

ORIGINAL ARTICLE

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Long-term stability of phosphate sorbed on an allophanic Andosol and a synthesized allophane

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Abstract

Allophane and ferrihydrite are the main hosts of phosphate in allophanic Andosols, which are vital soil resources that support high human population densities. However, the sorption mechanism of phosphate on allophane has not been elucidated, unlike that of ferrihydrite. In particular, the effects of residence time on phosphate sorbed on allophane remain unclear. Therefore, the objectives of this study were to (1) understand the effect of residence time on the stability of phosphate sorbed on allophanic Andosol and allophane by desorption experiments using arsenate and (2) elucidate the sorption mechanism of phosphate on allophane using solid-state ³¹P nuclear magnetic resonance (NMR). Consequently, the slow sorption of phosphate onto allophanic Andosol, allophane, and ferrihydrite continued for approximately 150 days. The ratio of total desorbable phosphate to phosphate sorbed onto the allophanic Andosol and allophane decreased with increasing residence time. In other words, phosphate sorption on allophanic Andosol and allophane was more irreversible with increasing residence time. The NMR spectra and X-ray diffraction patterns showed that the molecular environment of phosphate sorbed onto allophane and ferrihydrite did not change at any residence time. Therefore, the slow sorption and irreversibility of phosphate were caused not by surface precipitation but by internal diffusion. In addition, the NMR spectra showed that most of the phosphate sorbed on allophane was present as inner-sphere complexes.

1 | INTRODUCTION

Phosphorus (P) is a critical component of food production. However, because it strongly sorbs onto soils, the efficiency of P fertilizer is low, resulting in its overapplication in agriculture. The continuous application of excessive P also leads to

soil P buildup, referred to as “legacy P” (Sharply et al., 2013). A high level of legacy P carries a high risk of P loss from the field through surface runoff or leaching (King et al., 2015). Understanding the mechanism of P sorption is necessary to improve P utilization. Additionally, the availability of legacy P should be considered in P management.

Andosols, which are typical agricultural soils in Japan, are mainly derived from volcanic ash that contains a large amount of volcanic glass (Shoji et al., 1993). Andosols are mainly located on the Pacific rim, such as in Japan,

Abbreviations: ICP-OES, inductively coupled plasma-optical emission spectrometry; IR, infrared; MAS, magic angle spinning; NMR, nuclear magnetic resonance; SP, single pulse; XANES, X-ray absorption near edge structure; XRD, X-ray diffraction.

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New Zealand, and Indonesia, and are vital soil resources that support high human population densities (Takahashi, 2020; Takahashi & Shoji, 2002). As Andosols contain large amounts of active aluminum (Al) and iron (Fe), the efficiency of P fertilization in Andosols is particularly poor compared with that in other soils. Andosols are divided into two groups based on the active Al composition: allophanic and non-allophanic (Takahashi & Dahlgren, 2016). Allophanic Andosols are more commonly found worldwide than non-allophanic Andosols and contain many short-range order minerals, such as allophane and ferrihydrite, formed by the carbonic acid weathering of volcanic glass (Shoji et al., 1993). Allophane and ferrihydrite have large specific surface areas and can adsorb large amounts of phosphate (Dahlgren et al., 1993). Therefore, allophane and ferrihydrite determine the characteristics of P sorption in allophanic Andosols.

The sorption mechanism of phosphate primarily involves adsorption and precipitation (Wang et al., 2017, 2019). In general, phosphate precipitation is more stable in the natural environment than adsorption onto minerals. Many researchers have investigated the interaction between ferrihydrite and phosphate in detail (e.g., Arai & Sparks, 2001, 2007; Wang et al., 2017). For example, Wang et al. (2017) reported that phosphate forms a bidentate binuclear complex and a precipitate on ferrihydrite, and that precipitate formation begins once the 24-h P sorption loading reaches 895 mmol kg⁻¹. The sorption mechanism of phosphate on allophane has not been elucidated, unlike that of ferrihydrite. Uchida et al. (2022) suggested that phosphate forms a surface complex and precipitates onto allophane. However, Arai et al. (2005), who used arsenate as a phosphate analog, concluded that arsenate did not form a precipitate, but rather a bidentate binuclear complex, on allophane.

The reaction time between the sorbent and sorbate, referred to as “residence time” (Arai & Sparks, 2002), may affect the stability of phosphate on minerals (Landrot & Sparks, 2023). For example, Arai and Sparks (2007) reported that the amount of phosphate desorbed from ferrihydrite decreases with increasing residence time (<19 months). In addition, with increasing residence time, phosphate sorption onto minerals increases because of internal diffusion (i.e., intra- and inter-particle diffusion) and/or precipitation (e.g., Barrow, 1983; Ler & Stanforth, 2003; Willett et al., 1988). Although many researchers have reported the presence of internal diffusion (Li, Feng, et al., 2013; Makris et al., 2004; Willett et al., 1988), some have denied its occurrence (Zhang & Stanforth, 2005).

