Chronosequence of paddy soils and phosphorus sorption–desorption properties

Ping Zou · Jianrong Fu · Zhihong Cao

Abstract

Purpose Accumulated soil phosphorus (P) in agricultural lands due to long-term organic manure and mineral phosphate fertilizer input is considered one of the main non-point pollution sources to surrounding surface water bodies. A chronosequence of soils is a potent instrument for pedological investigation and allows assessment of the effect of duration of agricultural cultivation on the environmental risk to water bodies of P loss from soil.

Materials and methods The present study was conducted to evaluate the impact of pedogenesis on the retention of P in a chronosequence (25, 100, 300, 700, and 2,000 years) of rice paddy soils located on the south bank of Hangzhou Bay. Batch sorption–desorption experiments were performed on the samples of surface horizons from this chronosequence.

Results and discussion P retention differed moderately among the studied soils ranging from 17.8% to 22.6% when 2,500 mg P kg^{-1} was added. Subsequent desorption experiment revealed that 11.2% to 21.9% of the recently sorbed P might move into solution. The maximum P sorption capacity as estimated by Langmuir isotherm ranged from 521.9 to 850.9 mg kg^{-1}, with a mean value of 726.2 mg kg^{-1}, while the degree of P saturation was less than 5%. The results indicate that P sorption is influenced by soil development with the maximum sorption capacity of studied soils significantly positively correlated to the organic carbon content of these soil materials.

Conclusions The pH of the soil decreased from alkaline to neutral with increasing duration of rice cultivation due to continuing decalcification. The organic carbon content in the paddy surface soil materials increased with increasing duration of rice cultivation. The maximum P sorption capacity also slightly increased with increasing duration of rice cultivation likely due to organic carbon accumulation in topsoils. There is a very low risk of P in these paddy soils moving to the surrounding surface water bodies. This study of some possible long-term impacts helps to indicate that rice paddy agriculture is an environment friendly and sustainable land use.

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1 Introduction

Phosphorus (P) usually is the nutrient that limits algae growth in freshwater bodies (Zhang et al. 2003a). Consequently, increasing P concentration in surface waters is a major cause of eutrophication with detrimental impacts on quality of these waters. Eutrophication of most fresh water around the world has been accelerated by increasing P inputs (Sharpley et al. 1994). In China, 63.6% of lakes have been eutrophicated. Contemporary total P and total nitrogen (N) concentrations of the water in lakes located in densely populated areas (e.g., Taihu Lake, Chaohu Lake, and Dianchi Lake) can be ten times higher than they were in the 1980s (Zhou and Zhu 2003). P discharge from point

sources of pollution such as municipal sewage treatment outlet pipes are relatively easy to identify and, therefore, can be reduced by improving sewage treatment and decreasing industrial P output. However, "non-point" or "diffuse" sources such as agricultural land that may generate by runoff are much more difficult to identify, as their contribution to environmental pollution can exhibit substantial temporal and spatial variation. High P fertilizer inputs for intensive cropping system have been practiced for several decades. When P input from different sources is higher than P output due to crop removal, etc., then P accumulates in the soil (Gupta et al. 2007). Some researches have indicated that the P balance in agricultural land has been broken resulting in surplus P retained in topsoils (Zhang et al. 2003b; Lehmann et al. 2005), increasing the risk of P flux from soils to surface waters.

There have been many researches focused on P sorption–desorption and P movement in paddy or wetland soils. Zhang et al. (2002) found that the first few days after P application/incorporation in paddy soils was the main high-risk period for P export losses in drainage water. Hence, it was suggested that if either (or both) the time of P application or drainage could be adjusted, then the risk of P loss from rice fields could be appreciably reduced. Zhang et al. (2003c) conducted anaerobic incubation experiments (submerging with water in N_2 atmosphere) to study the effects of soil flooding on the transformation of Fe oxides and the adsorption/desorption of P of two paddy soils of Zhejiang province in Southeast China. They found that soil flooding significantly increased oxalate-extractable Fe, mainly at the expense of dithionite-soluble Fe (Fe_d), as well as oxalate-extractable P. Flooding largely increased both P adsorption and the maximum P adsorption capacity. Flooding also changed the characteristics of P desorption in the soils. Due to a decrease of the saturation index of the P sorption capacity, P adsorbed by flooded soils was much less desorbable than that from non-flooded soils. Finally, Zhang et al. (2003c) concluded that the adsorption and desorption behavior of P in paddy soils was largely controlled by the transformation of the Fe oxides.

Xie et al. (2004) conducted a field experiment to study P movement and leaching in flooded paddy soils in Taihu Lake region by using ^{32}P tracer method. The results showed that fertilizer P could quickly move in flooded paddy rice soils, and parts of it could enter into surface waters if the drainage or heavy rain immediately followed. Therefore, both P application and drainage should be well managed to reduce the risk of P loss. Guo et al. (2009) investigated paddy soil phosphorus adsorption characteristics affected by pig manure compost (PMC) or decaying rice straw (DRS) derived dissolved organic carbon (DOC). They found that P adsorption in paddy soil decreased with DOC extracted from PMC and DRS and could be well

fitted by Langmuir equation. Wang and Li (2010) collected sediments samples in Florida (USA), from an estuary, a marine environment, a wetland, a canal, a river, and a lake, respectively. The results from batch phosphorus adsorption and desorption experiments for each sediment showed that sediments from the canal and lake had the greatest native adsorbed P and the highest zero equilibrium P concentration, while sediment from the estuary had the highest P adsorption, followed by those from wetland and marine origins, respectively. Phosphorus desorption from sediments was obtained by replacing exchangeable P with Cl^- (20 mmol l^{-1} KCl) with an excellent fit of the data to an exponential desorption kinetic model. The fractions of retained P were as high as 85–98% in the studied sediments, which displayed strong P retention capacities by all these sediments.

