K_d$  values, for all three chemicals, was found in soils Bl, Go or Vi. Two of the soils (Vi and Go) that had the highest sorption also had the highest OC contents, 3.5 and 4.8%, respectively, and two of the soils with the lowest sorption (Bg and Cb) had the lowest OC contents, 0.9 and 0.6%, respectively (Table 1). There was no significant relationship between  $K_d$  values and OC for all three chemicals. However, removal of the average PFHxS  $K_d$  value for soil Bl resulted in a highly significant relationship ( $R^2=0.97$ ) (Fig. 1). There was no significant relationship between average  $K_d$  values and natural pH for all three chemicals (data not shown). One soil, Bl, had a similar OC content (1.8%) to soils Gu and Ly (2.0% and 1.8%, respectively), yet the average  $K_d$  value for Bl was 3-5-fold higher for PFOS and PFHxS and 36-fold higher for PFOA than

those values for Gu and Ly. The oxalate-extractable Al and Fe content, which is a measure of the amorphous Al and Fe oxides in soil, was approximately 1.5 times higher in soil Bl compared with soil Ly (Table 1). The isoelectric point for the common soil oxides is between pH 7 and 9 (Kämpf et al., 2012), so at lower pH values an oxide would become positively charged and thus provide considerable anion exchange capacity to the soil. Thus, the effect of pH adjustment on the surface charge of these soils, and subsequent sorption of these three chemicals, was further investigated.

### 3.2 Relationship between $K_d$ values and pH

Generally, the relationship between  $K_d$  and pH for PFOS, PFOA and PFHxS in all soils fitted a bent-stick model (Figs. 2-4; Supporting Information Figs. S1-S4). Of the soils studied there were three general responses of sorption behaviour of the chemicals with decreasing pH: (i) a marked increase in sorption with decreasing pH (Go and Gu, Fig. 2; Supporting Information Fig. S1), (ii) a small change in sorption until a specific pH was reached, after which sorption increased sharply as pH decreased (Ly, Bg, Vi, Bl, Fig. 3; Supporting Information Figs. S2-S4); or (iii) a relatively small change in sorption across the pH range studied (Cb, Fig. 4). There were strong ( $R^2=0.95$ ,  $P<0.001$ ) negative relationships for  $K_d$  for PFOS, PFOA and PFHxS with pH in the Go soil (Fig. 2). This soil had a high OC content (4.8%), a mid-range oxalate-extractable Fe content but a very high oxalate-extractable Al content (19400 mg/kg) that was nearly 3.5 times that of the next highest soil, Vi (with 5720 mg/kg) (Table 1). Similarly, sorption of PFOS and PFHxS to the Gu soil showed a significant ( $P<0.001$ ) negative relationship (Supporting Information Fig. S1;  $R^2 = 0.79$  and  $0.98$ , respectively) with pH. Sorption of PFOA to Gu varied little between pH 6.5 and 5 but at lower pH values a strong negative linear relationship was observed. While there

was a strong relationship between sorption and pH for Gu, the  $K_d$  values were the third lowest for the soils studied.

By contrast, sorption of all three chemicals to the Cb soil showed the least change across the pH range studied (Fig. 4). At the acidic pH values ( $<4.5$ ) sorption to Cb and Bg was generally the lowest (Fig. 4 and Supporting Information Fig. S2). At pH values  $<4.5$ , sorption to Bg increased markedly for all three chemicals. Interestingly, sorption of PFASs in some soils (e.g. for PFOA and PFHxS in Bg and for PFOS in Cb) showed a pronounced increase in sorption at pH values  $>6$ ; albeit the  $K_d$  values were relatively low. Of the seven soils studied, Cb and Bg had the lowest OC content and lowest oxalate-extractable Al concentrations. Soil Cb also had the lowest clay content, oxalate-extractable Fe and kaolin content (Table 1). Consequently, sorption sites for both phase partitioning and electrostatic interaction were the most limited in the Cb soil. For the other soils, there was a marked increase in sorption only when the pH had decreased below a certain value. For soil Bg this was pH 4.5 (Supporting Information Fig. S2) and for the other soils (Ly, Vi and B1) it was between pH 5 and 5.5 (Fig. 3, and Supporting Information Figs. S3 and S4, respectively). Bolan et al. (1999) broadly grouped sorption of ions into two groups: specific and non-specific retention. Nonspecific anion adsorption was defined as a process in which the negatively charged anions balance the positive charges on the soil particles and specific adsorption involves chemical bond formation. Nonspecific adsorption is characterised by high sorption at low pH and decreasing sorption with increasing pH as observed in this study while specific sorption occurs over a wide range of soil pH values (Bolan et al., 1999).

The sorption of ionisable chemicals would be expected to be dependent upon a range of soil properties. The pKa values of PFOS (-3.27), PFOA (-0.2) and PFHxS (0.14) (Krafft and Reiss, 2015) indicate that at the pH of the solutions in this study the PFAS chemicals would all be negatively charged (Deng et al. 2012). So the changes in pH would be expected

to affect the surface properties of the sorbent, rather than the charge of the PFAS molecules in the pH range studied here.

The effect of pH on sorption of PFASs to soils, sediments and pure mineral phases has been studied by others and some have observed increased sorption at lower pH values (Higgins and Luthy, 2006; Johnson et al., 2007). However, other studies on soils without variable charge properties have found only weak or no relationship between sorption and pH. For example, Milinovic et al. (2015) found no relationship between sorption of PFOS, PFOA and PFBS and pH for six sediments ranging in pH from 4.6 to 8.0. Kwadijk et al. (2013) found PFOS sorption increased from pH 4 to 6 but there was little difference in sorption values with further pH increases. A recent collation and analysis of the available literature  $K_d$  data for PFASs in soils and sediments found there was no significant relationship for  $K_d$  values and pH for PFOS (pH range 2.5 to 8.5,  $R^2 = 0.06$ ) or PFOA (pH range 4.5 to 10.0,  $R^2 = 0.07$ ) (Li et al., 2018). In order to understand the role of pH on sorption of PFASs the effect of changing pH and net surface charge of the whole soil was investigated.

### *3.3 Relationship between pH, net surface charge and $K_d$ values*

Electrostatic interaction is one of the major sorption mechanisms for PFASs and at environmental pH values (approximately pH 4-9) these chemicals usually exist as anionic species due to their low pKa values (Burns et al., 2008, Vierke et al., 2013). Electrostatic interactions can form between the negatively charged functional head of the PFASs and the positively charged surfaces of the adsorbents. Charge surfaces in soils can come from both organic and mineral phases. Silicate clay minerals derive their surface charge from isomorphous substitution of structural ions for ions of lower valence, which creates a charge imbalance, and the surface charge is fixed (permanent or constant charge) by the extent of substitution (Taylor et al., 1983). In weathered, tropical soils the surface charge can also be



strongly influenced by the Fe and Al oxide content and their kaolin clays. Their amphoteric surfaces are capable of sorbing and desorbing protons depending on pH and the ionic strength of the soil solution. This component of the soil surface charge is termed variable charge. Most soils contain a mixture of the variable- and constant-charge colloids and it is their relative proportions which control the net surface charge characteristics of a soil. Soils that contain appreciable amounts of oxides can give the soil a significant anion exchange capacity under acidic pH conditions (Taylor et al., 1983; Qafoku et al., 2004).

