Research Article

A Methodology to Estimate Net Proton: Phosphorus Co-Adsorption Ratios for Acidic Soils

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Abstract

Despite extensive research, the behaviour of the key nutrient element, phosphorus (P), in soil is not yet fully understood. This study focussed on the outstanding issue of the co-adsorption of protons (H^+) and P by soils. We developed a congruent set of measures to determine the net H^+:P co-adsorption ratio and tested it on goethite, for which a ratio of 1.6:1 had been estimated under CO_2-free conditions for additions of NaH_2PO_4. Under our conditions, and using additions of KH_2PO_4, the net H^+:P co-adsorption ratio was estimated to be 1.44:1, i.e., in passable agreement with the published value. Application of the protocol to acidic soils resulted in a net H^+:P co-adsorption ratio of 1.92:1, and substitution of H_3PO_4 for KH_2PO_4 gave a ratio of 1.96:1. These ratios for soils differ significantly from that for goethite. The soils for which we estimated net H^+:P co-adsorption ratios had a wide range of properties and two had received previous applications of P fertiliser ($Ca(H_2PO_4)_2$), which does not appear to have affected the net H^+:P co-adsorption ratios. The H^+:P co-adsorption

ratio method could benefit from refinement, and further study is required to explore how these findings may apply to commercial P fertilisers under field conditions.

1. Introduction

Phosphorus (P) is a critical element for all living systems, being widely involved in both terrestrial and marine biogeochemical cycles. P is an essential element for all biota, and is involved in cellular energy transport, structural components such as bones, teeth and plant tissues, and reproduction. P is an important component of global food production systems [1], and most global soils do not naturally contain sufficient P to support more than a few years of intensive crop production. Long-term, high-intensity crop production, needed to support a bourgeoning human population, requires P inputs, usually as manures or fertilisers. Fertilisers are mainly prepared (for the P component) from phosphate rock, a finite resource [2-4].

Soils are complex natural combinations of solids which themselves are intimate mixtures of organic and inorganic substances, a soil solution and a soil atmosphere [5]. The solids are bound together into structural units (peds) that vary in size, shape and stability in different soils, and even within any given soil profile. The soil atmosphere and solution fill the voids between the solids (pores), with the relative proportions varying widely over short time frames (rainfall will enter the soil pores to add to the soil solution, displacing the atmosphere; when the rain stops, water will gradually drain or evaporate allowing the soil atmosphere proportion to increase) [6]. Soils also have a living component, adding and removing substances from the solids, solution and atmosphere.

Phosphorus occurs in soils in a number of different forms in the solids, solution and living components of the soil. In the context of this study, most interest is in the behaviour of solution phase orthophosphate species (e.g., $H_2PO_4^-$), and interactions with the soil solids. Understanding how additions and losses of these species occur is vital for efficient and effective fertiliser use. The processes involved are summarised in the P cycle (Figure 1).

The addition of P materials to soils is aimed at enhancing the soil solution concentration of a soluble form of P that can be readily taken up by plants (mainly $H_2PO_4^-$ and HPO_4^{2-} [7]). When P fertilisers are added to soils, a complex set of interactions occurs such that only a proportion of the added P is taken up by the plants. Soluble P entering the soil solution as a phosphate ion, can be:

- *precipitated* by cations, especially Ca, Al and Fe ions, in the soil solution, as highly insoluble species [8];
- *adsorbed* on the surfaces of soil minerals, especially clay-sized oxyhydroxides of Al and Fe (e.g., gibbsite, goethite, ferrihydrite) and aluminosilicate clays (e.g., allophane, imogolite, kaolinite, smectite), which have a high affinity for phosphate [9]. P adsorption leads to the adsorbed ions contributing to the surface charge of the adsorbing particles [10];
- *absorbed* (taken in) by plant roots [7];

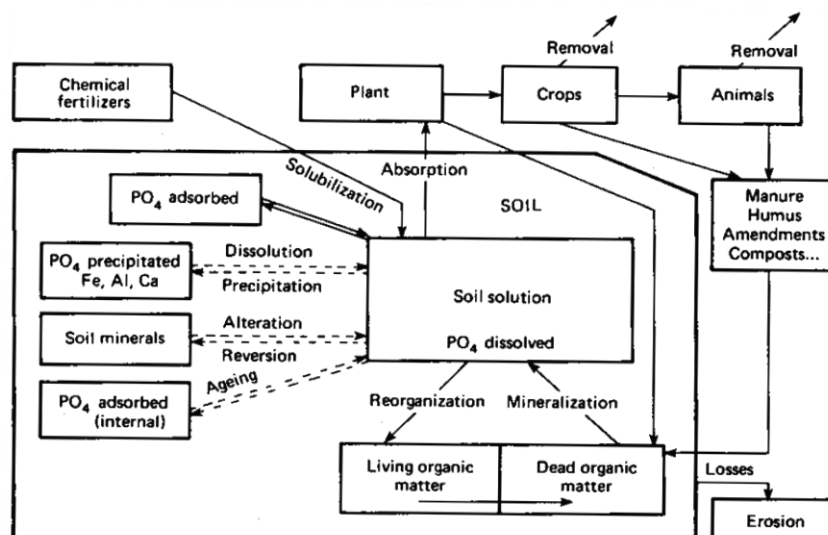- *retained* in the soil solution as phosphate ions in low concentration.

