Transformation of phosphorus forms and its regulation on phosphorus availability across differently degraded marsh soils

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Abstract

Soil phosphorus (P) is an essential nutrient that controls wetland productivity and ecological functions. However, the effects of soil P forms on P availability during wetland degradation are relatively unknown. Soil samples from differently degraded marshes, including relatively pristine marsh (RPM), lightly degraded marsh (LDM), moderately degraded marsh (MDM), and heavily degraded marsh (HDM), were collected to investigate the changes in soil P forms and its regulation on P availability in the Zoige Plateau, China. We observed that compared with RPM, the main changes in total P concentration were a significant increase of 31.6%–44.2% in the 0–30 cm soil layers of LDM and MDM, and the available P concentration increased in LDM and MDM but decreased in HDM with a lower P activation coefficient. Marsh degradation increased the concentration and proportion of dicalcium phosphates, P occluded in iron hydroxides, and organic P but decreased those of iron oxide surfaces adsorbed P and apatite P. Soil available P was mainly related to organic P and P non-occluded in iron oxide minerals that might also be non-negligible direct source of available P. The transformation from apatite P to organic P was an important regulation mechanism of P availability in soils during marsh degradation. This study revealed the risk of P limitation in heavily degraded marsh soils and established the mechanism by which marsh degradation significantly influences soil P availability. Therefore, some measure of on improving P availability should be implement for the ecological restoration of heavily degraded marsh in the future, such as grazing exclusion and the application of organic fertiliser.

Highlights

- Marsh degradation induced transformation from soil stable P to organic and labile P.
- Risk of P limitation occurred in heavily degraded marsh soil with low available P.
- Available P in alpine soils was mainly related to organic P and non-occluded P.
- Marsh degradation regulated soil P availability via transformation of apatite P.

Transformation of phosphorus forms and its regulation on phosphorus availability across differently degraded marsh soils

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Abstract: Soil phosphorus (P) is an essential nutrient that controls wetland productivity and ecological functions. However, the effects of soil P forms on P availability during wetland degradation are relatively unknown. Soil samples from differently degraded marshes, including relatively pristine marsh (RPM), lightly degraded marsh (LDM), moderately degraded marsh (MDM), and heavily degraded marsh (HDM), were collected to investigate the changes in soil P forms and its regulation on P availability in the Zoige Plateau, China. We observed that compared with RPM, the main changes in total P concentration were a significant increase of 31.6%–44.2% in the 0–30 cm soil layers of LDM and MDM, and the available P concentration increased in LDM and MDM but decreased in HDM with a lower P activation coefficient. Marsh degradation increased the concentration and proportion of dicalcium phosphates, P occluded in iron hydroxides, and organic P but decreased those of iron oxide surfaces adsorbed P and apatite P. Soil available P was mainly related to organic P and P non-occluded in iron oxide minerals that might also be non-negligible direct source of available P. The transformation from apatite P to organic P was an important regulation mechanism of P availability in soils during marsh degradation. This study revealed the risk of P limitation in heavily degraded marsh soils and established the mechanism by which marsh degradation significantly influences soil P availability. Therefore, some measure of on improving P availability should be implement for the ecological restoration of heavily degraded marsh in the future, such as grazing exclusion and the application of organic fertiliser.

Keywords: Zoige Plateau; Marsh degradation; Phosphorus forms; Phosphorus transformation; Phosphorus availability

1. Introduction
Phosphorus (P) plays a crucial role in maintaining microbial activity and plant growth (Cui et al., 2019a; Fan et al., 2021; Huang et al., 2015a; Oelmann et al., 2017; Sitters et al., 2019) and is anticipated to replace nitrogen as a limiting nutrient in natural ecosystems (e.g. wetland ecosystems) (Chen et al., 2020; Du et al., 2020; Turner et al., 2018; Vitousek et al., 2010). However, elevated P concentrations in soils and sediments are critical environmental problems (e.g. eutrophication) (Cheesman et al., 2012; Zhang et al., 2020; Zhou et al., 2019). In wetland ecosystems, P limitation risk and eutrophication primarily depend on labile P concentrations (e.g. soluble phosphate) that can be transformed into other P forms and then back again via biological or geochemical processes (Gao et al., 2019; Hu et al., 2022; Vitousek et al., 2010). Moreover, soil P transformation is strongly linked to carbon (C) cycles via the effect of the microbial community (Luo et al., 2021; Wang et al., 2021a; Zhai et al., 2022). The concentrations of P and the composition of P forms ultimately affect wetland ecological functions such as water conservation, CO₂ fixation, and climate regulation and health (Bai et al., 2020; Cui et al., 2019a; Liu et al., 2020; Sorrell et al., 2011). Therefore, soil P forms have received considerable attention in wetland ecosystems (Cheesman et al.; 2012; Dunne et al., 2011; Hamdan et al., 2012; Luo et al., 2021; Qu et al., 2021; Zhang et al., 2020).

