Phosphate sorption-desorption properties in volcanic topsoils along a chronosequence and a climatic gradient on the Galápagos Islands

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Abstract

Background: Phosphorus (P) retention behavior in the soil is one of the main factors driving ecosystem productivity and changes strongly during soil weathering. Volcanic soils are known for their high phosphate (PO4) sorption capacity (PSC). However, the changes of PO4 buffering properties and fixation processes in the course of their pedogenic development are not fully understood.

Aim: We investigated the short-term and longer-term PO4 sorption-desorption behavior in volcanic topsoils from the Galápagos Islands along a precipitation gradient (elevation sequence, 47–866 m asl) and a soil age gradient (chronosequence, 1.45–1070 ka) under humid climate.

Methods: Labile P (Mehlich-3, resin-P), P desorption (resin-desorbable P after 1 and 6 months incubation), PSC (sorption isotherms, equilibration time = 72 h) and sorption kinetics (4 h–62 days) were analyzed and compared against a broad range of topsoil parameters.

Results: Soils developed very high PSC within 4.3 ka of soil weathering (Langmuir Qmax = 18.2 g P kg⁻¹) due to the development of amorphous soil constituents. As the colloidal fraction changed to 2:1-type crystalline clays after 26 ka of soil weathering under humid climate, PSC declined rapidly, while labile P and resin-desorbable P reached a maximum. In older topsoils (> 165 ka), acidification and prevalence of aluminium (Al) and iron (Fe) (hydr)oxides led to increased P sorption again. Along the elevation sequence, increased precipitation favored the formation of amorphous constituents, resulting in a steep increase of P sorption capacity (from 0.9 to 19.9 g P kg⁻¹) from the arid lowlands to the very humid highlands.

Conclusion: Amorphous Fe and Al phases as well as Fe and Al bound to organic matter seemed to be the main driving factors for P sorption along the studied pedogenic gradients.

Key words: adsorption isotherm, andic, climosequence, pedogenesis, phosphorus, plant-available P
Phosphorus (P) is a crucial nutrient for all biomass production. Being a finite resource, the importance of understanding the P sorption dynamics in soils increases, as P is often not in readily available forms. Soil P behavior undergoes dramatic changes during pedogenic development. According to the model established by Walker and Syers (1976), plants tend to be nitrogen (N)-limited in younger soils, as enough P is provided by the parent material. As cations are leached and the solum thickness increases during pedogenesis, a shift to P limitation occurs (Laliberté et al., 2012; Walker & Syers, 1976). Advanced weathering results in low pH and prevailing (hydr)oxides of aluminium (Al) and iron (Fe) in the clay fraction, which can bind P very effectively. Strong P fixation is, therefore, one of the main challenges for agricultural production in (sub)tropical regions where highly weathered soils prevail, often necessitating high application rates of mineral P fertilizer (Syers et al., 2008). The latter not only poses a risk of cadmium (Cd) (and other toxic heavy metal) accumulation in the soils as apatite naturally contains Cd (McLaughlin et al., 1996) but may lead to water eutrophication if the soils’ retention capacities are exceeded and/or runoff and erosion occur.

Gradients of soil parent material age (chronosequences) and climate (climasesquences) are intriguing opportunities to study the evolution of soil P behavior in the course of weathering and soil formation. P sorption experiments along chronosequences formed on different parent materials such as alluvial sediments (< 20–500 years; Lair et al., 2009) and volcanic mudflows (77–1200+ years; Lilienfein et al., 2004) showed a build-up of soil P retention capacity in the early stages of soil development. An eight-fold decline of soil P over 120 ka of soil development under very wet conditions at the glacial Franz Josef Land soil chronosequence was associated with an increase of leaf N:P ratio and a general ecosystem decline (Richardson et al., 2004). Wardle et al. (2004) identified P limitation as the main driver of ecosystem decline observed along six different chronosequences. Furthermore, several P fractionation studies along chronosequences (e.g., Chen et al., 2015; Singleton & Lavkulich, 1987) and precipitation gradients (e.g., Brucker & Spohn, 2019; Galván-Tejada et al., 2014; Ippolito et al., 2010; Kitayama et al., 2000) were carried out to differentiate the mobile and immobile P fractions and their species. A recent study combining isotopic and sequential extraction methods along a precipitation gradient showed a dynamic turnover between the different fractions and concluded that while most of the P has a very slow turnover, a small, mobile fraction has a very rapid turnover (Helfenstein et al., 2018). These studies, however, lack a direct comparison of the soil-forming factors age and climate.

The pedogenesis of volcanic soils differs vastly from other soil ecosystems due to their unique mineralogical characteristics and, sometimes, the rapid development of andic properties (Ugolini & Dahlgren, 2002). In volcanic soils, which are generally known for their high fertility, exceptionally high P sorption capacities were found at early stages of pedogenesis up to 1000 years (Lilienfein et al., 2004). Amorphous constituents, such as allophanes and ferrihydrite, have especially strong P-binding capacity (Dahlgren et al., 1993). The binding mechanisms of anionic P forms to active Fe and Al are dominated by ligand exchange and inner-sphere complexes, rendering P sorption partly irreversible (Nanzo et al., 1993).

In contrast to most cations, P sorption behavior in soils is a rather slow process and therefore more difficult to investigate. Besides the rather fast ligand exchange, slow-term absorption processes can go on for months until an equilibrium state is reached (Munns & Fox, 1976). It is still unclear if clay minerals or rather Al/Fe oxides dominate the sorption of P in soils (Gérard, 2016). Brenner et al. (2019) recently pointed out that there is a lack of P sorption studies related to tropical soils, especially for Andosols where underestimation of P sorption maxima occurred frequently, as applied P concentrations were too low in most studies. Furthermore, their study could not show any relation between soil classification and Langmuir Qmax values for phosphate (PO4) sorption for a range of tropical soils. Axtoro et al. (2008) found a wide range of PO4 sorption maxima (0.048–52.4 g P kg−1) in topsoils with andic properties from the Azores, Portugal. However, the area is intensively used for agricultural production, and hence heavy fertilizer application may have influenced the results.

