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Supporting Information (SI)

Molecular level picture of the interplay between pH and phosphate binding at the goethite–water interface

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Modeling goethite with unsaturated active sites

In the following we introduce the idea behind our modeling approach and why we modeled the goethite with unsaturated active sites (bare surfaces):

1. In general, the main objective in the present study is to unravel the interplay between pH and phosphate binding at the goethite–water interface and how this is affected by the surface morphology and degree of saturation. So, it would be better to involve here bare surfaces with different surface saturation centers (Fe surface atoms were surrounded by 4 and 5 O^{2-}/OH^{-} groups) and different morphologies.

2. The reported goethite PZC values in literature data vary from 6.4 to 9.7 but mostly they are around pH 9 (see Table 3 in the main manuscript). This means that below pH 9 (or for some cases below pH 6.4) the surrounding water molecules will dissociate and donate more protons than hydroxyl groups to the goethite surface leading to a positively charged surface. This explains that the goethite surface at pH below pH 9 (or for some case pH 6.4) will be partially unsaturated and have the ability to attract/adsorb anions such as phosphate and/or hydroxyl groups at its surface. Considering the fact that most soils are acidic,[1,2] gives the motivation to model the goethite surface as a partially unsaturated one.

3. It is well-known from sorption experiments that the phosphate adsorption decreases with increasing the soil solution pH.[3–5] This means that in the presence of OH^{-} at high pH, OH^{-} groups can replace the adsorbed phosphate indicating a stronger adsorption for OH^{-} than for phosphate at mineral surfaces. This behavior has been observed and explained in more details at a molecular level by our group[6,7] and in the current contribution as well. The results indicated that phosphate can replace water molecules from the goethite surface, but phosphate could be replaced by OH^{-} groups. This shows that the reverse reaction, i.e. replacement of OH^{-} groups by phosphate, is mainly a non-spontaneous reaction and unlikely to take place. This indicates that formation of inner-sphere complexes of phosphate with goethite surfaces could happen mainly due to direct reaction of phosphate with the surface unsaturated centers and not with a ligand-exchange mechanism. Consequently, this points to the necessity of the presence of some unsaturated centers at the mineral surface to form inner-sphere complexes with phosphates. So, this means that one should model goethite surfaces with some unsaturation centers.

All these points motivated us to model the goethite surfaces with unsaturated centers (at different degree of saturations). This holds true unless one is studying a high pH range which, for this reason, we studied high pH by adding KOH molecules to simulate the existing hydroxyl groups at high pH.

Interaction Energy Calculations

In the following we comment on the calculation of interaction energies according to Eq. 1 of the main text. At the optimized geometry the total system can be decomposed into three sub-systems (fragments), i.e. phosphate (fragment1), goethite (fragment2), and water (fragment3). For each pair of fragments the interaction energy has been calculated within the BSSE counterpoise correction philosophy. That is, the interaction energy is calculated by performing five energy calculations using the same simulation box dimensions as follows: 1- total electronic energy of phosphate including only the phosphate basis functions ($E_{\mathrm{phosphate}}^{\mathrm{phosphate}}$), 2- goethite including only the goethite basis functions ($E_{goethite}^{goethite}$), 3- phosphate including the basis functions of phosphate and goethite ($E_{\mathrm{phosphate}}^{\mathrm{phosphate}+goethite}$), 4- goethite including the basis functions of phosphate and goethite ($E_{goethite}^{\mathrm{phosphate}+goethite}$), and 5- phosphate–goethite complex including the basis functions of phosphate and goethite ($E_{\mathrm{phosphate}-goethite\ complex}^{\mathrm{phosphate}+goethite}$). Eventually, the interaction energy between phosphate and goethite was calculated as $E_{int} = E_{\mathrm{phosphate}-goethite\ complex}^{\mathrm{phosphate}+goethite} - (E_{\mathrm{phosphate}}^{\mathrm{phosphate}+goethite} + E_{goethite}^{\mathrm{phosphate}+goethite})$, which corresponds to Eq. 1 in the main text where a simplified notation has been used. Similarly, the interaction energies between phosphate and water as well as between goethite and water have been calculated for each water–phosphate–goethite complex.

Adsorption Energy Calculations

In an alternative approach for calculating the adsorption energy (E_{ads}) of phosphate at the goethite surface, an explicit consideration for the surrounding water molecules has been introduced. For each phosphate–goethite model, a corresponding model involving phosphate as dissolved aqueous species (not bound to the goethite surface) has been created. Each model system has been optimized at the same level as for the inner-sphere phosphate–goethite complexes as described in the main text (see section 2.2). The adsorption energy (E_{ads}) has been calculated here as follows:

$$E_{ads} = E_{\mathrm{inner-sphere\ complex}} - E_{\mathrm{aqueous}} \qquad \text{(S1)}$$

where, $E_{\mathrm{inner\text{-}sphere\ complex}}$ and E_{aqueous} are the total electronic energies of the inner-sphere phosphate–goethite complexes and the corresponding cases in which phosphate is dissolved aqueous species involving surrounding water molecules. During the geometry optimization process, some structural changes for the water molecules are taking place which are not directly related to the phosphate adsorption process at the goethite surface. To avoid spurious effects due to such changes, the energy of the water molecules is omitted from the total energy, thus giving the corrected adsorption energy (E^c_{ads}) as follows:

$$E^c_{ads} = (E_{\text{inner-sphere complex}} - E_{\text{water/inner}}) - (E_{\text{aqueous}} - E_{\text{water/aqueous}}) \quad \text{(S2)}$$

where, $E_{\text{water/inner}}$ and $E_{\text{water/aqueous}}$ are the total electronic energies of the surrounding water molecules to the inner-sphere phosphate–goethite complexes and the corresponding cases in which phosphate is dissolved in water. It should be noted that the calculated adsorption energy values in Eqs. S1–S2 do not refer only to the phosphate adsorption energy on goethite, but they involve all other reactions/changes between structures of the inner-sphere complexes and the corresponding cases in which phosphate is dissolved in water. These values correspond to different processes such as water adsorption, water dissociation in solution and at the surface, proton transfer from and to phosphate, water, and goethite, formation of hydrogen bonds (HBs), and formation of water clusters such as dimers, trimers, and so on. Therefore, these calculated values are rather large and they depend on number of water molecules involved in the system. To eliminate this arbitrariness, the adsorption energies are given in Tables S1–2 per one water molecule i.e. they are calculated according to the above equations and then divided by number of water molecules involved for each phosphate–goethite complex.

It should be noted that there is no significant change between the calculated adsorption energies in Eqs. S1–S2 (see Tables S1–S2) for the different phosphate–goethite binding motifs. So, one couldn’t draw a conclusion on the phosphate–goethite binding mechanism and thus its pH-dependence using these values. This is because these values are related to all the reactions/changes taking place upon the structural change between the whole inner-sphere phosphate–goethite optimized geometry and the corresponding dissolved phosphate one. Therefore, the calculated interaction energies in Eq. 1 in the main manuscript are more specific and better to interpret the phosphate–goethite binding and the pH-dependence as well.