The forms of P in soils generally exhibit evident variations owing to the differences and changes in the pedogenic environments of wetlands, such as parent material, hydrothermal, and vegetation conditions (Cheesman et al., 2010, 2012; Cui et al., 2019b; Negassa et al., 2020; Qu et al., 2021; Wang et al., 2016a). Presently, climate change, rodent harm, and human disturbances such as drainage, overgrazing, and aquaculture have led to the degradation of more than half of wetlands worldwide to some degree (Huisman et al., 2017; Nguyen et al., 2016; Ren et al., 2019; Zuquette et al., 2020), which has completely altered the conditions of hydrology, salinity, vegetation, and soil characteristics in some wetland ecosystems (Cheng et al., 2020; Li et al., 2022; Zeng et al., 2021; Zhao et al., 2017a). This has further affected soil P accumulation and its forms via P transformation processes such as sorption/desorption, precipitation/dissolution, immobilisation/mineralisation, and weathering (Augusto et al., 2017; Barrow, 2015; Khosa et al., 2021; Qu et al., 2021; Smith et al., 2021). For example, cultivation and drainage stimulated the transformation of organic P to inorganic P and decreased organic P in freshwater wetlands of the Sanjiang Plain region, China (Wang et al., 2006), and in peatland wetlands of Mecklenburg-West Pomerania and Saxony-Anhalt, Germany (Negassa et al., 2020; Schlichting et al., 2002), resulting in reduced P accumulation. Grazing increased soil P accumulation in wetlands within the dairy pasture of the Okeechobee Basin wetlands in the United States (Dunne et al., 2011). However, existing studies have primarily focused on the varying effects of P forms in wetlands with low elevations, such as estuaries and coastal areas (Cheesman et al.; 2012; Dunne et al., 2011; Hu et al., 2021; Zhang et al., 2020), and minimal studies regarding this varying effect have been conducted in alpine wetlands where environmental factors are complex and shifting (Li et al., 2022; Wang et al., 2022; Wu et al., 2021).

The changes in P accumulation and forms would further alter P availability in wetland soils (Hu et al., 2021; Huang et al., 2015a; Wang et al., 2021b). For example, Huang et al. (2015a) observed that the exotic invasive plant Spartina alterniflora significantly increased the concentrations of P extracted by 1.0 mol L⁻¹ NH₄Cl, bicarbonate/dithionite-extracted P, and P extracted by 0.5 mol L⁻¹ NaOH in the Yancheng wetland of eastern China, leading to an increase in available P. Similarly, Hu et al. (2021) observed that an increase in wetland salinity might significantly enhance labile P release owing to Fe-bound P reduction in the Min River estuary wetland, China. Furthermore, the primary forms of P in soils that regulate P availability differ owing to the differences in environmental conditions such as vegetation (Gama-Rodrigues et al., 2014; Hou et al., 2016). For example, some studies have revealed that the major sources of the available P pool are organic P, oxalate-extractable P, and iron-bound P in tropical forest, tropical acid farmland, and temperate meadow soils, respectively (Gama-Rodrigues et al., 2014; Melese et al., 2015; Yang et al., 2013). In addition, wetland ecosystems have unique environmental characteristics, such as perennial waterlogging and anaerobic conditions, and multiple functions compared with terrestrial ecosystems (Ouyang and Lee, 2020; Shen et al., 2019). However, limited information is available on the main P forms that regulate available P in different wetland soils, particularly in alpine wetlands.

Marsh wetlands on the Zoige Plateau with alpine and fragile environments are located on the eastern edge of
the Qinghai–Tibet Plateau, China, and have undergone degradation to different degrees because of natural threats and human activities over the past 60 years (Li et al., 2015, 2019; Shen et al., 2019). Several studies have revealed that alpine marsh degradation has decreased soil C sink function by increasing C emission fluxes in the Zoige Plateau (Ma et al., 2016; Pu et al., 2020; Zhou et al., 2020). Furthermore, total P and available P significantly affect the concentration of organic C in the Zoige peatland soils (Luo et al., 2021). However, it remains unclear whether marsh degradation impacts P accumulation and availability in soils, further inducing P limitation of primary productivity of alpine wetland ecosystems. Solving this question would contribute to effectively assessing soil P supply and further implementing the measures of soil P regulation to improve the C neutrality potential and promote the ecological restoration of degraded alpine marshes. Therefore, we hypothesised that marsh degradation would have a pronounce effect on the accumulation and transformation of soil P owing to the desiccation accompanied with plant community and overgrazing, further influencing soil P availability. To test this hypothesis, this study selected Zoige marsh wetlands with different degradation degrees and aimed to (1) quantify the changes in soil P and its forms for exploring the characteristics of P accumulation and transformation during marsh degradation, (2) determine how marsh degradation influences soil P availability, and (3) elucidate the regulation of soil P forms on available P under marsh degradation.

2. Materials and methods

2.1 Study area and marsh degradation gradient

The study area is located in the Huahu Science Spot, Haqingqiao, and Heihe Village on the Zoige Plateau, China, northeast edge of the Qinghai-Tibet Plateau (between 102°25′–103°0′ E and 33°30′–33°55′ N) (Figure 1). The area is at an average altitude of ~3450 m and subjected to an alpine cold temperate monsoon humid climate, the wet season between May and September, and the dry season between October and April. The mean annual temperature is 0.4–1.1 degC, with a minimum mean monthly temperature of -10.8 degC in January and a maximum of 10.9 degC in July. The annual precipitation is 647–753 mm, with a relative humidity range of 64~73% and a potential evapotranspiration of 1100–1274 mm. The landform is characterized by a combination of broad valleys, low mounds, lake depressions, terraces and river flood plains that are associated with the Black River system (a tributary of the Yellow River).