In general, the molecular environment of phosphate sorbed on aluminum-containing minerals was investigated by X-ray absorption near edge structure (XANES) or ³¹P solid-state nuclear magnetic resonance (NMR) (e.g., Li, Pierre-Louis, et al., 2013; Uchida et al., 2022). Previous studies employed XANES to distinguish P adsorption from surface precipitation (Khare et al., 2005; Uchida et al., 2022). However, Abdala

Core Ideas

- We explored residence time’s effects on phosphate sorbed on allophanic Andosol and allophane.
- Phosphate sorption on Andosol and allophane continued for approximately 150 days.
- Nuclear magnetic resonance (NMR) spectra did not notably change during long-term phosphate sorption to allophane.
- Irreversibility of sorbed phosphate increased with residence time.
- Internal diffusion by soil in the phosphate sorption process is very important.

et al. (2015) pointed out that the authors in their studies relied on indirect observation. ³¹P solid-state NMR has often been used to investigate the molecular environment of phosphates sorbed onto minerals containing Al based on ³¹P chemical shifts (Johnson et al., 2002; Li, Pierre-Louis, et al., 2013; Li, Feng, et al., 2013; Lookman et al., 1994; van Emmerik et al., 2007). Therefore, we selected ³¹P solid-state NMR to investigate the molecular environment of phosphates sorbed onto allophane. According to the literature review by Li, Pierre-Louis et al. (2013), the chemical shifts at $\delta_p = -11$ to -30 ppm, $\delta_p = 0$ to -10 ppm, and $\delta_p = 10-0$ ppm could be attributed to surface precipitates, inner-sphere complexes, and outer-sphere complexes, respectively. Lookman et al. (1994) reported that the NMR chemical shift of phosphate sorbed on amorphous aluminum hydroxide tended to become more negative with increasing residence time (<120 days). Li, Feng et al. (2013) revealed that the residence time did not affect the molecular environment of phosphate adsorbed on boehmite (<21 days). However, this method has not been applied to investigate the molecular environment of phosphate sorbed onto allophane. Whether the residence time affects the molecular environment of phosphate sorbed on allophane remains unclear. Therefore, the objectives of this study were to (1) understand the effects of residence time on the stability of phosphate sorbed on allophane and allophanic Andosol and (2) elucidate the sorption mechanism of phosphate on allophane.

2 | MATERIALS AND METHODS

2.1 | Soil sample

Soil samples were collected from an experimental field at the National Institute for Agriculture (Kyushu-Okinawa Agricultural Research Center, National Agriculture and Food Research Organization) in Miyazaki Prefecture, Japan. This

soil sample was classified as an allophanic Andosol (Matsuyama et al., 2005). The soil sample was air-dried, ground, and sieved through a 2-mm mesh. The soil pH ($\text{pH}_{\text{H}_2\text{O}}$) was determined using a pH meter with a soil/solution ratio of 1:2.5. The soil organic matter content was determined using the dry combustion method (JM1000HCN; J-Science Lab Co. Ltd.). The amounts of acid oxalate-extractable Al (Al_{ox}), Fe (Fe_{ox}), and Si (Si_{ox}), citrate–dithionite-extractable Fe (Fe_{cd}), and pyrophosphate-extractable Al (Al_{p}) and Fe (Fe_{p}) were determined according to the methods described by Blakemore et al. (1981). These methods were described in detail in our previous study (Sato et al., 2023). The amounts of Al_{ox} , Fe_{ox} , and Si_{ox} are indicators of the fractions of poorly crystalline and noncrystalline minerals. The amount of Fe_{cd} is an indicator of the iron oxide fraction. The amounts of Al_{p} and Fe_{p} are indicators of the fraction of Al/Fe–humus complexes. Soil properties are summarized in Table S1 (Sato et al., 2023).

2.2 | Allophane and ferrihydrite synthesis

Allophane was synthesized according to the method described by Ohashi et al. (2002). Briefly, 100 mM Na_4SiO_4 and 100 mM $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ were mixed at a Si/Al atomic ratio of 0.75 to synthesize the allophane precursor. The suspension was stirred for 1 h at pH 6.0. The precursor was desalinated by centrifugation and autoclaved for 2 days at 105°C. The resulting material was then washed repeatedly with distilled water, freeze-dried, and finely ground. The X-ray diffraction (XRD) pattern, obtained using an Ultima IV (Rigaku Co., Ltd.), showed three broad peaks at 0.34, 0.22, and 0.14 nm (Figure S1a). The infrared (IR) spectrum, which was obtained using IR Prestige-21 (Shimadzu Co., Ltd.), showed broad bands at 800–1200 and 400–800 cm^{-1} (Figure S1b). The Si/Al atomic ratio of the materials was 0.70. These results are typical for allophane (Ohashi et al., 2002).

In this study, phosphate sorption on ferrihydrite was evaluated and compared with that on allophanic Andosol and allophane. Ferrihydrite was synthesized according to the method described by Schwertmann and Cornell (2000). Briefly, a solution of 0.1 M $\text{FeNO}_3 \cdot 9\text{H}_2\text{O}$ was adjusted to pH 7.5 through the dropwise addition of 5 M NaOH solution under continuous stirring. The precipitate was dialyzed, freeze-dried, and finely ground. The XRD pattern showed two broad peaks at 0.26 and 0.15 nm (Figure S1c). This is a typical characteristic of two-line ferrihydrite (Schwertmann & Cornell, 2000).