Figure 1 The soil phosphorus cycle.

The effectiveness of P fertiliser additions depends on these interactions, which are determined by soil properties (e.g., particle size distribution, soil structure, moisture content, mineralogy, organic matter content, pH), the nature of the added P [11, 12], and factors like temperature and redox conditions. The presence of several phosphate ion species adds to the complexity of the situation, and their behaviour is also influenced by involvement in a series of chemical equilibria (Figure 2), which are closely linked to the solution pH [13]. Soil solution P is usually a small proportion of the total P content (~0.01%); much more P exists in the soil solids [6].
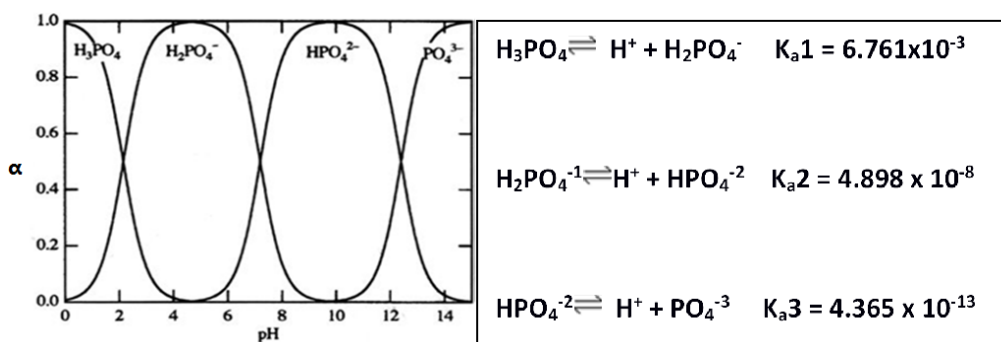

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \quad K_a1 = 6.761 \times 10^{-3}$$

$$H_2PO_4^{-1} \rightleftharpoons H^+ + HPO_4^{-2} \quad K_a2 = 4.898 \times 10^{-8}$$

$$HPO_4^{-2} \rightleftharpoons H^+ + PO_4^{-3} \quad K_a3 = 4.365 \times 10^{-13}$$

Figure 2 (left) pH dependent speciation of orthophosphate in solution; the Y axis indicates relative activity [14], (right) phosphate equilibrium constants at STP [5]. The phosphate equilibrium system also acts as a buffer of pH, shifting the degree of protonation to resist changes in acidity through consuming or releasing protons following Le Chatelier's Principle [15]. In natural water bodies, the aqueous concentration of phosphate (5--100 $\mu g.L^{-1}$ total P) [15] is generally too low for this buffering capacity to be significant. However, the initial P concentrations used in the net H^+:P co-adsorption study were approximately 1000 times greater. The impact of this buffering is highly relevant to the pH measurements undertaken.

Although P-soil interactions have been studied for over 100 years, we still do not have a sufficient understanding of all the processes occurring to accurately determine the quantity of fertiliser to be used in a given field (soil) for a selected plant and yield. Understanding of the P-soil interactions is also important to avoid adding too much P, since some of the surplus P will remain mobile in the soil and may be moved into adjacent surface waters leading to eutrophication of these waters through processes including algal blooms [16-18]. Eutrophication is a widespread global challenge; the annual economic losses from algal blooms in Australia are believed to be between AUD$180--240 million (US$125--175 million), with occurrences in coastal environments [19], agriculturally significant rivers such as the Murray-Darling [20], and world heritage habitats such as the Great Barrier Reef [21].

The bioavailable nutrient concentration of a soil is one of the crucial factors governing its agricultural productivity. In their natural state, Australian soils are heavily weathered due to their age and climate, and are comparatively deficient in nutrients when compared to younger soils of other continents [22]. Australian soil fertility has been greatly improved through the implementation of an extensive annual fertiliser regimes with as much as 5 million tonnes of fertiliser being applied on 50 million hectares of agricultural land in Australia in 2016-17 [23]. The annual additions of P to agricultural soils in Australia have increased dramatically since the 1950s, and are now in a relatively steady state varying only with seasonal fluctuations [24]. For most agricultural soils, P added through fertilisers exceeded the annual removal of P, creating a positive net balance of P and accumulating P in the soil [25].

While many factors influence the amount of P lost from the soil-plant system, and thus, the efficiency of applied fertiliser, the P adsorption capacity of the soil is one of the most important [26]. This property describes the ability of a soil to remove soluble P from the soil solution and retain it in a bound condition on the surfaces of soil components. Many P adsorption studies have tended towards understanding how sorption capacities vary with changing soil properties (e.g., mineralogical composition [9, 27], the effect of organic matter [28]), and using isotherm equations to create models which accurately quantify the process [17, 29].

Many studies have identified a variety of physico-chemical factors affecting the adsorption of phosphate; these include soil moisture content [30], soil mineralogy, especially oxyhydroxide (Al and Fe) content [31], pH [13], soil organic matter content [28, 32], and anion competition [33].