In this region, large marsh areas distribute on lowlands, terraces, and some underground stream gully zones due to the flat, low-lying ground and poor drainage of surface water. These marsh soils have the similar pedogenic conditions, such as soil parent materials of the Quaternary loose sediments from rivers and lakes, perennial waterlogging with water table depth greater than 10 cm, and the dominant hygrophytes of Carex L. (Carex muliensis, Carex lasiocarpa and Carex meyeriana). However, since the early 1960s, these marshes have occurred a regressive succession from original marsh to marsh meadow, meadow, desertified meadow with “black beach” due to climate change, rodents and human activities (Li et al., 2015, 2019; Huo et al., 2013; Zhao et al., 2017b). Taking comprehensively into account the diagnostic indices of the hydrologic conditions, dominant plant community and external disturbance (Huo et al., 2013; Wu et al., 2015), we divided degraded marshes into lightly degraded marsh (LDM), moderately degraded marsh (MDM) and heavily degraded marsh (HDM) according to the grading criteria of the degradation of relatively pristine marsh (RPM) (Table 1). Furthermore, the moderately and heavily degraded marshes are eroded by wind and easy to be sandy due to an increase in the area of surface soil exposed to sunlight. The soils of RPM, LDM, MDM and HDM are classified as Histi-Orthic Gleyosols, Molli-Orthic Gleyosols, Dark-Aquic Cambosols, Ochri-Aquic Cambosols in the Chinese soil taxonomy, respectively (Cooperative research group on Chinese soil taxonomy, 2001).

2.2 Soil sampling

To ensure degraded marshes from the degradation of RPM, we compared the remote sensing images recorded by the 1977 Landsat 2 MSS and 2015 Google Earth, and established sampling plots (100 m x 100 m) from differently degraded marshes following grading criteria of marsh degradation (Table 1) within the Huahu Science Spot, Haqingqiao, and Heihe Village in August 2017. After three subplots (1 m x 1 m) in each
sampling plot were randomly selected, we investigated the main habitat conditions (Table 2) and then clipped the aboveground parts of all standing plants (dead and alive) to measure the aboveground biomass. Subsequently, soil samples were taken at depths of 0–10, 10–20, 20–30, 30–40, 40–60, 60–80, and 80–100 cm in each subplot using a soil sampler (Eijkelkamp 07.53, SE, Netherlands) to determine soil bulk density and other properties. Three soil cores from the same soil depth in each plot were pooled to form a composite sample. 84 mixed soil samples were collected from 12 plots. Root biomass estimated from soil bulk density samples at a depth of 0–60 cm was washed through a 0.5 mm sieve to remove the soil, and all roots with a diameter of > 0.5 mm were collected and oven-dried at 65 degC (Table 2).

2.3 Soil basic physiochemical properties

The soil bulk density was calculated as the ratio of the oven-dried (105 degC) soil mass to the volume of the cylinder. The soil pH was determined in a soil-to-water mass ratio of 1:2.5, and particle size by the United States Department of Agriculture (USDA) were measured using the gravimetric method. The soil organic matter was analysed using the Walkley-Black potassium dichromate sulfuric acid oxidation method (Nelson and Sommers, 1982). The total N was measured using the semimicro-Kjeldahl method after complete digestion in CuSO_4-K_2SO_4-Se (100:10:1) at 400 degC (Bremner and Mulvaney, 1982), and available N was determined using NaOH-hydrolysation reduction-diffusion (Lu, 2000). The total P and available P were measured using the colorimetric molybdenum blue method via HNO_3-HClO_4-HF digestion and 0.5 mol L\(^{-1}\) NaHCO_3 (pH = 8.5) extraction, respectively (Murphy and Riley 1962; Olsen et al. 1954; Thomas et al. 1967). The basic soil physiochemical properties are listed in Table 3.

2.4 Sequentially extracted phosphorus forms

Given that the soils are derived from the calcareous parent material of lacustrine sediment, and the development of soils is weak in this study, we assumed that most of soil P was combined with primary minerals, existing in the form of “Calcium (Ca)-bound P”. Furthermore, the forms of Ca-bound P in the calcareous soils generally have a series of calcium phosphates with the complex transformation as follows: from dicalcium phosphate (i.e. CaHPO_4*2H_2O, Ca_2-P) to octacalcium phosphate (i.e. Ca_8H_2(PO_4)_6*5H_2O, Ca_8-P) and apatite (i.e. Ca_{10}(PO_4)_6F_2, Ca_{10}-P) (Jiang and Gu, 1989). Therefore, a sequential extraction procedure, provided by Jiang and Gu (1989) and modified by Adhami et al. (2006), was applied to determine P forms instead of the sequential extraction schemes according to Hedley et al. (1982) for distinguishing the series of Ca-bound P. Briefly, the NaHCO_3-soluble, CH_3COONH_4-soluble, NaOH-Na_2CO_3-soluble, citrate dithionite-soluble, and H_2SO_4-soluble phosphates was successively extracted with 0.25 mol L\(^{-1}\) NaHCO_3 (pH = 7.5), 0.5 mol L\(^{-1}\) CH_3COONH_4 (pH = 4.2), 0.5 mol L\(^{-1}\) NH_4F (pH = 8.2), 0.1 mol L\(^{-1}\) NaOH-Na_2CO_3, 0.3 mol L\(^{-1}\) CaH_2Na_2O_7plus 1.0 g Na_2S_2O_4 plus 1.0 mol L\(^{-1}\) NaOH (citrate dithionite) and 0.5 mol L\(^{-1}\) H_2SO_4, respectively. The above soluble phosphate was mainly composed of the form of Ca_2-P, Ca_8-P, aluminium oxide surfaces adsorbed P (Al-P), iron oxide surfaces adsorbed P (Fe-P), occluded P in iron oxide minerals (occluded P), and Ca_{10}-P, respectively (Jiang and Gu, 1989; Adhami et al., 2006), and was termed as Ca_2-P, Ca_8-P, Al-P, Fe-P, occluded P, and Ca_{10}-P respectively. Among these forms, Ca_2-P, Ca_8-P and occluded P are equivalent to NaHCO_3-extracted P, diluted HCl-extracted P and concentrated HCl-extracted P, respectively, in Hedley et al. (1982) scheme. The Ca_8-P, Al-P and Fe-P are inorganic P non-occluded in iron oxide minerals, and named as non-occluded P.

