

Development of soil phosphorus storage capacity for phosphorus retention/release assessment in neutral or alkaline soils

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Abstract: The concept of the soil phosphorus storage capacity (SPSC) was successfully used to evaluate the phosphorus (P) loss risk and the P retention capacity of acidic soil. This study extended the concept of SPSC from acidic soil to neutral or alkaline soil. A total of 95 surfaces (0–10 cm) soil samples were collected from the Yellow River Delta (YRD) for use in this study. Batch sorption experiments, correlation analysis, stepwise regression, and a split-line model were used to calculate the threshold value of the degree of P saturation (DPS). The SPSC was developed based on the DPS threshold value. Based on a DPS threshold value of 11.5%, we developed the following equation for calculating the SPSC: $SPSC = (11.5\% - \text{soil DPS}) \times (0.113 \times \text{SOM (soil organic matter)} + 1.343 \times \text{CaCO}_3)$. In the continuous system in this watershed, from wetland to farmland, the SPSC for vegetable fields (-94.7 ± 79.1 mg/kg) was lowest and that of the restored wetland (76.3 ± 26.1 mg/kg) was the highest. Along the transition zone in the YRD, both the natural soil development and human alternations significantly affected the soil P loss/retention capacity. In terms of P storage, the restored wetlands are the highlands for P retention and the vegetable fields contribute significantly to the P loss in the YRD. As a result, we strongly recommend that the restored wetlands be fully utilised for P retention and that P fertiliser no longer be applied to the vegetable fields to prevent P loss into the watershed.

Keywords: macronutrient; accumulation; environmental risk; external phosphorus pollution; land uses

Excessive phosphorus (P) is often applied to soils to increase food production, which results in the accumulation of P in the soils. Long-term P accumulation, also referred to as legacy P, leads to increased loss of P through the surface flow. The main consequence of P loss is the danger to surface water eutrophication, including harmful algal blooms and dead zones in freshwater systems and coastal oceans (Carpenter 2008). Several measures have been developed to evaluate the potential risk of P from loss agricultural fields. For example, soil P testing (STP) is used for agronomic purposes (e.g., Mehlich-3 P, Olsen P, and Bray-1P) and environmental purposes (e.g., water-extractable P (WEP) and CaCl_2 extractable P) and has been used to assess the risk of P loss from agriculture fields into water bodies (Ige et al. 2005a, Ulén and Jakobsson

2005, Blombäck et al. 2021). In recent decades, the degree of P saturation (DPS) has been widely used to predict the risk of P loss (Fang et al. 2002, Ige et al. 2005a, Fischer et al. 2017). In these approaches, the STP or DPS is regressed against the WEP, and then, a threshold (change point) is identified statistically using a non-linear equation (Ige et al. 2005b). Above the threshold, significant increases in the WEP in the soil solution are generally observed. However, these measures depend on the type of soil because different types of soil have different critical STP and DPS threshold values (Mukherjee et al. 2009). This makes it very difficult to compare the P loss potentials of different soils. To overcome these shortcomings, the concept of the soil P storage capacity (SPSC) was introduced by Nair and Harris (2004).

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The SPSC has been used to evaluate the amount of P that can be safely stored in the soil before that soil becomes an environmental risk (Nair and Harris 2004). Unlike the STP and DPS methods, SPSC evaluation is soil independent and was developed based on the DPS values, and it considers both the risk of P loss and the inherent P retention capacity of the soil (Nair and Harris 2014). The SPSC has been applied to the design, construction, and management of agricultural fields and wetlands. Chrysostome (2007) demonstrated the validity of using the SPSC as a means of estimating the P gain or loss under controlled laboratory conditions. Dari (2015) suggested that the SPSC concept could be a valuable tool for evaluating legacy P storage and the P release potential from both upland and wetland soils. Dari et al. (2018) reported that the SPSC index is applicable to acidic soils across a wide geographic range. In addition, the subsurface transport of phosphorus into groundwater in a soil profile supports the application of the SPSC index to deep soils (Liao et al. 2019).

