ORIGINAL ARTICLE

Soil order and management practices control soil phosphorus fractions in managed wetland ecosystems

B. A. Linquist · M. D. Ruark · J. E. Hill

Abstract Phosphorus, an essential element for plant and animal growth, can also impair water quality. Understanding management effects on P dynamics can aid in the management of these systems to reduce nonpoint source pollution and improve fertilizer use efficiency. A sequential P fractionation procedure was used to evaluate labile to recalcitrant inorganic (Pi) and organic (Po) fractions in wetland rice soils. In this study we evaluated 71 wetland soils in the Sacramento Valley, California, consisting of different soil orders (Alfisols, Entisols, Mollisols and Vertisols) and different management systems (conventional rice, organic rice and natural wetlands). Total soil P ranged from 165 to 784 $\mu g\ g^{-1}$ and averaged 415 $\mu g\ g^{-1}$. Mollisols contained significantly more Pi and Po than all other soils; especially more HCl-Pi and Po. Although most studies ignore Po in the HCl fraction, 9% of total P was recovered in this fraction, suggesting that this fraction should not be ignored in studies aimed at quantifying and understanding organic P. The HCl-Po fraction was closely correlated with HCl-Pi, suggesting that it may be Ca bound P. Soils managed under organic rice production had higher NaHCO$_3$-Pi and NaOH-Pi levels than conventional rice systems; while the natural wetland systems showed intermediate amounts. Organic or synthetic P fertilizers applied in excess of the amount of P that is removed during harvest was recovered as NaHCO$_3$-Pi and NaOH-Pi.

Keywords Wetlands · Rice · Fertility management · Phosphorus fractionation

Introduction

Although P is a non-renewable resource and is an essential nutrient for both plants and animals, it is also a leading water quality impairment (Sharpley et al. 2003). This is especially the case in managed wetland systems, such as in California where managed wetland rice systems are intermixed in the landscape with natural wetlands which are connected to each other and public water ways through a vast system of irrigation canals. It is critical to know how management affects soil P and its various forms which in turn affect its potential mobility (and potential as a pollutant) and its availability for plant uptake. A sequential chemical extraction of P from soils, as developed by Hedley et al. (1982), provides a methodology for examining soil P that allows for a better understanding of soil P dynamics. The sequential extraction procedure removes inorganic and organic P of increasing chemical stability as related

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to soil P bioavailability. Hedley et al. (1982) and Tiessen et al. (1984) reported that NaHCO$_3$-Pi is the most biologically available Pi form, NaOH-Pi is associated with amorphous and crystalline Al and Fe phosphates, and HCl-Pi represents stable Ca bound phosphates. NaHCO$_3$-Po is considered to be easily mineralized and may contribute to the plant available fraction while NaOH-Po is made up of chemically protected forms that involve long-term soil P transformations. HCl-Po has not been measured in most similar sequential P fractionation studies; however He et al. (2006) reported that the Po in this fraction is Ca bound hydrolyzable organic P. In an early study, Ivanoff et al. (1998), using a different fractionation procedure, suggested that HCl-Po was a moderately labile fraction.

This sequential extraction procedure, and modifications of it, have been used widely to evaluate soil P fractions as a function of pedogenesis (Cross and Schlesinger 1995; Sharpley et al. 1987; Tiessen et al. 1984); cultivation (i.e. Hedley et al. 1982); and land use and management (see review by Negassa and Leinweber 2009). However, there has been limited application of sequential P fractionation applied to lowland rice systems. The P chemistry of lowland rice soils is different from other soils because of the wetting and drying cycles imposed on these soils. While these processes are well understood in governing short-term P dynamics (Ponnamperuma 1972; Sah and Mikkelsen 1986) much less is known on the long-term dynamics. In rice systems, the few studies that have used the sequential P fractionation procedure have focused on how fertility management (both chemical and organic) affects the fate of P within soils (Yang et al. 2006; Zhang et al. 2006; Pheav et al. 2005; Saleque et al. 2004). These studies provided valuable insights into soil P dynamics in rice systems, but are limited to single locations in Asia.

California's Sacramento Valley provides an ideal region to study the dynamics of P in flooded soils. First, it is a major paddy rice growing region in the US with about 200,000 ha, including over 6,000 ha of organically produced rice. Second, the Sacramento Valley lies within the Pacific Flyway and was historically a wetland habitat. However much of this wetland habitat was converted for agricultural development beginning in 1850 (Frayer et al. 1989). Today, about 30,000 ha of "natural" wetland habitat (sometimes referred to as semi-natural wetlands) remains in

the Sacramento Valley and are managed to simulate historical water patterns. The rice and natural wetland systems provide habitat and a source of food for the 3–6 million waterfowl that migrate through the region each year (Sterling and Buttner 2009). Interestingly, natural wetlands have also been shown to function as sinks for P in agricultural landscapes (Maynard et al. 2009; Richardson 1999). The presence of rice ecosystems interspersed with natural wetlands makes it an ideal situation to study how wetland management impacts soil P dynamics. The objectives of this study were to characterize P fractions in wetland systems and how these are affected by ecosystem and fertility management. This will allow us to sustainably manage these systems within the landscape and minimize nonpoint source pollution.