According to the results of Jiang and Gu (1989) and Adhami et al. (2006), the solubility and bioavailability of Ca_2-P are higher than those of non-occluded P and thus Ca_2-P and non-occluded P was named as labile P and moderate labile P, respectively, whereas occluded P and Ca_{10}-P with a lowest solubility and bioavailability was termed as slowly cycling P (recalcitrant P or stable P). Total organic P was obtained as the difference in P through 0.5 mol L\(^{-1}\)H_2SO_4 extraction between ignition and non-ignition soils (Saunders and Williams, 1955). The correlation coefficient (r = 0.990) between total P determined by H_2SO_4-HClO_4 digestion and the sum of various P forms (including organic P) was significant (p < 0.001), which showed that the values of various P forms were reliable in our study.

2.5 Data calculations and statistical analyses
The soil P activation coefficient and available P were characterized by P availability, and the P activation coefficient was the proportion of available P content in total P content (Li and Zhang, 1994; Sharma and Chowdhury, 2021). All statistical tests were performed or produced using SPSS 18.0 software (IBM Corp., Armonk, NY, USA). All data were tested using a z-test for normality before analysis. Data meet normality if absolute z-scores for skewness or kurtosis (skew or kurtosis values dividing their standard errors) are less than 1.96 and 3.29 in small (n < 50) and medium-sized (50 < n < 300) samples, respectively. Thus, some data were square root transformed (total P, P activation coefficient) or log10 transformed (P forms excluding Ca10P), exponent transformed (pH) to meet normality. Two-factor analysis of variance was conducted to determine the effects of marsh degradation and soil sampling depth on soil P and its forms; one-way analysis of variance (ANOVA) followed by Duncan’s test was used to compare the differences in the concentrations of available P, P activation coefficient and other basic physiochemical properties among differently degraded marsh soils. Difference was considered to be significant when p < 0.05. The figures except for the structural equation model were drawn in Origin 9.0 (OriginLab Corp., Northampton, MA, USA). Structural equation model, combining factor analysis and path analysis, was broadly employed to analyse the relationship between variables (including unobserved variables) based on the covariance matrix of variables in natural ecosystems (Bai et al., 2020; Hou et al., 2016; Lefcheck, 2016; Melese et al., 2015). Therefore, we used a structural equation model to further identify the effects of different P forms in regulating available P variations and the complex interactions among P forms in soils.

Theoretical and experimental studies demonstrated that soluble P (available P) was regulated by the direct and indirect effect of various P forms (Gama-Rodrigues et al., 2014; Hou et al., 2016; Liu et al., 2019; Melese et al., 2015), and the changes in soil environments (e.g. plant community and hydrography) also influenced the transformation of P forms to available P (Hu et al., 2021; Wang et al., 2021b). Thus, a conceptual structural equation models of the direct and indirect effects of soil P forms on available P under marsh degradation are constructed in Figure 2 based the following hypothesis: (1) marsh degradation has an indirect effect on available P by the mobilisation of stable and moderate labile inorganic P, and organic P; (2) the mobilisation of soil P in alpine wetlands mainly follow a process from organic P to inorganic P, and from stable P to moderate labile P and labile P in turn (Hou et al., 2016). The model was fitted using a combined data from the three sites, four types of marsh degradation, and seven depths, totalling 84 observations, because P forms and available P from the same profile have the significant differences (Table 4; available P of one-way analysis of variance: F statistic value 5.185, p < 0.05). Thus, the minimum sample size can meet a general rule that the ratio of the total number of samples to the number of variables is 5 times (Lefcheck, 2016). The categorical variables of marsh degradation were indicated by the wetland degradation index that was calculated by Qinghai Provincial Standards “Degradation classification of alpine marsh wetlands” (DB63-T-1794-2020). The wetland degradation index was equal to the average of water area ratio and importance value of hygrophytes. Structural equation model was performed using the SPSS Amos 24.0 software package (IBM SPSS Inc., Chicago, IL, USA) after all variables excluding marsh degradation were log10 transformed. The best-fit model was derived using the maximum likelihood based on the relative/normed chi-square test (χ²/df), normed fit index (NFI), comparative fit index (CFI), and root square mean error of approximation (RMSEA) of model fit (Hooper et al., 2008; Grace and Bollen, 2005). Model fits with χ²/df ranges from 2.0 to 5.0, NFI > 0.95, CFI > 0.95, and RMSEA < 0.08 can be accepted as a good structural equation model (Hooper et al., 2008; Grace and Bollen, 2005).