There is little information on the long-term changes of P behavior in the different pedogenic stages of volcanic soils along weathering sequences that include over 100 ka-old soils. The fate of P is well studied along a chronosequence in Hawaii (Crews et al., 1995), where hotspot volcanism led to the opportunity to study a soil age gradient from 0.4 ka to 4100 ka with approximate annual precipitation of 2500 mm and mean annual temperature of 16°C across the sites. Plant-available P increased strongly until 150 ka of soil weathering, and then declined gradually along with an increased portion of occluded P in the soils. However, the Hawaiian ecosystems are considerably influenced by the deposition of P-containing Asian dust, making it difficult to study pedogenic P behavior (Chadwick et al., 1999).

The Galápagos Islands feature a similar tectonic setting as the Hawaiian archipelago. Situated approx. 1000 km west of the South American coast, they have been formed by a volcanic hotspot and consist of mostly tholeiitic and alkaline basaltic lava flows and pyroclastic materials (Geist et al., 1998). As the Nazca Plate moves eastward over the Galápagos hotspot with a speed of approximately 51 km per Ma (Argus et al., 2011), a chain of islands has formed with an age gradient from west to east. In contrast to the Hawaiian chronosequence, where amorphous constituents prevailed until at least 400 ka of soil development before kaolinite and gibbsite dominated the clay fraction (Chorover et al., 2004), the chronosequence in Galápagos formed under less humid conditions and shows only a relatively short period of andic properties (< 4.3 ka) followed by a transition to 2:1-type clay minerals (26 ka), and 1:1-type clays and oxides in the later stages (≥ 166 ka; Candra et al., 2021). The effect on soil P behavior by these mineralogical differences during soil development has not been studied.

Additionally, the volcanic slopes show distinctive moisture gradients from arid lowlands to very humid highlands. This gives the opportunity to study the factors parent material age and climate side by side in a study area with low human impact, as the archipelago had no human settlements until the early 20th century (Izurieta et al., 2018), and 97% of the terrestrial area is currently protected as a national
MATERIAL AND METHODS

Study sites and sampling

The topsoil samples used in this study are described in detail in previous studies (Rechberger et al., 2020; Zehetner et al., 2020). Briefly, the topsoil samples were taken in 2016 and 2017 on four of the Galápagos Islands (Isabela, Floreana, Santa Cruz, and San Cristóbal), Ecuador. On Santa Cruz Island, samples were taken along a climatic gradient (elevation sequence) comprising three climatic zones (arid, humid, very humid) and two parent material types, that is, scoria and lava (E1–E6; Table 1). The age of the parent materials was estimated to be in the range of 45–165 ka (40Ar/39Ar Geochronology Laboratory, Oregon State University). On the other islands, we did not achieve to establish comparable elevation sequences due to the heterogeneity of the parent materials and their age differences. After the islands had formed, volcanic activity continued often for hundreds of thousands of years, resulting not only in different types of parent materials but also in large age differences, as preexisting deposits were often only partially covered by subsequent ones (Geist et al., 2014).

Total annual rainfall was estimated to be 100–500 mm in the dry lowlands and up to 1600 mm in the humid highlands according to iso-hyets developed by Trueeman and d’Ozouville (2010). Mean annual temperatures are 24°C in the low-lying arid zone, 21–23°C in the intermediate humid zone, and 19–21°C in the very humid zone in the highlands (Lasso & Espinosa, 2018). Paleoclimatic studies suggest that the climate on the archipelago was slightly cooler in the time span of around 20–80 ka BP with ocean surface temperatures of 2°C less, compared to the present, but also witnessed a warmer period 120–135 °C (Lasso & Espinosa, 2018).}

The aim of this study was to systematically evaluate the P sorption-desorption behavior along a chronosequence (1.45–1070 ka) formed on basaltic scoria and an elevation gradient (47–866 m) including sites formed on basaltic scoria and lava, respectively, to assess the changes of P sorption and readily available P with soil weathering. For this purpose, PO4 sorption kinetics and isotherms were determined, and a longer-term incubation experiment was carried out to test resin-desorbable P. Based on the study of natural soils, we also derived implications for agricultural soils.

2  MATERIAL AND METHODS

2.1  Study sites and sampling

Selective dissolution analysis was performed as follows. Sodium pyrophosphate extracts (pH 10) were used to estimate Fe and Al bound to organic matter (OM; Feo, Alp; McKeague, 1967). With this method, however, other relatively labile Al fractions may also be extracted (García-Rodeja et al., 2004). The Fe and Al associated with crystalline and non-crystalline hydrous oxides were extracted with citrate-bicarbonate-dithionite (Feo, AIp; Mehra & Jackson, 1958). The concentrations of Fe, Al, and silicon (Si) measured in ammonium oxalate extracts (pH 3) correspond to amorphous constituents (Feo, Alto, Silo; Schwertmann, 1964). The extracted elements were measured by inductively coupled plasma (ICP)-mass spectrometry (Agilent 7700, Agilent Technologies). Furthermore, P was measured by ICP–optical emission spectroscopy (ICP-OES; Optima 8300, Perkin Elmer) in ammonium oxalate extracts (pH 3; Pox) to estimate the amount of already sorbed P in the soil (Leinweber et al., 1999).