2.3 | Residence time effects on sorbed phosphate stability

Suspensions of allophanic Andosol (20 g L^{-1}), allophane (2 g L^{-1}), and ferrihydrite (2 g L^{-1}) were pre-equilibrated at pH

6.7 with the background electrolyte of 0.1 M NaNO_3 before the addition of phosphate solutions. To achieve an initial phosphate concentration of 2 mM, 400 mM Na_2HPO_4 solution was added to the suspensions. After adding phosphate, the suspension pH was manually adjusted to 6.7 ± 0.2 every day for up to 1 week. Thereafter, we periodically adjusted the suspension pH to 6.7 ± 0.2 . The suspensions were shaken for 4–240 days. These kinetic experiments on phosphate sorption were conducted at 25°C. The suspensions were centrifuged to separate the supernatant from the residual solids. The supernatant solution was then filtered through a 0.22- μm filter. The final P concentration in the solution was measured using inductively coupled plasma-optical emission spectrometry (ICP-OES; ICPE-9000, Shimadzu Co., Ltd.). The amount of sorbed P was calculated as the difference between the concentrations in the final and initial solutions. The wet pastes (i.e., the residual solid after the centrifugation) of the allophane and ferrihydrite were washed with distilled water, followed by air-drying at 25°C. Air-dried allophane and ferrihydrite were used for solid-state ^{31}P NMR (see Section 2.5) and XRD measurements, respectively. XRD measurements of ferrihydrite were performed to check the formation of surface precipitates and the change in bulk mineralogy.

Furthermore, wet pastes of allophanic Andosol and allophane were used for desorption experiments. However, a desorption experiment was not conducted for ferrihydrite because its residual solid was easily dispersed, even after centrifugation. The stability of phosphate sorbed on allophanic Andosol and allophane was investigated using the replenishment method (Arai & Sparks, 2002), in which the phosphate on the solids was desorbed by the repeated addition of the solution. In this study, the desorption procedure was repeated 13 times: one with NaNO_3 and 12 with arsenate. The solution of 0.1 M NaNO_3 was added to the wet paste after the kinetic experiments, as described above. The suspensions were shaken for 1.5 h under the adjusted pH (6.7 ± 0.2) and constant temperature (25°C). The solution and solid containing the desorbed and sorbed P, respectively, were separated by centrifugation. The amount of the initial P desorbed by the NaNO_3 solution was estimated from the P concentration in the solution, which was measured using ICP-OES. Next, 2 or 10 mM arsenate was added to the residual solid. The suspensions were shaken for 24 h under identical conditions. The amount of P desorbed by the arsenate solution was similarly estimated. The desorption of P from the arsenate solution was repeated 12 times. As the agricultural soil (allophanic Andosol) contained native P owing to fertilizer application, the same desorption experiment was conducted without the addition of phosphate to evaluate the desorbable native P against arsenate. In addition, the P sorbed on allophane after the desorption experiments (using 10 mM arsenate) was measured by solid-state ^{31}P NMR (see Section 2.5).

2.4 | Surface loading effects on the sorption mechanism of phosphate

Suspensions of allophane (2 g L^{-1}) were pre-equilibrated at pH 6.7 with the background electrolyte of 0.1 M NaNO_3 before the addition of phosphate solutions. A desired amount of $400 \text{ mM Na}_2\text{HPO}_4$ solution was added to the suspensions. The initial phosphate concentrations in the suspensions were $0.5, 1, 2,$ and 4 mM . After adding phosphate, the suspension pH was manually adjusted to $\text{pH } 6.7 \pm 0.2$ daily. The suspension was shaken for 6 days and centrifuged to separate the solid and solution. This experiment was conducted at 25°C . The supernatant was analyzed using the method described in Section 2.3. After centrifugation, the collected wet pastes of allophane were washed with distilled water followed by air-drying at 25°C . Air-dried allophane was used for the NMR measurements, as described in Section 2.5.

2.5 | ^{31}P SP/MAS NMR measurements

The air-dried allophane described in Sections 2.3 and 2.4 was finely ground and packed in a zirconia rotor. Solid-state ^{31}P single pulse (SP) and magic angle spinning (MAS) NMR measurements with proton decoupling were performed using a 400 MHz solid-state NMR spectrometer (VARIAN) with a 4.0-mm double-resonance MAS probe. The ^{31}P chemical shifts (δ_{P}) were calibrated indirectly through $\text{NH}_4\text{H}_2\text{PO}_4$ ($\delta_{\text{P}} = 1.00 \text{ ppm}$). The rotors were spun at 10 kHz with ^{31}P 90° pulse width, relaxation delay, and total scans of $7.75 \mu\text{s}$, 120 s , 512 s , or 1024 s , respectively. A line broadening of 100 Hz was applied before Fourier transformation and phase correction (Cade-Menun, 2005). All NMR spectra were normalized to the maximum intensity.

