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Distribution of inorganic phosphorus in profiles and particle-size fractions across an established riparian buffer and adjacent cropped area at the Dian lake

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Abstract

Riparian buffer can trap sediment and nutrients sourced from upper cropland and minimizing eutrophication risk of water quality. This study aimed to investigate the distributions of soil inorganic phosphorus (Pi) forms among profile and particle-size fractions in an established riparian buffer and adjacent cropped area at the Dian lake, South-western China. The Ca-bound fraction (62 %) was the major proportion of the Pi in the riparian soils. Buffer rehabilitation from cropped area had a limited impact on total phosphorus (TP) concentrations after 3 years, but has contributed to a change in Pi forms. At 0–20 cm soil layer, levels of the Olsen-P, nonoccluded, Ca-bound and total Pi were lower in the buffer than the cropped area; however, the Pi distribution between the cropped area and the buffer did not differ significantly as depth increased. The clay fraction corresponded to 57 % of TP and seemed to be both a sink for highly recalcitrant Pi and a source for labile Pi. The lower concentration of Pi forms in the silt and sand particle fraction in the surface soil was observed in the buffer area, which indicating that the Pi distribution in coarse particle fraction has sensitively responded to land-use changes.

1 Introduction

Eutrophication of surface water has been linked to runoff of excess nutrients from agricultural soils in many parts of the world. The improper management or use of phosphorus (P) fertilizer during cultivation enhances the P transport affecting the water quality, leading to alterations in water ecosystems (Sharpley et al., 2003; Troitiño et al., 2008). Riparian buffer is an efficient and economical tool to reduce agricultural non-point source pollution (Correll, 2000). Because of the filtering function of soil, the effectiveness of riparian buffers in reducing sediment and nutrient loading in surface and subsurface flows from cropland has been shown across many geographic regions (Dosskey et al., 2010; Keesstra et al., 2012).

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In the basin of the Dian lake, Southwestern China, agriculture development from conventional field crop to intensive horticultural crop has occurred for more than 20 years. Due to severe eutrophication of the Dian lake, a conservation program of Dian lake was established in 2009. Since its inception, thousands of hectare of buffers have been established by converting strips of cropland around the lake riparian zones to permanent vegetation. It is critical to know how the change of land-use affects soil P and its various forms which in turn affect its potential as a pollutant.

Much experimental evidence from research on both arable and buffer soils indicates that P are transported from soil to water with eroded soil (Abrams and Jarrell, 1995). Minimizing the risk of P enrichment of surface water bodies with P transported from agricultural soils will require specific attention to forms of P in soils. Mooer and Reddy (1994) reported that soil inorganic P may represent a greater risk for eutrophication than the organic forms of P. P distribution in chemical fractions can vary among land uses. Chalmers et al. (2001) observed only a slight increase in extractable P in buffer area as compared with crop field after 3–5 years set-aside period. Schroeder and Kovar (2006) reported that levels of the iron (Fe)-P fractions were higher in the buffer area than crop field over a 20 year period.

The chemical fractions of inorganic P include iron (Fe)-P, aluminum (Al)-P, calcium (Ca)-P, and occluded P according to Chang and Jackson (1957) fractionation procedure.

Kuo (1996) developed a sequential extraction technique for separating soil inorganic P into various forms, which integrated several fractionation procedures. Application of the Kuo fractionation to particle-size fractions can achieve better understanding on Pi transformations because of soil texture is an essential factor dominating soil P dynamics (Christensen, 1992).

In the present study we applied the Kuo fractionation to whole soil samples and particle-size fractions of different land uses. The objective of this study was to identify the transformations of the inorganic P forms in the plateau lake riparian anthrosols after land-use changes from cropped area to vegetation buffer. This will allow us to sus-

tainably manage these systems within the landscape and minimize non-point source pollution.