3 Results

3.1 Soil total phosphorus concentration

The total P concentration was significantly affected by soil depth and marsh degradation degree (p < 0.05, Table 4). However, no significant differences were observed between the interaction effect of soil depth and marsh degradation degree (p > 0.05, Table 4). As the soil depth increased, soil total P concentration generally decreased (Figure 3a–d). However, marsh degradation generally increased soil total P concentrations, and their significant changes in soil total P concentration were primarily embodied in the shallow soils at 0–30 cm depth (Figure 3a–d). The total P concentrations of shallow soils significantly increased by 31.6%–38.5%
and 32.9%–44.2% in LDM and MDM ($p < 0.05$), respectively, but slightly increased in HDM compared with RPM (Figure 3a–d).

3.2 Soil phosphorus forms and their proportions

Soil depth and marsh degradation degree also significantly affected the concentrations of other P forms, except for Fe-P ($p < 0.05$, Table 4). As the soil depth increased, soil organic P, Ca$_2$P, Ca$_8$P, Al-P, and occluded P concentrations generally decreased, whereas soil Ca$_{10}$P concentration slightly increased. The Fe-P concentration increased in LDM soil but exhibited no apparent trend in other soils (Figure 3a–d).

As illustrated in Figure 3a–d, the organic P concentration generally increased in degraded marshes. Over the entire soil profile, the average organic P concentrations in the MDM, HDM, and SDM were significantly higher (79.9, 78.1, and 82.1%, respectively) than those in the RPM ($p < 0.05$). Along the marsh degradation gradient, the Ca$_2$P and occluded P concentrations increased, reaching a maximum in the MDM (Ca$_2$P) and LDM (occluded P) soils and subsequently decreased; Fe-P concentration decreased, reaching a minimum in the MDM soil and subsequently increased; Ca$_{10}$P concentration decreased gradually, whereas no apparent changes in Ca$_8$P and Al-P concentrations were observed. Compared with those in the RPM soil, the Ca$_2$P and occluded P concentrations from the entire profile of degraded marsh soils increased by 46.7%–137.7% and 31.7%–49.3%, respectively, whereas Fe-P and Ca$_{10}$P concentrations decreased by 17.2%–32.2% and 15.3%–27.8%, respectively.

Based on the proportion of each P form (ratio of various P forms to total P), Ca$_2$P (including Ca$_2$P, Ca$_8$P, and Ca$_{10}$P) was the dominant P form for the whole soil profile. However, marsh degradation altered the proportion of the P form. Compared with those in the RPM soil, Ca$_2$P, occluded P, and organic P proportions in the 0–30 cm soil layer from degraded marshes increased by 21.9%–70.7%, 8.1%–15.8%, and 35.2%–64.0%, respectively, whereas Al-P, Fe-P, and Ca$_{10}$P proportions decreased by 10.7%–43.4%, 19.9%–60.5%, and 32.2%–50.7%, respectively (Figure 4a). The changes in soil Ca$_2$P, occluded P, organic P, Fe-P, and Ca$_{10}$P proportions at 30–100 cm depth were similar to those at 0–30 cm because of marsh degradation, whereas Al-P and Ca$_8$P proportions at 30–100 cm in degraded marsh soils irregularly changed compared with those in RPM (Figure 4b). Moreover, organic P in soils changed to the first dominant form at 0–30 cm depth, accounting for 41.2%–50.0% (Figure 4a).

3.3 Soil phosphorus availability

The available P concentration and P activation coefficient first decreased and then slightly increased in the LDM soil but gradually decreased in other soils as the soil depth increased (Figure 5a–b). Compared with RPM soil, the available P concentration was 17.0%–234.0% and 0.0%–85.1% higher in all soil layers from the LDM and MDM, respectively, with a significant difference at the 10–30 cm and 60–100 cm layers in the LDM and the 0–20 cm layers in the MDM ($p < 0.05$) (Figure 5a); it decreased by 4.0%–30.7% at the 0–40 cm depth of HDM but hardly changed at the 60–100 cm depth (Figure 5a). The variations in P activation coefficient between the RPM and degraded marsh soils exhibited a trend similar to that of available P (Figure 5a–b). Furthermore, the P activation coefficient in the surface (0–10 cm) soil was lower than the threshold of soil P deficiency of 2.0% (Li and Zhang, 1994).

3.4 Soil available phosphorus related to phosphorus forms

The conceptual structural equation model in Figure 2 was successfully fitted to our data, and the goodness-of-fit metrics were satisfied ($\chi^2/df$ was approximately 1, NFI > 0.95, CFI > 0.99, and RMSEA < 0.08; Figure 6a). All P forms explained 79% of the variations in soil available P. The non-occluded Ca$_8$P and Al-P exhibited a strong effect on the variations in soil available P, whereas the effect of non-occluded Fe-P was so minor that it did not exhibit in the fitting structural equation model (Figure 6a).

Soil organic P had a strong total effect (0.784) on the variations in available P and was the most important positive factor influencing the variations in available P, followed by non-occluded P (0.578), occluded P (0.447), Ca$_2$P (0.409) and Ca$_{10}$P (-0.093) (Figure 6b). This indicated that the variations of available P
were mainly related to organic and non-occluded P in alpine wetland soils. The direct effect of soil non-occluded and organic P on available P was slightly less than that of Ca$_{10}$-P (Figure 6b), suggesting that soil non-occluded and organic P also might be non-negligible direct source of available P. Marsh degradation exhibited a high direct effect (0.455) on the variations in Ca$_{10}$-P. Meanwhile, Ca$_{10}$-P presented a high indirect effect (-0.402) on the variations in available P through the effect of organic and non-occluded P in soils (Figure 6a–b). These revealed that marsh degradation significantly influenced soil P availability via the transformation from Ca$_{10}$-P to organic and non-occluded P.