The effect of pH on sorption of PFASs has been reported to be due to pH-dependent changes in the sorbent (Higgins and Luthy, 2006; Chen et al., 2009). For all seven soils studied, the net surface charge became less negative with decreasing pH and all relationships were linear (Table 2; Figs. 2-4; Supporting Information Figs. S1-S4). Soils Cb and Bg had the least net negative charge at the most alkaline conditions (pH approximately 7), namely -3.3 and -5.4 cmol/kg respectively, (Fig. 4 and Supporting Information Fig. S2). They also had the smallest change in net charge across the pH range studied (2.59 and 3.63 cmol/kg, Table 2). Soils B1 and Ly had the highest negative net charge, namely -22.3 and -16.8 cmol/kg, respectively, at pH approximately 7.0 (Supporting Information Fig. S4 and Fig. 3), and they also had the largest change in net charge across the pH range studied (13.65 and 9.26 cmol/kg, Table 2). A high negative surface charge would be expected to repel the negatively charged functional head of the PFASs but, due to the hydrophobic properties of these chemicals, it has been suggested that they may prefer sorption onto solid surfaces rather than remaining in the water phase (Du et al., 2014). While Go and B1 had comparatively high net negative surface charge at pH >6 (Fig. 2 and Supporting Information Fig. S4) the higher OC contents in these soils, compared with the other soils studied, provided an alternative sorption site for partitioning of the hydrophobic PFAS tail.

Ullberg (2015) modelled net surface charge of one Swedish soil and found higher  $K_d$  values with decreasing negative surface charge for perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA), perfluorododecanoic acid (PFDoDa), and perfluorotetradecanoic acid (PFTeDA) but the trends for three perfluoralkyl sulfonates (perfluorobutane sulfonic acid (PFBS), PFHxS and PFOS) were not consistent. Campos Pereira et al. (2018) modelled net charge of soil organic matter as a function of pH and various concentrations of  $Al^{3+}$ ,  $Ca^{2+}$  and  $Na^+$  in a Swedish soil with a high carbon content (45%). They found sorption of PFHxA, PFHpA, PFOA, PFNA, perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), PFDoDA, PFTeDA, and perfluorooctane sulphonamide (FOSA) significantly ( $P < 0.01$  or  $< 0.001$ ) decreased with increases in the magnitude of the modelled net negative charge on soil organic matter. They found no significant relationship for the short-chained PFASs (perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA) and PFBS) and a weaker relationship for PFHxS and PFOS ( $P < 0.05$ ).

The rate of change in net charge ((cmol/kg)/pH) with decreasing pH in this study was in the order: Go (2.76) > Bl (2.64) > Ly (1.98) > Gu (1.77) > Vi (1.30) > Bg (0.79) > Cb (0.59) (Table 2). The soils with a high rate of change in charge (Bl, Ly and Gu) had a high kaolin content and Go had an exceptionally high oxalate extractable Al content. There was a significant linear relationship between the rate of change in net charge with pH and kaolin content (%) when the Go soil was excluded ( $R^2 = 0.82$ ) (Supplementary, Fig. S5). A weaker relationship was found with oxalate Fe content ( $R^2 = 0.36$ ) or total oxalate Fe and Al ( $R^2 = 0.47$ ) (Supplementary, Figs. S6 a and b). The point of zero charge (PZC) for kaolin is low (3-4) (Schroth and Sposito, 1997) while those of Al oxides are high (5-9). If the pH of a soil is above its PZC the soil surface will have a net negative charge and predominantly exhibit an ability to exchange cations, while the soil will mainly retain anions (electrostatically) if its pH

is below its PZC (Appel et al., 2003). The surface properties of kaolin are likely to greatly influence pH-induced change of net surface charge for Bl, Ly and Gu, while the properties of Al oxides are likely to greatly influence that for Go. One factor not considered in this study is the surface area of kaolin and Al oxides and this may be an important factor affecting rate of change of charge with pH.

To investigate the effect of net surface charge on the sorption of all three chemicals together, only the  $K_d$  data that increased with decreasing net surface charge (and decreasing pH) (called pH-responsive dataset) were considered. The pH-responsive dataset were normalised by dividing the  $K_d$  values for each individual chemical by the highest  $K_d$  value for that chemical in each soil. This was necessary given the very different range of  $K_d$  values for the three PFASs. Data for Cb was excluded since  $K_d$  values in this soil showed only a small change with decreasing pH. Plots of normalised  $K_d$  values for all three chemicals for each soil in this pH-responsive dataset are given in Supplementary, Fig. S7. Despite considerable scatter of the normalised  $K_d$  values the linear regressions with net charge ranged from  $R^2 = 0.64$  for Ly to  $0.82$  for Gu. Stepwise regression was also performed on this pH-responsive dataset to investigate what soil properties accounted for the  $K_d$  values (Table 3). For all three chemicals net surface charge, CEC, oxalate extractable Al and EC accounted for a large proportion of the  $K_d$  data for the pH-responsive dataset (PFOA  $R^2=0.88$ , PFOS  $R^2=0.88$ , and PFHxS  $R^2=0.84$ ). Including oxalate extractable Mn for the pH-responsive dataset for PFHxS improved the regression ( $R^2=0.87$ ,  $P<0.001$ ). Including oxalate extractable Mn, total kaolin and OC for the pH-responsive dataset for PFOA improved the regression ( $R^2=0.90$ ,  $P<0.001$ ).

This data demonstrates that sorption of PFOS, PFOA and PFHxS does involve electrostatic interactions and it is affected by pH. The extent of the importance of this mechanism for sorption of the PFASs varied between soils and was related to the Al and Fe hydroxide content of the soils.

Changes in pH can also affect the release of DOC from soils. Under acidic conditions the solubility of DOM is diminished by the high degree of protonation (Kalbitz et al., 2000). Under alkaline conditions the sorption of PFOS, PFOA and PFHxs may have increased due to the release of DOC. However, this is unlikely since at the alkaline conditions in this study (pH 7-7.5), and in the presence of  $\text{Ca}^{2+}$  as the background electrolyte, pH has been shown to have a minimal effect on DOC release (Curtin et al., 2016). Changes in soil pH may also affect the release of ions in solution, which may affect sorption. The relationship between pH and cations in solution is discussed below.