Materials and methods

All the soils in this study were collected in the Sacramento Valley which is the northern part of the Central Valley in California (Fig. 1) between 2005 and 2007. Soils were collected during April and May of each year to a depth of 15 cm. At each location three to six soil samples were collected and composited. Soils were collected from three systems: conventional and organic rice systems and natural wetlands. Soils from the nine natural wetland sites were taken in 2005 from areas within the wetlands that were seasonally flooded (not year-round ponds). Soil samples from 58 conventional rice fields and four organic rice fields were collected between 2005 and 2007 before planting and any fertilizer was applied. For conventional and organic rice the fertilizer management history was determined based on interviews with each grower. In conventional fields, P fertilizer was applied at rates ranging from 12 to 34 kg P ha year^{-1} and the organic growers applied poultry litter at rates varying from 4 to 10 t poultry litter ha^{-1}. For the natural wetland sites, we determined when the site became established as a natural wetland, previous land management, water source for irrigation and duration of flooding in the seasonal flood areas (Table 1).

All soils were air dried and ground to 2 mm or less. Soils were analyzed for pH (saturated paste—U.S. salinity laboratory staff 1954), organic carbon (modified Walkley–Black- Nelson and Sommers 1982), texture (hydrometer method - Sheldrick and

Fig. 1 Map showing the rice growing area, wildlife areas and the counties within the Sacramento Valley of California. The approximate study locations are shown indicating conventional (C), organic (O) and natural wetland (W) sites. System symbols followed by a number indicate the number of fields in that particular area. For example "C3" indicates that there were 3 conventional rice fields in that area. The "*star*" shows the location of the city of Sacramento
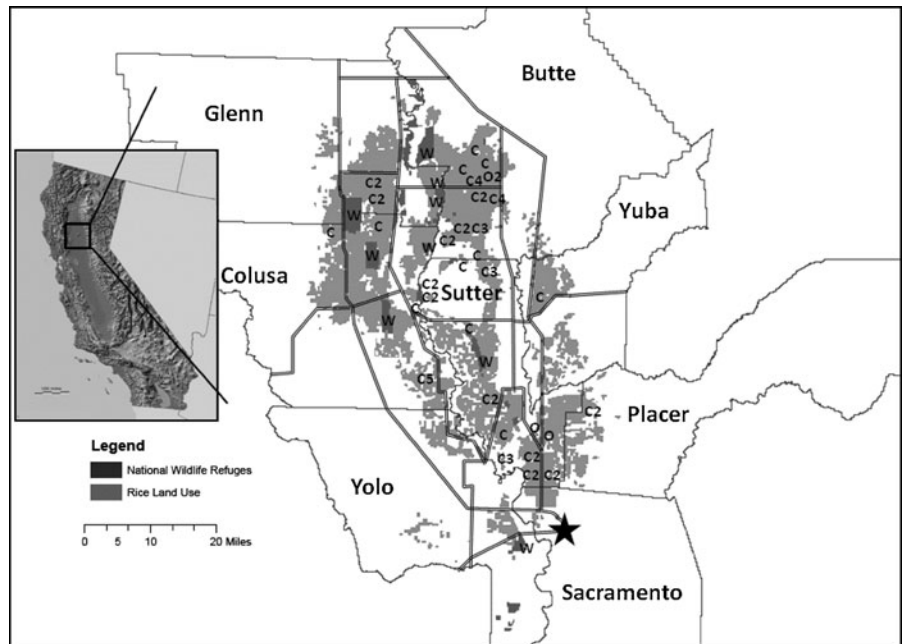

Table 1 Properties and management practices for natural wetland sites

	Year it became a wetland	Period wetland is flooded	Water source	Previous management
UBB-Llano–Seco	1992	August–April	Sacramento river	Rice
UBB-Howard Slough (216)	1992	August–April	Rice field drain water	Rice
UBB-Howard Slough (207)	1992	August–April	Rice field drain water	Rice
Sacramento NWR	1937	August–April	Mix of ag. drain water and fresh water	Rice/pasture
Delevan NWR	1962	August–April	Mix of ag. drain water and fresh water	Rice
Grey Lodge	1931	August–March	Mix of ag. drain water and fresh water	Unknown
Colusa NWR	1945	August–April	Mix of ag. drain water and fresh water	Rice
Sutter NWR	1945	September–April	Mix of ag. drain water and fresh water	Unknown
Yolo	1997	August–April	Mix of ag. drain water and fresh water	Agriculture

Wang 1993) and soil test P (Olsen and Sommers 1982). The soil order was determined from the Natural Resources Conservation Service web based soil survey (http://websoilsurvey.nrcs.usda.gov).

A sequential P fractionation procedure was conducted as outlined by Tiessen and Moir (1993) with four sequential P fractions being analyzed: NaHCO$_3$ extractable, NaOH extractable, HCl extractable and Residual. We modified the method by first not including an initial resin P; and second by analyzing for Po in the HCl extraction based on results from He et al. (2006) who showed significant amounts of Po can exist in this fraction. The fractionation was conducted on 0.5 g of soil by sequentially extracting with 0.5 M NaHCO$_3$, 0.1 M NaOH and 1 M HCl. Each extraction required 16 h of shaking. The Po content of each extract was calculated as the difference between Pi and total P. The total P content of each extract was determined after digesting with ammonium persulfate and H$_2$SO$_4$. The Pi was determined on neutralized extracts using the molybdate-colorometric method of Murphy and Riley (1962). Following the HCl extraction, the remaining P (Residual-P) was determined using microwave acid digestion/dissolution (Sah and Miller 1992) and the P concentration determined by Inductively Coupled Plasma Atomic Emission

Spectrometry (ICP-AES). Total P for each soil was calculated as the sum of P in all fractions. For this manuscript, C:P is the ratio of organic C to total organic P. The P fraction data were analyzed and are presented as absolute values and as a percentage of total P.