Tables

Table S1. Relative energies between dissolved phosphate species in water at the goethite surface and inner-sphere phosphate–goethite complexes at both 010- and 100-goethite surface planes.

species	Relative energies per H_2O molecule [kcal mol^{-1}]			
	010–surface plane		100–surface plane	
	M	**B**	**M**	**B**
H_3PO_4	-30.6	-28.8	-30.6	-30.2
KH_2PO_4	-30.7	-28.8	-31.0	-30.5
K_2HPO_4	-30.3	-27.5	-31.5	-30.0
K_3PO_4	-31.3	-28.9	-32.7	-31.0
K_3PO_4 + 10 KOH	-30.3	-27.5	-31.5	-30.0
K_2HPO_4 + 10 KOH	-31.3	-28.9	-32.7	-31.0

Table S2. Corrected relative energies between dissolved phosphate species in water at the goethite surface and inner-sphere phosphate–goethite complexes at both 010- and 100-goethite surface planes.

species	Relative energies per H_2O molecule [kcal mol^{-1}]			
	010–surface plane		100–surface plane	
	M	**B**	**M**	**B**
H_3PO_4	-29.0	-36.7	-29.8	-31.6
KH_2PO_4	-29.8	-38.9	-30.7	-32.2
K_2HPO_4	-30.4	-38.1	-30.7	-30.8
K_3PO_4	-32.0	-38.2	-31.5	-33.4
K_3PO_4 + 10 KOH	-30.3	-27.5	-31.5	-30.0
K_2HPO_4 + 10 KOH	-31.3	-28.9	-32.7	-31.0

Table S3. Change of pH during the P adsorption.

Time [h]	pH 4	pH 6	pH 8	pH 10	pH 12
0	4.028	5.988	8.026	10.031	11.953
2	4.026	5.144	7.333	8.180	11.736
24	3.904	4.810	6.307	7.170	11.619
168	3.926	4.982	6.683	7.553	11.561

Table S4. Total carbon content (C_{Total}) in the solid goethite samples prior to the P adsorption process and after an adsorption reaction time of 168 h.

prior to adsorption		after 168 h reaction time	
pH	C_{Total} [µmol m^{-2}]	pH	C_{Total} [µmol m^{-2}]
4	3.30	4	2.75
6	3.72	6	2.57
8	2.88	8	2.72
10	3.46	10	3.32
12	7.73	12	3.98

Figures

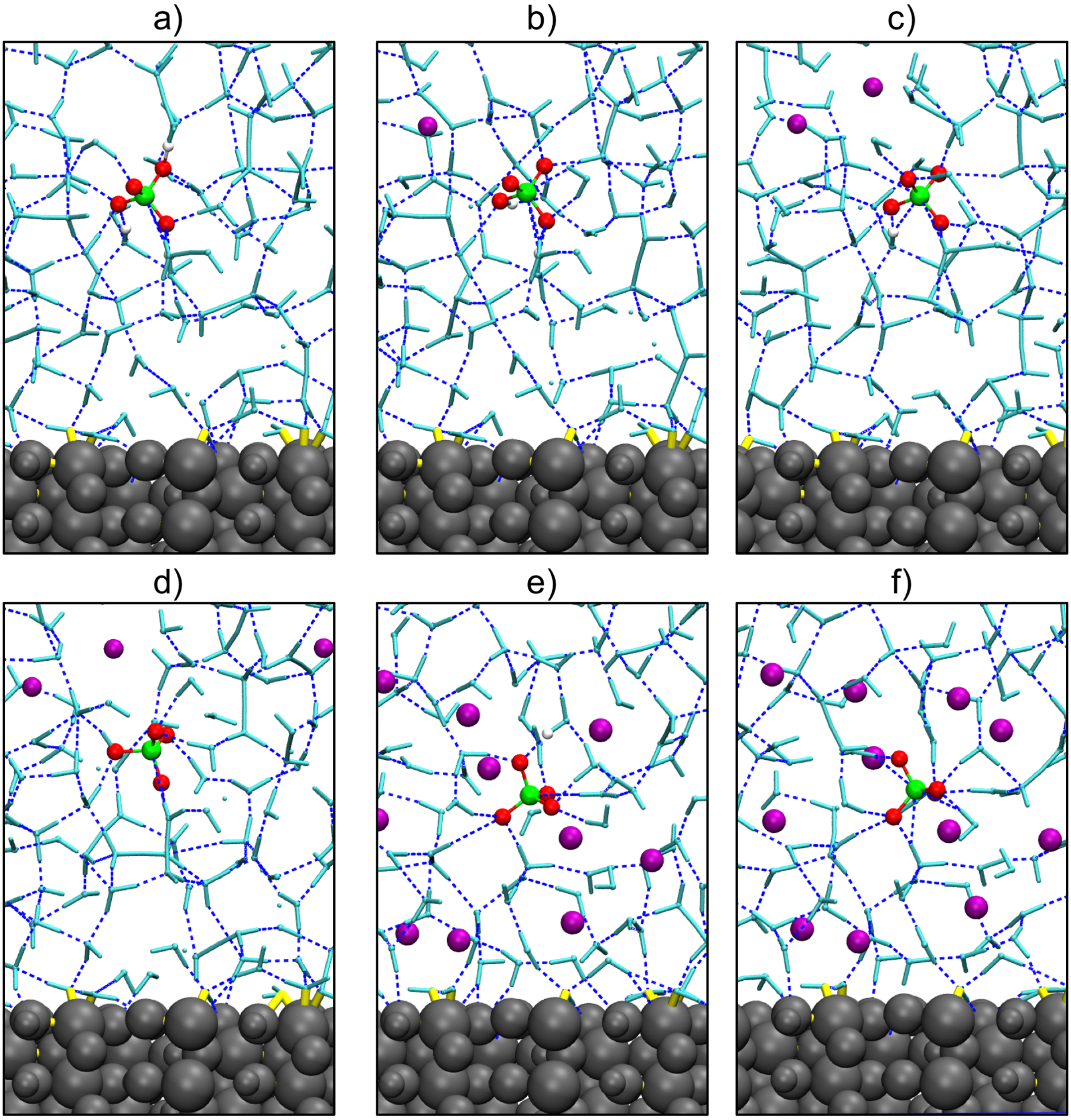

*Fig. S1. Geometry optimized structures of the dissolved phosphate species in water at the goethite surface for the H_3PO_4 species at the 010-goethite surface plane (a), KH_2PO_4 species (b), K_2HPO_4 species (c), K_3PO_4 species (d), K_2HPO_4 species in the presence of 10 KOH molecules (e), and K_3PO_4 species in the presence of 10 KOH molecules with two **M** motifs (f). Goethite, and water atoms are colored in gray and cyan, respectively. For phosphate, atoms are colored in green (P), red (O), white (H), and purple (K). Intramolecular and intermolecular covalent bonds including goethite atoms are colored in yellow and HBs are colored in blue.*