Mehlich-3 (M3) extraction (Mehlich, 1984) is a common method to account for “plant-available” or labile nutrients. Here, the procedure of Pierzynski (2000) was followed. The soil was extracted by shaking end-over-end (soil:solution = 1:10) with the M3 extracting solution for 5 min; the supernatant was filtered through Munktell folded filters (Grade 14/N; d= 150 mm; 80 g cm−1), and P was measured by ICP-OES. While the M3 method is a widely used test for agricultural soils due to its simplicity and cost-effectiveness, it does not represent exact plant-
TABLE 1  Site descriptions with selected chemical and physical topsoil parameters (modified after Rechberger et al., 2020); mean values ± standard deviation; n = 3; different letters indicate significant differences within the columns of one sequence (Tukey honestly significant difference; HSD); asterisks indicate significant differences between humid and dry comparison sites (Welch t-test)

| Site | Island | Rock age (ka) | Climate | Elevation (m asl) | Rock type | pH (in CaCl₂) | EC (µS cm⁻¹) | Corg (%) | DOC (mg kg⁻¹) | SSA (m² g⁻¹) | Particle size distribution |
|------|--------|--------------|---------|------------------|-----------|--------------|-------------|----------|---------------|-------------|--------------------------|
|      |        |              |         |                  |           |              |             |          |               |             | Sand (wt.%) | Silt (wt.%) | Clay (wt.%) | Allophane (wt.%) | Ferrihydrite (wt.%) |
| C1   | IS     | 1.45 ± 0.06  | Humid   | 371              | Scoria    | 6.7 ± 0.1 ab | 357 ± 27 a  | 25.4 ± 1.0 a| 960 ± 48 a   | 544 ± 27 a  | 48          | 35          | 17          | 4.7 ± 0.1     | 3.8 ± 0.1 c       |
| C2   | IS     | 4.29 ± 0.09  | Humid   | 375              | Scoria    | 6.3 ± 0.1 b  | 176 ± 29 b  | 18.3 ± 2.2 b| 616 ± 72 b  | 550 ± 48 a  | 41          | 36          | 23          | 7.8 ± 0.7     | 7 ± 0.4 a        |
| C3   | FL     | 26 ± 7       | Humid   | 344              | Scoria    | 6.7 ± 0.2 ab | 159 ± 28 b  | 8.9 ± 1.1 c | 530 ± 176 b | 550 ± 15 a  | 6           | 23          | 71          | n.d.         | 2.1 ± 0.1 d     |
| C4   | SC     | 165.5 ± 11.6 | Humid   | 497              | Scoria    | 5.8 ± 0.2 c  | 111 ± 20 bc | 6.7 ± 0.7 c | 367 ± 37 bc | 314 ± 10 b  | 3           | 35          | 62          | n.d.         | 4.8 ± 0.1 b     |
| C5   | CR     | 825.6 ± 11.2 | Humid   | 548              | Scoria    | 4.9 ± 0.1 d  | 50.4 ± 7.5 c| 5.5 ± 0.6 c | 157 ± 41 c  | 217 ± 14 c  | 3           | 37          | 59          | n.d.         | 2.6 ± 0.2 d     |
| C6   | CR     | 1070 ± 10    | Humid   | 586              | Scoria    | 3.9 ± 0.1 e  | 48.6 ± 3.6 c| 6.7 ± 0.8 c | 152 ± 13 c  | 223 ± 11 c  | 2           | 31          | 66          | n.d.         | 2.7 ± 0.1 d     |
| C3a  | FL     | 26 ± 7       | Very dry | 170              | Scoria    | 6.5 ± 0.1    | 46.1 ± 2.1 b| 21 ± 0.5 c  | 213 ± 37   | 115 ± 10 *  | 79          | 16          | 5           | n.d.         | 2.5 ± 0.4       |
| C5a  | CR     | 812.9 ± 9.6  | Dry     | 385              | Scoria    | 6.2 ± 0.1 *  | 139 ± 14 *  | 5.6 ± 0.5  | 351 ± 24 *  | 437 ± 14 *  | 3           | 29          | 68          | n.d.         | 1.8 ± 0.1 *     |
| E1   | SC     | Arid         | 47      | Lava             | 7.1 ± 0.1 a | 331 ± 67 a  | 12.1 ± 1.0 c| 1090 ± 222 a| 397 ± 27 ab | 46          | 47          | n.d.        | 0.5 ± 0.1 d    | n.d.            |
| E2   | SC     | Arid         | 57      | Scoria           | 6.3 ± 0.3 b| 115 ± 7.6 b  | 2.0 ± 0.1 d | 404 ± 59 a  | 116 ± 15 c  | 68          | 23          | 9           | n.d.         | 1.1 ± 0.3 cd    |
| E3   | SC     | Humid        | 424     | Lava             | 5.7 ± 0.1 b| 111 ± 18 b  | 9.8 ± 0.6 bc| 489 ± 51 b  | 417 ± 4 a   | 3           | 31          | 66          | n.d.         | 4.7 ± 0.2 bc    |
| E4   | SC     | Humid        | 497     | Scoria           | 5.8 ± 0.2 b| 111 ± 20 b  | 6.7 ± 0.7 c | 367 ± 37 b  | 314 ± 10 b  | 3           | 35          | 62          | n.d.         | 4.8 ± 0.1 b     |
| E5   | SC     | Very humid   | 800     | Lava             | 3.9 ± 0.1 c| 67.6 ± 9.6 b| 15.9 ± 2.2 a| 424 ± 75 b  | 424 ± 63 a  | 38          | 36          | 26          | 18 ± 0.6     | 9.8 ± 1.5 a     |
| E6   | SC     | Very humid   | 866     | Scoria           | 4.2 ± 0.2 c| 71.5 ± 0.5 b| 12.8 ± 0.6 ab| 314 ± 20 b  | 497 ± 21 a  | 26          | 38          | 36          | 17 ± 0.4     | 12.9 ± 2.2 a    |

Abbreviations: asl, above sea level; EC, electrical conductivity; Corg, organic carbon; DOC, dissolved organic carbon; SSA, specific surface area; n.d., not determined; IS, Isabela; FL, Floreana; SC, Santa Cruz; CR, San Cristóbal.

Climate zones according to PRONAREG–ORSTOM–INGALA (1987): arid = 12 dry months; very dry = 10 to 12 dry months; dry = 8 to 10 dry months; humid = 4 to 8 dry months; very humid = less than 4 dry months.

Values obtained from respective A-horizons (n = 1).

Calculated only for soils with andic properties, based on ammonium oxalate-extractable Si (7.1 × %Si₀).

Calculated based on ammonium oxalate-extractable Fe (17 × %Fe₀).
available nutrient contents and needs to be calibrated for actual plant P uptake for the respective soils, climate, and plant species (Mallarino, 1997).