4. Discussion

4.1 Marsh degradation increases soil phosphorus accumulation

In this study, the P accumulation (total P concentration) in all soil profiles ranged from 183.0 to 1433.8 mg kg$^{-1}$, with an average value of 683.3 mg kg$^{-1}$, indicating slight P enrichment according to the threshold of 500 mg kg$^{-1}$ (DeBusk et al., 2001). Similar to estuaries or coastal, depressional, and riparian wetlands (Huang et al., 2015a; Wang et al., 2006, 2013; Zhang et al., 2015), the P accumulation in all soils exhibited a decreasing trend with increasing soil depth (Figure 3a–d) because plant detritus was deposited, which led to P enrichment in surface soils (Meyerson et al. 2000; Reddy et al. 1999); however, no significant difference was observed in vertical variations among differently degraded marshes.

Marsh degradation primarily increased soil P accumulation at 0–30 cm depth (Figure 3a–d) owing to the comprehensive effects of hydrothermal environments, input of organic materials, and human activities. In RPM, long-term floods and highly anaerobic environments may stimulate the reductive dissolution of binding partners of phosphate (Kjaergaard et al., 2021) and increase soluble P concentrations in the overlying water (Dunne et al., 2011; Kröger et al., 2012; Qu et al., 2019; Zhou et al., 2019), further resulting in a significant loss of soluble P via runoff and leakage. However, marsh desiccation can greatly decrease the loss of soluble P, even under light or mediated grazing. Hence, the accumulation of shallow soil P in LDM and MDM significantly increased owing to marsh desiccation and a higher litter (approximate to aboveground biomass) input compared with RPM ($p < 0.05$, Figure 3a–c), which was inconsistent with the results that wetland degradation due to cultivation activities decreased soil P accumulation in the Sanjiang Plain, China (Wang et al., 2006) and Saxong-Anhalt, Germany (Schlichting et al., 2002). This might be because cultivation decreases the amount of soil P returned owing to crop absorption (Schlichting et al., 2002; Wang et al., 2006).

As meadows continued to degrade into desertified meadows, soil P accumulation in HDM was significantly lower than that in LDM and MDM. Two facts could explain this: (1) decrease in litter input and root biomass (Table 2) reduced the amount of soil P returned owing to overgrazing and severe rodent damage; and (2) decrease in vegetation coverage, soil clay, and organic matter (Tables 1 and 2) weakened the ability of soil fixation and increased P loss of dissolved P via runoff and leakage (Cui et al., 2018). Similarly, previous results demonstrated that the replacement of the native mangrove community by the invasive plant Phragmites australis reduced the ability of soil to adsorb immobilised P in the Minjiang River estuarine wetland, China (Wang et al., 2016a), and cultivations reduced P accumulation in the Sanjiang Plain wetlands, China (Wang et al., 2006). However, desiccation and excreta from bovines and sheep may supplement a certain amount of P to offset the partial loss of P. Thus, soil P accumulation in HDM was slightly higher than that in RPM, which is consistent with the result of Dunne et al. (2011) that soil P accumulation increased because of the input of organic fertiliser (cattle manure) in the Okeechobee Basin wetlands in the United States.

4.2 Marsh degradation influences the transformation of soil phosphorus forms

The most remarkable changes in P forms due to marsh degradation was an increase in organic P concentration and proportion, and organic P became the predominant P form in surface soils (Figures 3a–d and 4a–b) in Zoige, which is consistent with the results of the Min River Estuary, China (Zhang et al., 2015). However, some studies have revealed that the concentration and proportion of organic P in wetland soils decreased because cultivation and drainage stimulated the transformation from organic P to inorganic P and increased organic P loss (Negassa et al., 2020; Schlichting et al., 2002; Wang et al., 2006). Negassa et al. (2020)
demonstrated that the proportion of organic P was higher in long-term rewetted peatlands than in drained peatlands. This result was closely associated with marsh desiccation, combined with the changes in the plant community or overgrazing. The alpine marsh experienced light or moderate degradation, and the dense plant communities of hygrophytes and mesophytes, such as Carex, Blysmus sinocompressus, and Kobresia tibetica (Table 2), increased plant coverage, aboveground biomass (Table 2), and biodiversity and richness owing to water table drawdown (Zeng et al., 2021) and drying-rewetting (Wang et al., 2021b). Consequently, plant roots might take up more bioavailable inorganic P and then return more organic P (Huang et al., 2015b) via a high litter input compared to RPM, particularly in surface soil (Table 2). Although livestock foraged some plant shoots during grazing, this effect was very minor and hardly altered the above increase in soil organic P because of the limitation of flooding or excess water during the outdoor grazing season (wet season) in LDM and MDM. Alpine marshes are heavily degraded, and more livestock excreta can compensate for the decrease in organic P owing to livestock foraging and an increase in the bioaccumulation of organic P in surface soils during overgrazing. Furthermore, the improvement in aerobic environments in degraded marshes can enhance the microbial activity and decomposition rate of litter and livestock excreta (Gyaneshwar et al., 2002; Jones et al., 2018; Prado and Airoldi, 1999; Qian et al., 2010), which can induce labile organic P migration from the upper to lower layers of natural soil profiles through soil porewater to further increase the organic P concentration in subsurface soils (Pan et al., 2021).