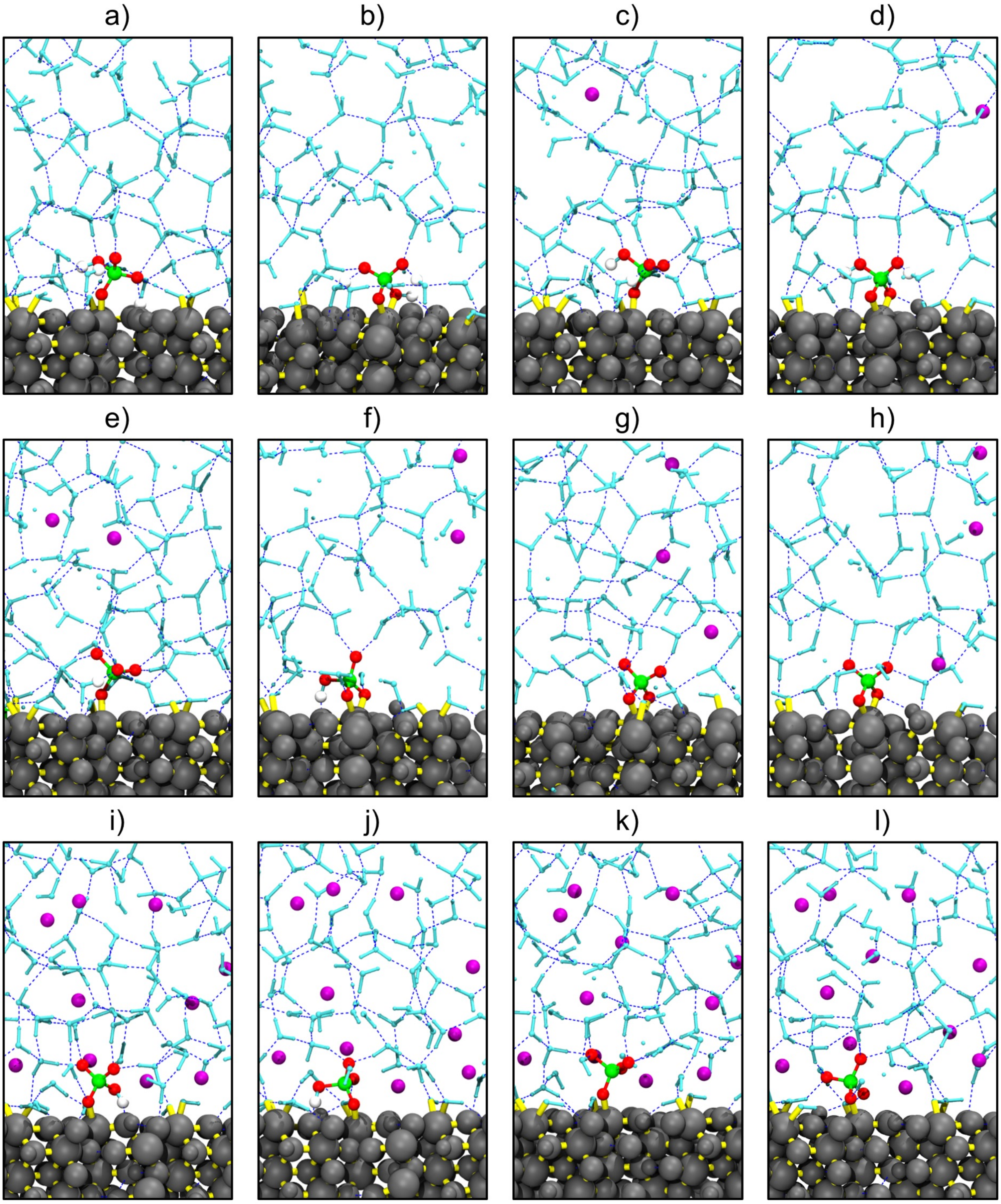

*Fig. S2. Geometry optimized structures of the inner-sphere phosphate–goethite–water complexes for the H_3PO_4 species at the 010-goethite surface plane (**M** motif (a), **B** (2O+1Fe) motif (b)), KH_2PO_4 species with **M** motif (c) and **B** (2O+1Fe) motif (d), K_2HPO_4 species with **M** motif (e) and **B** (2O+1Fe) motif (f), K_3PO_4 species with two **B** (2O+1Fe) motifs (g and h), K_2HPO_4 species in the presence of 10 KOH molecules with two **M** motifs (i and j), and K_3PO_4 species in the presence of 10 KOH molecules with two **M** motifs (k and l). Goethite, and water atoms are colored in gray and cyan, respectively. For phosphate, atoms are colored in green (P), red (O), white (H), and purple (K). Intramolecular and intermolecular covalent bonds including goethite atoms are colored in yellow and HBs are colored in blue.*