### *3.4 Relationship between polyvalent cations in solution and $K_d$ values*

Several studies have shown that polyvalent cations in solution can affect the sorption behaviour of PFASs (Higgins and Luthy, 2006; You et al., 2010; Chen et al., 2012.) and adjusting pH may change the concentration of polyvalent cations in solution. Higgins and Luthy (2006) studied the effect of  $\text{Ca}^{2+}$  and  $\text{Na}^+$  on sorption of anionic PFASs and found the average increase in  $\log K_d$  per log unit  $[\text{Ca}^{2+}]$  was  $0.36 \pm 0.04$ . However, increasing concentrations of  $\text{Na}^+$  did not increase sorption of PFASs. The increased sorption of the anionic PFASs with increased concentrations of  $\text{CaCl}_2$  has been attributed to the neutralization of the negative charge on the sediment surface and decreased electrostatic repulsion and the salting-out effect of the increased content of dissolved ions (You et al., 2010). The salting out effect occurs when the water molecule becomes more ordered and compressible in the presence of dissolved ions and the cavity volume available to accommodate the neutral solutes decreases (Turner and Rawling, 2001). Consequently, the aqueous solubility of organic chemicals was inversely related to the content of dissolved ions (You et al., 2010). The increased ions in solution have been proposed to affect the sorption behaviour of the hydrophobic tail of the PFAS chemicals (You et al., 2010). Others have also described a mechanism where divalent cations, such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Cu}^{2+}$ , could form a

bridge between the anionic functional groups in soil organic matter and the anionic organic pollutants (Hyun and Lee, 2005). Consequently, the effect of pH adjustment on the cations in solution was investigated.

In this study, the concentrations of polyvalent cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$ ) in solution in all soils increased with decreasing pH and generally were dominated by  $\text{Ca}^{2+}$  at low pH values (Supporting Information, Figs, S8 a-g). For some soils (Go, Gu, Bg and Vi) the concentrations of  $\text{Al}^{3+}$  and  $\text{Fe}^{n+}$  increased under alkaline conditions, but at the pH values in this study (approximately pH 6 – 7.5) these metals would not exist as dissolved polyvalent cations and would most likely be complexed with DOC. The increase in concentrations of polyvalent cations in solution was not related to the sorption of PFOS, PFOA or PFHxS. For example, soil Ly showed increased sorption at approximately pH 6.0 for PFOS and PFOA and 4.5 (Fig. 3) for PFHxS but the concentrations of polyvalent cations increased linearly from pH 7.3 to 4.0 (Supporting Information, Fig. S8c). Similarly for soil Bg, sorption generally did not begin to increase until the pH decreased to 4.5 (Supporting Information, Fig. S2) but the total polyvalent cations steadily increased, albeit at low concentrations, from pH 5.9 (Supporting Information, Fig. S8e). This would suggest that the effect of decreasing pH on sorption of PFOS, PFOA and PFHxS in these soils is not related to the concentrations of polyvalent cations in solution.

This is the first study in the published literature that has determined the effect of surface charge of whole soils on sorption behaviour of PFASs. This study has shown that sorption of PFASs in soils is complex and a number of properties are contributing to the sorption. Others have found sorption of several PFASs onto three mineral phases in the order hematite>kaolinite> montmorillonite even though at the pH of their study (6.9) kaolinite and hematite were negatively charged (Zhao et al., 2014). They suggested other interactions beside electrostatic attraction were involved in sorption of PFASs. While OC is an important

factor controlling sorption of PFASs, as soil pH decreases the role of surface charge becomes important in variable charge soils (containing significant amounts of Al and Fe oxides) but the degree of importance is moderated by the contents of OC and oxides. In this study the sorption of PFOS, PFOA and PFHxS increased for 6 of the 7 soils below pH  $\approx$ 5. This has implications for management of acidic soils in the region since any increase in pH, such as liming, potentially could decrease the sorption of these PFASs and increase their potential for transport and bioavailability. Conversely lowering the pH of soils that carry a variable charge may increase the sorption of these chemicals, but on-going monitoring would be required to ensure the pH remained acidic.

**ASSOCIATED CONTENT**

Fig. S1-S4. Relationship between  $K_d$  values for a) PFOS, b) PFOA and c) PFHxS and pH and net charge for soils Gu, Bg, Vi and Bl.

Fig. S5. Relationship between rate of change in total surface charge and kaolin (%) content in whole soil.

Fig. S6. Relationship between rate of change in net charge and oxalate Fe content (mg/kg).

Fig. S7. Relationship between normalised  $K_d$  values ( $K_d$  values normalised to a fraction of the highest  $K_d$  value measured in that soil) for PFOS, PFOA and PFHxS and net charge only for data in the pH range where the  $K_d$  values increased (i.e. excluding the data where  $K_d$  values were linear) for a) soils Bg, Ly and Gu and b) soils Vi, Bl and Go.

Fig. S8. Total polyvalent cations (meq/g) at designated pH values for a) soil Go, b) soil Gu, c) soil Ly, d) soil Bl, e) soil Bg, f) soil Vi and g) soil Cb.

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**Notes**

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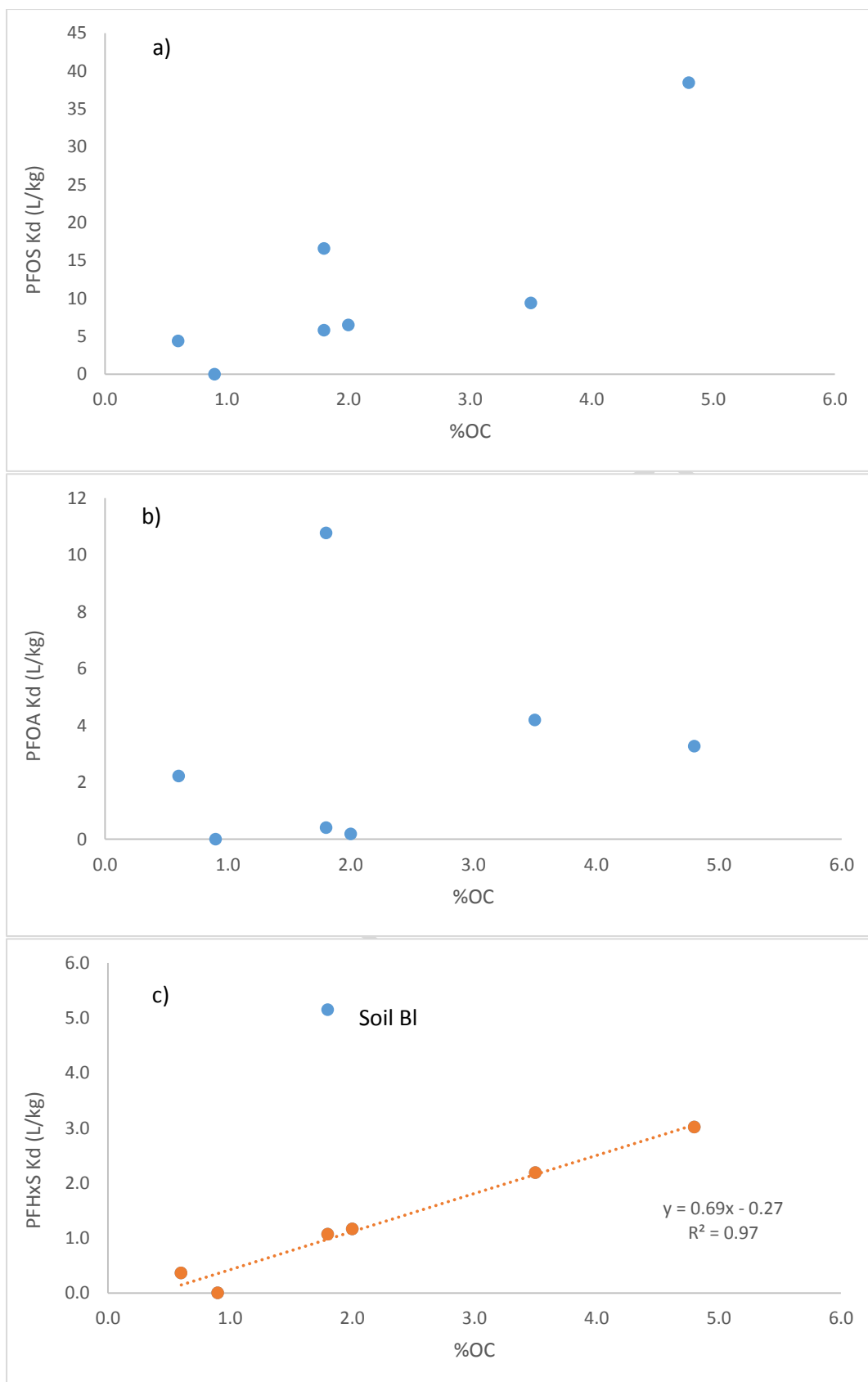