Pearson correlation coefficients were calculated to determine the degree of association between and among P fractions (absolute and relative values) and other soil properties. In addition, the P fractions (absolute and relative values) and other soil data (pH, organic carbon, texture and Olsen-P) were analyzed using the PROC MIXED procedure of SAS (Littel et al. 1996). An initial analysis was conducted for the soil order classification and because of the large effect of soil order on P fractions and as not all ecosystems were represented by all soil orders, a separate analysis was conducted using only Vertisol sites for comparing conventional rice, organic rice and natural wetland systems.

A canonical discriminant analysis (CDA) was used to investigate the two dimensional association of relative P fractionation with the levels of the three factors (fixed effects: conventional, organic and natural wetland). Data were analyzed with the canplot macro that utilizes the CANDISC procedure of SAS (SAS Institute, 1999). The results of the CDA were summarized in a two-dimensional canonical discriminant structure plot. Scores for the first two canonical variates were plotted as points in the ordination space. Means for each treatment were plotted along with the corresponding 95% confidence limits as circles around each corresponding mean. The variable vectors (correlation between the canonical variate and original data) for the different P fraction-methods were plotted as a point at the end of vectors projecting from the origin into various positions in the ordination space. Each vector was calculated as the hypotenuse of the right triangle formed by the angle associated with the variable vectors for the two canonical variates. The coincidence of vectors and a level(s) of a factor in the same area of the ordination space suggested a probable affinity of P fraction-methods for that level(s).

Results

The total amount of soil P measured across all soils in our study ranged from 165 to 784 $\mu g\ g^{-1}$ and averaged 415 $\mu g\ g^{-1}$ (Table 2). On average,

inorganic P (228 $\mu g\ g^{-1}$) was roughly twice as much as organic P (116 $\mu g\ g^{-1}$). As a percentage of total P, 53% was present as Pi, 29% as Po and 18% as Residual-P. Within the extractable fractions most of the inorganic P was in the HCl fraction (28%), followed by the NaOH fraction (16%) and the $NaHCO_3$ fraction (9%). For organic P, most was found in the NaOH fraction (16%) followed by HCl (9%) and $NaHCO_3$ (4%).

Correlations of the absolute amount of P in each fraction with other soil properties show that soil clay content was not correlated with any of the fractions (Table 3). However, pH was positively correlated with $NaHCO_3$-Pi, HCl-Pi, and HCl-Po, and negatively correlated with $NaHCO_3$- Po and NaOH-Po. Organic C was positively correlated with NaOH-Po. The C:P ratio was negatively correlated with all fractions with the exception of $NaHCO_3$- and NaOH-Po. Olsen-P and the other P fractions showed a high degree of positive correlation with each other. The fractions which were exceptions to these positive correlations were $NaHCO_3$-Po and NaOH-Po which were only correlated with each other.

Correlations coefficients based on the relative amount of P within each fraction indicated that Po, in particular $NaHCO_3$ and NaOH, were positively correlated with clay content (Table 4). Soil pH was positively correlated with HCl-Pi and -Po was negatively correlated with NaOH-Pi and NaOH-Po. Soil organic C was negatively correlated with $NaHCO_3$- and NaOH-Pi and Residual-P. The C:P ratio was negatively correlated with HCl-Po and positively correlated with Residual-P. Olsen-P was not correlated with either HCl fraction but was positively correlated with many of the Pi fractions and negatively correlated with Po fractions and Residual-P. There was a high degree of positive and negative correlation among the P fractions. In general, HCl-Pi and -Po fractions were negatively correlated with $NaHCO_3$- and NaOH-Pi and -Po fractions and Residual-P. HCl-Pi and -Po fractions were positively correlated with each other.

Vertisols were the most common soil order (n = 48) and was represented by all ecosystems. Mollisols (n = 9) were found in both conventional rice systems and natural wetland systems, whereas Entisols (n = 8) and Alfisols (n = 6) were only found in conventional systems. Soil orders differed significantly in soil pH, clay content and P fractionation.

Table 2 Summary statistics on absolute amounts and the percentage of P within each fraction for the 71 wetland soils

	NaHCO$_3$		NaOH		HCl		Residual	Total		Total
	Pi	Po	Pi	P	Pi	Po	P	Pi	Po	P*
Absolute amount of P within each fraction (µg g^{-1})										
Mean	36.3	15.4	65.1	58.9	126.3	41.2	71.8	227.8	115.5	415.1
Standard deviation	17.4	5.3	32.2	19.0	91.7	34.4	27.0	115.1	39.0	158.0
Min	11.5	5.4	20.2	18.6	19.8	0.0	28.0	53.6	56.9	164.8
Max	82.9	31.9	150.5	111.2	382.1	169.6	148.0	544.9	229.4	784.0
Percentage of P within each fraction (%)										
Mean	8.9	4.3	16.0	16.1	27.6	9.0	18.1	52.5	29.4	
Standard deviation	2.9	2.2	6.0	7.5	13.0	4.8	5.8	9.5	8.4	
Min	3.4	0.9	6.1	2.7	8.4	0.0	10.0	30.4	13.5	
Max	16.9	10.4	29.2	38.4	52.7	21.6	40.0	73.1	55.1	

* Total P is the sum of total Pi, total Po and residual P

Table 3 Pearson correlation coefficients among soil characteristics and the absolute amount of P in each fraction. Only significant ($P < 0.05$) correlations are shown