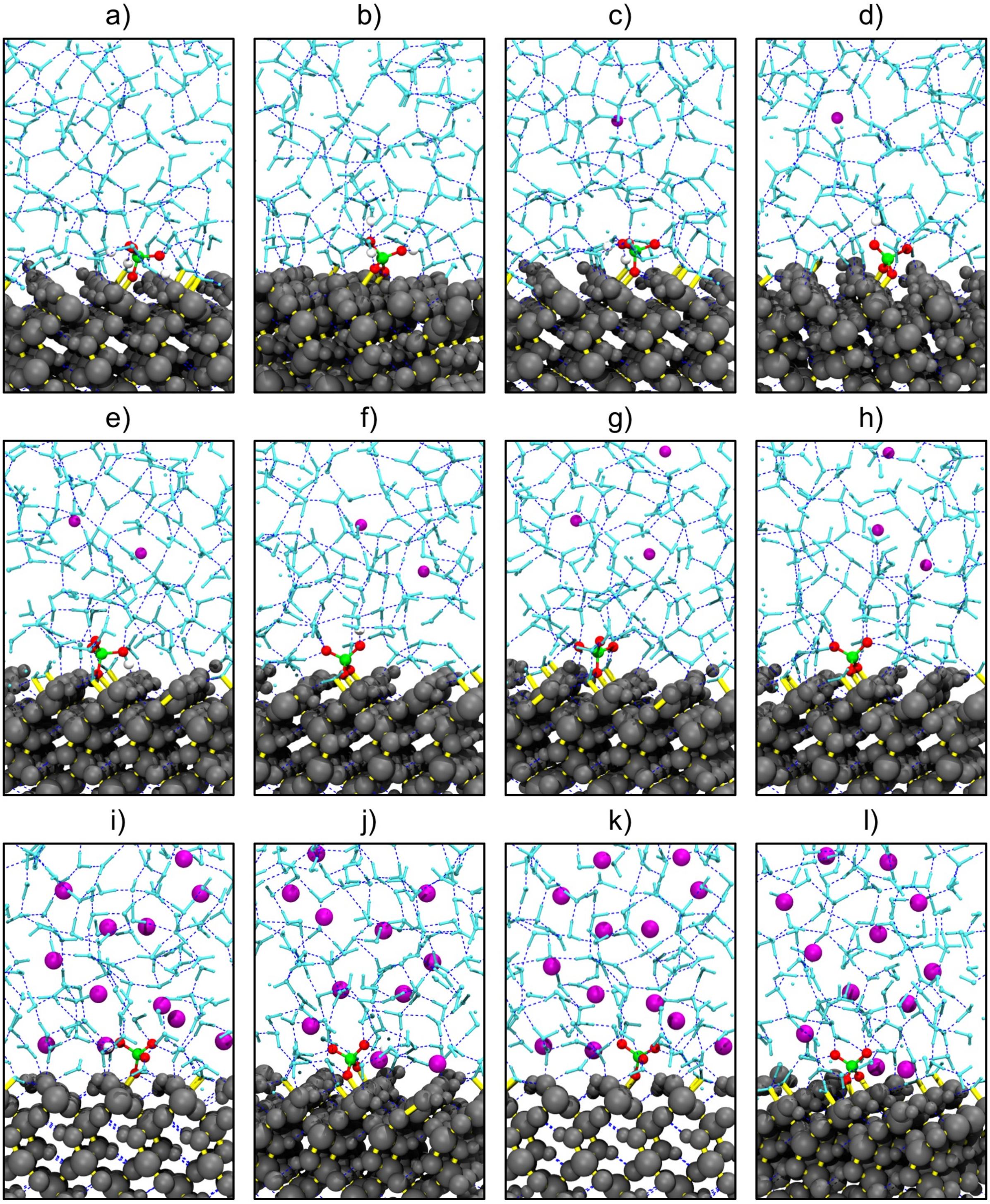

*Fig. S3. Geometry optimized structures of the inner-sphere phosphate–goethite–water complexes for the H_3PO_4 species at the 100-goethite surface plane (**M** motif (a), **B** (2O+2Fe) motif (b)), KH_2PO_4 species with **M** motif (c) and **B** (2O+2Fe) motif (d), K_2HPO_4 species with **M** motif (e) and **B** (2O+2Fe) motif (f), K_3PO_4 species with **M** motif (g) and **B** (2O+2Fe) motif (h), K_2HPO_4 species in the presence of 10 KOH molecules with **M** motif (i) and **B** (2O+2Fe) motif (j), and K_3PO_4 species in the presence of 10 KOH molecules with **M** motif (k) and **B** (2O+2Fe) motif (l). Goethite, and water atoms are colored in gray and cyan, respectively. For phosphate, atoms are colored in green (P), red (O), white (H), and purple (K). Intramolecular and intermolecular covalent bonds including goethite atoms are colored in yellow and HBs are colored in blue.*

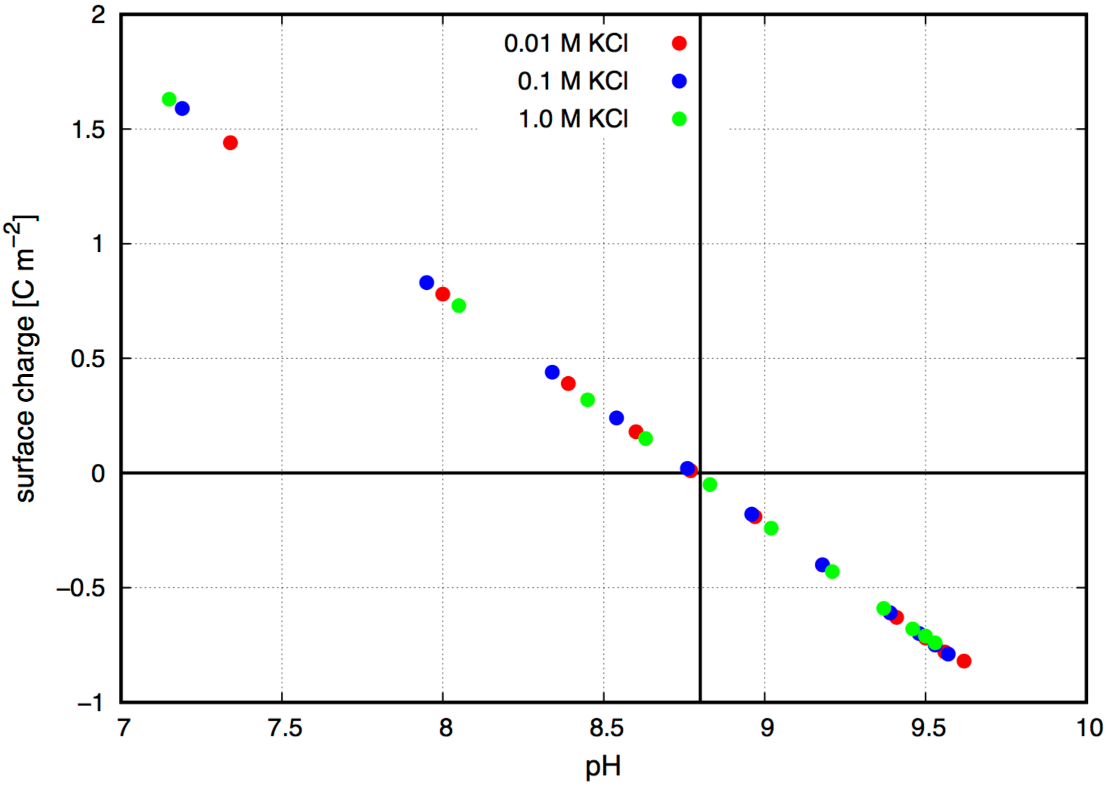

Fig. S4. Goethite surface charge in C m^{-2} versus the solution pH at different ionic strengths of the KCl background electrolyte. Here the data refer to a point of zero charge (PZC) for goethite at 8.8.