Zhang et al. (2008) reported that P adsorption capacity of paddy soils was medium, with the maximum P adsorption capacity of the soil examined, as calculated by Langmuir model, ranging from 415.2 to 809.2 mg kg^{-1} in the aerobic conditions, and from 567.0 to 1505.0 mg kg^{-1} in the anaerobic conditions. The anaerobic conditions (representing paddy soil conditions) significantly increased P sorption because of a remarkable increase in amorphous (poorly crystalline) iron oxides. They also proved that the degree of P saturation (DPS, the ratio of maximum P sorption capacity and Olsen-P content) was a good environmental indicator for phosphorus loss risk assessment in paddy soils. In the Netherlands, DPS has been used as sensitive critical indicator for P environmental risk assessment (Schoumans and Groenendijk 2000): When DPS is more than 25%, the risk of phosphorus release and export from the soil is significantly increased.

Soil chronosequences are potent instruments for pedological investigations, and they have a starring role to play in the testing of pedological theories (Huggett 1998). There are several reports recently relating to paddy chronosequences. Zhang and Gong (2003) focused on the redox condition and iron oxides dynamics in three sets of paddy chronosequences, which commonly originated from alluvial plains, a bog area, and terraced hill slopes in China. They found that management practices for paddy cultivation differed between the different landscape settings and that these fundamentally influenced soil processes. Recently, Cao (2008) reported one paddy chronosequence that developed on the same parent material, in the same ecological environment, and from essentially the same cropping system. This chronosequence had several rice planting ages, which were 50, 100, 300, 500, 700, 1,000, and 2,000 years, respectively. Cheng et al. (2009) compared this paddy chronosequence with a corresponding non-paddy chronosequence and found that paddy management has had a profound impact on soil formations. Soil organic

carbon accumulation in surface horizon, the increase of clay content in horizons below 40-cm depth, horizon differentiation characterized by distribution/redistribution patterns of total Fe and free Fe oxyhydrates, and net losses of total Mn from the profiles are the characteristics of soil-forming processes of paddy soils.

The sorption capacity of soil for P has been shown to change over time in response to soil development (Lilienfein et al. 2004; Zehetner and Miller 2006). To our knowledge, an assessment of environmental risk associated with P in paddy soils as a result of their distinctive pedogenic development has not been studied in China. The objective of this research was to (1) investigate pedogenic properties and the P status of soils in a paddy chronosequence, (2) evaluate the effect of these pedogenic properties on P sorption–desorption in the paddy chronosequence, and (3) assess the environmental risk of P of this paddy chronosequence.

2 Materials and methods

2.1 Outline of study area and soil chronosequence identification

The study area is located on the south bank of Hangzhou Bay, Cixi city, East China, with a longitude range of 121° 12′–121°42′, and a latitude range of 30°21′–30°24′. It is in the southern margin of the north subtropical monsoon climate zone. Mean annual air temperature is about 16.3°C, with a year range from −4.8°C to 37°C. Mean annual precipitation is 1,325.8 mm, of which 73.3% is concentrated in the rice paddy flooding season (i.e., the period from April to October). The soils in the study area that mostly originate from marine deposits from Yangtze River delta have been indicated by several studies (Su and Wang 1989; Chen et al. 1990). The approximate commencement of rice

planting in these soils was identified according to local chorography and the construction dates of different dikes in study area. The local rice cropping system was single-crop rice, and the paddy density was about 300,000 rice plants hm^{-2}. The conventional P fertilizer application rate was 60 kg P_2O_5 hm^{-2} $year^{-1}$ with P fertilizer usually used as base fertilizer. A detailed description of this chronosequence of paddy soils was given by Cheng et al. (2009).

2.2 Sample preparation and analysis of basic soil property

A paddy chronosequence with 25-, 50-, 100-, 300-, 700-, and 2,000-year durations of rice cultivation was sampled in present study. The sampling protocol was the same to what Cheng et al. (2009) had stated. There were two soil sampling campaigns. The field sampling was conducted in June 2008 just before flooding of rice paddies. The chronosequence of paddy soils with 50, 100, 300, 700, and 2,000 years (the years here represent the number of years that the site has been used for paddy farming) was sampled. At each site in the chronosequence, a pit (approximately 1.0 m in depth and 1.2 m in width) was excavated, and the soil profile was identified according to both the Chinese Soil Taxonomy (Revised Scheme) (Gong 2003) and World Reference Base for Soil Resources (IUSS Working Group WRB 2006). The supplementary field sampling was completed in February 2010. Only topsoil samples of paddy soils with 25-year cultivation time was sampled. The specific locations, soil classification, and some description of all the sites are given in Table 1. About 5 kg of soil was sampled from each horizon, mixed, put into plastic bags, and transported to the laboratory. At the laboratory, all samples were air-dried, passed through a 2-mm sieve, and stored in plastic containers.