### 2.3 P desorption

Resin-P was desorbed by anion exchange membranes before and after longer-term incubation of the soils with and without spiked P (Sharpley et al., 1989). The membranes mimic the uptake of PO₄-P by plant roots by acting as an ion sink and keeping the PO₄ concentration in the soil solution low, which promotes the mobilization of the labile P fraction in the soil. To this end, 1-g aliquots of soil were treated with five different concentrations of KH₂PO₄ solutions between 0 and 120 mg P kg⁻¹ and incubated for 1 and 6 months, respectively. Soil moisture was initially brought to 90% water holding capacity (WHC) to ensure even distribution of the P spiking solution and subsequently kept near 50% WHC during incubation at 21°C, which corresponds to the approximate mean annual temperature in the humid zone. For the subsequent P desorption, the protocol of Wuenscher et al. (2015) was followed. Briefly, the PO₄ was desorbed for 16 h by shaking the incubated soils end-over-end with 40 mL of Milli-Q water containing an anion exchange membrane strip (AMI-7001; Membranes International Inc.; size: 1 x 7.5 cm; anion exchange capacity: 0.49 mmol.e). After rinsing, the strips were placed in 40 mL of 0.5 M HCl or NaCl was preferred over HCl because the latter reduced the stability of the ammonium heptamolybdate complex during P measurement), shaken for 90 min, and the P was measured in the extractant. Photometric PO₄ determination was carried out using the molybdenum blue colorimetric method established by Murphy and Riley (1962). For lower concentrations (0.05–2.5 mg P L⁻¹), the adaptation by Wuenscher et al. (2015) was followed.

### 2.4 P sorption experiments

Longer-term sorption kinetics and short-term sorption isotherm experiments were conducted following the OECD guidelines (OECD, 2000). Based on the calculated PO₄ sorption capacity (PSC, see Chap. 2.5), P concentrations were chosen accordingly for the sorption isotherm experiments and kinetic studies. For sorption isotherms, soil samples (2 g) were treated with 20 mL PO₄ spiking solutions (KH₂PO₄ in 0.01 M KCl; concentrations: 0, 0.12, 1, 5, and 10 g P kg⁻¹) in 50 mL polypropylene (PP) centrifuge tubes with polyethylene (PE) caps. Soils with high P sorption capacity were additionally treated with 30 g P kg⁻¹ to obtain more accurate Freundlich and Langmuir isotherms. Potassium chloride (KCl) as a background electrolyte was preferred over CaCl₂ to avoid precipitation of calcium PO₄. For the sorption isotherms, microbial growth was not inhibited, as chloroform or toluene may increase dissolved P concentrations due to lysis of microbial cells (Reddy et al., 1998) and NaCl may alter the pH of the soil solution (Wolf et al., 1989). After shaking end-over-end for 72 h at 24 (±1)°C, samples were immediately centrifuged (RCF = 2714 g) for 15 min and filtered through 0.45 μm nylon syringe filters. After their pH was recorded, the filtrates were stabilized with 30 μl-concentrated HCl and stored in the dark at 4°C until measurement.

For the sorption kinetics experiment, 15 g of soil was weighed into 200 mL opaque PE bottles, pre-equilibrated in 0.01 M KCl solution for 24 h, and filled with PO₄-spiking solutions to 150 mL of the total solution. The solutions were spiked with NaN₃ at a concentration of 2600 mg kg⁻¹ soil to prevent microbiologically induced reducing conditions after longer periods of shaking that may provoke P remobilization. Due to the vast difference in sorption capacities, the soils were divided into three classes, and P loadings were adapted as follows: 50 g kg⁻¹ (C1, C2), 30 g kg⁻¹ (C3–C6), and 10 g kg⁻¹ (C3a, C5a). At each sampling step, 1–1.5 mL of suspension was drawn with a syringe and filtered directly (0.45 μm) to obtain at least 500 μl of filtrate. Sampling times were set at 4, 8, 24, and 72 h and 10, 30, and 62 days. After 72 h of shaking end-over-end, the samples were shaken horizontally twice a day for 30 min to limit the destruction of aggregates through physical force.

The amount of sorbed P was calculated by subtracting the PO₄-P concentrations of the filtrates from the concentrations in the spiking solutions, both determined colorimetrically.

### 2.5 Calculations and statistical analyses

All soil parameters and element contents referring to soil mass relate to oven-dry soil (105°C). The PSC was calculated based on the linear relationship of Al₀ and Fe₀ with the maximum P sorption discovered originally by Beek (1979) and further developed by van der Zee and van RIemsdijk (1988) to the equation:

\[
PSC = \gamma (A_l + F_{e0}).
\]

The factor \(\gamma\) was set to 0.5.

The degree of PO₄ saturation (DPS) was further calculated to evaluate the portion of P sorption sites that are occupied by P:

\[
DPS (\%) = \left(\frac{P_{c}}{P_{sc}}\right) \times 100.
\]

The P desorption coefficient was derived from the slope of the linear regression of the PO₄ desorption values at the different PO₄ spiking loads and describes the degree of availability of added P.

If not stated otherwise, values are depicted as mean ± standard deviation of the three field replicates for each site. Statistical analyses were performed in R, version 3.5.1 (R Core Team, 2018) and Excel, version 2016. Repeated measures ANOVA and Bonferroni post hoc test were calculated in SigmaPlot, version 13. For those tests, as well as for the two-tailed Welch-test, one-way ANOVA, and Tukey’s post hoc test, \(\alpha\) was set to 0.05. Tukey’s post hoc test was conducted with the R package agricolae. For stepwise regression with stepwise parameter selection, the R packages MASS and leaps were used.

Sorption isotherm data were fitted with the Freundlich model as well as the Langmuir model using the R-package PUPAIM. The lin-
earized Freundlich equation was used to fit the data:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e,$$

where $q_e$ = quantity of adsorbate sorbed by the soil at equilibrium state (g kg$^{-1}$), $C_e$ = adsorbate concentration in solution at equilibrium state (g L$^{-1}$), $K_f$ = Freundlich constant (L kg$^{-1}$), and $n$ = Freundlich exponent.