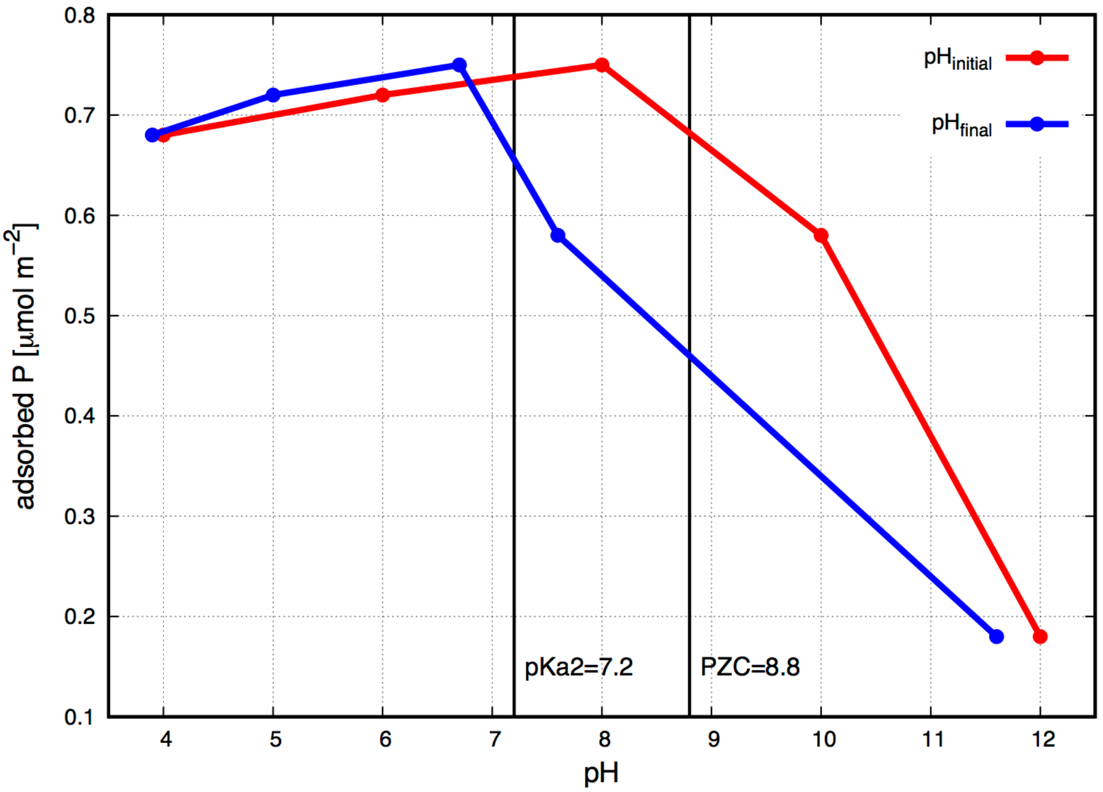

Fig. S5. Effect of pH on the phosphate (P) adsorption for the present study (considering the initial pH in red and the final pH in blue.

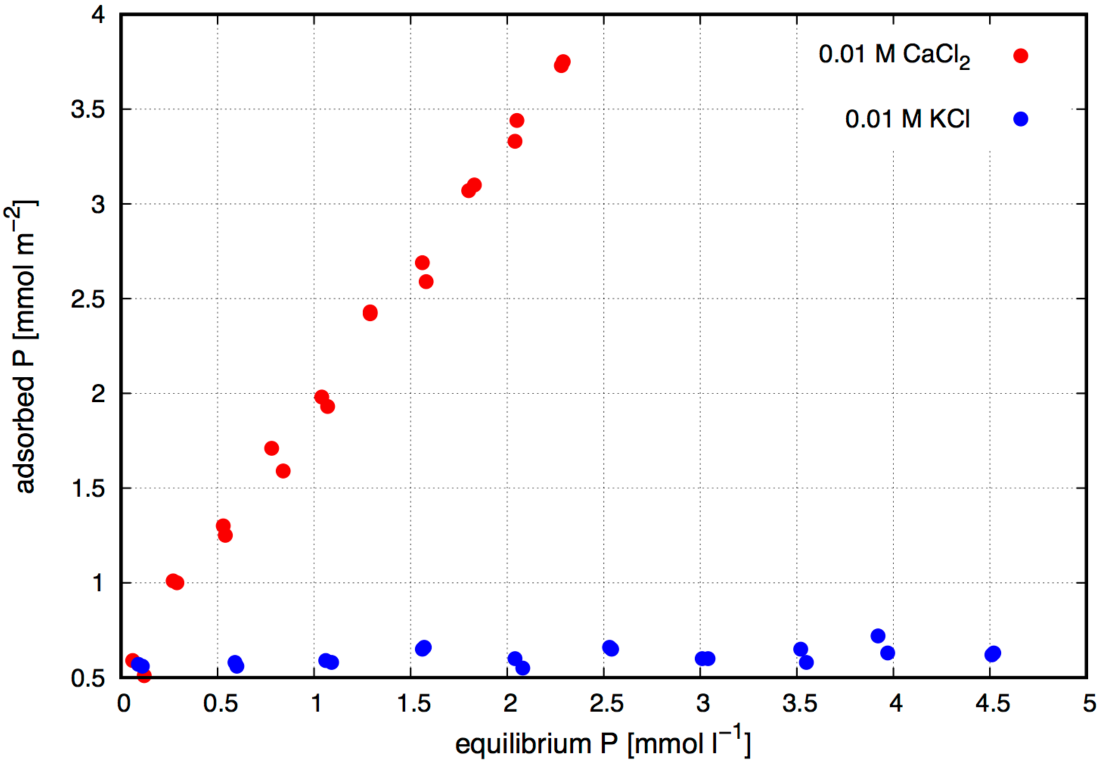

Fig. 6. Effect of background electrolyte solution on the P adsorption at goethite surfaces. Here, two background electrolyte solutions (0.01 M $CaCl_2$ and 0.01 M KCl) were used at pH 6.