Fig. 1. Relationship between average K<sub>d</sub> values (L/kg) for a) PFOS, b) PFOA and c) PFHxS and soil organic carbon (OC).



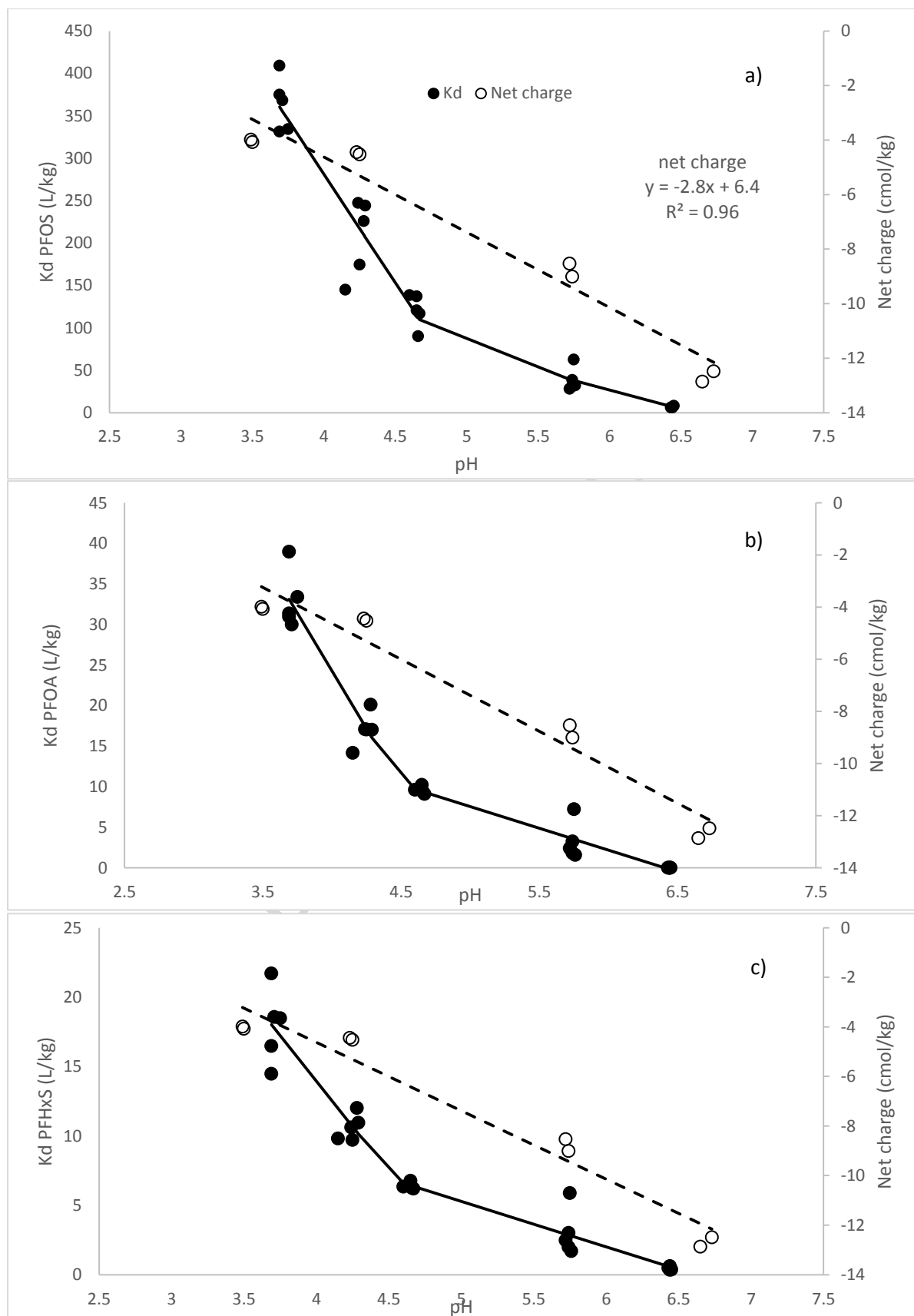


Fig. 2. Relationship between  $K_d$  values for a) PFOS, b) PFOA and c) PFHxS and pH and net charge for the Go soil.