3 | RESULTS

3.1 | Sorption kinetics

The sorption kinetics of phosphate are shown in Figure 1. The amounts of phosphate sorbed on the allophanic Andosol were $77.1, 88.1, 91.6, 93.1,$ and $94.2 \text{ mmol kg}^{-1}$ for 6, 48, 105, 152, and 240 days, respectively. The amounts of phosphate sorbed on the allophane were $546, 692, 745, 782,$ and 784 mmol kg^{-1} for 6, 45, 102, 149, and 237 days, respectively. The amounts of phosphate sorbed on the ferrihydrite were $839, 935, 940, 958,$ and 960 mmol kg^{-1} for 6, 45, 102, 149, and 237 days, respectively. Similar to the results reported by Uchida et al. (2022), ferrihydrite sorbed more phosphate than allophane. Compared with the amount of sorbed phosphate at approximately 240 days, 81.8% (allophanic Andosol), 69.6% (allophane), and 87.4% (ferrihydrite) were sorbed within the first 6 days. That is, fast sorption was followed by slow sorption. The slow

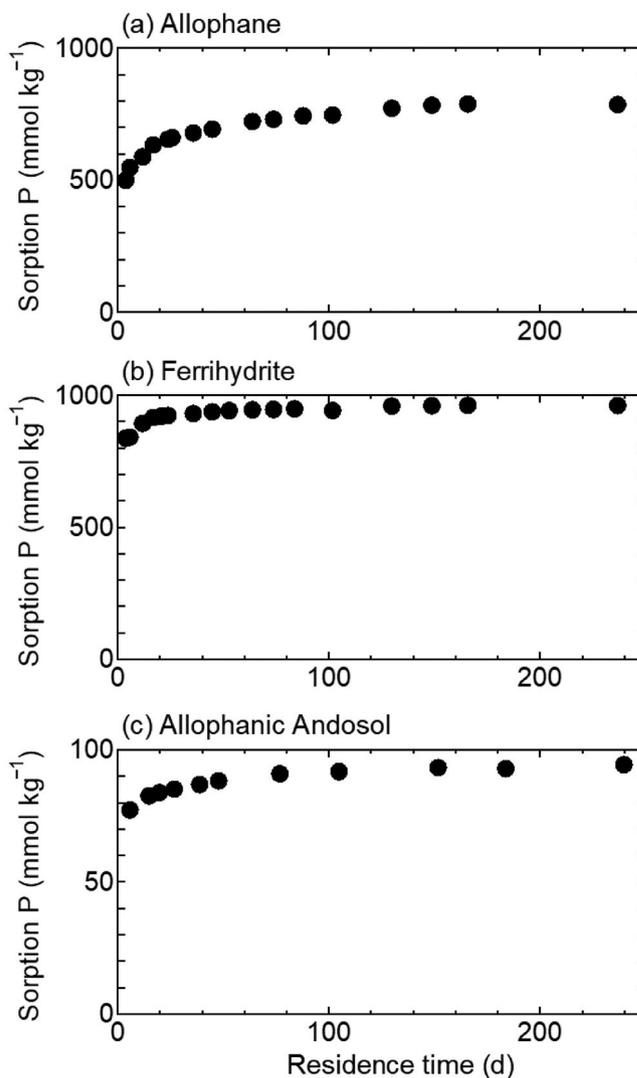


FIGURE 1 Phosphate sorption kinetics of (a) allophane, (b) ferrihydrite, and (c) allophanic Andosol. The initial phosphate concentration was 2 mM at pH 6.7. Suspension density was 2 g L^{-1} for allophane and ferrihydrite and 20 g L^{-1} for allophanic Andosol.

sorption of phosphate continued for approximately 150 days. These results are consistent with those of some studies that reported that the sorption of phosphate onto minerals and soil continues for months (Arai & Sparks, 2007; Parfitt, 1989; Tanaka et al., 2023; Willett et al., 1988).

Phosphate sorbed on allophane as a function of residence time was analyzed using ^{31}P SP/MAS NMR spectroscopy (Figure 2). The NMR spectra showed an asymmetric broad peak at $\delta_{\text{P}} = -7$ to -10 ppm , which appeared to be slightly flattened with residence time. This might be caused by the phase correction. In addition, we tried the subtraction of NMR spectra at 6 days from that at 237 days. However, in the difference spectrum, any peaks were indistinguishable from noise. This indicates that the residence time can hardly affect the molecular environment of the phosphate sorbed on allophane under these experimental conditions.