For the Langmuir model, the non-linearized equation was preferred, as the different forms of linearization may lead to alteration of the weight placed on the respective data points (Bolster & Hornberger, 2007):

$$q_e = \frac{Q_{max} \cdot b \cdot C_e}{1 + b \cdot C_e},$$

where $q_e$ = quantity of adsorbate sorbed by the soil at equilibrium state (g kg$^{-1}$), $C_e$ = adsorbate concentration in solution at equilibrium state (g L$^{-1}$), $b$ = Langmuir binding strength coefficient (L g$^{-1}$), and $Q_{max}$ = maximum sorption capacity of the soil (g kg$^{-1}$).

### RESULTS

#### 3.1 Dissolution analysis

The results of the selective dissolution analysis are summarized in Table S3. Along the chronosequence, there was a general trend toward an increase in the elements extractable by ammonium oxalate during the initial 4.3 ka with a subsequent decrease, as amorphous constituents became increasingly crystalline, indicated by decreasing Fe$_o$/Fe$_d$ ratios. Despite high C$_{org}$ contents at C3 (8.9 ± 1.1%), Fe$_o$ and Al$_o$ contents reached their minimum at this site. Ammonium oxalate-extractable elements showed an increasing trend with increasing precipitation along the elevation sequence. The same trend was observed for Fe and Al bound to OM (Fe$_o$, Al$_o$) as well as hydrous oxides (Fe$_p$, Al$_p$).

#### 3.2 P sorption and availability indices

P sorption and availability indices are reported in Table 2. The younger sites on Isabela Island (C1, C2) exhibited high P$_o$ contents of over 2 g kg$^{-1}$. While topsoil P availability was also high initially (1.45 ka), the quantity of mobile P decreased until 4.3 ka as indicated by a drastic reduction of more than 50% of M3- and resin-desorbable P. At C3, P was readily available again before available P decreased again with soil age. Except for the dry comparison site C3a, M3 and resin-P were in the same range for lower concentrations until around 15 mg kg$^{-1}$; above 15 mg kg$^{-1}$ (C1, C3), resin-P was significantly higher than M3-extractable P.

Along the elevation sequence, M3-extractable P was extremely high on the arid site E1 (1007 ± 266 mg kg$^{-1}$) and still high for non-agricultural topsoil on site E2 (50.4 ± 18.4 mg kg$^{-1}$). The exceptionally high labile P contents at site E1 may be of biogenic origin as a tortoise nesting site was found there. For the humid and very humid zones (E3–E6), labile P showed a decreasing trend.

PSC calculated from Fe$_o$ and Al$_o$ estimated PO$$_4$$^2$$-$P sorption maxima of over 10 g P kg$^{-1}$ for the sites C1, C2, C4/E4, E5, and E6. Lower
FIGURE 1  Freundlich sorption isotherms of Phosphorus (P) along the elevation sequence [right; elevation in parentheses; parent material: lava (black), scoria (gray)] and the chronosequence (left; rock age in parentheses; mean values ± standard deviation; n = 3).

P sorption maxima (< 5 g P kg⁻¹) were calculated for the sites in the arid climate zone (E1, E2) as well as for the dry comparison site on San Cristóbal (C5a). DPS, an indicator of the saturation of P sorption sites, stayed < 18% on all sites, except for E1 where it exceeded 340%.

3.3 | Sorption–desorption experiments

PO₄ sorption isotherms were conducted for both the chronosequence and elevation sequence (Figure 1).

Isotherms were fitted to the experimental data with the Freundlich and Langmuir isotherm models, with $R^2 \geq 0.95$ for both models (Table S4). Sorption maxima ($Q_{\text{max}}$), as determined by the Langmuir equation, varied between 2.42 and 18.21 g P kg⁻¹ for the chronosequence and from 0.92 to 19.93 g P kg⁻¹ for the elevation sequence. $Q_{\text{max}}$ followed the order C2 > C1 > C6 > C5 ≥ C4 ≈ C5a ≈ C3 > C3a indicating a rapid development of P sorption capacity within 4.3 ka under humid conditions followed by a steep decline (C3, 26 ka) and a subsequent slower build-up with increasing soil age (C4–C6).

The elevation sequence showed increasing PO₄ sorption with increasing humidity and soil acidification. Noteworthy are the extremely high sorption capacities (> 17 g P kg⁻¹) of the two andic topsoils in the very humid zone (E5, E6; Table S4). In contrast to the (very) humid sites, the topsoil formed on scoria under arid conditions showed considerably lower PSC than its counterpart formed on lava.

In addition to simple correlation analysis (Table S1), stepwise regression (Table S5) identified the parameters Fe₀, Al₀, Al₀′, Fe₀, Cₐ₉g, and total N ($N_t$) to be the most effective predictors for $Q_{\text{max}}$. For the chronosequence, Al₀ correlated well with $Q_{\text{max}}$ ($R^2 = 0.87$) and $R^2$ could be improved to 0.91 if $N_t$ was considered in the equation. For the elevation sequence, the sum of Al₀ and Fe₀ correlated well with $Q_{\text{max}}$ ($R^2 = 0.93$) and was, together with Cₐ₉g content, also considered useful to predict $Q_{\text{max}}$ if all sites were considered for the model.

FIGURE 2  Kinetics of P sorption along the chronosequence (mean values ± standard deviation; n = 3) for 62 days; respective P loadings indicated with brackets; different letters indicate significant differences within one site (Bonferroni post hoc test).

PSC values were generally higher than $Q_{\text{max}}$ values obtained from the sorption isotherm experiments, especially on the sites with high sand contents (E2, C3a), where PSC values were three times higher than $Q_{\text{max}}$ values (Tables 2 and S4). Accordingly, the kinetic study showed that P sorption continued significantly after 72 h (= 3 days) equilibration time at all sites, and the sorbed PO₄ portion at 3 days in comparison to 62 days varied between 55% and 76% (Figure 2). The ratio of PO₄ sorption after 3 and 62 days, respectively, (3:62 d) correlated strongly with Fe₀ ($r = 0.87, p < 0.01$) and Al₀ ($r = 0.70, p < 0.01$) as well as with Langmuir $Q_{\text{max}}$ sorption values ($r = 0.71, p < 0.01$) (Table S2). Up to 65% (at C1) of the PO₄ sorption at 62 days equilibration occurred within 24 h, whereas for the sites C3 and C4, it was less than 50% (Figure 2). These two soils were also the only ones showing a significant increase in sorption after 30 days suggesting that longer-term P fixation played a greater role in these soils.