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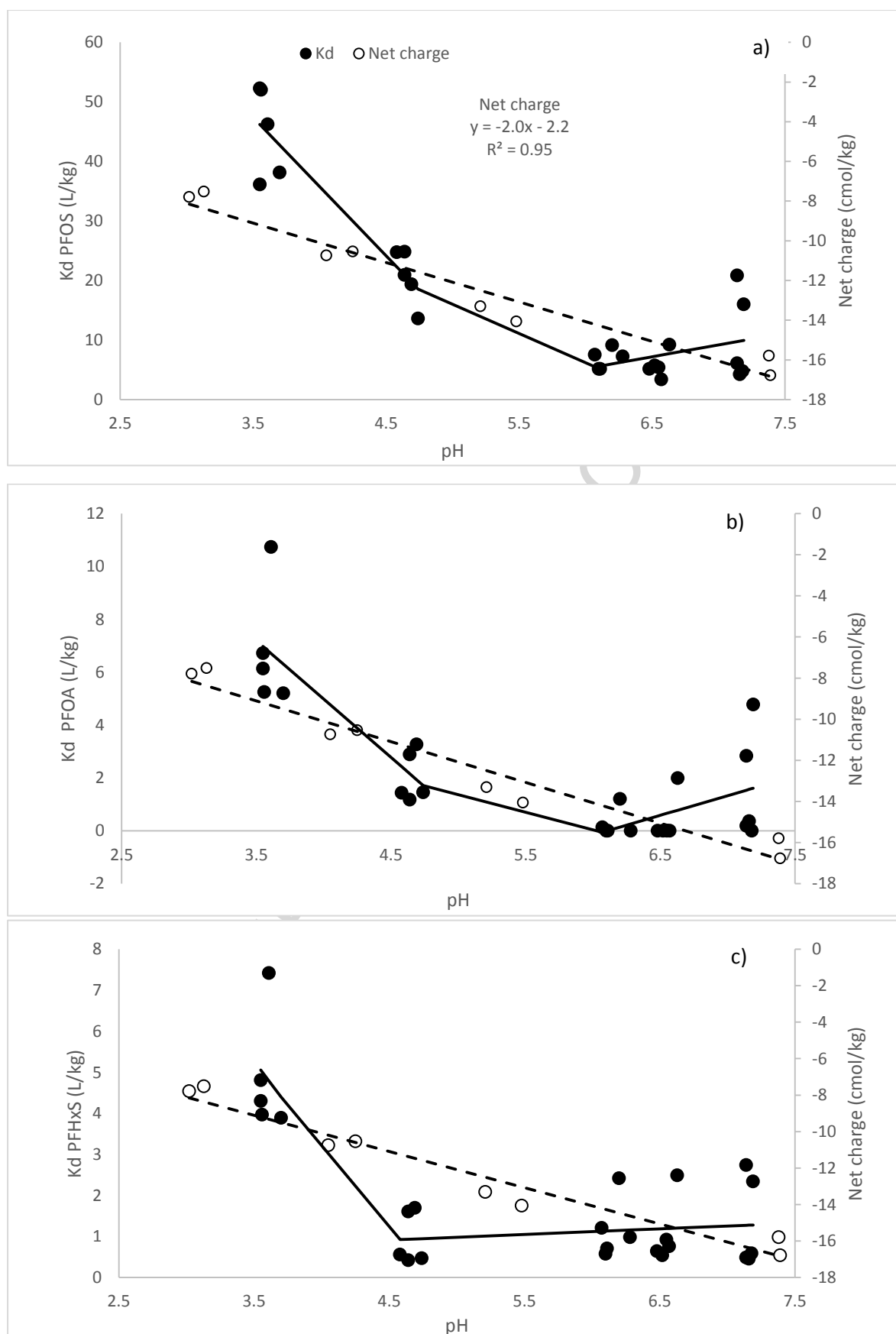


Fig. 3. Relationship between  $K_d$  values for a) PFOS, b) PFOA and c) PFHxS and pH and net charge for the Ly soil.

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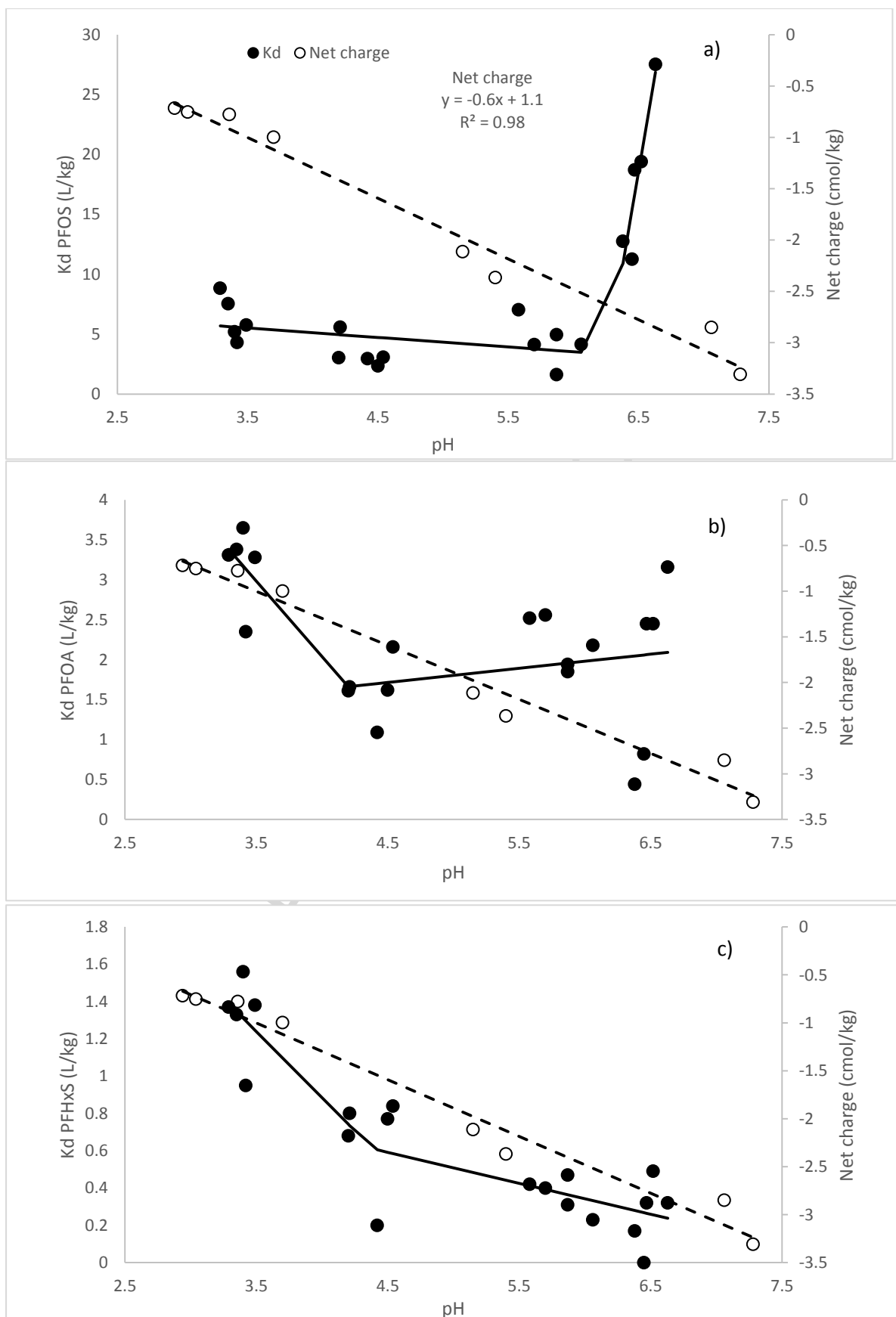


Fig. 4. Relationship between  $K_d$  values for a) PFOS, b) PFOA and c) PFHxS and pH and net charge for the Cb soil.