Soil particles are charged, because of ionic substitutions within the (mainly aluminosilicate) minerals forming part of the soil solids (these are usually permanent charges) and variable charges occurring as a result of interactions between surfaces of soil mineral matter and the ions in the soil solution. Positive and negative overall charges are found, with the majority being overall negative charges [14]. As PO_4^{3-} groups adsorb onto soil particle surfaces, the surfaces will tend to become more negative (Figure 3) unless co-adsorption of positive ions occurs.
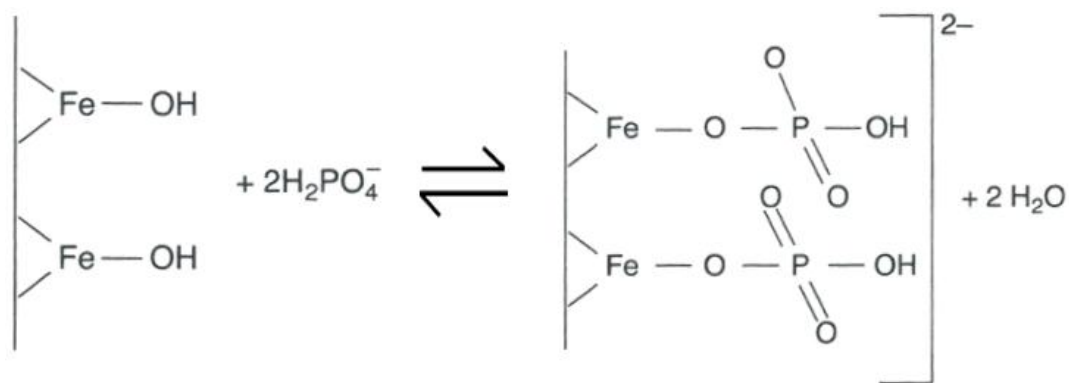
Figure 3 Sorption equilibrium of phosphate onto iron oxyhydroxide surfaces.

Prior to the present study, proton (H^+) co-adsorption (co-sorption) with P in soils has not been investigated, although Rahnemaie et al. [34] observed that a pH decrease occurred that corresponded with the quantity of added P for goethite at pH 3.98. The net H^+:P co-adsorption ratio for $H_2PO_4^-$ was ~1.6:1, i.e., less than the stoichiometric ratio for the $H_2PO_4^-$ ion itself of 2:1, excess H^+ being left in solution causing a pH decrease. If similar behaviour occurred in field soils, this would lead to the addition of P fertilisers causing a decrease in soil pH. It is not accurately known whether inorganic P additions to soils using certain types of fertilisers changed the pH of soil over time, although Schumann [35] reported that from limited field trials, non-nitrogenous P fertilisers, such as superphosphate, appeared to produce no measureable effect on soil pH.

Both the chemical complexity and biological activity in soils present challenges in producing experimentally valid data for H^+:P co-adsorption. Therefore, a significant portion of this study was dedicated to the development of a credible methodology using samples of three soils. The methods were then applied to soil samples from six sites under pasture, two of which had undergone varying degrees of P fertiliser treatment. We also explored other factors potentially impacting estimates of net H^+:P co-adsorption.

2. Materials and Methods

2.1 Samples

The sample of goethite was prepared in-house for general laboratory investigations [36]. It was not synthesised under CO_2-free conditions. Samples of nine topsoils were used: three (EMAI, TG1, ULL2) in method development and six for the H^+:P co-adsorption studies (KA, FL, MO, MA, D, RO) (Table 1). The six sites were located in New South Wales and South Australia, and bulk topsoil samples (0–15 cm) had been taken prior to this study and amended with varied amounts of triple superphosphate ($Ca(H_2PO_4)_2$) equivalent to 0–2158 mg P kg^{-1} [37]. We subsequently sampled a subset of the soil × $Ca(H_2PO_4)_2$ combinations, cleaned them of macroscopic organic materials, and ground and sieved them to < 1 mm for storage. We further subsampled, ground and sieved them to < 250 μm. The properties are presented in Table 1, and other properties are described in [37] and [38].

Table 1 Locations, Australian classification and key properties of soil samples used in this study.

Location	Sample ID	Depth (cm)	Classification[+]	OC %	Sand (%)	Silt (%)	Clay (%)	pHCa[#]	Olsen P mg kg^{-1}	Al$_{ox}$ mg kg^{-1}	Fe$_{ox}$ mg kg^{-1}	Role
Camden	KA	0-10	Brown Chromosol	2.98	53	17	31	5.4	7.8	2244	3196	H$^+$:P
Flaxley	FL	0-10	Brown Chromosol	3.50	52	19	29	5.5	11.2	3730	2999	H$^+$:P
Glenmore	MO	0-10	Red Chromosol	3.42	23	34	43	4.7	11.4	2900	5100	H$^+$:P
	MO6			3.39				4.9	13.6	5711	5904	H$^+$:P
Bowral	MA	0-10	Brown Kurosol	4.78	27	30	43	4.3	4.8	7460	4293	H$^+$:P
Richmond	D	0-10	Red Kandosol	1.24	85	5	10	4.5	5.2	1767	917	H$^+$:P
Robertson	RO	0-10	Red Ferrosol	6.11	27	19	54	4.4	4.4	11940	10363	H$^+$:P
Robertson	RO3	0-10	Red Ferrosol	6.13				4.3	5.6	12200	9824	H$^+$:P
	RO6	0-10		6.23				4.3	12.8	11710	10555	H$^+$:P
	RO10	0-10		6.10				4.4	34	12410	10704	H$^+$:P
Menangle	EMAI	0-25	Haplic Eutrophic Brown Chromosol	3.35	28	36	36	4.7	68	3517	4310	M.D.
Ulladulla	TGI	0-15	Grey Kurusol	1.67	74	21	5	4.1		<100	717	M.D.
Ulladulla	ULL2	0-15	Brown Dermasol	5.74	29	18	53	4.8		4012	4500	M.D.