	Clay	pH	Org C	C:P ratio*	Olsen-P	NaHCO$_3$ Pi	NaOH Pi	HCl-Pi	Total Pi	NaHCO$_3$ Po	NaOH-Po	HCl-Po	Total Po	Residual P
pH														
Org C														
C:P ratio			0.56											
Olsen-P	0.25			−0.48										
NaHCO$_3$ Pi	0.25			−0.53	0.96									
NaOH-Pi				−0.43	0.75	0.75								
HCl-Pi	0.69			−0.27	0.44	0.46								
Total Pi	0.54			−0.42	0.71	0.73	0.55	0.92						
NaHCO$_3$-Po	−0.29													
NaOH-Po	−0.43	0.42					0.29			0.50				
HCl-Po	0.55			−0.54	0.38	0.46		0.71	0.70					
Total Po		0.29		−0.57	0.38	0.45	0.38	0.55	0.61	0.26	0.49	0.83		
Residual-P				−0.26	0.50	0.48	0.64	0.37	0.54			0.30	0.28	
Total P	0.49			−0.49	0.69	0.73	0.60	0.87	0.97			0.77	0.74	0.64

* The C:P ratio is the ratio of organic C to total organic P

On average, Mollisols had the highest pH (6.8) of all the soil orders and Entisols the lowest (5.3) (Table 5). Vertisols had the highest clay content (45%), followed by Mollisols (35%), Entisols (30%) and Alfisols (24%). Mollisols had a higher P content (641 µg g^{-1}) than any other soil order (average of 359 µg g^{-1} for other soil orders) and contained more total Pi and Po (Table 6). Mollisols had 110% more total-Pi and 67% more total-Po than the average of the other soils. Mollisols had significantly more HCl-Pi and -Po and NaHCO$_3$-Pi than the other soils. On a relative basis, Mollisols also had the highest amount of P in the HCl-Pi (40%) and -Po (14%) fractions but the lowest amount of P in the NaOH-Pi and -Po fractions. Entisols had the highest percentage of NaHCO$_3$-Po and NaOH-Po and -Pi.

To evaluate the effects of management, only sites with Vertisols were included because this was the only soil order represented by all the systems. Soil properties among these systems had similar pH, clay

Table 4 Pearson correlation coefficients among percentage of P in each fraction and soil properties. Only significant (P < 0.05) correlations are shown

	Clay	pH	Org C	C:P ratio*	Olsen-P	NaHCO$_3$ Pi	NaOH Pi	HCl Pi	Total Pi	NaHCO$_3$ Po	NaOH Po	HCl Po	Total Po
NaHCO$_3$-Pi			−0.41		0.55								
NaOH-Pi		−0.70	−0.25		0.28	0.60							
HCl-Pi		0.73			−0.46		−0.71						
Total Pi		0.49			0.57			0.78					
NaHCO$_3$-Po	0.34	−0.48			−0.51			−0.63	−0.76				
NaOH-Po	0.31	−0.61			−0.48			−0.70	−0.81	0.78			
HCl-Po		0.47		−0.51			−0.37	0.37		−0.40	−0.42		
Total Po	0.30	−0.41			−0.48				−0.57	−0.80	0.72	0.85	
Residual-P			−0.25	0.25	−0.24				−0.45	−0.48		−0.47	

* The C:P ratio is the ratio of organic C to total organic P

Table 5 Soil properties of the different soil orders present in the Sacramento Valley

System	n	Olsen-P mg kg^{-1}	pH	Organic carbon %	Clay %	C:P ratio*
Alfisol	6	11.5	5.8 bc	1.07	23.9 c	127
Entisol	8	12.2	5.3 c	1.26	29.9 bc	112
Mollisol	9	22.0	6.8 a	1.46	34.9 b	89
Vertisol	48	13.9	5.9 b	1.22	45.3 a	122
P value		0.057	<0.001	0.233	<0.001	0.228

Different letters grouped together within a column represent significantly different values (P < 0.05)

* The C:P ratio is the ratio of organic C to total organic P

contents, organic C and C:P ratio (Table 7). However, the organic fields had higher labile P (28.7 µg g^{-1}) than the conventional rice fields (11.5 µg g^{-1}) and the wetland systems showing intermediate values (18.1 µg g^{-1}).

Conventional rice systems had lower NaHCO$_3$- and NaOH-Pi than organic and natural wetland systems on both an absolute and relative basis (Table 8). Organic systems had the highest amount of P in these fractions with 31 and 16 µg g^{-1} more NaHCO$_3$-Pi than in the conventional rice and natural wetland systems, respectively; and 43 and 21 µg g^{-1} more NaOH-Pi than the conventional rice system and wetlands, respectively.

Canonical discriminant analysis (CDA) showed that the horizontal dimension, which explained 79.5% of the variability, was associated with significant differences between conventional systems and the organic and natural wetland systems (Fig. 2). Confidence limits indicate that the conventional rice systems were different from natural wetland and organic systems, which were not different from each other. The differences were due to the higher levels of NaHCO$_3$-, NaOH- and total-Pi associated with the organic and natural wetland systems, confirming results of the analysis of variance (Table 8).