2 Materials and methods

2.1 Site description

The study area is located on the southeastern basin of the Dian lake in the mid-Yunnan Plateau (24°42′–46′N, 102°41′–43′E), China, which is the last large agricultural production area in the basin of the Dian lake. This semi-humid region within the sub-tropical climatic zone is characterized by a dry winter and a moist summer. Mean annual air temperature in the area is 14.7°C and mean annual rainfall is 953 mm, of which 80 % falls between June and October. The soil at the site is a paddy soil (Soil Taxonomy: Anthrosols, according to IUSS Working Group WRB, 2014). The cropped area has been in vegetable cropping (4–6 harvests per year) in plastic greenhouse for more than 20 years. After each harvest in a year, the field is rotary plowed to a 0.15 m-depth. A large amount of chemical fertilizer and animal manure is applied in those production area, resulting in P application of approximately 136–195 kg ha⁻¹ in each year. The buffer area, which is approximately 100–200 m wide, was converted from the cropped area in 2009 and planted indigenous tree plantation (*Salix babylonica* L. and *Metasequoia glyptostroboides*).

2.2 Soil sampling

All the soils in this study were collected in the Niulian (NL), Haigeng (HG) and Xinglong (XL) sites which are located at the southern part of the basin of the Dian lake in 2012 (Fig. 1). In the drought season, the shallow ground water levels were about 0.3, 0.7 and 1.2 m deep in the buffer at NL, HG and XL, whereas the shallow ground water levels were about 0.1, 0.4 and 1.0 m deep at NL, HG and XL in the rainy season, respectively. Because of drainage, the shallow ground water levels were below 1.0 m

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deep in the cropped area both at NL and HG. Soils were collected during April and May of 2012 to a depth of 100 cm at 20 cm-interval. At each site five cores were collected from randomly selected locations across a 50 by 50 m area of both the buffer and the cropped area with a soil drill. There were 15 cores samples of soil profiles for buffer and cropped area respectively. All soil samples were air dried, passed through a 2 mm sieve, and stored at 20 °C.

2.3 Laboratory analyses

Soil subsamples were ground with a mortar and pestle prior to total soil nutrient analysis. Subsamples were analyzed for pH (soil : water = 1 : 2.5); Soil organic carbon and total nitrogen were determined by the oil-bath potassium dichromate ($K_2Cr_2O_7$) titration method and the macro-Kjeldahl method (Shi, 1998). Particle size distribution of soil was determined by the hydrometer method (Gee and Bauder, 1986). Particle density of soil ($Mg\ m^{-3}$) was measured using the liquid pycnometer method, with desired water as the displacing liquid (Blake and Hartge, 1986). All the measurements were triplicated.

The particle-size fractionation followed a fractionation procedure of Christensen (1992) and Neufeldt et al. (2000). 50 g of soil in 100 mL deionised water was intensely shaken for 3 h to disaggregate the coarse-sand fraction. The coarse sand ($> 250\ \mu m$) was obtained by passing the suspension through a $250\ \mu m$ sieve, and dried at 40 °C. The remaining suspension was exposed to $1500\ J\ ml^{-1}$ ultrasonic energy using a probe-type disintegrator. The clay fraction ($< 2\ \mu m$) was freeze-dried after separating it from the fine sand and the silt by repeated centrifugation until the supernatant was clear. The fine sand ($250\text{--}50\ \mu m$) was obtained by passing through a $50\ \mu m$ sieve, and dried at 40 °C, whereas the remaining silt ($2\text{--}50\ \mu m$) in the remaining suspension was freeze-dried. Due to the low recovery of sand fractions, it was necessary to combine coarse-sand and fine-sand fractions to give one sample for chemical analyses.

Total soil P was determined using wet oxidation (Shi, 1998). Olsen P was determined by adding 20 mL of 0.5 M $NaHCO_3$, pH 8.5 extractant to 1.00 g of soil, shaking for 30 min, and filtering through Whatman 42 filter paper (Kuo, 1996). Inorganic P fractions were

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conducted by Kuo fractionation schemes (Zhang and Kovar, 2000). A 0.5 g soil sample was placed in a 50 mL centrifuge tube and sequentially extracted with 25 mL each of 1.0 M NH_4Cl , 0.5 M NH_4F (loosely bound Pi), and 0.1 M NaOH (non-occluded Pi) in that order. Each extraction was performed for 0.1, 1, and 17 h using a horizontal shaker followed by centrifugation at 3300 rpm for 15 min, respectively. The occluded Pi was subsequently extracted by adding 20 mL of 0.3 M $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, 2.5 mL of 1 M NaHCO_3 , and 0.5 g $\text{Na}_2\text{S}_2\text{O}_4$ to the residue in each tube and heating for 15 min at 85 °C, followed by centrifugation at 3300 rpm for 15 min. The calcium-bound Pi was subsequently extracted by adding 25 mL of 0.25 M H_2SO_4 followed by centrifugation at 3300 rpm for 15 min. All the measurements were triplicated.