Note: Adapted from Dougherty et al. [37] and Choruk and Morrison [38]

The alpha characters identify the soils, and the numeric co-identifiers indicate different Ca(H$_2$PO$_4$)$_2$ additions,

i.e., MO6 received 71 mg P kg^{-1}, and RO3, RO6and RO10 respectively received 79, 306 and 1038 mg P kg^{-1}

[+] classification using Isbell [39].; # pH measured in CaCl$_2$ (0.01M); M.D. = method development; H$^+$:P = co-adsorption study

2.2 Methods

Soil pH protocols vary, but ratios of 1:5 or 1:10 are common [40], and we measured the pH of soil suspensions (5 g : 25 mL) shaken with 10 mM $CaCl_2$ solution for 1 h. All pH measurements were made to at least 2 decimal places (Dual Star, Orion Pacific Pty Ltd, Australia). The Ag/AgCl/Cl reference electrode was refillable with ~4 M KCl and fitted with a ring junction (Orion 91578N, Thermo Scientific). Water was ultrapure (MilliQ HX7000, Merck Millipore) and the pH was close to 7. Equipment was soaked in 10% HCl and rinsed until acid-free using pure water before use. Suspension temperatures were maintained at 20.8-21.3^{o}C during pH measurements and batch H^+:P co-adsorption studies. Key soil parameters for Al and Fe relating to P adsorption are the quantities extracted by acid oxalate solution [17]. The oxalate extractions were performed in the dark, and the co-extracted Al and Fe were measured by inductively coupled plasma emission spectroscopy [40].

We used measures of acid:base stoichiometry and of P adsorption to estimate net H^+:P co-adsorption ratios for suspensions of goethite, because this material has been studied previously though under strictly CO_2-free conditions [34]—and of soils, for which no data appear to exist.

Supernatants from some co-adsorption studies were analysed for potentially competitive species, e.g., dissolved organic carbon (DOC), and sulfur (S), assuming that the S was predominantly present as sulfate. In addition, the cations NH_3, Ca, Na and Mg were measured to evaluate the degree to which cation exchange may be buffering H^+ release. The results were inconclusive and are not presented here, although they are described in detail elsewhere [41].

2.2.1 Acid/Base Stoichiometry

Microbial activity is a major threat [42] to pH stability of soil suspensions, and the effect of the potent antimicrobial, $HgCl_2$, was investigated. Subsamples (4 g) of ULL2 were shaken with 20 mL of 0.01 M KCl background electrolyte with varying additions of $HgCl_2$ for 16 h. When the $HgCl_2$ concentration reached 6.6 mM, the suspension pH before and after 16 h of shaking was within measurement uncertainty, i.e., 4.84 ± 0.01. We consequently used 6.6 mM $HgCl_2$ as part of the background electrolyte throughout the remainder of the study. This concentration of $HgCl_2$ stabilised the pH of suspensions of goethite and soil during shaking for 16 h, whether or not P was added (data not presented).

Acid/base stoichiometry was examined for the background electrolyte and for goethite and soils suspended in it. For goethite, 1 g aliquots were suspended in 19 mL of 10 mM KCl containing 6.6 mM $HgCl_2$ and the pH measured. Then 1 mL of 0.0375 M HCl was added, the suspensions shaken for 16 h, and pH was back titrated to the original value using 0.04 M NaOH. There were four replicates. We also suspended varying masses (0.5–2 g) of ULL2 soil in 19 mL of the same electrolyte and followed the acid:base neutralisation procedure described for goethite. There were eight replicates. Five replicate electrolyte solutions were also taken through the same procedure.

Assessment of acid/base stoichiometry might also be affected by imbalance of the CO_2/H_2CO_3/HCO_3^- buffer system. To achieve CO_2-free conditions, for suspensions of goethite or soil, this requires lowering the suspension pH to (say) 5 to convert bicarbonate to H_2CO_3 and exhaustive purging, for which CO_2-free N_2 was used [34]. This procedure is acceptable for synthetic substrates such as goethite, but may affect the properties of the less well-characterised

P sorbents in soils; consequently, the acid/base stoichiometry and net H^+:P co-adsorption ratio were tested without stripping the HCO_3^-/CO_2, i.e., at the current ambient atmospheric CO_2 concentration of ~400 μL L^{-1} [43].