Discussion

General relationships among fractions

There is a relatively high degree of correlation among most of the P fractions and some general patterns are as follows. The Fe/Al fractions (NaOH-Pi and -Po) were negatively correlated with the Ca fractions (HCl-Pi and -Po) (Table 4). Furthermore, pH was negatively correlated with the Fe/Al P fractions and positively correlated with the Ca bound P fractions. The Residual-P fraction was most closely correlated

Table 6 Phosphorus fractions for each soil order expressed as the absolute and relative amount (%) of P in each fraction

Soil order	n	NaHCO3		NaOH		HCl		Residual	Total		Total
		Pi	Po	Pi	Po	Pi	Po	P	Pi	Po	P
Absolute amount of P within each fraction (µg g^{-1})											
Alfisol	6	31.0 b	12.5	70.9	51.4	70.5 b	27.6 b	87.8	172.4 b	91.5 b	351.7 b
Entisol	8	32.1 b	18.9	67.6	69.6	62.1 b	23.5 b	62.3	161.8 b	111.9 b	336.0 b
Mollisol	9	52.0 a	13.7	72.2	62.7	259.4 a	95.7 a	85.6	383.6 a	172.1 a	641.2 a
Vertisol	48	34.5 b	15.4	61.7	56.3	117.7 b	34.9 b	67.8	213.9 b	106.6 b	388.3 b
P value		0.032	0.128	0.760	0.200	0.000	0.000	0.091	0.000	0.000	0.000
Percentage of P within each fraction (%)											
Alfisol	6	8.6	3.8 ab	19.0 a	14.4 ab	20.4 b	7.7 b	26.2 a	48.0	25.8	
Entisol	8	9.7	5.7 a	19.1 a	21.5 a	18.9 b	7.1 b	18.0 bc	47.8	34.3	
Mollisol	9	8.1	2.4 b	11.2 b	10.6 b	40.0 a	14.1 a	13.6 c	59.3	27.1	
Vertisol	48	8.9	4.5 a	16.1 ab	16.5 a	27.5 b	8.5 b	18.0 b	52.5	29.5	
P value		0.761	0.019	0.026	0.028	0.003	0.004	0.000	0.053	0.276	

Different letters grouped together within a column represent significantly different values (P < 0.05)

with the Fe/Al fractions, possibly suggesting that the Residual-P fraction may be recalcitrant and or occluded Fe/Al bound P.

P fractionation and soil order

Mollisols had more total P than any of the other soils in our study (Table 6). The question remains whether high soil P values are due to properties associated with Mollisols or to differences in management practices. Within the Mollisol order there were no sites where organic rice was grown. Organic rice systems had high amounts of NaHCO$_3$-Pi and NaOH-Pi which lead to slightly higher total P levels than the other systems (Table 8), thus the high amount of P in the Mollisol soil order occurred in the absence of organically managed rice systems. Mollisols had higher pH (Table 5), higher amounts of HCl-Pi and HCl-Po on both an absolute and relative basis, and showed the lowest amounts of NaOH-Pi, NaOH-Po and Residual-P on a relative basis (Table 6). This negative relationship between Fe/Al bound P and Ca bound P was also apparent when the analysis was conducted across soil orders (Table 4). High amounts of Ca bound P (HCl-P) have been attributed to younger soils that are less weathered and have a high Ca content (Cross and Schlesinger 1995; Sharpley et al. 1987; Tiessen et al. 1984). Sharpley et al. (1987) also reported that soil weathering results in a shift from Ca to Fe bound phosphates. The combination of the high HCl-Pi and low NaOH-Pi (Fe-bound), in relative terms, suggest that the Mollisols are dominated by Ca bound phosphates and are less weathered than the other soils tested in our study. Mollisols are considered slightly weathered soils and are defined as having greater than 50% base saturation and thus high amounts of Ca bound P (HCl-P) are expected. However, in a study comparing P fractions among natural, unfertilized and uncultivated soils, Cross and Schlesinger (1995) found that Mollisols had less HCl-Pi than Vertisols and that both soils had similar amounts of total P, contradicting the findings reported here. There are several possible explanations for the differences between these two studies. First, in the study by Cross and Schlesinger (1995) only three Vertisols were compared to 42 Mollisols, and the Vertisols were highly variable both with respect to total P (289–736 µg g^{-1}) and HCl Pi (65–430 µg g^{-1}). Second, the soils used in their study were not cultivated and, it seems, were non-flooded

Table 7 Soil properties of the Vertisol fields as affected by ecosystem management

System	n	Olsen-P mg kg^{-1}	pH	Organic carbon %	Clay %	C:P ratio*
Conventional	37	11.5 b	5.9	1.3	46	126
Organic	4	28.7 a	5.8	0.9	47	84
Wetland	7	18.1 ab	6.1	1.0	43	122
P value		0.001	0.664	0.066	0.831	0.227

Different letters grouped together within a column represent significantly different values (P < 0.05)

* The C:P ratio is the ratio of organic C to total organic P

Table 8 Phosphorus fractions for the Vertisols expressed as the absolute and relative amount of P in each fraction for conventional and organic rice systems and wetland systems

	n	NaHCO$_3$		NaOH		HCl		Residual	Total		Total
		Pi	Po	Pi	Po	Pi	Po	P	Pi	Po	P
Absolute amount of P within each fraction (µg g^{-1})											
Conventional	37	29.6 b	15.6	54.8 b	57.8	118.9	35.3	65.3	203.3	108.7	377.3
Organic	6	61.0 a	14.0	97.4 a	64.0	83.8	33.6	80.6	242.3	111.6	434.5
Wetland	7	44.6 a	15.5	76.7 ab	44.4	131.3	33.1	73.3	252.5	93.0	418.8
P value		0.001	0.833	0.009	0.098	0.429	0.579	0.480	0.491	0.525	0.645
Percentage of P within each fraction (%)											
Conventional	37	8.0 b	4.7	14.9 b	17.5	28.3	8.9	17.8	51.2	31.0	
Organic	6	13.8 a	3.2	22.0 a	14.6	19.4	7.6	19.3	55.2	25.4	
Wetland	7	11.0 a	4.4	18.6 ab	12.3	28.5	7.0	18.3	58.0	23.7	
P value		0.000	0.499	0.015	0.239	0.429	0.579	0.843	0.206	0.112	