2.4 Statistical analysis

All data was submitted to analysis of variance (ANOVA) and treatment means were detected using Fisher's LSD and Duncan's Multiple Range Tests. Statistical analyses were performed with the PASW Statistics 17.0.2 for Windows (SPSS Inc., 2009).

3 Results and discussion

3.1 Land-use effects on soil physicochemical properties

Summarized results from particle size analysis are presented in Fig. 2. The soils in the Xinglong (XL) and Haigeng (HG) sites have less clay than those at the Niulian (NL) sites. Soil textures under the buffer and cropped fields were determined as a clay in all soil depths at the NL sites, whereas a clay loam both at the XL and HG sites, according to soil texture classification of USDA system. The higher percentages of sand in the buffer upper soils (0–40 cm) at the NL and HG sites indicated that the buffer has acted as a sink for coarse sediments but not for finer particles.

Soil organic carbon (SOC) and nitrogen (N) concentrations at the NL sites were significantly higher than the HG and XL sites (Fig. 3). This was probably related to the

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shallower groundwater table and higher clay content of the soils (Parton et al., 1987). Organic carbon and nitrogen concentrations in the buffer soils (0–100 cm at the NL sites and 0–20 cm at the HG and XL sites) were significantly higher than in the cropped soils (Fig. 3). The greater accumulation of plant debris by the revegetation and the slower rate of organic matter decomposition by the lack of cultivation might have contributed to the build up of soil organic carbon (SOC) in the buffer soils (Reddy et al., 2008). There was a significant relationship between SOC and N at the research area. Several studies have indicated that the rate of SOC accumulation is controlled by the rate of N accumulation in the early stages of vegetation regeneration of abandoned agricultural soils (Knops et al., 2000; Poulton et al., 2003). Differences of SOC and N between the cropped and the buffer soils were less significant as depth increased at the HG and XL sites but at the NL sites. The organic-rich subsurface soil in the buffer area at the NL sites may be due to the buried river channel sediment or peat.

The higher pH of surface soil (0–20 cm) in the cropped area reflected the regular fertilization increasing salt concentration in the soil solution (Godsey et al., 2007). In addition, the pH of the NL soils was 0.2 to 0.5 higher than the pH of the XL and HG soils. Compared as the cropped soils, the lower pH of subsurface buffer soils in the NL sites may be partly explained as the higher soil organic matter which can be a potential source of soil acidity (Coleman and Thomas, 1967). Soil particle density (ρ_d) of the NL sites was significantly lower than that of the XL and HG sites.

3.2 Land-use effects on P fractions in whole soil samples

Fertilizer application has a significant effect on increasing the available P forms in the cropped soils (Fig. 4). Comparison of Olsen-P levels in the cropped and buffer soils indicated that higher amount of available P (99.3 mg kg^{-1}) was accumulated in topsoil (0–20 cm) in cropped areas. The higher extractable P in the cropped soil implicated that it would be more easily depleted by movement from the soil surface by erosion and leaching (Sharpley et al., 2003). Also, non-occluded, Ca-bound and total inorganic P (Pi) levels at 0–20 cm layer were higher in the cropped soil than in the buffer soil.

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This may be due to the regular fertilization in surface soil for crop growth. Sharply and Smith (1985) and Negassa et al. (2009) also reported amounts of soil Pi increased with fertilizer application, with non-occluded and Ca-bound Pi constituting the major proportion of the change. Neufeldt et al. (2000) reported that fertilizer P has also been sorbed in a highly recalcitrant form and suggested that all P fractions are linked. No significant difference in loosely-bound and occluded Pi and total P distribution between these cropped and buffer soils was observed in this study. However, Sharply and Smith (1985) reported that cultivated soils had lower occluded Pi as compared with their virgin analogues. Cooper and Gilliam (1987) reported that topsoil total P concentrations has significantly increased in riparian areas as compared with an adjacent cropland over a 20 year period.