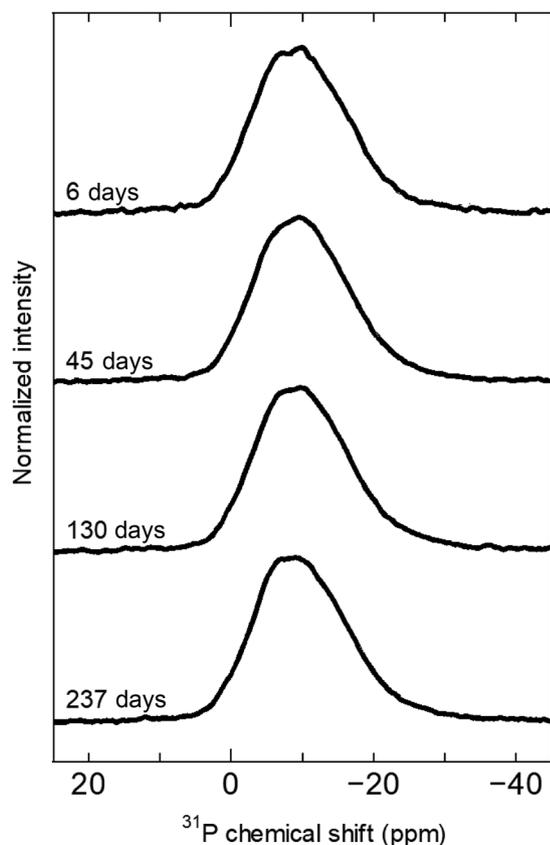


FIGURE 2 ^{31}P single pulse/magic angle spinning (SP/MAS) nuclear magnetic resonance (NMR) spectra of phosphate sorbed on allophane as a function of residence time. Samples were prepared at pH 6.7 with an initial phosphate concentration of 2 mM for the indicated time.

Ferrihydrite reacted with phosphate as a function of residence time and was analyzed using XRD (Figure 3). Although XRD cannot detect low concentrations of surface precipitates (Li, Pierre-Louis, et al., 2013), the XRD pattern of the phosphate-reacted ferrihydrite did not show a broad peak at 0.308 nm, suggesting that significant amounts of surface precipitates such as amorphous FePO_4 were not formed (Wang et al., 2017). In addition, common ferrihydrite transformation products, such as goethite and hematite, were not observed.

3.2 | Residence time effects on sorbed phosphate stability

The amount of the initial desorbed phosphate, which represented weakly adsorbed phosphate on allophanic Andosol, decreased from 5.90 (7.73%) to 2.20 mmol kg^{-1} (2.33%) with an increase in residence time from 6 to 240 days (Figure 4). In addition, the total desorbable phosphate in the allophanic Andosol against 2 mM arsenate (i.e., sum of the phosphate released in the replenishments) decreased from 50.7 (66.3%)

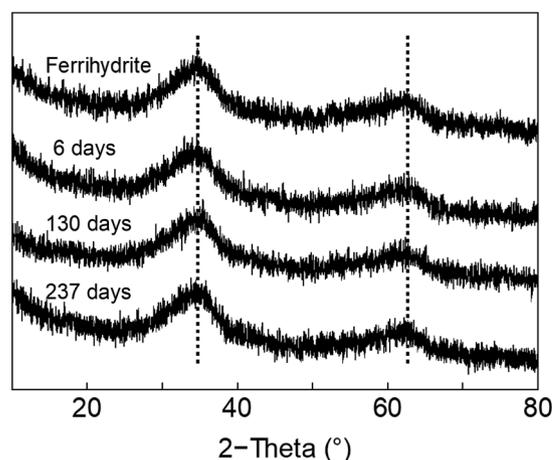


FIGURE 3 X-ray diffraction (XRD) pattern was of aged ferrihydrite suspensions at pH 6.7 with an initial phosphate concentration of 2 mM for the indicated time.

to 39.2 mmol kg^{-1} (41.6%) with an increase in residence time from 6 to 152 days, although the total desorbable phosphate did not change with increasing residence time after 152 days (Figure 4a). It should be noted that the allophanic Andosol contained 4.78 mmol kg^{-1} of the native P, which could be released from the soil by the repeated addition of 2 mM arsenate solution (Figure 4b).

The amount of weakly adsorbed phosphate on allophane decreased from 58.0 (10.6%) to 33.6 mmol kg^{-1} (4.28%) with an increase in residence time (Figure 4c). The total desorbable phosphate in the allophane against 2 mM arsenate decreased from 307 (57.1%) to 293 mmol kg^{-1} (37.4%) with an increase in residence time from 6 to 149 days, although the total desorbable phosphate did not change with increasing residence time after 149 days (Figure 4d). More phosphate was desorbed when an arsenate solution with a higher arsenate concentration (10 mM) was added (Figure S2). However, the phosphate desorption trend in the experiment using a high arsenate concentration was similar to that using a low arsenate concentration.

Figure 5 shows the NMR spectrum after the sorption of phosphate on allophane for 237 days and the removal of 40% of the sorbed phosphate by the repeated addition of 10 mM arsenate. Although many surface complexes of phosphate on allophane were expected to be removed by arsenate, there was no significant change in the NMR spectra before and after the desorption experiment.