To assess longer-term P fixation along the studied soil age gradient, resin-desorbable PO₄ was measured 1 and 6 months after the addition
of PO₄, respectively (Figure 3). Only a small fraction of the added PO₄ was desorbable in the Andosol (C2) and in the ≥ 165 ka old soils. At C4, P addition of up to 60 mg kg⁻¹ resulted in hardly any change of resin-desorbable P already after 1 month of incubation. On the dry comparison sites, P addition led to a clear increase of resin-extractable P. At C5a, significantly lower P values after 6 months in comparison to the 1-month incubation indicate secondary, slow-term P fixation. The slope of the linear regression, as indicated in the formulae embedded in Figure 3, corresponds to the P desorption coefficient and is a measure of the degree of P availability. Interestingly, no significant correlation between sorption maxima (PSC, Qmax) and the P desorption coefficient could be found (Table S2).

4 DISCUSSION
4.1 Soil development as driving factor for P sorption and availability

Along the studied chronosequence, the two youngest sites showed the highest P sorption despite their pH range of 6.3–6.7 where high P mobility is anticipated. Maximum sorption capacity was developed after 4.3 ka (C2); in line with this, labile P decreased from C1 to C2 (Tables S4 and 2). These patterns can be attributed to the development of andic properties in the soil, accompanied by the formation of allophane (as estimated by the Si₆ content) and ferrihydrite (Table 1), both known for their exceptionally high affinity to PO₄ (Dahlgren et al., 2004). Even though high OM presence may compete for sorption sites and hence reduce P sorption capacity, PO₄ might be sorbed directly by allophane and ferrihydrite or via OM-metal-PO₄ complexes (Guppy et al., 2005). PO₄ sorption to ferrihydrite was found to be less pH-dependent in the presence of humic acids (H. Wang et al., 2015). Similar effects have been reported for the abundance of base cations such as Ca²⁺ and Mg²⁺, where a synergistic effect for PO₄ sorption to ferrihydrite was found via ternary complex formation along with a reduction of pH sensitivity of the sorption process (Mendez & Hiemstra, 2020). Especially exchangeable Ca²⁺ was high in the two youngest topsoils with values of over 100 cmol_c kg⁻¹ (data derived from effective cation exchange capacity measurement by Rechberger et al., 2020) 160.5 ± 12.6, 128.0 ± 15.7, 82.2 ± 8.2, 34 ± 5.8, 8.7 ± 1.4, and 0.7 ± 0.1 cmol_c Ca²⁺ kg⁻¹ in C1, C2, C3, C4, C5, and C6, respectively).
As amorphous constituents diminished and 2:1-type clay minerals formed (Candra et al., 2021) during further soil weathering (C3; 26 ka) while still maintaining a soil pH > 6, P became highly mobile. Accordingly, the initially high contents of P\(_2\) (Table 2), which likely reflect the P sorbed by amorphous constituents, were drastically reduced at site C3. Also, Fe (hydr)oxide content was lowest in this soil as indicated by the Fe\(_2\) and Fe\(_3\) contents (Table S3). Strikingly, the topsoils at C3 and C4 exhibited similar PO\(_4\) sorption capacities (Q\(_{\text{max}}\) 3.9 and 4.15 g P kg\(^{-1}\), respectively; Table S4) but differed strongly in extractable P (Table 2) as well as in the degree of P availability as indicated by the desorption coefficients (Figure 3). Even though the soil at C4 was only slightly acidic (pH 5.8 ± 0.2), P availability was exceptionally low. This may be attributed to the very high binding strength of amorphous Fe (hydr)oxides, which accumulated strongly with soil weathering in C4 (165 ka; Table S3). Additionally, poorly ordered kaolinite was detected in C4 (Candra et al., 2021). Depending on the Fe content and crystallinity, kaolinite was found to sorb considerable amounts of PO\(_4\), where the pH optimum shifted from near-neutral at low PO\(_4\) concentrations to pH 3 at very high PO\(_4\) concentrations (Gérard, 2016). Upon further soil weathering, progressing crystallization processes, which generally reduce P sorption sites, were obviously counterbalanced by soil acidification enhancing PO\(_4\) sorption to Al and Fe (hydr)oxides in the oldest topsoils (C5, C6; 825–1070 ka). Even though maximum PO\(_4\) sorption was not correlated linearly with P availability (Table S1), there was overall a mirroring trend between the two. Sorption isotherms revealed much higher sorption capacities in the andic topsoils, compared to the ≥165 ka old topsoils while maintaining similar desorption behavior as the latter highly weathered soils. This can be attributed not only to favorable pH levels for P mobility in the andic soils but also to high OM and DOC contents and a competition on Al and Fe sorption sites (Meason et al., 2009). Furthermore, the organic P pool may enhance P availability in these soils (Guppy et al., 2005).