Soil pH was measured using a pH electrode in distilled water (mass/volume ratio of 1:2.5). Soil organic carbon (OC) content was determined by acid dichromate digestion.

Table 1 Characteristics of the studied chronosequence of paddy topsoils

Site no.	Age	Sampling location		Land use/soil type	Soil classification[a]	Groundwater level (cm)
		East	North			
1	25	120°6.848′	30°54.645′	Rice/paddy	Stagnic Anthrosols	85
2	50	121°21.366′	30°11.031′	Rice/paddy	Stagnic Anthrosols	90
3	100	121°20.971′	30°09.827′	Rice/paddy	Stagnic Anthrosols	55
4	300	121°30.280′	30°06.437′	Watermelon/paddy	Stagnic Anthrosols	80
5	700	121°09.180′	30°10.408′	Rice/paddy	Stagnic Anthrosols	>100
6	1,000	121°06.957′	30°09.763′	Rice/paddy	Stagnic Anthrosols	>100
7	2,000	121°26.775′	30°05.425′	Rice/paddy	Stagnic Anthrosols	Ground[b]

[a] Soil classification was given based on *Chinese Soil Taxonomy* (*Revised Scheme*) (Gong 2003)

[b] Ground means the field was flooded before sampling, with drainage for at least 1 week before sampling

Calcium carbonate equivalent was measured by the following procedure: All the soil samples were reacted with 10% H_3PO_4, and the CO_2 evolved were measured by IR absorption (C-mat 550 PC, Ströhlein GmbH, Kaarst, Germany). Total nitrogen was measured by Kjeldahl method; total phosphorus was determined by wet acid digestion procedures with perchloric and sulfuric acid, and then measured by molybdenum blue method. Total potassium (K) was measured by flame photometer method. Soil available phosphorus was determined by Olsen method. Total Fe and total Mn in soils were digested with HF–HNO_3–$HClO_4$. Free Fe and Mn oxyhydrates were extracted using dithionite citrate bicarbonate. Extracted Fe and Mn were measured by flame atomic absorption spectroscopy. All the details of these chemical methods were described by Sparks (1996) and Lu (2000).

2.3 Phosphorus adsorption and desorption experiment

Surface horizons of selected soils in the paddy chronosequence with 25-, 100-, 300-, 700-, and 2,000-year durations of rice paddy cultivation were used to conduct the phosphorus adsorption and desorption experiment. A soil sample of 1.0 g was added into a 100-ml pre-weighed centrifuge tube and then equilibrated with 25 ml of 0.01 M $CaCl_2$ solution containing phosphorus(as $H_2PO_4^-$) concentration of 0, 1, 5, 10, 20, 50, 75, and 100 mg P l^{-1}. The suspensions were shaken on constant temperature oscillator at 25±1°C for 18 h. After centrifugation at 4,000 rpm for 5 min, the supernatants were filtered through P-free filter paper. The phosphate P in solution was determined by UV–visible spectrophotometer using the molybdate blue method. Two often-used isotherms for P sorption are the Langmuir and the Freundlich isotherms, with the Langmuir having an advantage over the Freundlich in that it provides valuable information on the P sorption maximum (S_{max}) and a constant k, related to the P bonding energy.

Sorbed P (S') was calculated by difference between initial and final solution P concentrations after equilibrium. Phosphorus sorption parameters were determined by fitting experimental data to the Langmuir models using the SigmaPlot software. The Langmuir model is expressed as:

$$\frac{C}{S} = \frac{1}{kS_{max}} + \frac{C}{S_{max}} \tag{1}$$

where C is the equilibrium P concentration (mg L^{-1}); k is a constant relating to bonding strength; $S = S' + S_0$, S is the total amount of P sorbed (mg kg^{-1}); S' is the sorbed P (mg kg^{-1}) calculated by difference between the initial and the final P concentrations; S_0 is the original sorbed P (mg kg^{-1}) determined by the P release at 0 initial P concentration, estimated from the isotherms using a least-squares fit of S' measured at low equilibrium concentrations (C) (i.e., the linear part of the isotherm):

$$S' = k'C - S_0 \tag{2}$$

where k' is the linear sorption coefficient (L kg^{-1}), generally referred to as buffer capacity (Olila and Reddy 1993). In addition, equilibrium P concentration (EPC$_0$) is expressed as the final phosphorus solution concentration at which no net sorption occurred ($S'=0$). So, EPC$_0$ is equal to S_0/k'.

After removing the supernatant solution from the sorption experiment, each tube was weighed to estimate the volume of the residual solution and account for P entrapped in that solution. Then, each soil was shaken in an aliquot of 50 ml 0.01 M P-free $CaCl_2$ solution. The same analytical procedure was used for the P desorption experiment as in the sorption experiment. All of the above analyses were duplicated, and the data were presented as arithmetic means.

2.4 Statistical analyses

Statistical analyses including fitting experimental sorption data to nonlinear sorption isotherm equations, correlation analysis, and variance analysis were performed using program SigmaPlot version 11.0 (Systat Software, Inc., SigmaPlot for Windows, CA, USA).