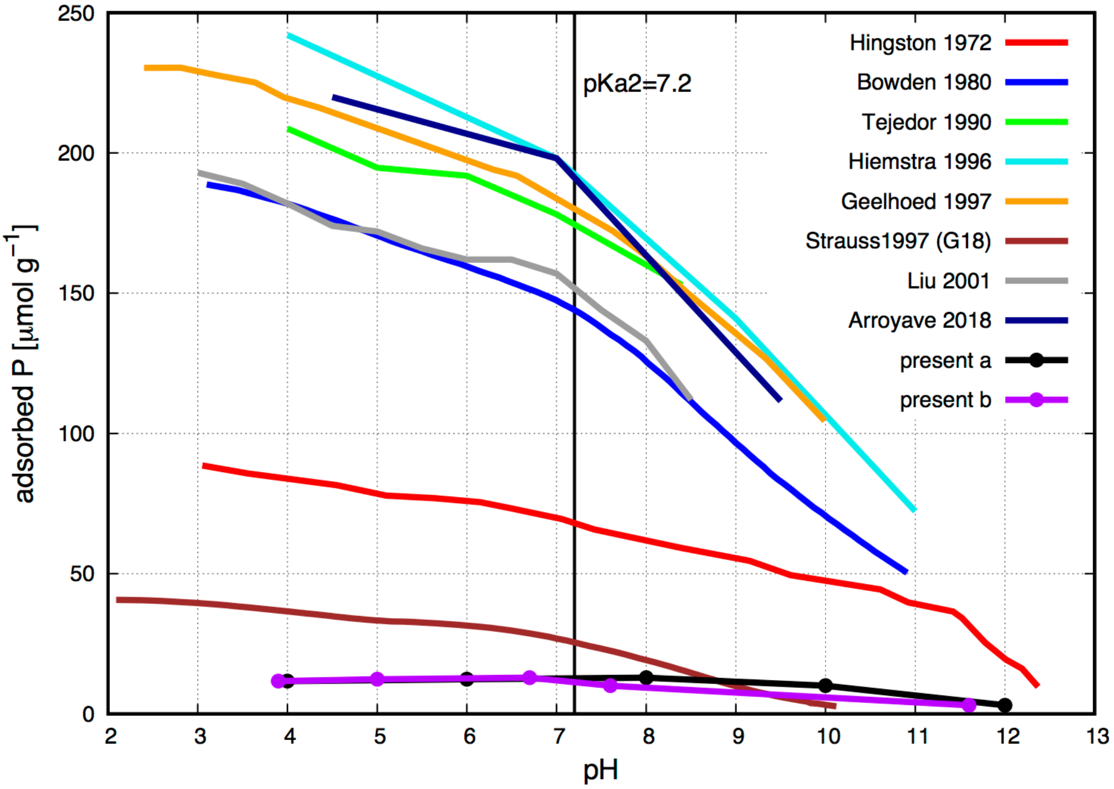

Fig. S7. Effect of pH on the phosphate (P) adsorption for the present study (considering the initial pH in black "present a" and the final pH in magenta "present b") and from literature. The latter includes data by Hingston et al.,[1] Bowden et al.,[2] Tejedor-Tejedor and Anderson,[3] Hiemstra and Van Riemsdijk,[4] Geelhoed et al.,[5] Liu et al.,[6] and Arroyave[7]. This figure is exactly the same as Fig. 7 in the main text but here the amount of adsorbed P is calculated with respect to the mass of goethite sample i.e. in μmol g^{-1}.

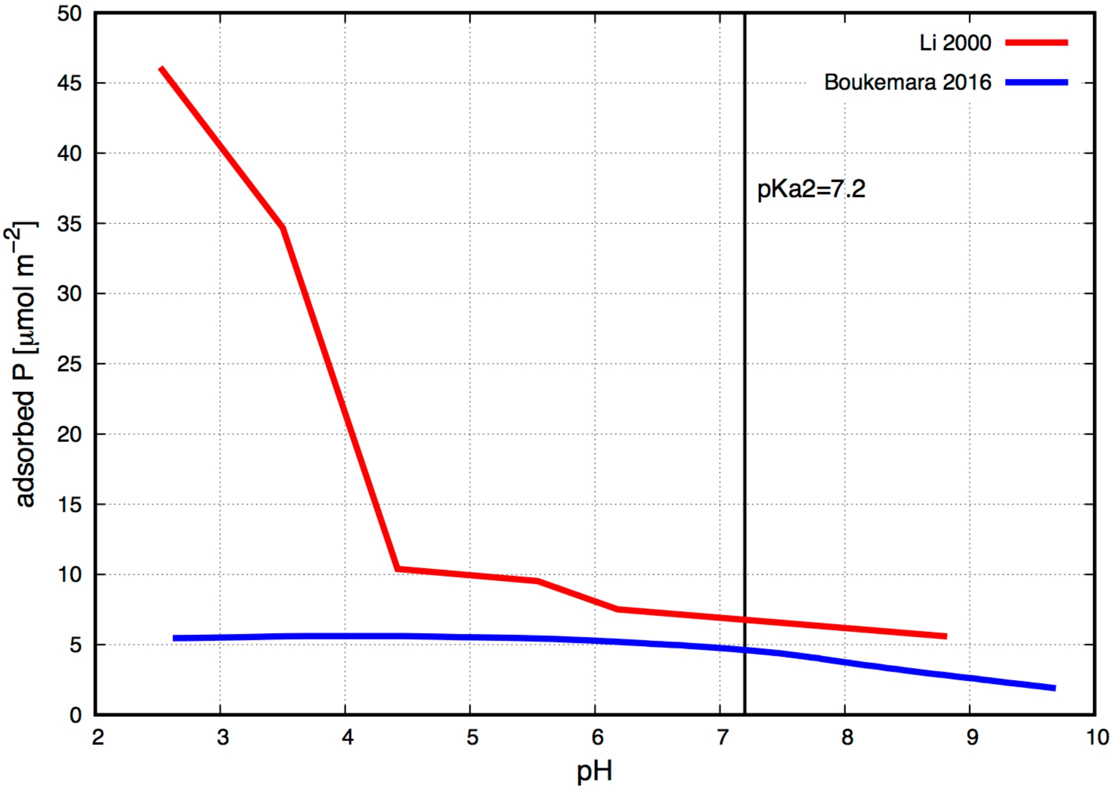

Fig. S8. Effect of pH on the P adsorption at high P surface coverage. The plotted data are collected from previous studies by Li and Stanforth[8] and Boukemara et al.[9]

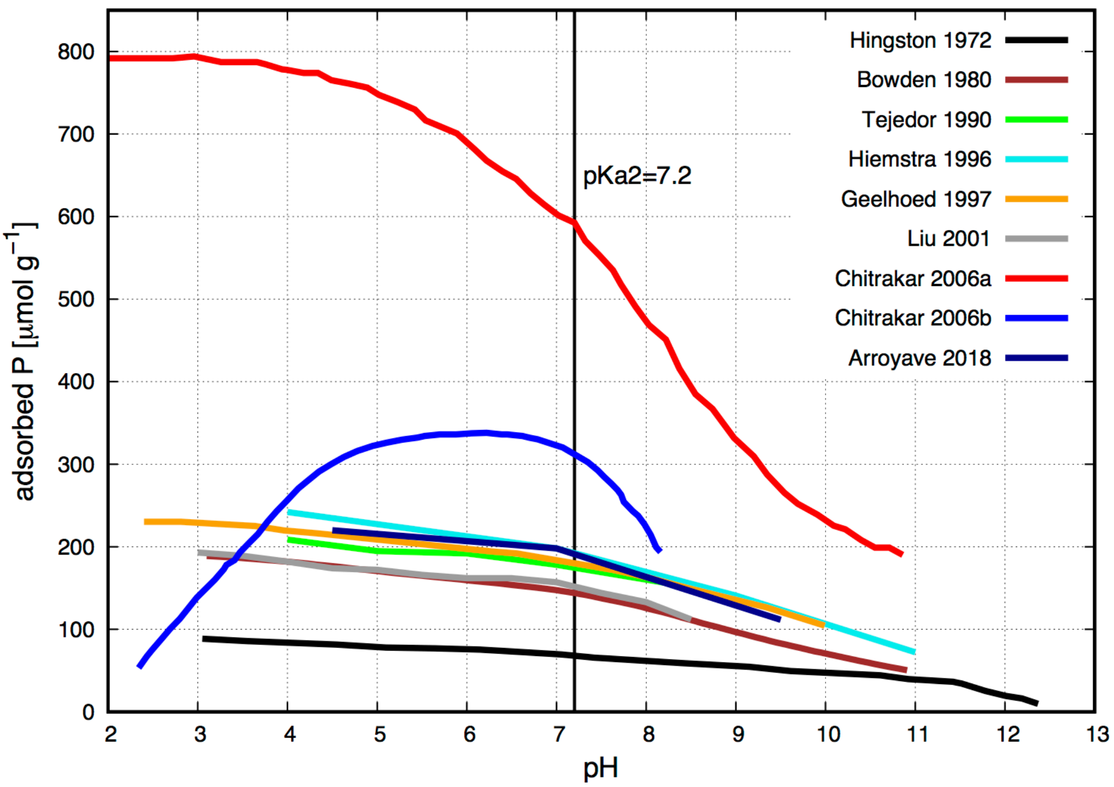

Fig. S9. Effect of pH on the P adsorption at goethite surfaces for a previous study by Chitrakar et al.[10] (adsorption in pure water is represented in red "Chitrakar 2006a" and in sea water in blue "Chitrakar 2006a"). To show how different this study than other literature studies, the studies by Hingston et al.,[1] Bowden et al.,[2] Tejedor-Tejedor and Anderson,[3] Hiemstra and Van Riemsdijk,[4] Geelhoed et al.,[5] Liu et al., [6], and Arroyave[7] are represented as well. Here the amount of adsorbed P is expressed in µmol.g^{-1}.