Due to its similar geological setting, similar chrono- and climosequences were established on the Hawaiian archipelago, which can serve as valuable comparison sites for the Galápagos Islands and vice versa to validate the respective observations and arrive at more general conclusions. Crews et al. (1995) proposed a unimodal trend of plant-available P with soil age after studying resin-P along a chronosequence (0.3 ka to 4100 ka, mean annual precipitation and temperature 2500 mm and 16°C, respectively). However, they did not measure resin-P for soils in the range of > 0.3 to < 20 ka, missing the drastic changes of soil sorption behavior in the early phase of soil weathering (Rechberger et al., 2020). In our study, we found that the natural P availability, as well as the degree of availability of added P, had a first maximum in the 1.45-ka-old soil before P was increasingly immobilized as andic properties became more expressed. While Crews et al. (1995) found plant-available P to be highest at the 150-ka-old site, our study showed the highest P-availability after 26 ka and lowest available P contents as well as very high P fixation after 165 ka of soil weathering. A possible explanation for these differences could be the relatively high rainfall levels in the Hawaiian chronosequence. Chadwick and Chorover (2001) showed that soil weathering is retarded not only under very dry conditions but also at high rainfall levels of over 2000 mm annually. Overall, the climatic conditions at the Hawaiian chronosequence are closer to our sites in the very humid zone of the elevation sequence, where similar pedogenic processes were observed, that is, rapid loss of base cations and resulting soil acidification as well as stabilization of metal-organic complexes (Chorover et al., 2004). Paleoclimate studies suggest, however, that the soils on the Hawaiian sites ≥ 20 ka were exposed most of the time to drier and cooler climates (Hotchkiss et al., 2000). Another explanation could be the significant atmospheric P inputs with Asian dust reported for the Hawaiian Islands (Chadwick et al., 1999). These rejuvenate the soils’ P biogeochemistry and may also delay the peak of P availability along the chronosequence. The Galápagos archipelago is hardly reached by Asian dust; however, dust inputs originating from the South American continent via prevailing south-east trade winds are likely but yet to be analyzed in terms of quantity and (elemental) composition.

Along the studied elevation sequence, P sorption capacity increased with increasing moisture availability at the higher elevations. The sandy topsoil at E2 (arid climate, on scoria) displayed an especially low P sorption ability, while the comparison site developed on lava (E1) already displayed similar P adsorption characteristics as the topsoils in the humid zone (E3, E4) along with a considerable accumulation of C\(_{\text{org}}\) and clay (Table 1). The latter was attributed to enhanced soil formation driven by increased water retention on the denser lava and a more favorable microrelief for the accumulation of plant residues on E1, compared to E2 (Rechberger et al., 2020). Noteworthy in this regard is the relatively high sorption capacity at site E1 even though the DPS exceeded 340%. For comparison, depending on soil type, proposed thresholds for risk of P release into the environment range from 10% to 25% in agricultural soils (Nair, 2014). The P sorption of the scoriaceous topsoil in the very humid zone (E5) exceeded that of all chronosequence topsoils. This can be attributed to the soil’s low pH favoring P immobilization in combination with very high contents of active Fe and Al sites (Shoji et al., 1993). Especially Al and Fe complexed with OM seem to play an important role for P sorption in this soil. The high prediction power of Al\(_2\) and Fe\(_3\) in the multiple regression models (Table S5) supports the hypothesis that OM-metal complexes had a significant influence on P sorption in the studied soils.

Despite low oxalate-extractable P in the topsoils of the very humid zone (< 0.5 g kg\(^{-1}\) in E5 and < 0.3 g kg\(^{-1}\) in E6) and highest PO\(_4\) sorption capacities, M-3-extractable P was in the range of the soils in the humid zone (E3, E4; Table 2). This is in contrast to a study along a precipitation gradient from 280 to 3100 mm on 150 ka old basaltic lava parent material in Hawaii (Helfenstein et al., 2018), where plant-available P decreased significantly with increasing precipitation, and along with that, biological P cycling predominated over geochemical processes. Accordingly, higher contents of OM and, hence, a higher fraction of P in the organic cycle might have elevated P availability in the very humid zone (E5, E6). Also, P\(_5\), as well as M3-extractable P, was higher in all sites developed on lava, compared to their respective scoriaceous counterparts. This could again be explained by higher OM contents found in the soils on lava (cf. Table 1), as the EDTA in the M3 solution is an effective extractant for ions sorbed to OM. By binding the cationic metals, especially Al, from OM-metal-P complexes, the EDTA may...
have led to $\text{PO}_4$ being released from those complexes. Vitousek and Chadwick (2013) studied the pedogenic processes along a 150-ka and a 4100-ka-old rainfall sequence on the islands Hawaii and Kauai, respectively. They found a close relationship between exchangeable Ca (extracted at pH 7) and resin-P, especially at the younger sites. We found that exchangeable Ca correlated significantly with resin-P ($r = 0.67$, $p < 0.01$) along the chronosequence, whereas no relation with M3-extractable P was evident in either of the sequences.

4.2 | Longer-term $P$ fixation processes

Our kinetic experiment showed considerable P sorption even after 3 days of equilibrium time. Especially the topsoils at sites C3, C4, and C3a stood out with a delayed $\text{PO}_4$ fixation in the kinetics experiment (Figure 2). In contrast to a study with topsoils from a variety of parent materials in Northern Ireland that found significant sorption in the period beyond 1 month (Maguire et al., 2001), our study showed little additional sorption between day 30 and 62 (except for C3 and C4). The results of the P desorption experiment (Figure 3) confirmed this trend. While most of the P fixation happened during the first month of incubation, desorption coefficients showed a significant decrease beyond 1-month incubation for the topsoils at sites C4, C3a, and C5a. Meanwhile, the younger topsoils (C1, C2) showed little change of P desorption coefficients between 1 and 6 months of incubation. In line with this, de Campos et al. (2016) studied $\text{PO}_4$ sorption kinetics in humid tropical soils and found that differences in kinetic trends between 21, 42, and 83 days were apparent in soils with low to medium $\text{PO}_4$ sorption capacities, while soils with high $\text{PO}_4$ sorption capacities showed little additional sorption after 7 days equilibrium time. Lower P sorption capaciries in the study of Maguire et al. (2001) might also be a reason for the differences in sorption kinetics, compared to our study. They used topsoils with an average PSC of 4.4 g kg$^{-1}$, well below the values in our study.

$\text{PO}_4$ sorption rates differ depending on aggregates and sorbent characteristics (X. Wang et al., 2000). Fast P sorption processes are followed by secondary, slow-term, and diffusion processes. $\text{PO}_4$ was found to be rapidly sorbed onto ferrihydrate, with a lightly slower sorption rate to goethite and hematite (X. Wang et al., 2013). This fits well with the differences in clay mineralogy at our study sites. We found more rapid $\text{PO}_4$ sorption at the youngest sites with soil constituents exhibiting high affinity to $\text{PO}_4$ (i.e., allophane) as well as in the highly weathered soils at the older sites, where the prevalence of Fe oxides and low pH provided favorable conditions for $\text{PO}_4$ sorption. In the intermediate-aged soils (C3, C4), however, slower-term diffusion into micro-aggregates could have played a greater role.