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

Soil code	Soil Order <sup>a</sup>	TC	OC	ECEC (Amm. Acet.)	Clay <0.002 mm	Silt 0.002-0.05 mm	Sand 0.05-2 mm	pH <sub>w</sub> <sup>b</sup>	pH <sub>Ca</sub> <sup>c</sup>	EC (1:5) <sup>d</sup>
		%	%	cmol+/kg	%	%	%			dS/m
Cb	Kandasol	0.6	0.6	2.8	7	1	91	6.9	6.3	0.07
Bg	Dermosol	0.9	0.9	3.6	30	22	48	5.7	5.1	0.10
Ly	Kandasol	1.8	1.8	20.4	52	6	42	7.4	6.9	0.29
Bl	Ferrosol	1.8	1.8	27.7	52	21	27	7.9	7.3	0.37
Gu	Ferrosol	2.0	2.0	6.8	47	29	24	5.6	5.0	0.12
Vi	Kandasol	3.5	3.5	10.0	22	8	70	6.5	5.7	0.10
Go	Ferrosol	4.8	4.8	17.3	13	24	49	5.9	5.0	0.06

<sup>a</sup> CSIRO 2018; <sup>b</sup> 1:5 water measurement ; <sup>c</sup> 1:5 0.1M CaCl<sub>2</sub> measurement; <sup>d</sup> Electrical

conductivity 1:5 water measurement

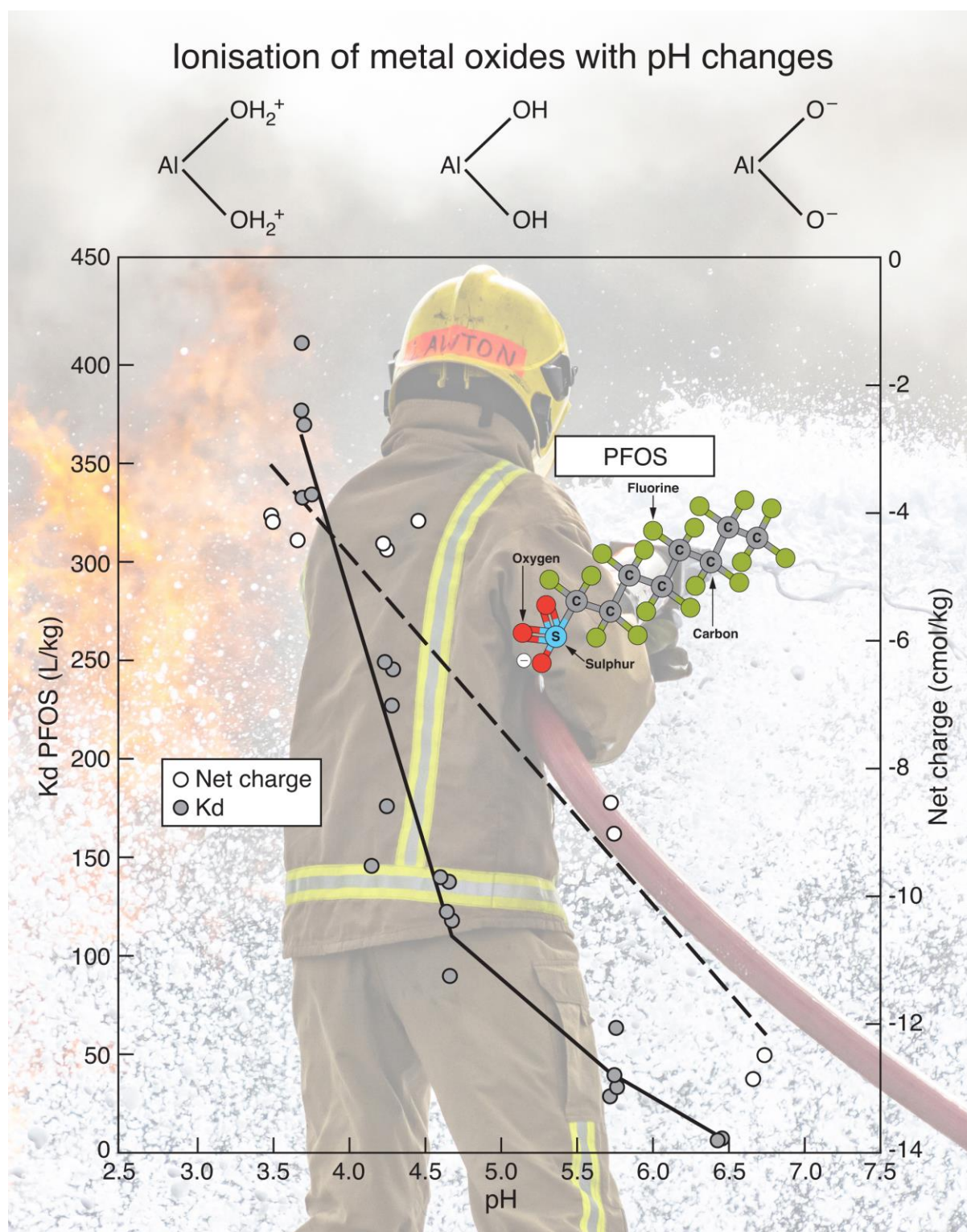
Table 2. Range and rate of change of net surface charge across the pH range assessed.

Soil	Net charge (cmol/kg)			pH			Rate of change in net charge across pH range studied (cmol/kg.pH)
	min	max	range	min	max	range	
Cb	-3.31	-0.72	2.59	2.94	7.28	4.34	-0.592
Bg	-5.44	-1.80	3.63	2.95	7.2	4.25	-0.791
Ly	-16.78	-7.51	9.26	3.02	7.39	4.37	-1.984
Bl	-22.30	-8.65	13.65	3.06	7.91	4.85	-2.641
Gu	-8.88	-2.21	6.68	3.01	6.85	3.84	-1.774
Vi	-7.65	-2.63	5.01	3.25	7.13	3.88	-1.299
Go	-12.87	-3.99	8.88	3.49	6.73	3.24	-2.760



Table 3. Results from stepwise regression of  $K_d$  values (L/kg) for PFHxS, PFOS and PFOA when the dataset was restricted to those values that were found to increase with decreasing pH.

	$K_d$ PFHxS			$K_d$ PFOS			$K_d$ PFOA
	Estimate	Std Error	P-value	Estimate	Std Error	P-value	Estimate
Intercept	0.47	0.12	<0.001	2.21	0.46	<.001	3.08
Net charge	0.30	0.04	<0.001	1.19	0.15	<.001	0.49
CEC	0.14	0.03	<0.001	0.50	0.13	<.001	0.31
Oxalate Al	$1.3 \times 10^{-4}$	$7.91 \times 10^{-6}$	<0.001	$5.57 \times 10^{-4}$	$3.00 \times 10^{-5}$	<.001	$2.86 \times 10^{-4}$
EC	0.35	0.11	0.0013	1.97	0.43	<.001	0.59
$R^2$ for regression	0.84			0.88			0.88
P value for regression	<0.001			<0.001			<0.001
Oxalate Mn	$5.13 \times 10^{-4}$	$1.27 \times 10^{-4}$	<0.001				$3.33 \times 10^{-4}$
Total kaolin							-0.10
OC							-0.74
$R^2$ for regression With extra terms	0.87			0.88			0.90
P value for regression With extra terms	<0.001			<0.001			<0.001



Graphical abstract

## Highlights

The role of surface charge and pH changes in tropical soils on sorption behaviour of per- and polyfluoroalkyl substances (PFASs).