3 Results and discussion

3.1 Basic properties of the studied soil chronosequence

Basic properties of the studied paddy soil chronosequence are summarized in Table 2. Soil pH (mean, 7.81±0.65) showed moderate variation among all the samples. The soil pH decreased to neutral conditions with increased duration of rice paddy cultivation, with the average pH value in soil profile decreasing from 8.33 after 50 years of rice paddy cultivation to 7.08 after 2,000 years. It is well established that flooded rice management tends to converge soil pH to neutral whether soil had previously been acidic or alkaline (Ponnamperuma 1978). It is also clear from Table 2 that the pH values of the topsoils are lower than those in the subsoils due to soil organic materials accumulation and leaching effects of irrigation. Organic matter accumulation in topsoil could increase proton concentration in soil solution because of organic matter decomposition under submergence. Irrigation water could leach basic material in topsoil. Therefore, soil pH value in topsoil would decrease.

OC content in the paddy topsoils gradually increases with increased durations of rice paddy cultivation and when it gets an ecological stable capacity, organic carbon content

Table 2 Basic characteristics of paddy chronosequence in Cixi city

| Age	Soil profile		pH	OC[a]	CaCO₃	TN[b]	TP[c]	TK[d]	Feₜ[e]	Fe_d[f]	Mnₜ[g]	AP[h]
	Depth (cm)	Horizon	(H₂O)	g kg⁻¹								mg kg⁻¹
25	0–20	Alp	n.m.[i]	13.49	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	8.72
50	0–7	Alp	7.83	17.58	7.40	1.74	1.05	21.5	36.8	n.m.	777	26.19
	7–14	Arp	8.10	14.56	n.m.	1.50	0.92	21.3	37.6	n.m.	820	n.m.
	14–23	Ardp	8.42	4.18	24.4	0.57	0.60	22.0	40.3	n.m.	987	1.73
	23–35	Bwg1	8.45	3.13	28.0	0.57	0.58	21.7	38.9	n.m.	989	1.16
	35–50	Bwg2	8.50	2.67	27.6	0.81	0.61	20.5	35.7	n.m.	978	2.30
	50–70	Bwg3	8.52	3.31	30.3	0.60	0.62	20.6	35.8	9.09	999	0.22
	70–100	Blg	8.52	3.42	30.7	0.47	0.63	21.1	37.0	8.90	715	1.14
100	0–9	Alp	6.55	18.21	0	2.04	0.77	20.1	34.4	8.38	607	12.27
	9–15	Alp	7.23	13.05	0	1.61	0.80	20.8	36.2	8.99	853	10.75
	15–21	Ardp	8.25	4.81	0	0.71	0.68	21.3	37.5	9.77	1,430	5.98
	21–30	Bwg1	8.26	3.31	21.8	0.62	0.62	22.1	39.0	11.06	1,020	1.96
	30–50	Bwg2	8.23	3.89	20.5	0.68	0.58	22.7	41.4	11.12	1,214	2.03
	50–75	Bwlg1	8.31	3.31	22.9	0.62	0.62	21.3	37.8	10.56	1,092	5.55
	75–100	Bwlg2	8.4	3.31	23.2	0.59	0.63	21.3	37.7	11.41	874	5.55
300	0–18	Alp	7.36	19.43	0	2.13	0.96	20.8	34.2	8.92	617	17.33
	18–24	Ardp	8.36	7.54	0	0.81	0.73	21.3	35.7	9.86	778	10.65
	24–30	Bwdl	8.53	4.23	11.5	0.50	0.62	21.9	37.8	10.21	726	2.49
	30–50	Bwl	8.51	3.77	0.80	0.56	0.63	21.9	36.9	11.24	674	1.75
	50–70	Bwlg1	8.51	3.6	13.4	0.48	0.60	23.0	40.3	10.79	802	2.92
	70–100	Bwlg2	8.55	3.13	17.8	0.47	0.59	22.2	39.2	11.88	1,025	4.11
700	0–10	Alp1	7.47	26.33	0	2.16	0.92	20.2	33.6	8.84	580	37.47
	10–16	Alp2	7.22	18.68	0	1.86	0.71	20.2	31.5	8.84	474	25.60
	16–22	Ardp	7.67	10.15	0	1.26	0.61	20.8	32.5	9.41	480	6.23
	22–45	Bg	7.94	5.45	0	0.92	0.50	20.8	31.4	8.30	671	2.69
	45–69	2Ahgb	7.95	5.57	0	0.77	0.28	23.9	40.4	12.90	388	0.72
	69–106	2Blg1	7.92	3.77	0	0.93	0.45	25.2	55.2	27.84	477	10.32
	106–116	3Ahlgb	n.m.	n.m.	0	n.m.	n.m.	n.m.	n.m.	3.94	n.m.	5.12
	116–130	3Blg	n.m.	n.m.	0	n.m.	n.m.	n.m.	n.m.	7.00	n.m.	6.14
2,000	0–15	Alp	5.66	30.34	0	2.55	0.74	18.8	23.6	n.m.	354	34.75
	15–20	Ar(d)p	6.61	21.11	0	2.52	0.55	18.7	23.7	6.59	318	26.28
	20–27	Bdg	7.13	11.95	0	1.59	0.32	18.8	22.0	16.89	274	3.61
	27–35	2AhgB	7.36	4.87	0	0.69	0.20	19.3	25.1	9.48	612	1.50
	35–50	2Bg1	7.46	2.84	0	0.51	0.19	21.5	40.8	24.82	424	2.08
	50–70	2Bg2	7.57	2.26	0	0.51	0.24	21.6	39.2	15.35	470	0.80
	70–100	2Blg	7.78	2.26	0	0.51	0.58	21.1	45.0	14.19	759	0.88