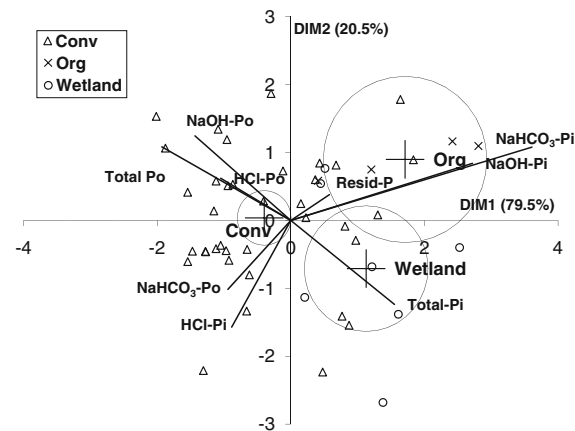Different letters grouped together within a column represent significantly different values (P < 0.05)

Fig. 2 Canonical discriminate analysis of the relative amount of P in each fraction on Vertisol soils. The factors were conventional rice (Conv), organic rice (Org) and natural wetlands (Wetland)

soils. In contrast, soils in this study have been cultivated and flooded for extensive periods of time, experiencing many flooding and drying cycles. Sah and Mikkelsen ([1986](#)) reported short-term increases and/or decreases in Ca–P, Fe–P and Al–P due to flooding and drainage. While their results were not consistent across soils and are related to within-season effects, it does indicate that flooding and draining of soils affects inorganic P transformations—at least in the short term.

Management effects on P fractionation

The systems only differed with respect to NaHCO$_3$-Pi and NaOH-Pi (Table 8). Organic rice systems had the highest amount of NaHCO$_3$-Pi and NaOH-Pi both in absolute and relative terms while conventional rice systems showed the lowest amount of P in these fractions. This suggests that conventional rice systems depleted these P fractions and/or that organic and natural systems sequestered P in these fractions. Conventional rice growers seek to maximize their returns on fertilizer investment thus their goal is to

apply only the P fertilizer that is needed to assure optimum crop growth. Theoretically, the long-term effect of such management decisions would be that soil P levels remain constant as inputs equal outputs. However, it must be recognized that matching crop demand with fertilizer input is far from exact and inputs may be far higher or lower than crop demand. While the goals of organic rice growers may be similar, these farmers have less choice in fertilizers and there is a tendency to over apply P when farmers apply manure to meet crop N demands. Organic rice producers often apply poultry litter at rates of 4–10 t ha^{-1}. Assuming a moisture content of 55% and a P concentration of 0.65% for poultry litter (Dobermann and Fairhurst 2000) this would be equal to an annual application of 12–30 kg P ha^{-1}. Assuming an average yield of 6,000 kg ha^{-1} (dry weight basis) for organically produced rice and a grain P concentration of 0.21% (Dobermann and Fairhurst 2000), the amount of P removed in the rice grain at harvest (straw is retained in the field in organic rice systems) is about 13 kg P ha^{-1}. Thus, on an annual basis there is an average net gain of 8 kg P ha^{-1} leading to higher amounts of P in organically managed rice cropping systems P. Sharpley et al. (2003) also reported that the continued use of manure can result in an accumulation of P in the soil. In contrast, in the conventional rice fields annual P applications of the growers in this study averaged 21 kg P ha^{-1} with average yields of about 9,500 kg ha^{-1} (dry weight basis-data not shown). Using the same assumptions for grain P concentration (and that no straw is removed), the net annual balance of P in these systems is about +1 kg ha^{-1}, indicating that P inputs closely balance outputs. Richardson (1985) has shown that with continued high P inputs the ability of a soil to retain P diminishes and increases the risk of P losses. Thus organic systems may be at a higher risk of dissolved P losses if they continue to receive high P inputs. While P leaching is likely to be low in these rice soils due to their impermeability and risk of soil runoff is low, it is important to manage P fertility in organic systems to prevent soil P from building up to levels that are considered a problem or where the soil can no longer retain P. One solution may be to use manure to meet the P (instead of N) requirements of the crop. The additional N requirement could be made up using an organic N source that has low concentrations of P.

Natural wetlands, on the other hand, do not receive direct inputs of P fertilizer and there is no P removal through harvest events but may receive P inputs in the form of agricultural runoff and waterfowl defecation. Water fowl defecation has been shown to lead to higher P loads (Olson et al. 2005; Kitchell et al. 1999). Both rice fields and wetland habitats in the Central Valley serve as important waterfowl wintering area in the Pacific Flyway, supporting up to 60% of the total flyway population (Central Valley Joint Venture 2006). The total annual water bird count (including migrants) in the region has been estimated as high as 10–12 million (Gilmer et al. 1982). Thus, there is considerable potential for P loading due to water fowl defecation. P inputs from waterfowl are likely to be greater in natural wetlands than rice fields as the natural wetlands serve as year-round habitat. Another possible reason for the relatively high total P values in the natural wetland systems is that natural wetland can be a sink for P in agricultural landscapes as they filter agricultural runoff (Maynard et al. 2009; Richardson 1999). Long-term retention of P in wetlands is controlled by two main processes: (1) the deposition and burial of sediment and organic P and (2) the sorption of dissolved P to soil particles (Richardson 1985, 1999). While we did not quantify P inputs into these systems our results suggest that these systems may be functioning as sinks for P. As with organic systems, continued long-term exposure to elevated P inputs may diminish the effectiveness of wetlands to retain P (Richardson 1985).