Furthermore, Olsen-P, Pi fractions and TP levels were higher in the 0–20 cm samples compared to other sampling depths in both areas, suggesting that P was stratified in both areas. Within each sampling site (cropped or buffer soil), TP concentrations decreased as sampling depth increased. Loosely-bound, non-occluded, occluded and total Pi differed significantly in the 0–40 cm depth but not below the 40 cm depth in these soils. Additionally, the percentage of loosely-bound, non-occluded Pi also decreased as sampling depth increased except occluded and Ca-bound Pi (Fig. 4).

Distribution of total Pi in the soils was, on the average, 5 % loosely-bound, 9 % non-occluded, 24 % occluded and 62 % Ca-bound. High levels of Ca-P in these soils suggested that at least some of the soil's alluvial parent material probably originated from the limestone bedrock in the area above the catchment of the Dian lake (Schroeder and Kovar, 2006). Except for the occluded Pi in 0–20 cm layer, the percentages of Pi fractions did not differ significantly between the cropped and the buffer soils. Compared with the cropped area topsoils (0–20 cm), the higher percentages of occluded Pi was found in the buffer topsoils (Table 1). In general, this observation suggests the increasing possibility of occlusion of P with Fe/Al hydrous oxides or formation of insoluble Al/Fe phosphates in buffer soils relative to cropped soils.

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Although subsoil Ca-P (below 0–20 cm) alone did not differ among those areas, the others Pi fractions were greater in the XL soils than in the HG and NL soils (Fig. 4). The NL soil had the lowest loosely-bound, non-occluded, occluded and total Pi (Fig. 4). However, total P concentration did not differ significantly among those areas. Soil TP concentration was positively correlated with clay content ($r = 0.508$, $n = 30$, $P < 0.01$). However, there was not a significant relationship between Pi fractions and clay content. Occluded Pi was negatively correlated with soil pH ($r = -0.621$, $n = 30$, $P < 0.01$). Furthermore, there were strong correlations among the P fractions.

3.3 Land-use effects on inorganic phosphorus fractions in particle-size fractions

Although the error of individual fractions was up to 12 %, the sum of all Pi fractions in the particle-size fractions was similar to Pi in the whole soil (Table 2). In these soils, the proportion of P froms decreased continuously with increasing particle size of the fractions. The high proportion of P froms in the clay fraction reflected that the clay fraction not only seemed to be a sink for highly recalcitrant Pi but also a source for labile Pi forms (Neufeldt et al., 2000; Suñer and Galantini, 2015). The concentrations of Pi forms in the sand fraction were both significantly lower than in the clay and silt fraction, whereas the concentrations of Pi forms did not differ significantly between the clay and silt fraction. The higher concentration of TP in the clay fraction could be attributed to the enrichment of organic phosphorus in the finer particle size class. Christensen (2001) reported that in arable soils, clay-sized complexes ($< 2\mu\text{m}$) have the largest concentrations of OM, silt-sized ($2\text{--}20\mu\text{m}$) particles are less enriched, and size separates $> 20\mu\text{m}$ usually contain little OM.

Figure 5 shows the complex distribution of surface soil (0–20 cm) Pi fractions in the particle-size fractions under different land-use types. Buffer rehabilitation had no effect on the concentration of Pi fractions within clay fraction, but the coarse particle fraction exhibited an decrease in the concentration of loosely-bound, nonoccluded, occluded (not in the silt fraction) and Ca-bound Pi. Chen et al. (2015) also reported that topsoil

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nutrients stored in coarse particle fractions were more sensitive than those stored in the fine fraction to soil recovery. However, Suñer et al. (2014) reported that the coarse fraction of the cultivated field had low levels of Pi as a consequence of the particulate organic matter decomposition and coarse mineral particle weathering. The reduction of Pi in coarse particle fractions in the buffer soil could have a positive influence on the function of the buffer to act as a sink for P. In the cropped soil, however, the accumulation of labile Pi in coarse particle fractions was considered to be more susceptible to lose P via leaching. Zheng et al. (2003) reported that soil particles containing high amounts of extractable P suggested to have a higher P release potential. The higher nonoccluded and occluded Pi in the sand and silt fractions of the cropped soil indicated that the dissolved fertilizer P was easily transformed into more stable Pi forms (Neufeldt et al., 2000). The significant accumulation of Ca-bound Pi in the sand and silt fractions of the cropped soils as compared to the buffer soils could be explained by the presence of undissolved P fertilizer granules in these fractions, because of rock phosphate had been often used together with soluble P fertilizers in these areas. Tiessen et al. (1983) also observed a similar enrichment of recalcitrant P in the coarse silt fraction of a cropped soil. Below 20 cm, the concentrations of Pi fractions in the particle-size fractions did not differ significantly between the cropped and buffer soils.