However, the previous usage of the SPSC for P assessment has mainly focused on acidic soils (Nair and Harris 2014). There is little information about calculating the SPSC values of alkaline soils. The method of calculating the SPSC of alkaline soil is hypothesised to be significantly different from that for acidic soil because of the different P retention mechanisms of these types of soils (Reddy et al. 1999, Ige et al. 2005a). In generally, for soils with a pH of < 6.5, amorphous Fe and Al oxides determine the P sorption; however, for soils with a pH of > 7.5, Ca and Mg species tend to dictate the P sorption (Reddy et al. 1999). For alkaline soils, the P sorption capacity (PSC) estimated using the Mehlich-3 calcium (Ca) and Mg was highly correlated with the maximum amount of P adsorbed (Ige et al. 2005b). Hongthanat et al. (2011) observed that the PSC is significantly correlated with both oxalate-extracted iron (Fe_{ox}) and aluminium (Al_{ox}) or with the Mehlich-3 extracted Ca and Mg, which suggested that both indices are suitable for neutral to alkaline soils in Iowa. Renneson et al. (2015) found that the multiple regression equation $PSC = a \times Al_{ox} + b \times pH$ is better suited for estimating the PSC of pH-neutral soils. Therefore, an in-depth study of the environmental index for the P retention and loss assessment of alkaline soils is imperative since such soils are widely distributed and agriculturally important.

The Yellow River Delta (YRD) was formed by the large amount of sediment carried by the Yellow River from the upland area (Yu et al. 2015). The land-use types

vary significantly from land to sea due to the natural soil development and human alternations. Therefore, the wide range of soil properties and P characteristics in YRD should be employed to fully understand the P retention or release of alkaline soils (Li et al. 2016a). Furthermore, the sea adjacent to the YRD is threatened by external P pollution, so it is necessary to calculate the P retention and loss risk in the YRD (Zhou et al. 2021). As a result, the goals of this study were (1) to develop an SPSC for phosphorus retention/release assessment based on DPS evaluations in alkaline wetland soils; and (2) to compare the SPSC values of soils from six typical land uses from land to sea in the YRD.

MATERIAL AND METHODS

Study area. The Yellow River Delta (118°07'–119°18'E, 36°55'–38°12'N) is situated to the south of the Bohai Sea, China (Figure 1). It has a temperate, semi-humid continental monsoon climate, with an annual average temperature of 12.1 °C and an annual average rainfall of 552 mm. A huge amount of sediment was carried by the Yellow River from the Loess Plateau and was deposited in the delta where a vast area of floodplain and wetland formed. The main soil types include Calcaric Fluvisols, Salic Fluvisols, and Gleyic Solonchaks (Li et al. 2016a).

The land-use types in the YRD mainly include tidal wetlands, restored wetlands, abandoned fields, cotton fields (cotton), cereal fields (corn/wheat), and vegetable fields. From the tidal wetlands to the vegetable fields, the soil fertility significantly increases with decreasing soil salinity along with the continuous system (Li et al. 2016b). The tidal wetlands are characterised by high soil salinity, sparse vegetation, and low organic matter content. The restored wetlands have proven to be effective at reducing the soil salinity and increasing the vegetation community and soil organic matter (SOM) content (Cui et al. 2009). Because the cotton has a strong salt tolerance, it is the pioneer species in the soil reclamation area in the YRD. After long-term cultivation of cotton in a field, the soil salinity significantly decreases and the soil fertility improves, and then, the soil can be planted with corn or wheat. With successive soil reclamation, the soil has become almost completely desalinated and vegetables can be planted in the YRD. The abandoned fields consist of the degraded cotton fields where the soil fertility was greatly reduced due to improper land management (Li et al. 2016b).