Notably, additions of P in organic form, in excess of what is removed by the crop, did not increase Po levels when compared to the application of inorganic P fertilizer. In fact, the CDA indicated that organic rice and natural wetland systems were associated with Pi fractions - in particular the NaHCO$_3$ and NaOH (Fig. 2). Such an association between organic P inputs and Pi fractions has also been reported for both lowland rice (Saleque et al. 2004) and upland rice systems (Paniagua et al. 1995; Oberson et al. 1993) and suggests that organic P is mineralized and stored as inorganic P in these systems. In contrast, Yang et al. (2006) reported that following 4 years of organic matter additions, soil Po levels increased relative to a treatment receiving only chemical fertilizer-P. However, in their study, soil organic C also increased dramatically and in some cases more than doubled due to the large inputs of organic

materials (15–25 Mg ha^{-1}). Thus, with high organic input loads it may be possible to increase Po. Similar to organic P, synthetic fertilizer P applied in excess of crop demand has also been reported to be recovered in the NaHCO$_3$-Pi and NaOH-Pi (Fe bound P) fractions in both lowland (Zhang et al. 2006; Pheav et al. 2005; Saleque et al. 2004) and upland soils (Negassa and Leinweber 2009). The increase in NaHCO$_3$-Pi and NaOH-Pi concentrations will have to be taken into consideration when developing improved soil P tests.

HCl-Po fraction

The total amounts of P in these wetland soils were between 165 and 784 μg P g^{-1} which are all within the range of 56–1,434 μg P g^{-1} reported by Sharpley et al. (1987) in an examination of 120 soils from around the world. The sequential fractionation procedure developed by Hedley et al. (1982) and subsequently modified and used by others does not include an analysis for HCl-Po. Tiessen and Moir (1993), who developed a widely used modification of Hedley et al. (1982) indicated that there was usually little Po in this extract. In our study, we found that while the HCl-Po fraction averaged 9% of total P; in one case it represented almost 22% of the total P. Furthermore, this particular P fraction was sensitive to differences among soil orders. Turner et al. (2005), based on a review of the literature, indicated that a quantitative analysis of organic P must include a determination of Po in both acid and alkali extracts. In methods proposed by Hedley et al. (1982) and Tiessen and Moir (1993) all of the Po is determined in the alkali extracts. A scheme was developed by Ivanoff et al. (1998) for analysis of Po in wetland soils and they included an analysis of the HCl-Po fraction; however the HCl extraction was conducted before the NaOH extraction rather than after as in our study. Ivanoff et al. (1998) found that 1–5% of total P in Histisols was in the HCl-Po fraction and suggested that the HCl-Po is a moderately labile fraction. In a more recent study, He et al. (2006) reported that the 1 M HCl extraction in the Hedley sequential fractionation procedure (Hedley et al. 1982) may contain significant amounts of Po.

The amount of HCl-Po was most closely correlated with HCl-Pi (Table 3). Like HCl-Pi, it is positively correlated with pH and negatively correlated with the NaOH-Pi and -Po, NaHCO$_3$-Po and Residual-P (Table 4). This similarity to HCl-Pi, which is considered to be Ca bound P (Hedley et al. 1982), suggests that the HCl-Po fraction is also associated with Ca bound P in the soil. Our findings are consistent with those of He et al. (2006) who reported that the HCl-Po was Ca-bound hydrolyzable P. Including this fraction allows for a more complete description of P in the Hedley sequential fractionation method and it should be considered in further studies.

Summary and conclusion

The total amount of soil P measured across all soils averaged 415 μg g^{-1}. Mollisols had significantly higher concentrations of Pi and Po, in particular HCl-Pi and Po. Organic rice and natural wetland systems showed the greatest amount of NaHCO$_3$-Pi and NaOH-Pi which is likely due to a more positive soil P balance than for the conventional rice systems. P applied in excess of that removed by the crop was found in labile to moderately labile Pi fractions (NaHCO$_3$-Pi and NaOH-Pi) and others have also found that excess organic or synthetic P is found in these fractions. In the long-term, continued exposure to high P inputs may diminish the ability of organic rice and natural wetland systems to retain P and increased P runoff from these systems may ensue. On average, 9% of P was in the HCl-Po fraction, a fraction which is often not been taken into consideration. As this fraction is correlated with the HCl-Pi fraction, it suggests that it is associated with Ca bound P and can be an important component of soil P.

References

Central Valley Joint Venture (2006) Central valley joint venture implementation plan–conserving bird habitat. U.S. Fish and Wildlife Service, Sacramento, CA

Cross AF, Schlesinger WH (1995) A literature review and evaluation of the Hedley fractionation: applications to the biogeochemical cycle of soil phosphorus in natural ecosystems. Geoderma 64:197–214

Dobermann A, Fairhurst T (2000) Rice: nutrient disorders and nutrient management. International Rice Research Institute, Los Banos, Philippines, p 191 p

Frayer WE, Peters DD, Pywell HR (1989) Wetlands of the California Central Valley status, trends: 1939 to mid-1080's. U.S. Fish and Wildlife Service, Washington, DC

Gilmer DS, Miller MR, Bauer RD, LeDonne JL (1982) California's Central Valley wintering waterfowl: concerns and challenges. Proceedings North American Wildlife and Natural Resources Conference, pp 441–452

He Z, Fortuna AM, Senwo ZN, Tazisong IA, Honeycutt CW, Griffin TS (2006) Hydrochloric fractions in Hedley fractionation may contain inorganic and organic phosphates. Soil Sci Soc Am J 70:893–899

Hedley MJ, Stewart JWB, Chauhan BS (1982) Changes in inorganic and organic soil phosphorus fraction induced by cultivation practices and by laboratory incubations. Soil Sci Soc Am J 46:970–976