To enable a better understanding of P transformations in those riparian soils, regardless of land uses, the average proportions of the P fractions in the particle size fractions are presented in Fig. 6. Compared with the sand and silt fractions, the proportions of occluded Pi was increased in the clay fraction, which should be related to the increasing adsorption to Fe/Al hydrous oxides with finer particle size classes. Agbenin and Tiessen (1995) and Neufeldt et al. (2000) also reported a similar change of the proportions in entisols, inceptisols and oxisols from Brazil. The proportions of Ca-bound Pi in the clay and silt sand fraction were significantly lower than that in the sand fractions, which suggested that the increase in occluded Pi with finer particle size fractions may be at the expense of Ca-bound Pi. The occluded Pi, which consisted of insoluble Al/Fe

phosphates, are progressively sequestered in finer particle size fractions and therefore more difficult to extract.

The proportion of nonoccluded Pi was nearly twice as high in the silt and clay fractions as compared to the sand fractions, which could be attributed to their comparatively higher amounts of discrete Fe/Al hydrous oxides. However, Neufeldt et al. (2000) reported that the proportions of NaOH-Pi showed no consistent trends between the particle-size classes. In contrast, the proportions of loosely-bound Pi did not differ significantly between the particle-size classes, which suggested the potential of labile Pi lose would not decrease with decreasing the particle-size fractions.

4 Conclusions

Inorganic phosphorus forms and their distribution in particle-size fractions were different between the conservation buffer and the continuously cropped area. Amounts of Pi increased in the surface soil of crop field associated with fertilizer P application, with nonoccluded and Ca-bound Pi constituting the major proportion of the change. Lower concentration of Pi forms in the silt and sand particle fractions was found in the surface soil of the buffer, suggesting that P in these fractions had a lower release potential. The enrichment of labile Pi in the coarse particle fraction of cropped soil implicated that it would be more easily depleted by movement from the soil surface by leaching. More important, the application of particle-size separation of P forms determination can be represented to a better understanding of soil P distribution between different land uses.

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Table 1. Percentage of inorganic phosphorus forms on total Pi at 0–20 cm soil layer of different sites. Data followed by the same lower case letter at same column indicate that the percentage of Pi forms were not significantly different at $P < 0.05$ according to lsd test.

	Percentage of Pi forms on total Pi			
	loosely-bound	non-occluded	occluded	Ca-bound
Niulian site				
Buffer area	5c	5c	26b	64b
Cropped area	4c	4c	23c	69a
Haigeng site				
Buffer area	7b	11b	31a	51d
Cropped area	6b	12b	26b	56c
Xinglong site				
Buffer area	11a	18a	28ab	42f
Cropped area	11a	18a	25c	46e

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Table 2. Phosphorus forms in particle-size fractions of the riparian soil. For each phosphorus form, data followed by the same capital case letter indicate that the P concentrations between particle size fractions were not significantly different at $P < 0.05$ according to lsd test. Data in parentheses followed by the same lower case letter indicate that the proportion of P forms between particle size fractions were not significantly different at $P < 0.05$ according to lsd test.

P forms	Particle size classes			Σ g kg^{-1}	Whole soil g kg^{-1}
	$< 2 \mu\text{m}$ g kg^{-1}	$2\text{--}50 \mu\text{m}$ g kg^{-1}	$50\text{--}2000 \mu\text{m}$ g kg^{-1}		
loosely-bound	0.05A(49a)	0.05A(38b)	0.04B(13c)	0.05	0.05
non-occluded	0.09A(46a)	0.11A(44a)	0.06B(10b)	0.09	0.09
occluded	0.25A(53a)	0.23B(33b)	0.19C(14c)	0.24	0.21
Ca-bound	0.52A(51a)	0.51A(34b)	0.42B(15c)	0.50	0.48
TPi	0.91A(51a)	0.91A(35b)	0.71B(14c)	0.87	0.82
TP	1.75A(57a)	1.25B(28b)	1.21B(15c)	1.48	1.39