We also used initial and final pH measurements, and a measure of pH buffering for the particular adsorbent, to calculate the H^+ release resulting from P adsorption, but this proved unreliable and no data are presented.

2.2.2 H^+:P Co-Adsorption Protocol

Optimising the estimate of the H^+:P molar sorption ratio requires accurate values of both terms in the ratio. For KH_2PO_4 additions and net H^+:P co-adsorption ratios of ~2, this is a conflicted situation. The concentration of adsorbed P is more accurately measured when most of the added P is sorbed; however, this limits the accuracy of back-titration of a potentially small excess of H^+. A compromise between these two conflicting demands was found by trial and error [41]. Unsurprisingly then, we added larger amounts of P than would be applied as fertilisers in the field. In addition, the amount of KH_2PO_4 added was varied both for the one soil depending on the P-fertiliser pre-treatment, and also between soils. In this regard, the RO soil (Red Ferrosol) contained the greatest concentrations of Al_{ox} and Fe_{ox}, and was the strongest P- sorbing of the soils.

To provide information on the effect of the P added species on the measured net H^+: P co-adsorption ratio, we also tested additions of H_3PO_4. The high P adsorption capacity of goethite [17] eased the preceding conflict. Data for net H^+ release and sorbed P are presented where the experimental uncertainty was deemed acceptable.

For goethite, 1 g aliquots were suspended in 20 mL of 10 mM KCl containing 6.6 mM $HgCl_2$ in 25 mL polypropylene, screw capped centrifuge tubes, and the pH measured. Aliquots of 1 M KH_2PO_4 were added, the tubes were closed and the suspensions shaken end-over-end at 5 revolutions min^{-1} for 17 h. The final pH was measured and the suspensions back-titrated to the initial pH using carefully standardised 0.04 M NaOH solution. The suspensions were centrifuged at 7000 revolutions min^{-1} (rcf 5800 x g) and an aliquot of the supernatant was put through a 0.45 μm filter before P measurement (see below). There were five replicates.

For soils, 0.5--2.0 g of soil were suspended in 20 mL of 10 mM KCl solution containing 6.6 mM $HgCl_2$ in 25 mL capacity polypropylene centrifuge tubes, and conditioned by shaking the suspension end-over-end at 5 revolutions min^{-1} for 1 h. The pH was measured then aliquots of 1 M KH_2PO_4 in 10 mM KCl were added to different tubes and the suspensions were shaken for a further 16 h, and the final pH was measured. The suspensions were restored to their initial pH by titration using 0.04 M NaOH and centrifuged as described for goethite to provide clear supernatants for P analysis (see below). The number of replicates varied from 2–5.

To test whether the estimated net H^+:P co-adsorption ratio was impacted by the species of added phosphate, an additional H^+:P co-adsorption test was applied to the RO soil using the preceding protocol except that 7.3 M H_3PO_4 was substituted for KH_2PO_4.

Aqueous P concentrations were measured on the clear supernatants using a flow injection analyser (QuikChem 8500, Lachat Instruments, USA) employing a modified version of the Murphy and Riley [44] molybdenum blue method (molybdate reactive P) measuring absorbance at 880 nm. Calibration standards were prepared in the background electrolyte to minimise matrix effects. Any colloids present would have caused positive bias due to light scattering and soils may release

soluble organic phosphate species into solution [45] some of which may react with molybdate. The extent to which these effects may have occurred was not quantified.

2.3 Calculations

Sorbed P was estimated from the difference between the initial and final measured P concentrations, and the mass: volume ratio. The H^+_{sorbed} values measured by titration were adjusted for the separately measured acid:base stoichiometry for goethite and soils, to calculate the net H^+:P co-adsorption ratios. The pH changes and the estimated net H^+:P sorption ratios are reported.