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## Highlights

- Net surface charge on 7 tropical soils became less negative with decreasing pH.
- Sorption of PFOS, PFOA and PFHxS increased linearly on 2 soils with decreasing pH.
- On 4 other soils sorption of PFOS, PFOA and PFHxS showed little change until pH <5.
- Sorption of PFOS, PFOA and PFHxS generally followed the net charge in these soils.
- The pH of variable charged soils needs to be managed to minimise leaching of PFASs.

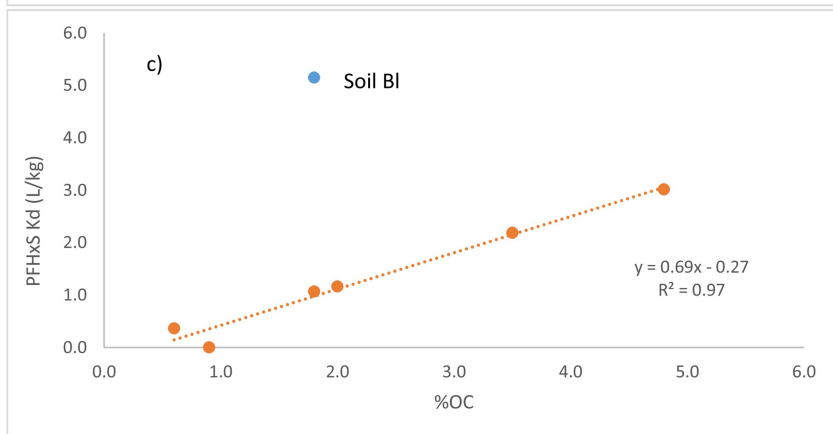
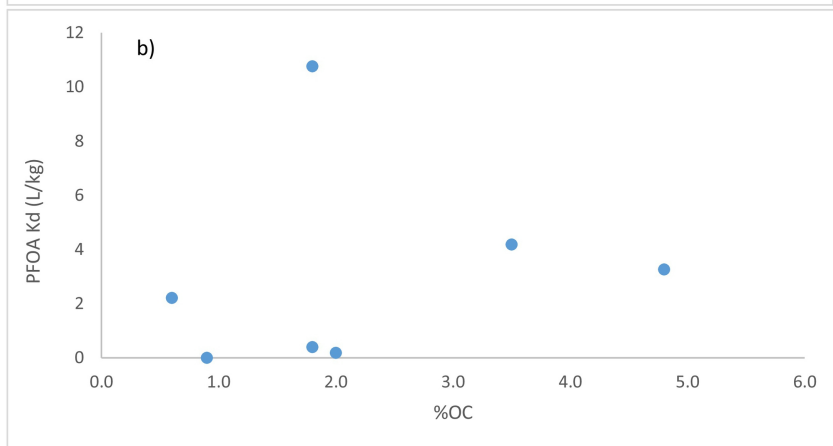
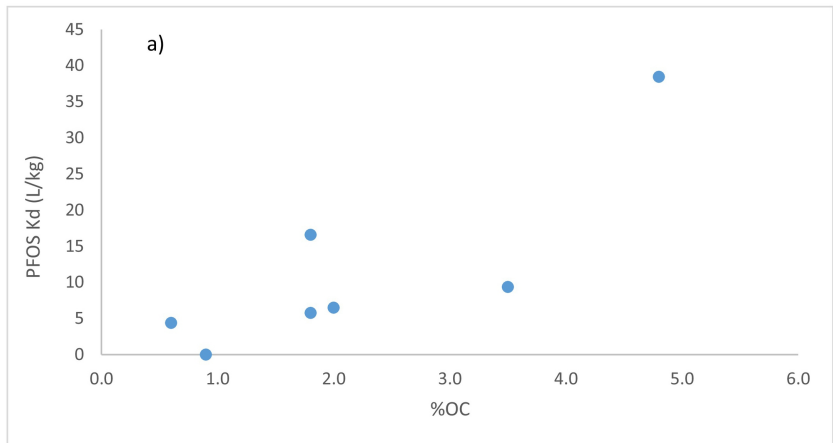