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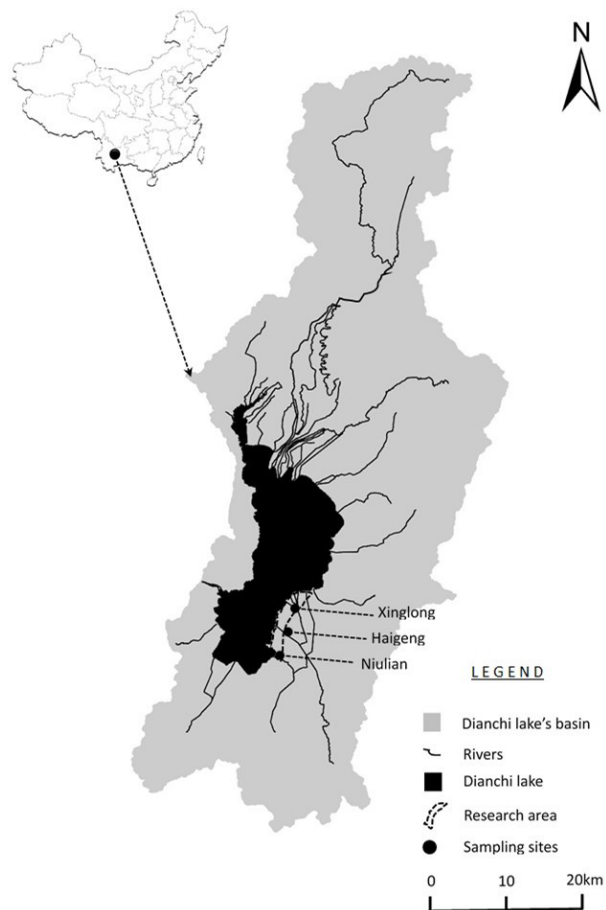


Figure 1. Map of the research area with sampling sites

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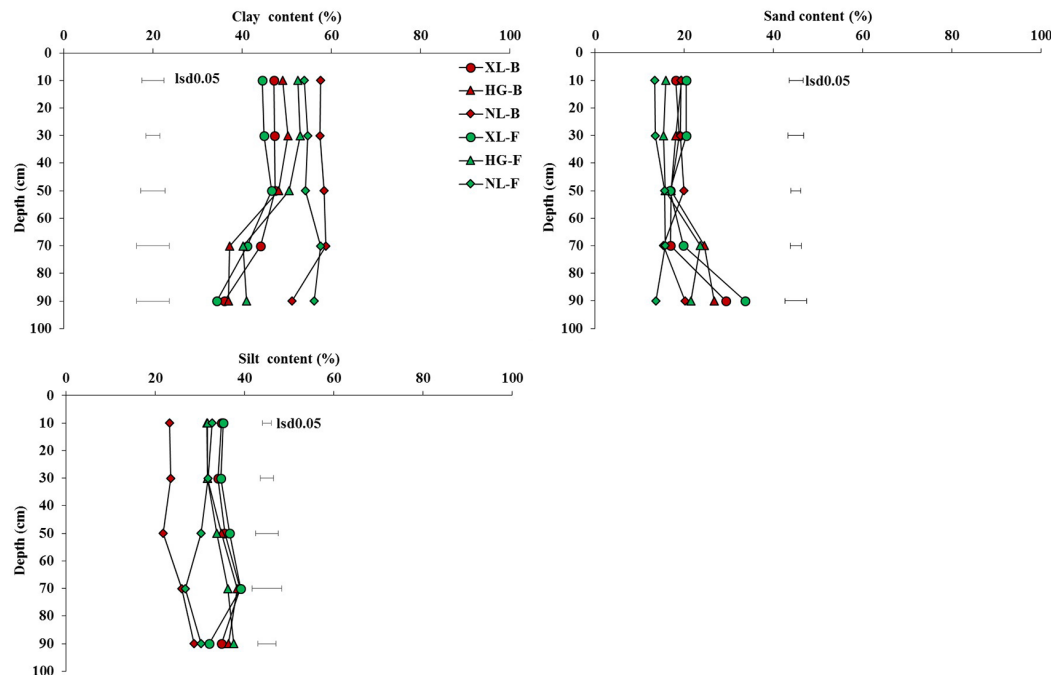


Figure 2. The distribution of soil particle size fractions in profile at different land use sites. Buffer of Xinglong site (XL-B); Buffer of Haigeng site (HG-B); Buffer of Niulian site (NL-B); Cropped field of Xinglong site (XL-F); Cropped field of Haigeng site (HG-F); Cropped field of Niulian site (NL-F).