3. Results and Discussion

3.1 Acid / Base Stoichiometry

The acid:base stoichiometry for 10 mM KCl containing 6.6 mM $HgCl_2$ was 1.02:1 (Figure 4), i.e., there is a ~2% overestimate of H^+. This stoichiometric difference may have been due to buffering by bicarbonate. Whatever the cause, the bias was consistent within a system, and we inferred that it would not be unreasonable to adjust measured H^+:P co-adsorption ratios on that basis. The corresponding values for goethite and the soil of 1.23:1 and 1.07:1 respectively (Figure 4), were reduced to 1.21:1 and 1.05:1 to adjust for the overestimation.
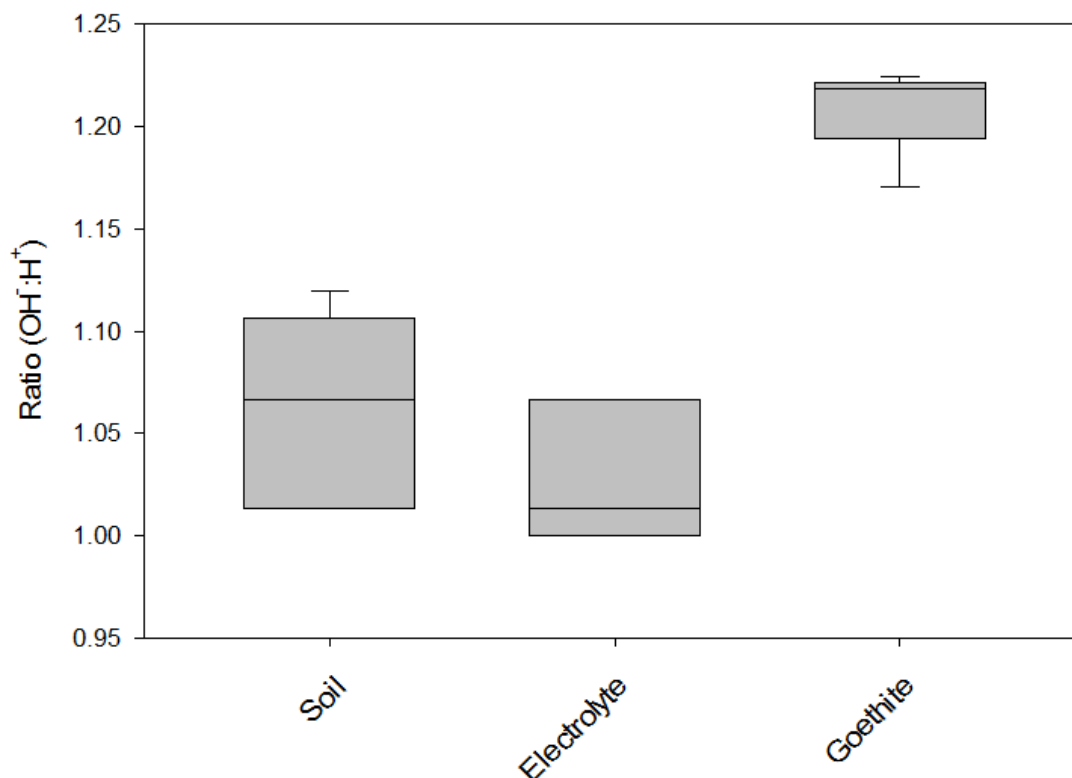

Figure 4 Acid-base stoichiometry of 10 mM KCl containing 6.6 mM $HgCl_2$, and of soil ULL2 and goethite suspensions in the same electrolyte. The boxes represent the 25th and 75th percentiles, the lines within the boxes, the median and the whiskers represent the 10th and 90th percentiles.

3.2 Net H^{+}:P Co-Adsorption Ratio for KH$_2$PO$_4$ and Goethite

The initial pH of the goethite suspensions in the background electrolyte was 3.91–3.94. After reaction with added P for 16 h, the net co-adsorbed quantities of H^{+} and P were linearly related (*P* < 0.001) with a slope of 1.74 (standard error ± 0.03, Figure 5). Adjustment for the net 1.21 acid: base stoichiometry for goethite suspensions (Section 3.1) gives a value of 1.44:1 for the adjusted H^{+}:P co-adsorption ratio, which is in reasonable agreement with the value of 1.6:1 obtained in a CO$_2$-free environment at pH 3.98 [34]. The relatively small disparity between the studies indicates that our H^{+}:P co-adsorption protocol may also produce useful estimates of the net H^{+}:P co-adsorption ratio for soils.
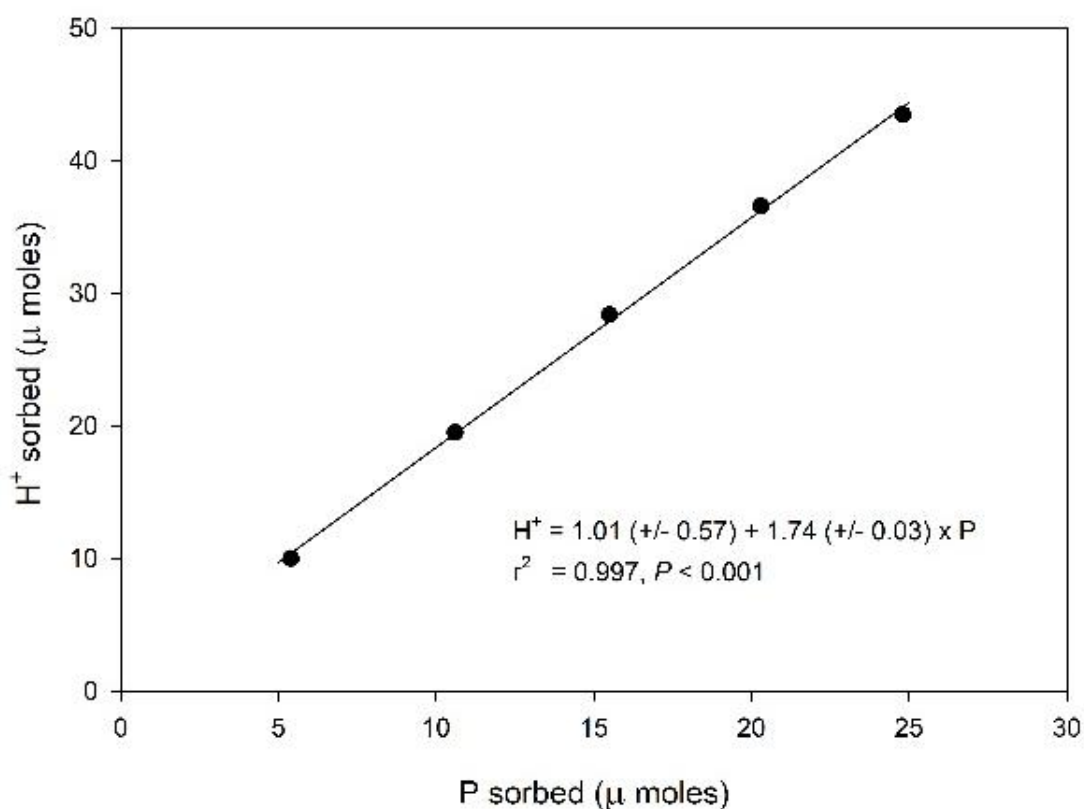