Ca-P was not only the dominant inorganic P form but also the majority of total P for the whole soil profile in this study (Figures 3a–d and 4a–b) because the soil was derived from the calcareous parent material of lacustrine sediment, where the concentration of calcium carbonate equivalent ranged from 61.3 to 240.6 g kg$^{-1}$ (data from an investigation of soil series survey in Sichuan Province, China). For Ca-P forms, a remarkable change was observed in the concentration and proportion of available Ca$_2$-P increased under marsh degradation, whereas those of unavailable Ca$_{10}$-P decreased (Figures 3a–d and 4a–b). This is because marsh desiccation accompanied by the transition of the plant community or overgrazing may enhance the activity and/or quantity of phosphate-dissolving bacteria, such as Pseudomonas, Bacillus, and Erwinia (Liu et al., 2015; Susilowati et al., 2019) and increase the organic acids from plants, microbes, and/or livestock excreta (Almeida et al., 2020; Gyaneshwar et al., 2002; Miao et al., 2013; Nuryana et al., 2019). Improved phosphate-dissolving bacteria and organic acids can further stimulate the transformation of Ca$_{10}$-P to other labile inorganic P forms such as Ca$_2$-P, Ca$_8$-P, and Al-P (Almeida et al., 2020; Susilowati et al., 2019). Similarly, Jamil et al. (2016) revealed that Calcisols with greater biological activity under sugarcane crop cover had a high concentration of Ca$_2$-P in the estuary plains of Pakistan. However, the input of external P fertiliser from surrounding pasture uplands resulted in an increasing trend of exchange P (primarily Ca$_2$-P) with increasing hydroperiod in isolated Lake Okeechobee in Florida, USA (Cheesman et al. 2010), which was contrasting with our result, owing to a significant loss of soluble P (e.g., Ca$_3$-P) and lack of external P in RPM with perennial flooding. Another remarkable change in inorganic P forms was that marsh degradation decreased the concentration and proportion of soil Fe-P but increased those of soil occluded P similar to the changes in Al-P or Fe-Al-P during soil drying (Bai et al., 2019; Zhang et al., 2015). This is primarily because soil Fe$^{2+}$ is oxidised and transformed into colloidal ferric hydroxide and amorphous hydrated iron oxide (Ding et al., 2016; Wang et al., 2021b), which can adsorb and immobilise more phosphate during soil desiccation, resulting in the transformation from Fe-P to occluded P (Sah and Mikkelsen, 1986, 1989).

In summary, the differences in P forms among marsh soils with different degrees of degradation likely indicates that marsh degradation primarily induced the transformation from recalcitrant Ca$_{10}$-P to organic P and labile Ca$_2$-P via litter return or livestock excreta combined with marsh desiccation.
4.3 Marsh degradation alters soil phosphorus availability

Our results showed that P availability in alpine wetland soils decreased with soil depth owing to organic matter accumulation in shallow soils and ‘surface aggregation’ of soil nutrients, particularly surface soils (Ockenden et al., 2014; Wu et al., 2020). This result conforms with those of previous studies on freshwater and salt wetland soils (Negassa et al., 2020; Qu et al., 2019; Wang et al., 2008; Xu et al., 2012). Soil P availability hardly had significant differences in the vertical variations among differently degraded marsh soils. However, it generally increased along the marsh degradation gradient from the RPM, reaching a maximum in the LDM or MDM soil and subsequently decreasing to the lowest in HDM (Figure 5a–b). This pattern can be primarily attributed to the changes in factors affecting soil P availability, such as the hydrological regime, vegetation presence, and external disturbance (Duhamel et al., 2017; Ganjegunte et al., 2018; Kroger et al., 2012; Qu et al., 2018; Wang et al., 2021a, b). As RPM evolved into marsh meadow, the drying-rewetting and changes in vegetation community promoted the dissolution of slowly cycling P, decomposition of extracellular polymers and dead microorganisms containing labile monoester and diester P and plant debris containing phytate P, and the release of colloid-bound P through the breakdown of soil aggregates (Stevens and Tullos, 2011; Wang et al., 2021b). Thus, soil P availability was significantly higher in LDM than in RPM (Figure 5a–b), although the released soluble P might have been slightly lost because of inundation (Kroger et al., 2012; Zhou et al., 2019) in wet season. This was similar to the results previously observed in the water-level fluctuation zones of the Three Gorges Reservoir area, China (Wang et al., 2021b), estuarine wetlands with different vegetation in the Yellow River Delta, China (Qu et al., 2021, 2018; Xu et al., 2012), and managed wetland cells of Mississippi, USA (Kroger et al., 2012).