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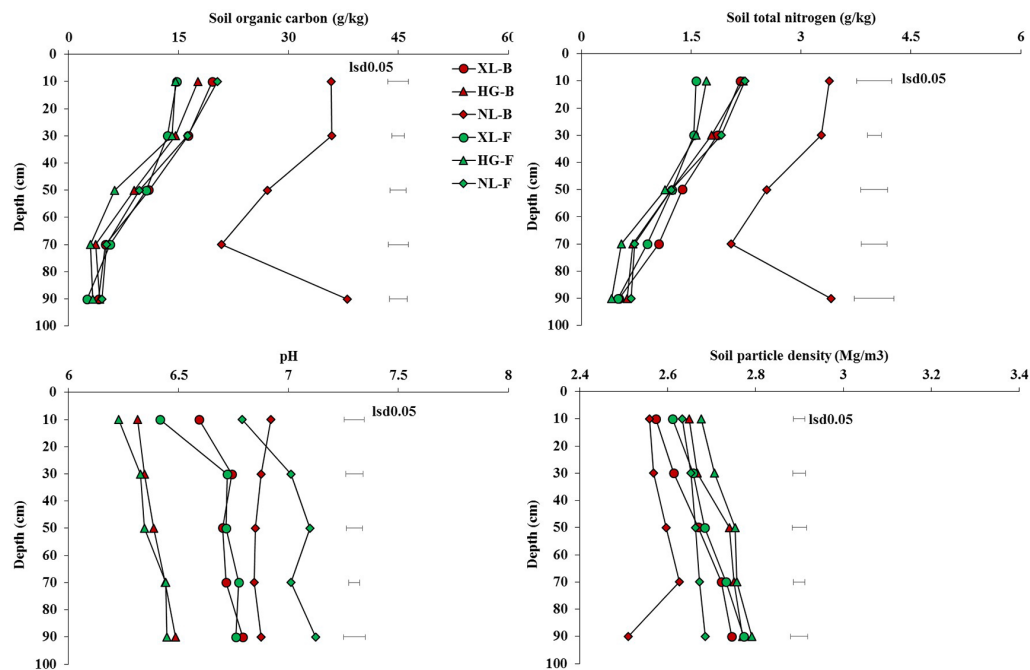


Figure 3. The distribution of soil physicochemical properties in profile at different land use sites. For abbreviations, see Fig. 2.

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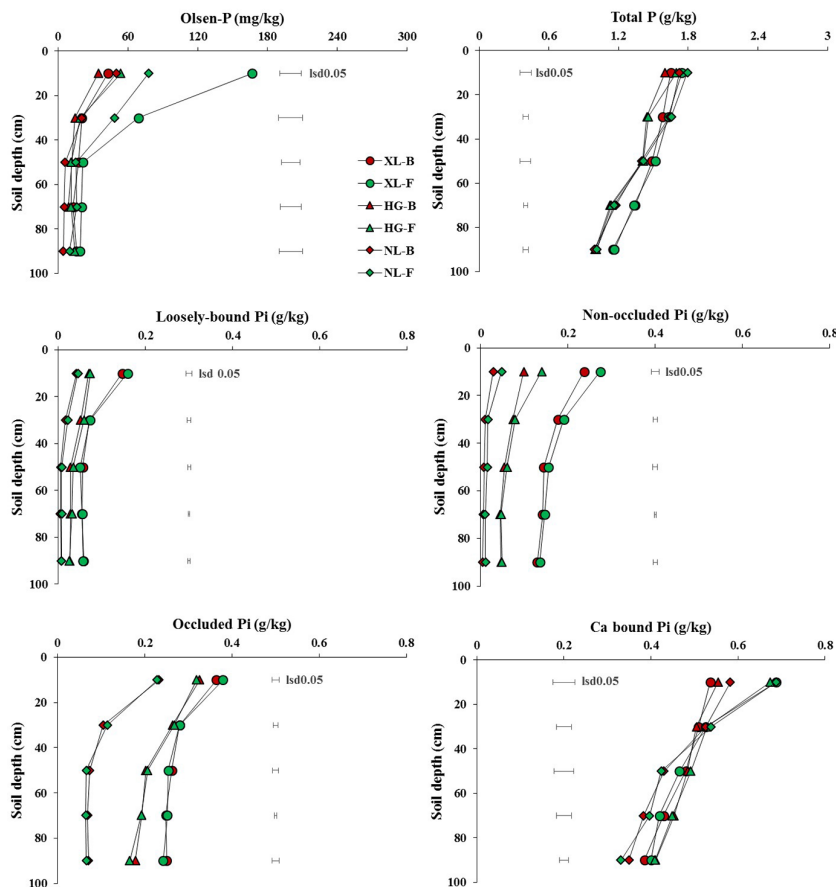