$$H^+ = 1.01\ (+/-\ 0.57) + 1.74\ (+/-\ 0.03) \times P$$
$$r^2 = 0.997,\ P < 0.001$$

Figure 5 Molar sorption of H^{+} and P (µ moles) by goethite for additions of KH$_2$PO$_4$.

3.2.1 Net H^{+}:P Co-Adsorption Ratios for KH$_2$PO$_4$ and Soils

The measured H^{+}:P co-adsorption ratio for soils was 2.02 (± 0.02):1 for the 26 soil × P fertiliser combinations tested (Figure 6). The relation was linear and very strong (r^2 = 0.997, *P* = 0.001). Adjustment of the slope for the measured acid: base stoichiometry of 1.05:1 (Figure 4) gave a H^{+}:P co-adsorption ratio of 1.92:1. That is, where sufficient acid was released to provide confidence in the accuracy of the titration using 0.04 M NaOH, the H^{+}:P co-adsorption ratio appears independent of the soil × P fertiliser combinations. The value of 1.92:1 for soils is well in excess of the similarly adjusted ratio of 1.44:1 for goethite (Section 3.2).
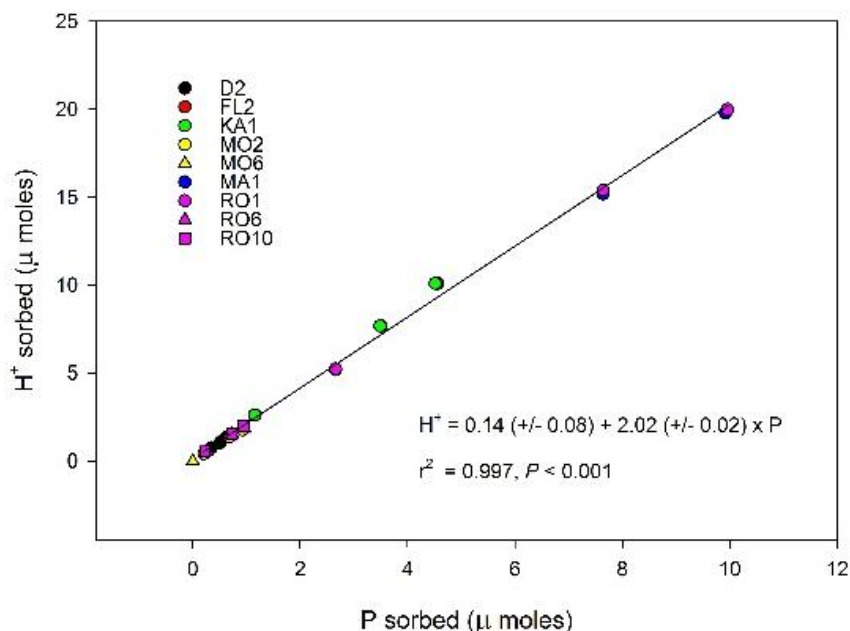
Figure 6 Sorption of H$^+$ and P by 26 soil × P fertiliser combinations for additions of KH$_2$PO$_4$.