[a] Organic carbon

[b] Total nitrogen

[c] Total phosphorus

[d] Total potassium

[e] Total Fe

[f] Dithionite extractable Fe

[g] Total Mn

[h] Available phosphorus extracted by Olsen method

[i] Not measured

in subsoil will also eventually increase with time (Cao 2008). Organic carbon data in Table 2 substantiate that OC content in paddy topsoils increases with increased durations of rice paddy cultivation. After 700-year rice cultivation, OC content in paddy topsoils reaches a relatively stable level; this may be one of the important evidence of the development of a mature paddy profile (see Fig. 1).

The results indicate that with increased durations of rice paddy cultivation, the whole soil profile has been in the process of decalcification from calcium carbonate content showed in Table 2. The 700- and 2,000-year paddy soils are devoid of CaCO$_3$. Decalcification is relatively fast in these soils and is first apparent in the paddy topsoils most likely due to leaching by irrigation water.

The study area is within a very intensive and highly productive agriculture area. Therefore, high input of mineral fertilizer is necessary. As shown in Table 2, the levels of both total N and total P in the soil layers are relatively high, especially in topsoils. The total potassium content (mean, 21.48±1.64 g kg^{-1}) shows little variation among all the samples. This may be the evidence that parent materials of theses soils have a similar marine origin. Although the total potassium contents of the samples are very high, the available potassium contents of these soils are relatively low. Hu et al. (2008) conducted a pot culture experiment with no fertilizer added to test the relationship between soil natural productivity and rice planting time. The results showed that soil productivity increased with increased duration of rice paddy cultivation, and the sustainability of the paddy soils in this chronosequence was mainly based on a combination of the recycling of straw, manure, biological N fixing during long history, as well as the input of mineral fertilizers in recent 50 years.
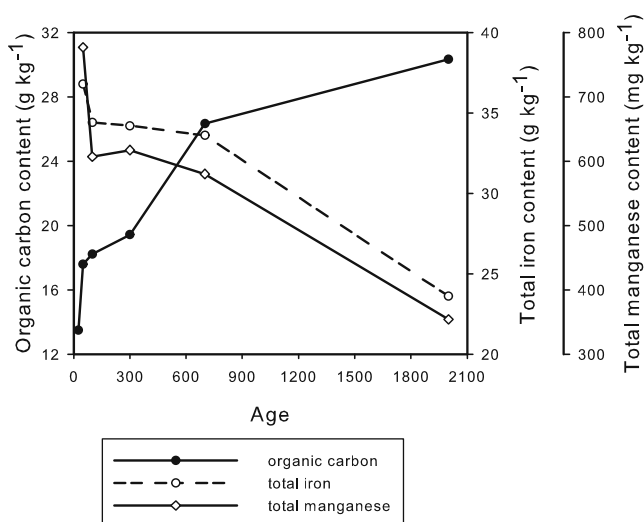
The transformation of iron and manganese oxides is one of characteristic feature in paddy soils. Downward leaching and successive re-irrigation or precipitation accounts for the formation of an iron-rich illuvial horizon in these soils (Zhang and Gong 2003). Relative enrichment of Fe$_d$ in the subsoil is diagnostic for Hydragric Anthrosols (IUSS Working Group WRB 2006), and a ratio of 2:1 of Fe$_d$ in a hydragric horizon to that in the surface layer is indicative of an iron-rich subtype. The subsoils of 700- and 2,000-year paddy soils have a relative high concentration of Fe$_d$; this indicates an enrichment of iron crystalline oxides. As the duration of rice paddy cultivation increases, a decrease of Fe$_d$ content in the surface layers is more pronounced, as is the relative accumulation of Fe$_d$ in the subsoil. It is also clear (see Fig. 1) that total iron and manganese content in surface horizons of the paddy chronosequence significantly decreases with duration of rice paddy cultivation. This indicates that the leaching of manganese oxides occurs more rapidly than that of iron oxides in the first 100 years of rice paddy cultivation.

The available P content was high in the paddy chronosequence topsoils compared with upland topsoils in the same region. However, the available P content of the subsoil materials was much lower. This could be attributed to a surficial high input of mineral fertilizer P if the paddy topsoils have a high P sorption capacity. According to the results from some studies (Dobermann et al. 1998; Gibson 1998), when the Olsen-P content is higher than 20 mg kg^{-1}, there is enough P available to enable optimal crop production in paddy soils. In the present study, the average available P concentration in the paddy topsoils of the chronosequence was 25.60±10.58 mg kg^{-1}, a level that should be sufficient for rice production without excessive P fertilizer application.