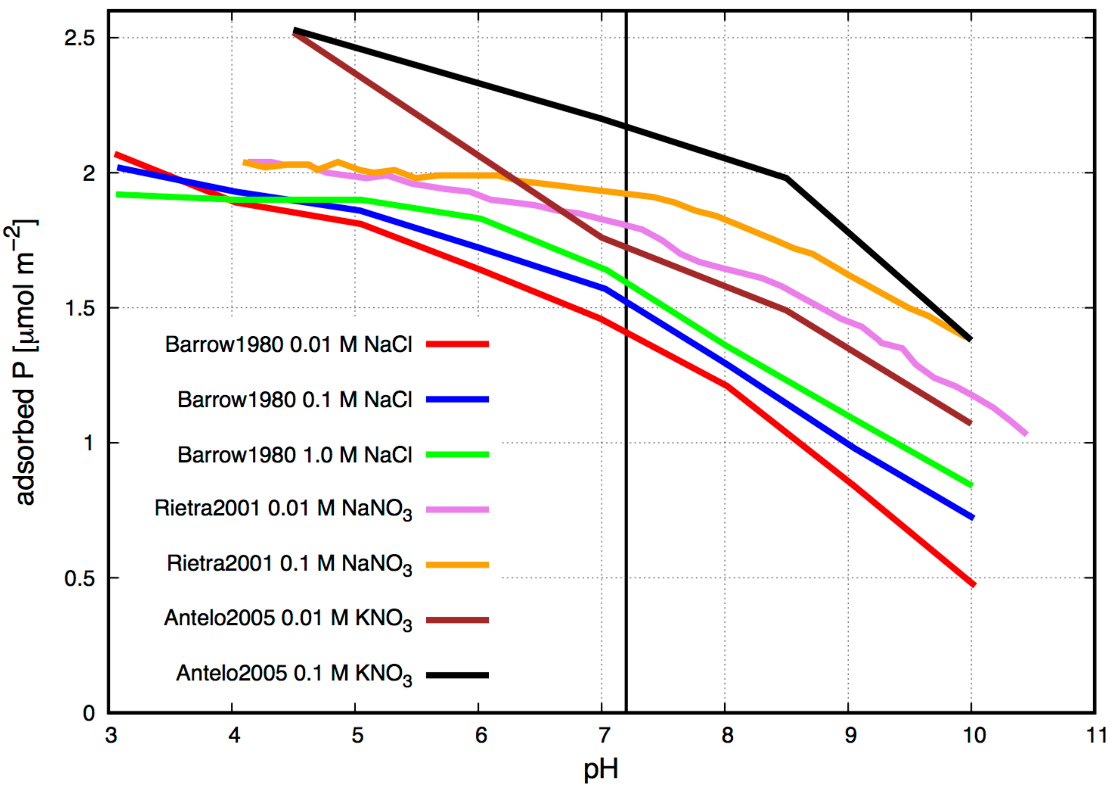

Fig. S10. Effect of pH on the P adsorption at goethite surfaces at different background electrolyte solutions and with different electrolyte concentrations. The plotted data are collected from previous studies by Barrow et al.,[11] Rietra et al.,[12] and Antelo et al.[13]

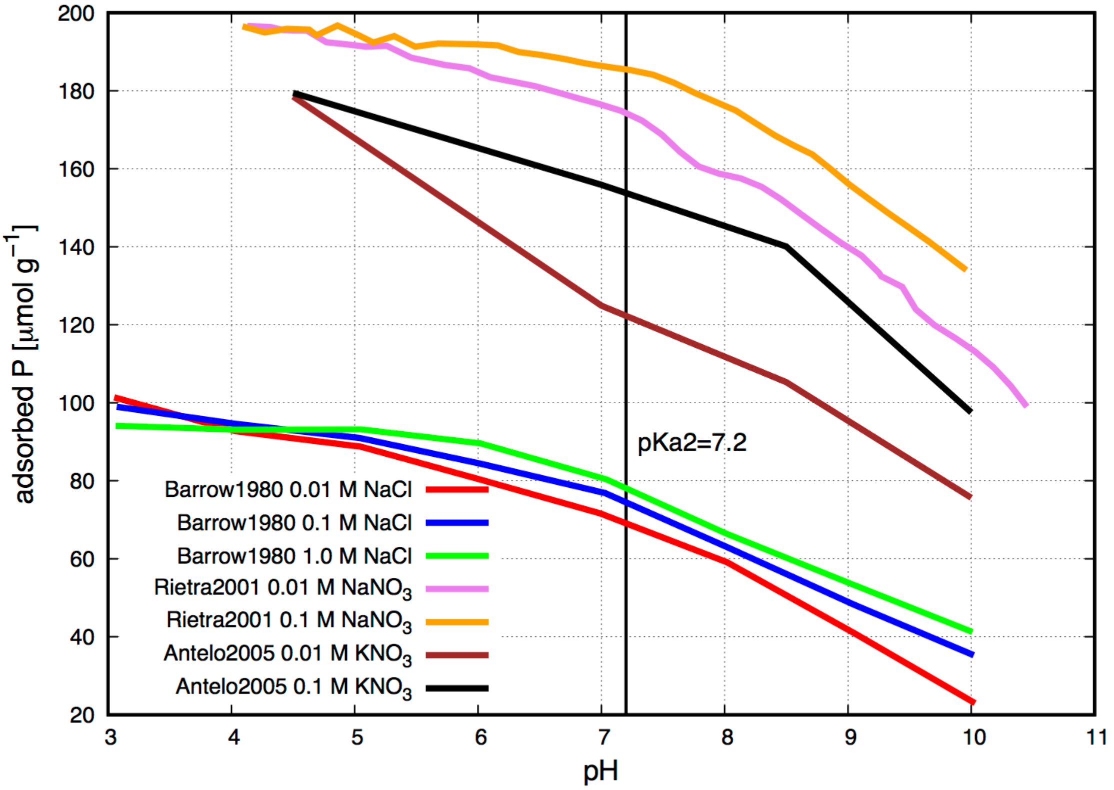

Fig. S11. Effect of pH on the P adsorption at goethite surfaces at different background electrolyte solutions and with different electrolyte concentrations. This Figure corresponds exactly to Fig. S9 but here the amount of adsorbed P is calculated with respect to the mass of goethite sample i.e. in µmol g^{-1}.