3.2.2 Net H$^+$:P Co-Adsorption Ratio for H$_3$PO$_4$ and the RO Soil

An operational benefit in substituting H$_3$PO$_4$ for KH$_2$PO$_4$ is that for a H$^+$:P co-adsorption ratio near 2:1, there was a more substantial balance of H$^+$, and a correspondingly larger and more accurate back titration using 0.04 M NaOH. When applied to the RO soil, the measured net H$^+$:P co-adsorption ratio was 2.06 (±0.09):1 (Figure 7). Adjustment for acid:base stoichiometry of 1.05, (Section 3.2) gives a ratio of 1.96:1. We consequently infer that, within experimental limits, addition of P as either H$_2$PO$_4$ or H$_3$PO$_4$ did not affect the net H$^+$:P co-adsorption ratio. Therefore, the use of H$_3$PO$_4$ might provide a means to improve the typical measurement accuracy of the H$^+$ balance and thereby increase the accuracy of H$^+$:P co-adsorption ratios for acidic soils.
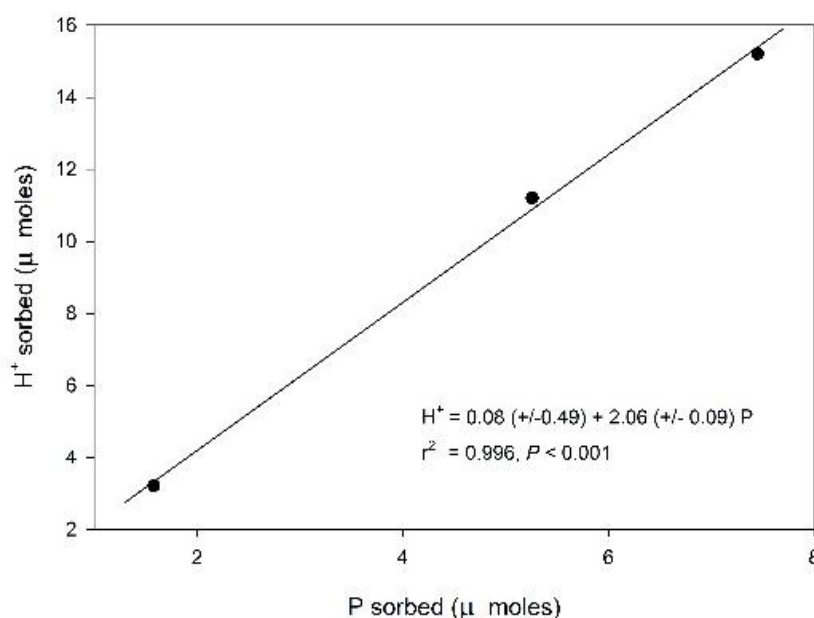

Figure 7 Sorption of H$^+$ and P by soil RO for additions of H$_3$PO$_4$.

4. General Discussion and Recommendations

The protocol we developed gives a credible (adjusted) net H^+:P co-adsorption ratio of 1.44:1 for goethite; the published value is 1.6:1 [34]. By analogy, we argue that the ratio of 1.92–1.96:1 we obtained for acidic soils is also likely to be credible. This ratio appears independent of the diverse soil × P-fertiliser combinations of our samples (Table 1) and of the form of added P (KH_2PO_4 or H_3PO_4). That is, the results indicate that similar P-ligand soil surface complexes were formed under a wide variety of conditions.

Soil system chemistry is extremely complex, and soils contain a selection of P-sorbents, including a variety of clay minerals as well as organic materials [46]. Goethite is only one of the many P-sorbents in soils, e.g. Al substituted goethites occur [47] and are strong P sorbents [48]. In acidic soils, dissolution of Al (mostly as $Al(OH)_2^+$ and $Al(OH)^{2+}$) can occur and sorb or precipitate P sufficiently to influence its rapid adsorption by soils [49]. Consequently, it is unsurprising that the (adjusted) net H^+:P co-adsorption ratio for soils differs from that for goethite.

The developed protocol is a credible first step towards quantitatively estimating net H^+:P co-adsorption ratios for acidic soils; nonetheless it may benefit from refinements. For example, substitution of H_3PO_4 for KH_2PO_4 increased the size of the back-titration, and therefore presumably its accuracy and, consequently, the accuracy of the estimated net H^+:P co-adsorption ratios. $HgCl_2$ is an effective microbial suppressant, but a less toxic antimicrobial would be desirable. It is possible that less potent antimicrobials may suffice in combination with pasteurisation of the soil suspensions [42, 50]. Other factors worthy of investigation include: 1) eliminating HCO_3^- and CO_2 from the system, which may interact with suspension pH to affect acid:base stoichiometry; 2) the effect of added K^+ (as KH_2PO_4)—though the apparent indifference of the measured net H^+:P co-adsorption ratios to additions of KH_2PO_4 and H_3PO_4—argues that any such effect may be relatively small; 3) our samples contained small amounts of organic fragments whose impact on soil pH [51] was unknown [52]; 4) measuring anions competitively desorbed by the P additions, e.g., sulfate [53-55]; and, 5) H_3PO_4 additions may allow ΔpH values to conveniently access net H^+ balance in soil suspensions.

Soil acidity is a critical issue pertaining to agriculture within an Australian context [24] and also more widely [56, 57]. However, in applying the knowledge gained from this study, several limitations need consideration. Firstly, key differences include the fine grinding required for replication in the laboratory [58], which not only destroys the natural soil structure exposing a greater surface area, but also disperses residual plant fragments. Secondly, sufficiently accurate acid/base measurement necessitated greater additions of P than used to fertilise soils, and the chemical forms of P added in the laboratory are unlike those typically used as fertilisers [23]; nonetheless, any P solubilised from these materials is likely to be as orthophosphate [59]. That said, prior amendment of the RO soil with large additions of $Ca(H_2PO_4)$, or triple superphosphate, had little if any effect on pH (Table 1). Lastly, soil atmospheres can have instantaneous changes in % concentrations of CO_2.

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Author Contributions

Paul Taglieri contributed to project design, carried out most of the experimental work and made a significant contribution to writing the first draft of this paper.

Paul Milham played a major role in the concept development, project design, and data interpretation, and contributed to the manuscript writing.

Paul Holford contributed to the data interpretation and the manuscript writing.

John Morrison contributed to the project design and laboratory work planning and coordinated the preparation and writing of the manuscript.

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Competing Interests

The authors have declared that no competing interests exist.

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