3.2 Phosphorus sorption

The P sorption data fitted a Langmuir curve very well (Fig. 2; $p<0.01$, Table 3). The fraction of P sorbed varied moderately among the studied soil materials ranging from 17.8% to 22.6% when 100 mg P l^{-1} was added to the samples. When the equilibrium P concentration was low, the amount of sorbed P on soil solid increased dramatically. This stage is the rapid adsorption stage for P to soil solids and may be attributed to chemical adsorption onto amorphous iron and aluminum oxides and covalent adsorption for basal ions onto colloidal particles. When the equilibrium P concentration was high, the P adsorption capacity increased slowly, gradually reaching a plateau. This is the slow adsorption stage, which may be caused by soil solid physico–chemical and physical adsorption of phosphorus (Gale et al. 1994). As described previously, Langmuir isotherms were used to simulate P sorption dynamics in this study. It was clear (see Fig. 2) that only

Fig. 1 The characteristic variation with time in surface horizons of paddy chronosequence
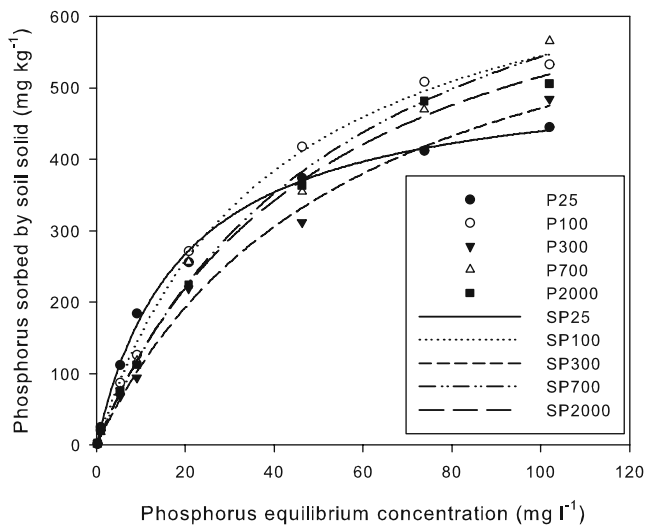
Fig. 2 Phosphorus sorption isotherm of surface horizons in the chronosequence of paddy soils, P25 and SP25 ,represent for phosphorus sorption scatter plot and simulated Langmuir isotherm curve, respectively. The rest is similar

the P adsorption capacity of surface horizon sample from 25-year-old paddy soil reached a plateau at high equilibrium P concentrations, likely due to saturation of sorption sites. Sorption isotherm parameters based on the Langmuir model are presented in Table 3. Sorption of P by the samples was adequately described by the simple Langmuir equation. Coefficient of determination (R^2) values ≥0.99 were observed for all of the paddy soil materials examined in the chronosequence.

S_{max} is the maximum sorption capacity of inorganic P by a soil material. The maximum P sorption capacity estimated by Langmuir sorption isotherms ranged from 521.9 to

850.9 mg kg^{-1}, with a mean value of 726.2 mg kg^{-1} (see Table 3). These values are higher than those obtained by Zhang et al. (2008) for the plow layers of typical paddy soils in nearby Hangzhou–Jiaxin–Huzhou Plain and the mean value (456.2 mg kg^{-1}) obtained by Zhou and Zhu (2003) for surface paddy soil samples (0–20 cm) in the southern Taihu Lake area, but are comparable with the values obtained for 23 surface horizon samples from representative purple soils in the upper reaches of the Yangtze River (Li et al. 2007). The wide range of maximum P sorption capacity in paddy soils is likely due to variations in paddy soil properties such as soil texture, the content of amorphous and crystalline iron and aluminum oxides, clay content, and organic carbon content.

Our study indicates that S_{max} slightly increases with increased duration of rice paddy cultivation when that duration is no more than 700 years ($R^2=0.761$, $p<0.1$). This may be attributed to the observed pattern of organic carbon accumulation in topsoils with increased duration of rice paddy cultivation. Organic matter accumulation will facilitate the increasing quantity of organic–inorganic complexes in topsoils, including organic–Fe complexes. Thus, organic matter accumulation can expand the number of the reaction sorption sites in paddy topsoils. The R^2 between organic carbon and S_{max} was 0.882 and statistically significant when the 2,000-year paddy soil data were excluded. Cao (2008) has found that 700 years was the threshold of mature paddy soil.

The maximum sorption capacity in a chronosequence of paddy soils increased with increasing duration of cultivation. When this duration was longer than 700 years, the S_{max} of the paddy soil materials became relatively stable. The maximum buffer capacity (MBC) describes the resistance

Table 3 Phosphorus sorption characteristics of selected soil samples

Soil		Langmuir isotherm			MBC[a]	EPC$_0$[b]	DPS[c]
Sample[d]	Layer cm	S_{max}[e] mg kg^{-1}	k[f] L mg^{-1}	R^2	L kg^{-1}	mg L^{-1}	%
P25	0–20	521.9±18.10	0.052±0.006	0.999[g]	27.27±3.94	0.060	1.671
P100	0–9	641.7±85.35	0.026±0.008	0.995[g]	16.68±7.65	0.064	1.912
P300	0–18	773.6±46.20	0.019±0.003	0.999[g]	15.02±2.85	0.169	2.240
P700	0–10	850.9±71.30	0.018±0.007	0.993[g]	15.03±7.64	0.043	4.404
P2000	0–15	843.0±64.65	0.020±0.003	0.999[g]	16.51±3.43	0.131	4.122