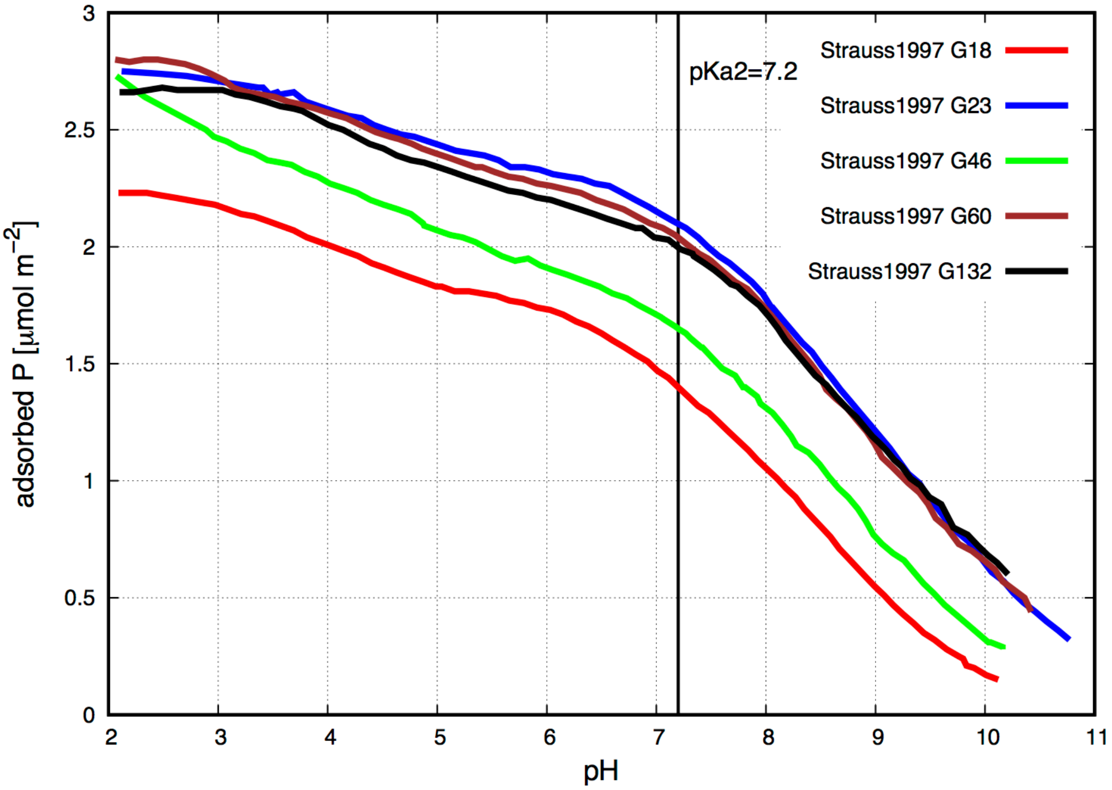

Fig. S12. Effect of pH on the P adsorption at goethite surfaces with different specific surface area (SSA) in the range from 18 to 132 m² g^{-1}. G18 to G132 refer to goethite samples with SSA values of 18 to 132 m² g^{-1}, respectively. Here the amount of adsorbed P is calculated with respect to the surface area i.e. in µmol m^{-2}. The plotted data are collected from a previous study by Strauss et al.[14]

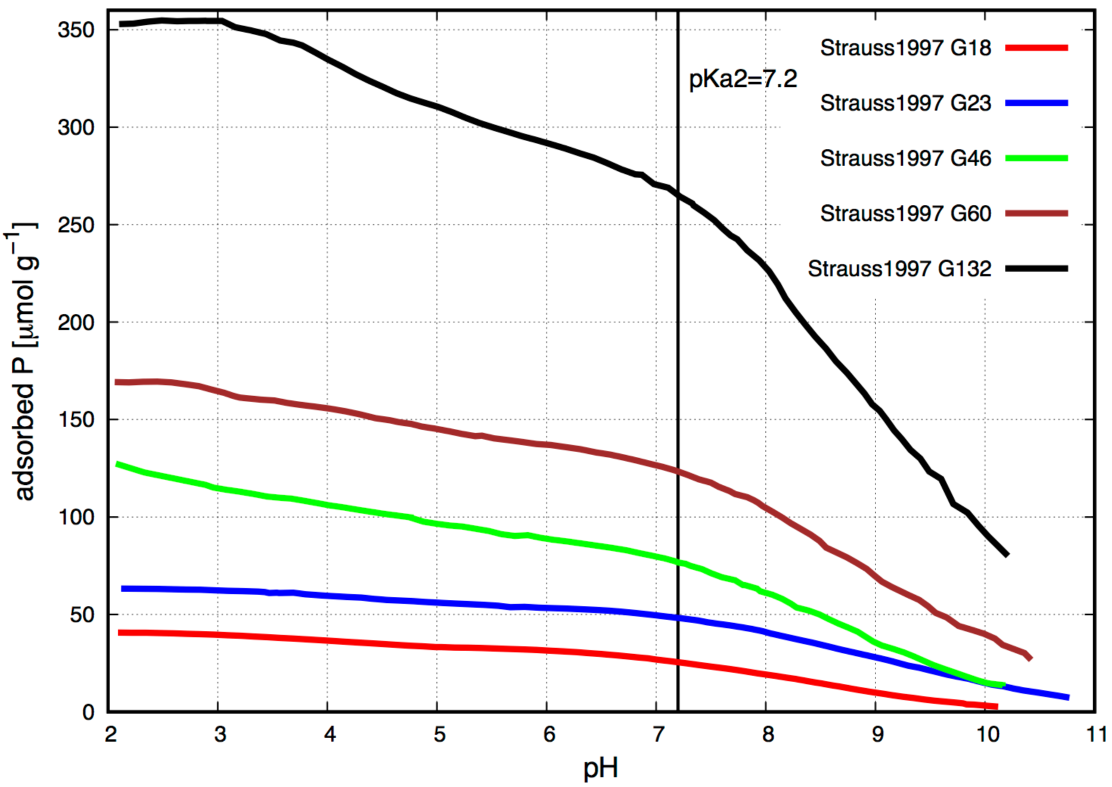

Fig. S13. Effect of pH on the P adsorption at goethite surfaces with different specific surface area which corresponds exactly to Fig. S10. Here the amount of adsorbed P is calculated with respect to the mass of goethite sample i.e. in µmol g^{-1}.

Note: The Figures S7–S13 are plotted based on data collected from pervious literature of phosphate sorption experiments.

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