Ivanoff DB, Reddy KR, Robinson S (1998) Chemical fractionation of organic phosphorus in selected Histisols. Soil Sci 163:36–45

Kitchell JF, Schindler DE, Herwig BR, Post DM, Olson MH, Oldham M (1999) Nutrient cycling at the landscape scale: the role of diel foraging migrations by geese at the Bosque del Apache National Wildlife Refuge, New Mexico. Limnol Oceanogr 44:828–836

Littel RC, Milliken GA, Stroup WW, Wolfinger RD (1996) SAS system for mixed models. SAS Institute, Cary, NC, p 656 p

Maynard JJ, O'Geen AT, Dahlgren RA (2009) Bioavailability and fate of phosphorus in constructed wetlands receiving agricultural runoff in the San Joaquin Valley, California. J Environ Qual 38:360–372

Murphy J, Riley JP (1962) A modified single solution method for the determination of phosphate in natural waters. Anal Chim Acta 27:31–36

Negassa W, Leinweber P (2009) How does the Hedley sequential phosphorus fractionation reflect impacts of land use and management on soil phosphorus: a review. J Plant Nutr Soil Sci 172:305–325

Nelson DW, Sommers LE (1982) Total carbon, organic carbon and organic matter. In: Page AL et al. (eds) Methods of soil analysis: part 2. Chemical and microbiological properties. ASA Monograph Number 9, pp 539–579

Oberson A, Fardeau JC, Besson JM, Stcher H (1993) Soil phosphorus dynamics in cropping systems managed according to conventional and biological agricultural methods. Biol Fert Soils 16:111–117

Olsen SR, Sommers LE (1982) Phosphorus. In: Page AL et al (eds) Methods of soil analysis: part 2. Chemical and microbiological properties. Agron. Mongr. 9, 2nd edn. ASA and SSSA, Madison, WI, pp 403–430

Olson MH, Hage MM, Binkley MD, Binder JR (2005) Impact of migratory snow geese on nitrogen and phosphorus dynamics in a freshwater reservoir. Freshwater Biol 50:882–890

Paniagua A, Mazzarino MJ, Kass D, Szott L, Farnadez C (1995) Soil phosphorus fractions under five tropical agro-ecosystems on a volcanic soil. Aust J Soil Res 33:311–320

Pheav S, Bell RW, White PF, Kirk GJD (2005) Phosphorus mass balances for successive crops of fertilized rainfed rice on a sandy lowland soil. Nutr Cycl Agroecosyst 73:277–292

Ponnamperuma FN (1972) The chemistry of submerged soils. Adv Agron 24:29–96

Richardson CJ (1985) Mechanisms controlling phosphorus retention capacity in freshwater wetlands. Science 228:1424–1427

Richardson CJ (1999) The role of wetlands in storage, release and cycling of phosphorus on the landscape: A 25-year retrospective. In: Reddy KR et al (eds) Phosphorus biogeochemistry in subtropical ecosystems. CRC Press, Boca Raton, FL, pp 47–68

Sah RN, Mikkelsen DS (1986) Transformations of inorganic phosphorus during the flooding and draining cycles of soils. Soil Sci Soc Am J 50:62–67

Sah RN, Miller RO (1992) Spontaneous reaction for acid dissolution of biological tissues in closed vessels. Anal Chem 64:230–233

Saleque MA, Naher UA, Islam A, Pathan ABMBU, Hossain ATMS, Meisner CA (2004) Inorganic and organic phosphorus fertilizer effects on the phosphorus fractionation in wetland rice soils. Soil Sci Soc Am J 68:1635–1644

SAS Institute, Inc. (1999) SAS OnlineDoc®, Version 8. Statistical Analysis Systems Institute, Inc., Cary, NC, p 1176

Sharpley AN, Tiessen H, Cole CV (1987) Soil phosphorus forms extracted by soil tests as a function of pedogenesis. Soil Sci Soc Am J 51:362–365

Sharpley AN, Weld JN, Beegle DB, Kleinman PJA, Gburek WJ, Moore PA Jr, Mullins G (2003) Development of phosphorus indices for nutrient management planning strategies in the United States. J Soil Water Conserv 58:137–152

Sheldrick BH, Wang C (1993) Particle-size distribution. In: Carter MR (ed) Soil Sampling and methods of analysis. Canadian Society of Soil Science, Lewis Publishers, Ann Arbor, MI, pp 499–511

Sterling J, Buttner P (2009) Wildlife known to use the California ricelands. California Rice Commission, Sacramento, CA

Tiessen H, Moir JO (1993) Characterization of available P by sequential extraction. In: Carter MR (ed) Soil sampling and methods of analysis. Lewis Publishers, Ann Arbor, pp 75–86

Tiessen H, Stewart JWB, Cole CV (1984) Pathways of phosphorus transformations in soils of differing pedogenesis. Soil Sci Soc Am J 48:853–858

Turner BL, Cade-Menun BJ, Condron LM, Newman S (2005) Extraction of soil phosphorus. Talanta 66:294–306

US Salinity Laboratory Staff (1954) pH reading of saturated soil paste. In: Richards LA (ed) Diagnosis and improvement of saline and alkali soils. USDA Agricultural Handbook 60. U.S. Government Printing Office, Washington, DC, p 102

Yang C, Yang L, Jianhua L (2006) Organic phosphorus fractions in organically amended paddy soils in continuously and intermittently flooded conditions. J Environ Qual 35:1142–1150

Zhang Q, Wang GH, Feng YK, Sun QZ, Witt C, Dobermann A (2006) Changes in soil phosphorus fractions in a calcareous paddy soil under intensive rice cropping. Plant Soil 288:141–154