[a] Maximum buffer capacity of phosphorus, MBC=S_{max}×k

[b] Equilibrium P concentration

[c] Degree of phosphorus saturation, calculated from the equation DPS=100×Olsen-P/S_{max}

[d] P25, P100, P300, P700, and P2000 represent for paddy soil which has cropped for 25, 100, 300, 700, and 2,000 years, respectively

[e] Sorption maximum
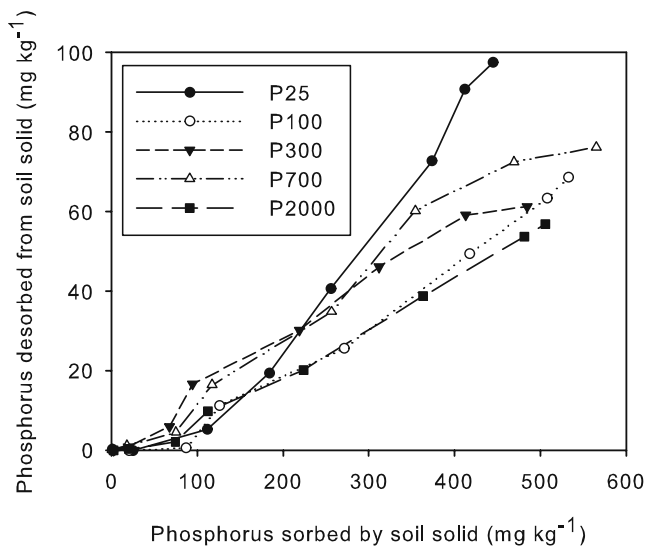
[f] A constant relating to bonding strength

[g] Significant at the 0.01 probability level

to change in P concentration of the soil solution or the labile solid phase (Holford 1979). The lower range of MBC obtained in this study did not necessarily translate to high EPC_0 as was observed by Villapando and Graetz (2001).

3.3 Phosphorus desorption

Soil P desorption is the reverse process of soil P adsorption; it may be more important than the adsorption process because it involves not only adsorbed P re-use and increases the availability of P in the soil but also is involved in environmental problems.

As it can be seen from Fig. 3, P adsorbed by the soil solid phase can be partially desorbed, and the amount of P desorbed increases with the amount of P sorbed by soil. There is a substantial proportion of phosphate remaining in the solid phase after 18 h of desorption. There was about 11.2% to 21.9% of recently sorbed P that could be desorbed when 100 mg P l^{-1} was added. This result is consistent with the findings of many desorption studies (Barrow 1983; Dubus and Becquer 2001; Villapando and Graetz 2001; Li et al. 2007; Dossa et al. 2008). Most sorbed P has been retained by the soil which reflects the irreversible sorption of phosphate by soil constituents due to a shift in the form of P held at the surface from a loosely bound to a more tightly bound type. Mechanisms proposed for this process have included precipitation of discrete phosphate minerals (Van Riemsdijk et al. 1984; Dubus and Becquer 2001), a shift from monodentate to bidentate forms of sorbed P (Gimsing et al. 2007; Wisawapipat et al. 2009), and diffusive penetration of surface-sorbed P into soil components (Pierzynski 1991). There was no significant differ-

ence ($r=-0.589$, $p=0.296$) between P desorbed (initial P concentration of 100 mg l^{-1}) and the duration of rice cultivation.

Linear equations of the form $Y = a \times X + b$ were used to fit the amount of P desorption and adsorption capacity of selected paddy soils, where X is the amount of P adsorbed by soil solid, Y is the amount of P desorbed, a is the slope, and b is the intercept. This equation fits the relationship between P desorbed and the amount of P adsorbed by soil solid very well, with the square of determination coefficients higher than 0.95 and significant at 0.01 probability level (Table 4). Slope a characterizes the rate of P desorption, indicating the amount of phosphorus desorbed in per volume of P adsorption. The larger the value of a, the greater the reversibility of P adsorption. It can be seen from Table 4 that the reversibility of P adsorption in all of the paddy soils examined in this chronosequence was low. This indicates that the duration of rice paddy cultivation has little effect on the reversibility of P adsorption.

3.4 Phosphorus environmental risk assessment in the chronosequence of paddy soils

Several phosphorus parameters that assess the potential for P movement from agricultural land to surface waters, either via surface runoff or subsurface percolation, have been used extensively, of which DPS is increasingly being utilized by soil and agricultural scientists around the world. P release (or desorption) from soil solids closely correlates to the process of soil adsorption. As described previously, the potential for P desorption increases with the amount of phosphorus adsorption capacity, so DPS will increase at the same time.