3.3 | Surface loading effects on the molecular environment of phosphate sorbed on allophane

The amounts of phosphate sorbed on the allophane were 231, 390, 591, and 819 mmol kg^{-1} for initial phosphate concentrations of 0.5, 1, 2, and 4 mmol L^{-1} , respectively. The NMR

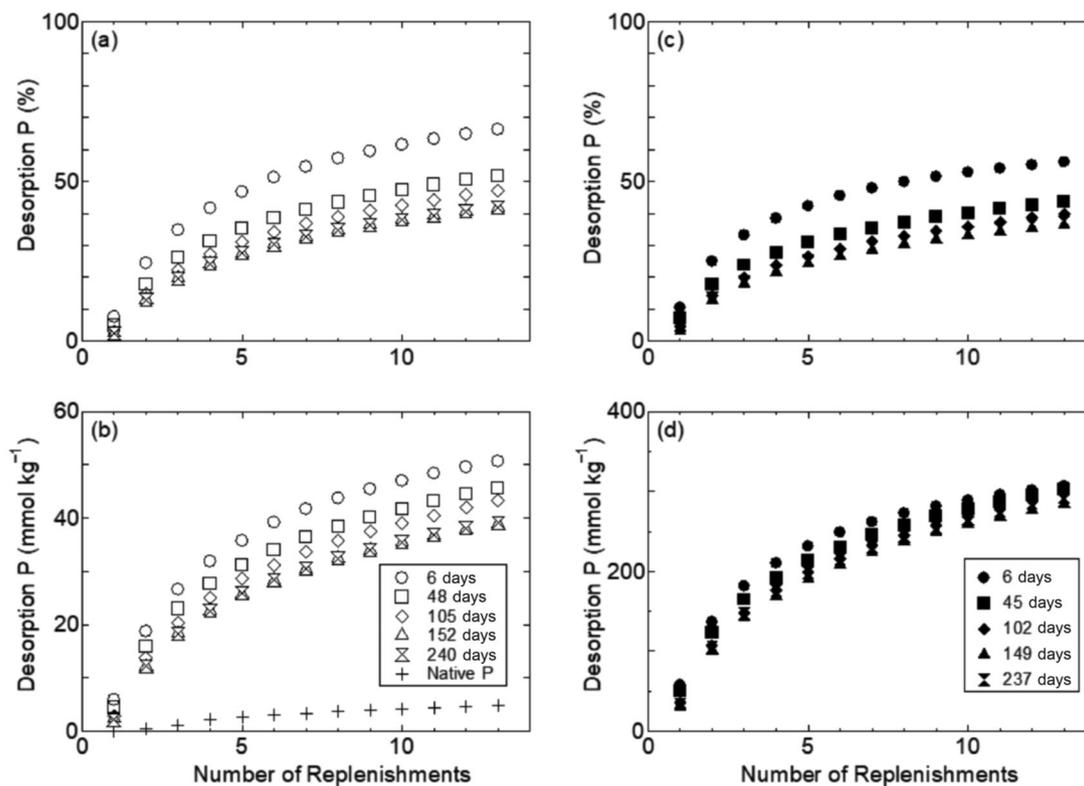


FIGURE 4 Residence time affects (a) and (c) the ratio of total desorbable phosphate to sorption phosphate and (b) and (d) the amount of total desorbable phosphate from (a) and (b) allophanic Andosol and (c) and (d) allophane against 2 mM arsenate. Before the desorption experiment for phosphate-reacted allophanic Andosol and allophane, the samples were prepared under the following reaction conditions: pH 6.7, suspension density 20 g L⁻¹ for allophanic Andosol and 2 g L⁻¹ for allophane, initial phosphate concentration 2 mM, and residence time as indicated.

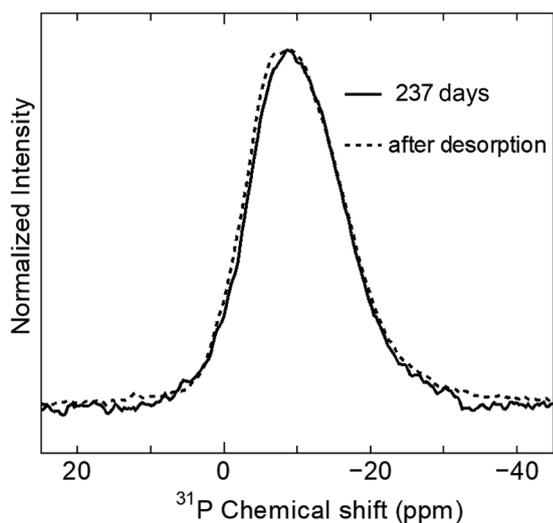


FIGURE 5 ³¹P single pulse/magic angle spinning (SP/MAS) nuclear magnetic resonance (NMR) spectra of phosphate before and after the desorption experiments for the samples reacted with phosphate under the following conditions: pH 6.7, initial phosphate concentration 2 mM, and residence time 237 days. Desorption experiments were conducted by replenishment with 0.1 M NaNO₃ and 12 times with 10 mM arsenate.

spectrum at the initial concentration of 0.5 mM was slightly different from that at initial concentrations of 1, 2, and 4 mM (Figure 6). The subtraction of the NMR spectrum at the initial concentration of 0.5 mM from that obtained at the initial concentration of 4 mM showed a positive peak at $\delta_p = -15$ ppm and a negative peak at $\delta_p = -3.5$ ppm (Figure 7). That is, chemical species assigned at $\delta_p = -15$ ppm became slightly apparent at high phosphate concentrations, and those assigned at $\delta_p = -3.5$ ppm became slightly apparent at low phosphate concentrations. The molecular environment could not be evaluated in detail by the peak deconvolution of the Gaussian curves because of the lack of characteristics in the NMR spectra.