Figure 1

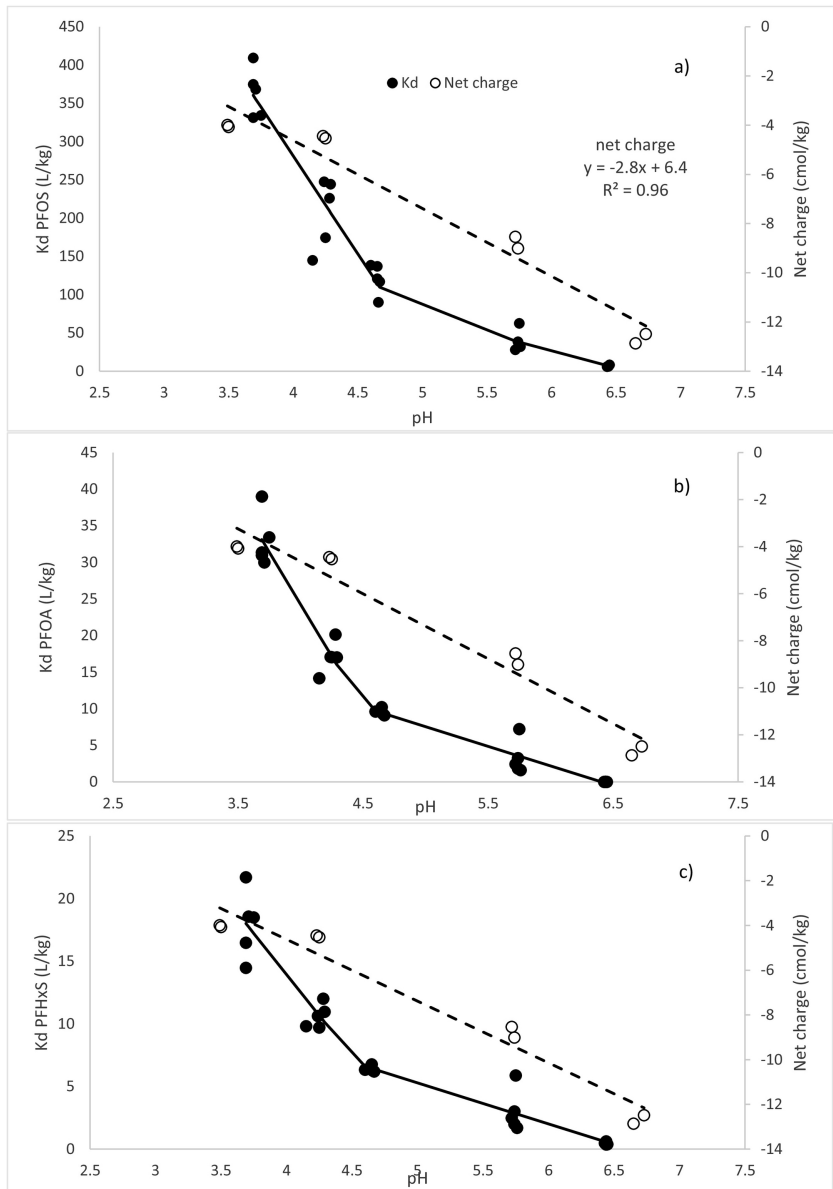


Figure 2

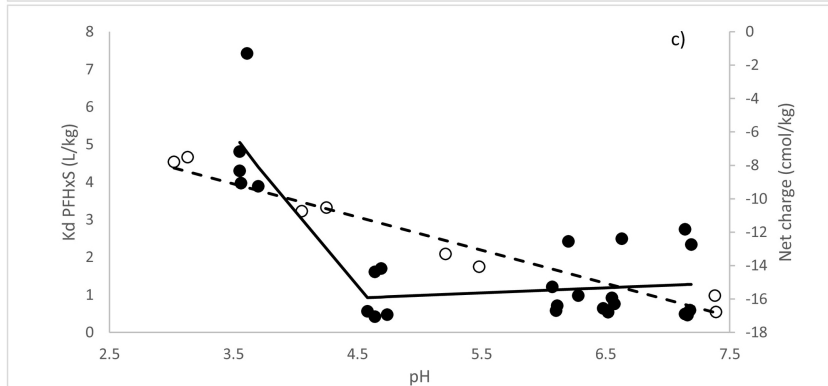
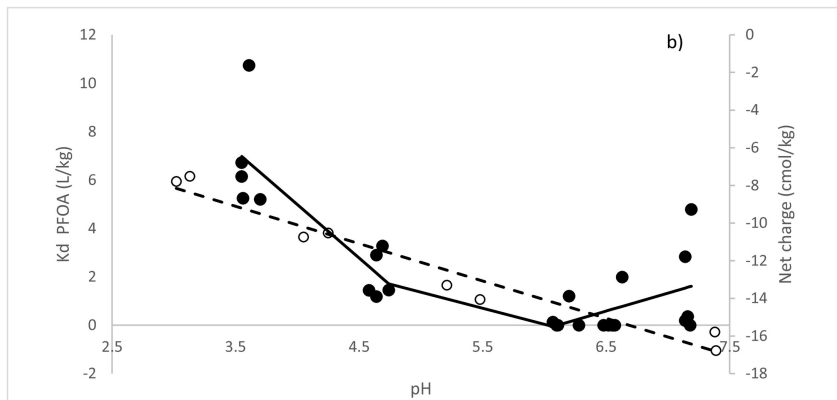
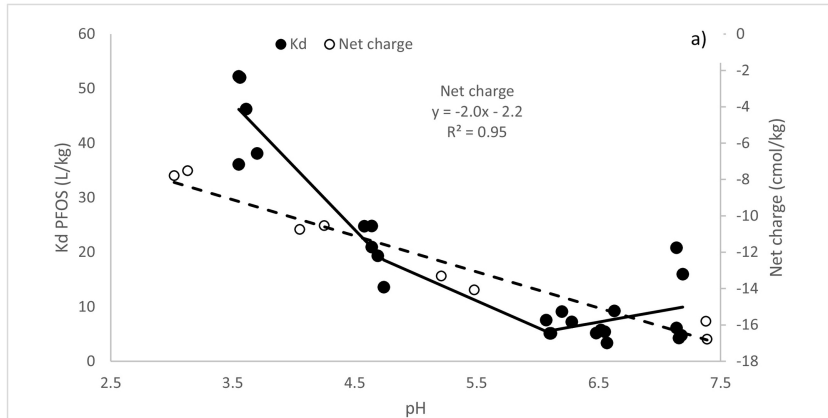


Figure 3

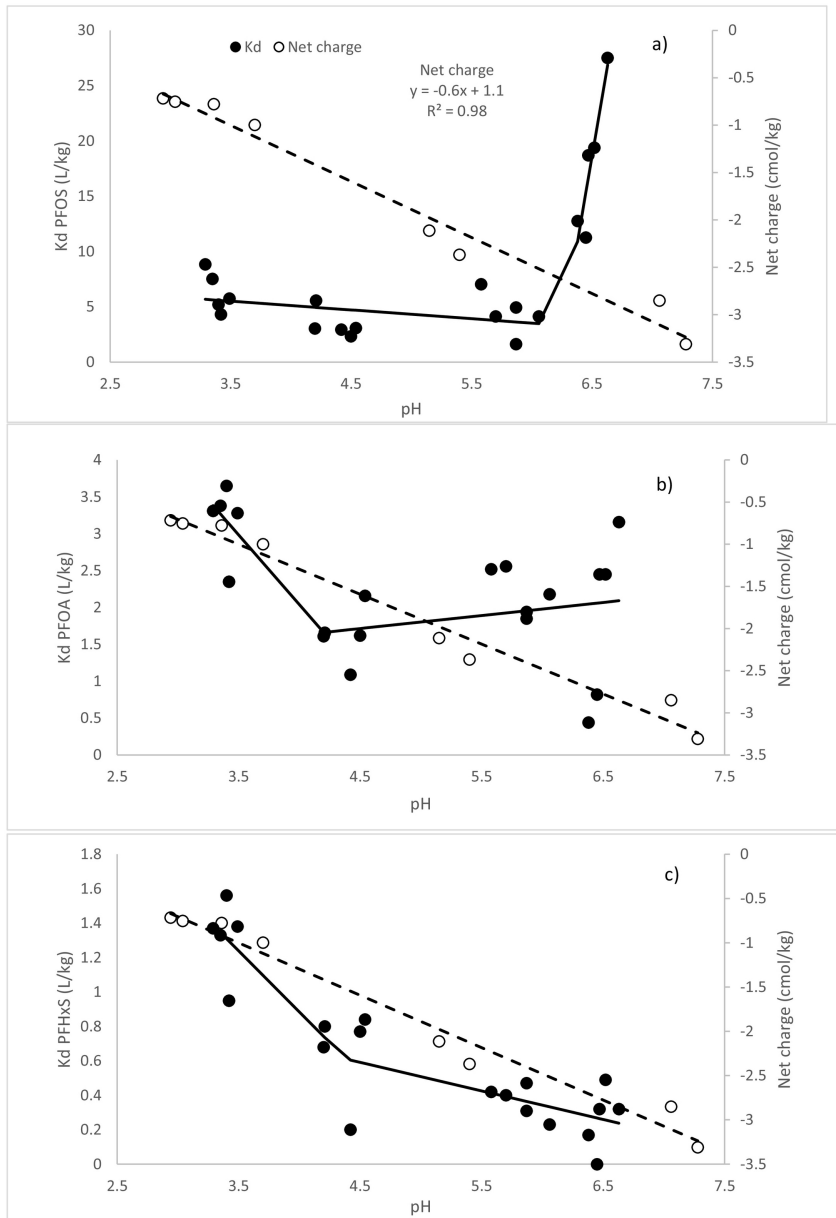


Figure 4