As marsh meadow continuously degraded into the meadow, the comprehensive effects of desiccation and vegetation resulted in a significant increase in soil P availability (Figure 5a–b) through the decrease in labile P loss, according to Kroger et al. (2012), and transformation from slow inorganic P and organic P to bioavailable P owing to the activation of organic acids from microbes and plant roots and debris (Hallama et al., 2019; Qualls and Richardson, 2000; Schelfhout et al., 2021; Wang et al., 2021a). However, when the marsh was heavily degraded, soil microbes significantly decreased by 39.3%–94.1% compared with the other three types of wetlands (Pu et al., 2022), and the activities of phosphomonoesterase, phosphodiesterase, and phytase were lower than those in the other wetlands by 50.5%–55.9%, 44.3%–52.6%, and 34.2%–70.5% (data from unpublished results), respectively. These results indicate that the mobilisation of soil in slowly cycling P was inhibited by the low activities of microbes and phosphatase through overgrazing and rodent damage stress. Therefore, P availability in the HDM soils decreased compared with that in RPM (Figure 5a–b), and P activation coefficient in surface soil was lower than the threshold of soil P deficiency (Figure 5b). This decrease indicated a risk of P limitation via plant biomass removal in HDM soils. Similarly, Shang et al. (2016), Teng et al. (2020) and Zhai et al. (2022) revealed that P limited plant growth in degraded alpine meadow and saline wetland ecosystems.

4.4 Regulation of soil phosphorus forms on available phosphorus under marsh degradation

Organic P can directly or indirectly transform into available P by mineralization, and some labile organic P, such as nucleic acids, phospholipids, and mononucleotides, might be directly available forms of P for plant uptake (Gatiboni et al., 2021; Tiessen et al., 1984). Thus, soil organic P not only acted as a dominant P form of regulating available P, but also was an important direct source of available P (Figures 6 a–b), because Zoige wetland soils had higher organic P concentration compared with other wetlands (e.g. estuarine wetland) soils (Cheesman et al., 2010; Li et al., 2018; Shao et al., 2019; Zhang et al., 2015). The moderate labile non-occluded P, similar to labile Ca$_2$-P, had a high regulation on available P, which was accorded to the reports from Gama-Rodrigues et al. (2014) and Hou et al. (2016), and also supported by a previous result exhibiting the significant correlations between available P and Al-P in albic-bleached meadow soils (Yang et al., 2013). Meanwhile, non-occluded P is easy to be mobilized into labile P (e.g. Ca$_2$-P) due to the activation of organic acids and phosphate-dissolving bacteria (Almeida et al., 2020; Susilowati et al., 2019), and indirectly regulate available P (Hou et al., 2016). Hence, soil non-occluded P was the second P form of regulating available P (Figures 6 a–b). Soil available P was primarily related to organic and non-occluded
P that might also be non-negligible direct source of available P in alpine wetland ecosystem. However, to confirm organic and non-occluded P considered as the direct source of available P, further examination of the contribution of soil organic and non-occluded P to plant P uptake is required in future studies.

Marsh degradation significantly influenced soil available P through the transformation from soil Ca₁₀⁻P to organic and non-occluded P, especially organic P (Figure 6a–b). This can be ascribed to the differences in hydrography, vegetation, and grazing between RPM and degraded marshes. For degraded marshes, soil organic P increased (Figures 3a–d and 4a–b) via plant uptake of bioavailable inorganic P and a high litter input in LDM and MDM with drying-rewetting and/or dense vegetation (Table 1 and 2); an increase in input of livestock excreta in HDM with overgrazing. Moreover, the risk of P limitation occurred with low available P in HDM. Some studies confirmed that the frequent drying-rewetting and organic acids from litter and/or organic fertiliser (e.g., livestock excreta) might induce direct and indirect transformation from apatite and organic P to labile and moderately labile inorganic P (Hallama et al., 2019; Schelfhout et al., 2021; Wang et al., 2021b), organic acids could dissolve occluded P into non-occluded P (Gatiboni et al., 2021; Touhami et al., 2020; Wang et al., 2016b), and organic and occluded P might be potential sources of available P in P-deficient soils (Turner et al., 2014; Yu et al., 2019). Additionally, the loss of carbon pools owing to marsh degradation may also result in the release of moderate labile inorganic P such as Fe-P and Al-P from organic matter (Yuan et al., 2015; Zhang et al., 2015). In this study, an increase in organic acids associated with a mobilisation of phosphate-dissolving bacteria and a loss of organic carbon (Gatiboni et al., 2021; Almeida et al., 2020; Susilowati et al., 2019; Pu et al., 2020) can improve the activation from soil Ca₁₀⁻P to organic P, non-occluded P and Ca₂⁻P under marsh degradation. Therefore, the transformation from Ca₁₀⁻P to organic P was an important regulation mechanism of P availability in soils during marsh degradation on the Zoige plateau.

5. Conclusions

Overall, our results verified our primary hypothesis that marsh degradation significantly influenced the accumulation and transformation of soil P owing to the desiccation accompanied with plant community and overgrazing, further altering soil P availability. Lightly and moderately degraded marsh soils had significantly higher total P and P availability than relatively pristine marsh soils. However, soil P availability in the heavily degraded marsh was lower than that in the relatively pristine marsh. Marsh degradation primarily induced the transformation from soil slow P to organic and labile P via litter return or livestock excreta combined with marsh desiccation. For alpine wetland ecosystem, soil available P was mainly related to organic and non-occluded P that might also be non-negligible direct source of available P. Marsh degradation regulated soil P availability via the transformation of apatite P to organic P. Our work illustrates that the risk of P limitation occurred in heavily degraded marsh soils with low available P. Future research should focus on measures to improve P availability for the ecological restoration of desertified meadows, such as grazing exclusion and the application of organic fertiliser. In addition, the variations of organic P fractions in differently degraded marsh soils also should be investigated to understand the transformation of organic P fractions and their effects on soil P supply, which has great significance for the ecological restoration of alpine degraded marshes.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability statement

Data available on request from the authors

References


Hosted file


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