4 | DISCUSSION

4.1 | Sorption mechanism of phosphate on allophane

Despite removing 40% of the phosphate sorbed by arsenate, there was no significant change in the NMR spectra before and after the desorption experiments (Figure 5). If a large amount of surface precipitation is formed, the NMR spectra

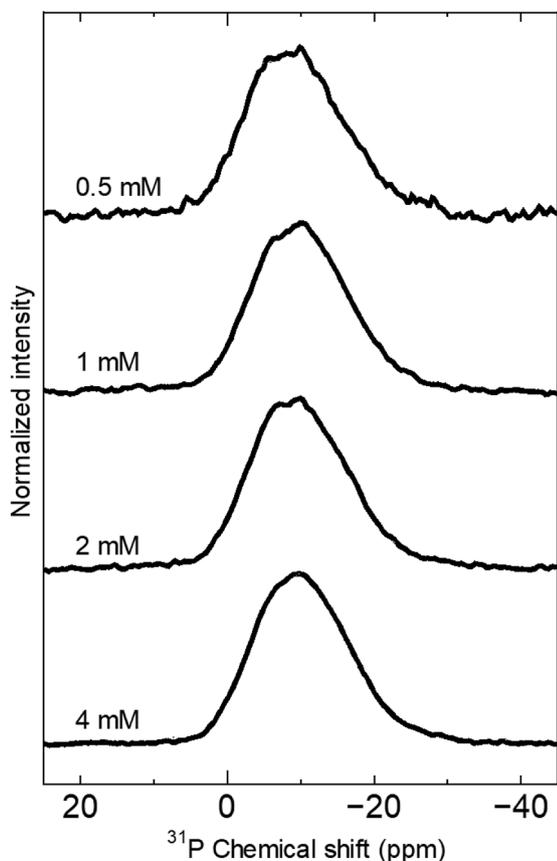


FIGURE 6 ^{31}P single pulse/magic angle spinning (SP/MAS) nuclear magnetic resonance (NMR) spectra of phosphate sorbed on allophane as a function of phosphate concentration. Samples were prepared at pH 6.7 with the indicated initial phosphate concentration for 6 days.

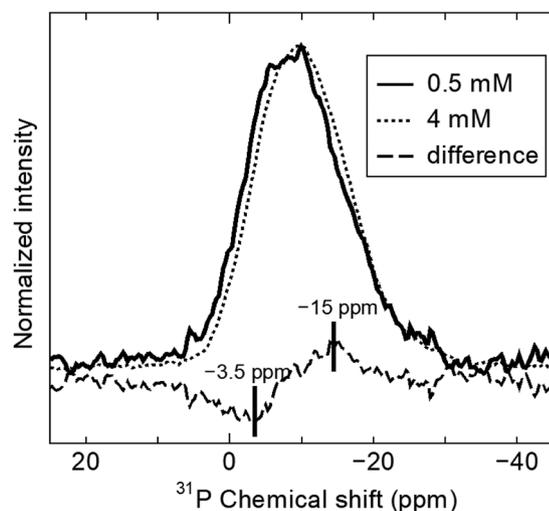


FIGURE 7 Subtraction of ^{31}P single pulse/magic angle spinning (SP/MAS) nuclear magnetic resonance (NMR) spectrum at 0.5 mM from that at 4 mM. Samples were prepared at pH 6.7 with the indicated initial phosphate concentration for 6 days.

after the desorption experiment should show a more negative chemical shift owing to the removal of surface complexes by arsenate. In other words, under the conditions of this experiment (suspension density, 2 g L^{-1} ; pH, 6.7; initial phosphate concentration, $<4 \text{ mM}$; and sorption P, $<820 \text{ mmol kg}^{-1}$), there was no or little surface precipitation. This result is consistent with those of Arai et al. (2005), who reported that arsenate does not precipitate on allophane. However, we cannot exclude the possibility that surface precipitation occurred on the allophane, because many researchers have reported the formation of surface precipitation during the reaction of phosphate with aluminum-containing minerals (e.g., Khare et al., 2005; Uchida et al., 2022). Uchida et al. (2022) and Wang et al. (2019) reported the formation of surface precipitation of phosphate on allophane (suspension density, 1 g L^{-1} ; pH, 6; and sorption P, $<500 \text{ mmol kg}^{-1}$). Wang et al. (2019) quantitatively distinguished between surface complexes and surface precipitation in the reaction of amorphous aluminum hydroxide with phosphate and reported that only 5.5% of surface precipitation was present under the similar experimental conditions of our study (suspension density, 2 g L^{-1} ; pH 7; and initial phosphate concentration, 2 mM). In addition, we observed that chemical species assigned at $\delta_{\text{p}} = -15 \text{ ppm}$ became slightly apparent at a high phosphate concentration, and those assigned at $\delta_{\text{p}} = -3.5 \text{ ppm}$ became slightly apparent at a low phosphate concentration (Figure 7). As mentioned in the Introduction, the chemical shifts at $\delta_{\text{p}} = -11$ to -30 ppm and $\delta_{\text{p}} = 0$ to -10 ppm could be attributed to surface precipitates and inner-sphere complexes, respectively (Li, Pierre-Louis, et al., 2013). In summary, most of the phosphate sorbed on allophane was present as inner-sphere complexes, and surface precipitation was present, albeit in small amounts.