The relatively short desorption time of 16 h in our desorption experiment does not account for slow-term P replenishment of the soil solution, which might differ among the sites. This slow-term transfer to the labile P pool is, besides plant species and root architecture, an important aspect in the assessment of the ecosystem’s nutrient status (Syers et al., 2008). Furthermore, also the subsoils may contribute considerably to the (longer-term) P supply.

4.3 | Implications for agriculture

Compared to generalized M3 threshold values established for agricultural soils of the southeastern United States (Zhang et al., 2014), M3-extractable P was (very) low at all sites except for C1 and C3, which showed medium P status, and the arid sites of the elevation sequence (E1, E2), where P contents exceeded by far the threshold for high soil P status ($> 35\, \text{mg P kg}^{-1}$; Table 2). While P fertilization requirements for agricultural soils are typically assessed by measuring soil P status, the P desorption coefficient is of special interest, as it gives an estimation of the P fertilization efficiency and, hence, a more accurate assessment of the amount of P that needs to be applied to ensure optimum plant growth and, at the same time, prevent leaching of excess P to the surrounding environments. In Galápagos, agricultural activity is concentrated in the humid zones of the islands Santa Cruz and San Cristóbal (and to some extent also Isabela Island), where P fixation is of great concern as shown by the low P desorption coefficients ($< 0.2$; Figure 3) on the two first mentioned islands. In comparison, Zehetner and Miller (2006) applied the same method as in our study to determine P desorption coefficients of agricultural soils in the Andes and found values of 0.74 and 0.75 in an Entisol and 0.31 and 0.19 in an Andisol after 1 and 6 months of incubation, respectively.

As the applied method is rather labor-intensive, different approaches have been tested to estimate the P desorption coefficient in tropical soils (X. Wang et al., 2000). Soil clay content is most commonly used to predict the P desorption coefficient (Cox, 1994; Shuai et al., 2011) assuming higher P fixation as clay contents increase. In contrast, along the studied chronosequence, clay content did not correlate with P desorption coefficients at all. This may be attributed to the dramatic changes in colloidal constituents/clay mineralogy along with decreasing pH values in the course of soil weathering and highlights the exceptional nature and properties of volcanic soils. In the humid zone, higher levels of labile P corresponded to higher P desorption, whereas the dry comparison sites showed low labile P but high P desorption coefficients due to their low P sorption capacities. The discrepancies between P sorption capacity (Figure 1) and labile P (Table 2; Table S1) confirm the observation by Syers et al. (2008) that even soils with high P retention capacities may provide sufficient plant-available P over time.

Organic soil amendments, such as the incorporation of plant residues could help to reduce the requirement for high mineral P inputs while also reducing Al toxicity in the strongly acidic soils (Haynes & Mokolobate, 2001). Considering the high priority to protect the natural terrestrial and marine ecosystems of Galápagos, awareness should be raised in the communities to prevent over-fertilization on the more vulnerable sites.

5 | CONCLUSION

In a previous study (Rechberger et al., 2020), we found pronounced changes in key soil properties, such as electrical conductivity EC, cation
FIGURE 4  Development of P behavior along the chronosequence with lines (humid climate) and symbols (dry comparison sites) of normalized values: P sorption (≈ Langmuir $Q_{\text{max}}$), availability of added P (≈ P desorption coefficient after 6 months incubation), amorphous Fe and Si (≈ oxalate-extractable elements); changes of soil pH and mineralogy for the humid sites indicated in the graph along the timeline.

exchange capacity, and crystallinity of Fe (hydr)oxides, along the studied gradients of soil age and precipitation. This, in turn, led to logarithmically decreasing cationic (Cu) sorption ability with increasing weathering along these gradients. As expected, topsoil PO$_4$ sorption followed the opposite trend and increased with increasing moisture availability along the elevation sequence. The moisture gradient from arid to very humid had a greater effect on the development of PSC than the 1-million-year soil age gradient under humid conditions. This could be explained by the rapid depletion of base cations and the resulting soil acidification in combination with the formation of metal-a complexes and active Al and Fe sites under a very humid (and cooler) climate. The strong impact of precipitation was also evident at the dry comparison sites, which both showed much lower P sorption than their humid counterparts.

However, the changes of PO$_4$ sorption behavior and P availability were more complex along the chronosequence and very dynamic in the early stages of soil development. In Figure 4, the changes of topsoil P behavior along with changes in soil mineralogy and pH are summarized. The rapid build-up of amorphous aluminosilicates, that is, allophanes and imogolites (as represented by Si$_0$), and amorphous Fe (hydr)oxides (represented by Fe$_0$) was paralleled by high PO$_4$ sorption and reduced P availability after 4.3 ka of soil development. As amorphous soil constituents were replaced by 2:1-type clays (illite, vermiculite), P availability peaked after 26 ka of pedogenesis. With further soil weathering, acidification and increasing formation of Fe (hydr)oxides led yet again to increased PO$_4$ sorption, rendering soil P less available at the older sites of the chronosequence.

In contrast to the findings of Crews et al. (1995), who proposed a unimodal trend of P availability during ecosystem development, our results followed a bimodal pattern (with maxima at the youngest site, C1, and then again at site C3) and indicated shifts of sorption mechanisms and binding strengths in the course of soil weathering. Multiple regression models show that P sorption behavior was closely related to amorphous Al and Fe phases as well as Al and Fe bound to OM. The strong diversity of soil development has led to a wide range of PO$_4$ sorption behavior and P status in the soils, including sites with P scarcity and excess P, across the different Galápagos Islands and among different climatic zones. The observed contrasts in P sorption and availability are not only of interest for agricultural land management on the inhabited islands but may also have important bearings on natural ecosystem productivity and species distribution on this unique archipelago.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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SUPPORTING INFORMATION

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