Although there are many reports about the threshold of DPS for risk assessments of P loss, it is not considered suitable to directly use the values gained from other studies. It needs to site a specific evaluation of the relationship

Fig. 3 Phosphorus desorption isotherm in surface horizons of selected paddy soils, P25, P100, P300, P700, and P2000 represent for paddy soil which has cropped for 25, 100, 300, 700, and 2,000 years, respectively

Table 4 Relationship between the desorption (Y) and the adsorption (X) of phosphorus

Soil		$Y = a \times X + b$			
Sample[a]	Layer cm	a	b	R^2	SSE[b]
P25	0–20	0.23±0.020	−11.35±5.67	0.955[c]	525.0
P100	0–9	0.13±0.007	−5.35±2.28	0.983[c]	101.7
P300	0–18	0.14±0.007	−0.04±1.87	0.984[c]	71.2
P700	0–10	0.15±0.010	−1.49±2.92	0.976[c]	174.1
P2000	0–15	0.12±0.004	−3.36±1.24	0.992[c]	31.2

[a] Abbreviations of the samples are the same as described in Table 3

[b] Sum of square error

[c] Significant at the 0.01 probability level

between DPS and P loss. Pearson correlation analysis between DPS and soil properties measured in this study showed that DPS was highly correlated ($R^2 = 0.837$, $p < 0.05$) to soil organic carbon content, indicating that the potential for P release mainly depends on the organic matter content. The DPS in our study was less than 5% even if rice paddy has been used for 700 or 2,000 years (see Table 3). The EPC_0 in the study was also very low, also indicating that the risk of release of P from these soil materials is low. The mode of construction of lowland rice paddy fields results in a semi-closed system (bounded by ridges and its bottom sealed by plow layer), and accordingly, the risk of P movement from these paddy soils to surrounding water bodies is negligible via runoff or percolation. These data on P retention support paddy farming on these soils as being a sustainable land use that is environmentally friendly and has ecologically secure functions (Cao and Zhang 2004).

There have been many studies on the status of the available P content and that have assessed the environmental risk flow from soils to water bodies causing, for example, eutrophication of lakes (Edwards and Withers 1998; Zhang et al. 2002). Field research in uplands and grasslands have shown that the P loss in subsurface flow, as well as surface runoff, increases with soil test P concentration (e.g., Olsen-P) when other factors (such as vegetation, climate, soil ecology, and agricultural management) are similar in the study area. But, before the rate of soil P accumulation reaches a critical value, the P loss in surface runoff increases very slowly. Once the available phosphorus concentration in topsoil is over this critical value, the P loss in surface runoff will increase dramatically. This critical value is called the "break point" or "change point" and is critical for P movement from soil. Heckrath et al. (1995) found that soil test P (Olsen-P) values greater than 60 mg kg^{-1} in the plow layer of a silt loam soil material caused the dissolved P concentration in tile drainage water to increase dramatically (0.15 to 2.75 mg L^{-1}). They postulated that this level (60 mg kg^{-1}), which is well above that needed by major crops for optimum yield, is a critical point above which the potential for P movement through the soil profile greatly increases. Cao et al. (2005) proposed that break point for the P loss of surface runoff in paddy field of Taihu Lake region is around 26–30 mg kg^{-1}. This threshold for soil phosphorus could be used as a reference in our study since there are similar environmental conditions between the Taihu Lake region and the south bank of Hangzhou Bay. The Olsen-P contents in the paddy soils of the chronosequence are shown in Table 2. It is clear that the Olsen-P content in the 700- and 2,000-year paddy soils were above this threshold value of Cao et al. (2005), indicating that the P in these two paddy soils pose a potential environmental risk of P being mobilized to the surrounding river and lakes.

Adjustment of fertilization schemes should be taken into account for mature paddy soils of 700- and 2,000-year age. Such adjustments include stopping P fertilizer application for 2–3 years or at least reducing the amount of phosphate fertilizer to reduce the P content in the field below the threshold value without no effect to rice production and quality. However, for young paddy soils still under 700 years of age, the application of phosphate fertilizer should be continued to be used to improve the fertility of soil phosphorus.

4 Conclusions

The present study revealed that soil age and development had a significant effect on several soil properties. The pH of the soil decreased from alkaline to neutral with increasing duration of rice cultivation due to continuing decalcification. Decalcification is very fast and firstly appears in topsoils of the paddy chronosequence because of abundant irrigation water input in paddy field. OC content in paddy topsoil increases with rice growing duration; however, when rice cultivation time exceeds 700 years, OC content in the topsoils of paddy profile reaches a relatively stable level.

P sorption data fitted to Langmuir isotherms very well. S_{max} slightly increased with increasing duration of rice paddy cultivation when rice cultivation time was no more than 700 years. When the duration of paddy cultivation was longer than 700 years, the S_{max} in paddy soils became relatively stable. This may be attributed to the pattern of organic carbon accumulation in topsoils with increasing duration of rice cultivation. The results of P desorption experiments indicate that about 11.2% to 21.9% of recently sorbed P (when 100 mg P l^{-1} were added) can be desorbed. Most sorbed P was retained by the soil material. The reversibility of P adsorption in a chronosequence of paddy soils is low. DPS in our study was less than 5%. The EPC_0 was also very low, indicating a low potential for P release from these soils. The mode of construction of lowland rice paddy fields results in a semi-closed system (bounded by ridges and its bottom sealed by plow layer), and accordingly, the risk of P movement from these paddy soils to surrounding water bodies is negligible via runoff or percolation. These data on P retention support paddy farming on these soils as being a sustainable land use that is environmentally friendly and has ecologically secure functions.

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