4.2 | What causes the slow sorption stage of phosphate?

The sorption of phosphate onto minerals is initially rapid, followed by a slow stage. In general, slow sorption can be explained by two factors: internal diffusion (Li, Feng, et al., 2013; Willett et al., 1988) and the formation of surface precipitation (Ler & Stanforth, 2003). In our study, the NMR spectra of phosphate sorbed on allophane indicated that slow sorption was not mainly due to the formation of surface precipitation because the NMR spectra did not change with increasing residence time (Figure 2). If slow sorption was caused by the formation of surface precipitation, the NMR spectra of phosphate sorbed on allophane would change because the precipitation of 200 mmol kg^{-1} , which increased during the slow sorption stage from 6 to 237 days, would cause a negative shift of the NMR spectra. Similarly, the XRD pattern of phosphate-reacted ferrihydrite suggested that

the slow sorption of ferrihydrite might not have been due to surface precipitation, because it did not change with increasing residence time (Figure 3). In addition, Wang et al. (2017) showed that precipitation on ferrihydrite occurred when the 24-h phosphate sorption loading reached 895 mmol kg⁻¹. In this study, the sorption of phosphate on ferrihydrite after 6 days was 839 mmol kg⁻¹. Therefore, it is expected that no surface precipitation of phosphate occurs on the ferrihydrite. Our results indicated that the slow sorption of allophane and ferrihydrite was caused by internal diffusion into the aggregates. This is supported by the fact that allophane and ferrihydrite typically exist as submicron nanoparticle aggregates (Dahlgren et al., 1993; Karube et al., 1996). In addition, the freeze-drying of allophane and ferrihydrite causes the irreversible aggregation of submicron aggregates (Karube, 2004; Scheinost et al., 2001).

The slow sorption of allophanic Andosols might also be caused by internal diffusion due to the presence of an aggregate hierarchy down to the submicron scale in allophanic Andosols (Asano & Wagai, 2014). However, as discussed later, the possibility that this was due to the formation of surface precipitates on the allophanic Andosols cannot be ruled out.

4.3 | Residence time effects on the stability of sorbed phosphate

The ratio of the total desorbable phosphate to sorbed phosphate decreased with increasing residence time (Figure 4). This result indicates that the phosphate sorbed on allophane became chemically or physically more stable with increasing residence time. However, the NMR spectra did not change with increasing residence time (Figure 2), indicating that the molecular environment of the phosphate sorbed on allophane did not change. If internal diffusion occurs as the residence time increases, the phosphate adsorbed within the aggregate via internal diffusion process is expected to become more stable than the phosphate adsorbed on the outer surface because of the physical protection (Makris et al., 2004). Therefore, the stabilization of phosphate sorbed on allophane with increasing residence time was mainly caused by internal diffusion. A similar observation regarding phosphate sorption on boehmite was reported by Li, Feng et al. (2013). Interestingly, these results were inconsistent with those of previous studies that reported the effects of residence time on the molecular environment (Arai & Sparks, 2007). Wang et al. (2017), Hunger (2003), and Lookman et al., 1994 indicated that the percentage of surface precipitation in sorption phosphate correlated with sorption levels. In addition, Wang et al. (2019) indicated that phosphate more readily precipitates on amorphous aluminum oxide than on ferrihydrite. Therefore, this discrepancy may be due to the difference in the sorption levels and of the species

of minerals. For example, Lookman et al. (1994) and Hunger (2003) used high phosphate sorption levels (more than twice those in our study and that by Li, Feng, et al. [2013]). Arai and Sparks (2007) used the same phosphate sorption level in their study, they observed the effects of residence time on the molecular environment on ferrihydrite. However, we could not identify the cause of this discrepancy, and further research is required.

5 | CONCLUSION

Phosphate sorption on allophanic Andosol and synthesized allophane continued for approximately 150 days. Furthermore, the sorption–desorption hysteresis increased with increasing residence time. The residence time didn't affect the molecular environment of the phosphate sorbed on allophane. The results indicated that the long-term duration of sorption and the increase in the irreversibility of sorption–desorption were caused mainly by internal diffusion. Phosphates sorbed on allophane were present as surface complexes with a small amount of surface precipitation. To understand phosphate sorption by the soil, not only phosphate sorption on the outer surface of soil aggregates, but also the intraparticle sorption of phosphate must be evaluated.

AUTHOR CONTRIBUTIONS

Kenji Sato: Conceptualization; data curation; formal analysis; investigation; methodology; visualization; writing—original draft. **Takehide Hama:** Conceptualization; data curation; formal analysis; funding acquisition; methodology; resources; software; supervision; writing—original draft; writing—review and editing. **Hiroaki Ito:** Formal analysis; methodology; resources; writing—review and editing. **Kayoko Kobayashi:** Formal analysis; methodology; resources; writing—review and editing. **Kimihito Nakamura:** Resources. **Shinji Sakurai:** Resources.

CONFLICT OF INTEREST STATEMENT

The authors declare no conflicts of interest.

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SUPPORTING INFORMATION

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