Figure 4. The concentrations of P forms in soil profile at different land use sites. For abbreviations, see Fig. 2.

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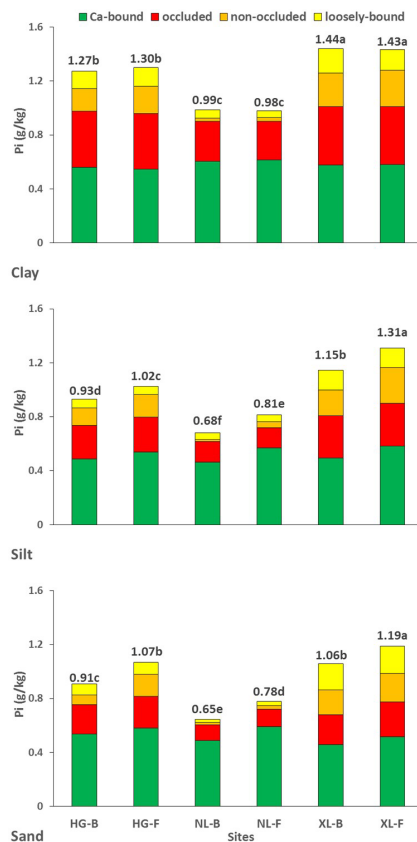


Figure 5. The P storage in particle size fractions for Pi fractions of different land use sites. Values on the column are the sum values of Pi fractions at same site. Values followed by a similar letter are not significantly different at $p < 0.05$ level of significance according to lsd test. For abbreviations, see Fig. 2.

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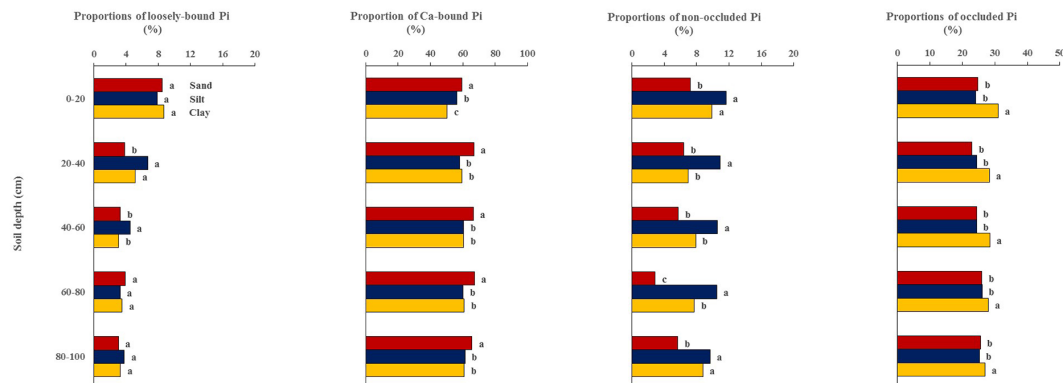


Figure 6. The proportion of Pi forms in particle size fractions in soil profile. Values followed by a similar letter in same layer are not significantly different at $p < 0.05$ level of significance according to lsd test.

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