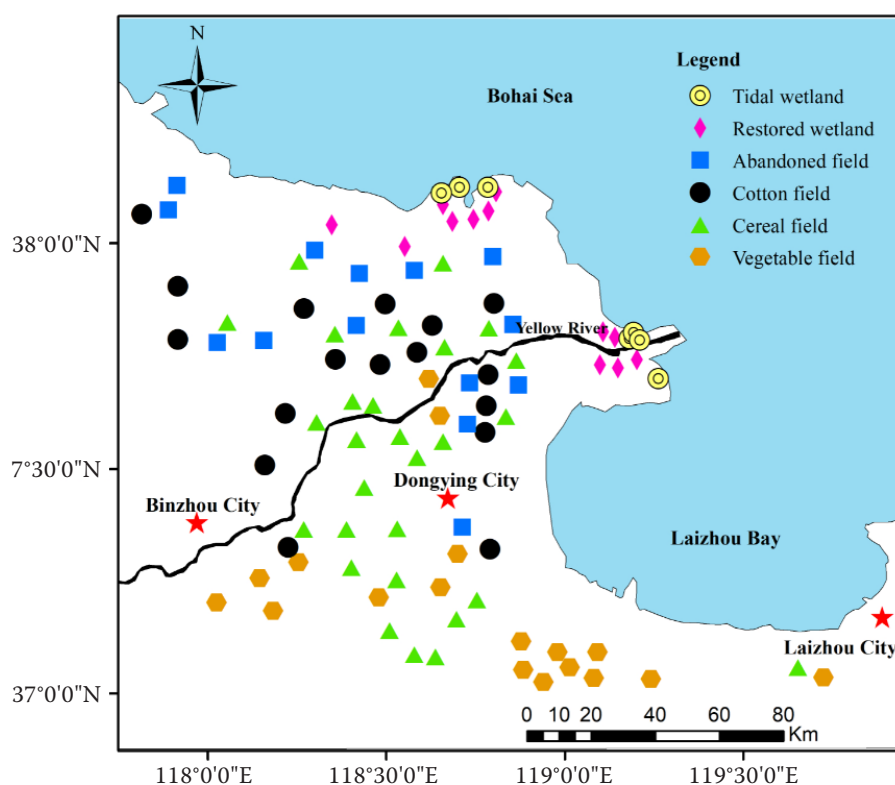


Figure 1. Distribution of sampling sites in the Yellow River Delta

Soil sampling. As already discussed, six typical land-use types, including tidal wetlands (sampling sites $n = 7$), restored wetlands ($n = 12$), abandoned fields ($n = 14$), cotton fields ($n = 17$), cereal fields (corn/wheat) ($n = 27$), and vegetables fields ($n = 18$), were selected for analysis in this study (Figure 1). A total of 95 surface soil samples (0–10 cm) were collected from 95 sites across the YRD in November 2018 (Figure 1). At each sampling site, three randomly distributed soil samples were collected and combined to obtain a more representative sample (~1 kg). All of the soil samples were air-dried. The visible roots and rocks in the samples were removed, and the samples were ground, passed through 0.149 mm (for soil organic matter and CaCO_3 analysis) and 2 mm (for P analysis and other soil properties determination) sieve, and stored in a refrigerator at 4 °C for future use.

Soil chemical analysis. A pH meter was used to measure the soil pH using a soil/water ratio of 1:2.5. Soil electric conductivity was measured in the suspension of 1:5 soil/water (m/v) using an electrical conductivity meter. The water-extractable P was performed by adding 25 mL distilled water into 1 g soil and shaking for 1 h (Pote et al. 1996). The P in the solution was determined using the molybdenum blue colourimetric method (Murphy and Riley 1962). The total P (TP) content was measured after

soil digestion in a mixture of concentrated sulfuric acid and perchloric acid. The SOM content was analysed as the loss on the ignition after heating at 500 °C for 2 h. The carbonate content was determined *via* the acid neutralisation method (Richards 1954). The appropriate soil sample was reacted with excessive standard HCl solution, thereafter the remaining acid is titrated with standard NaOH solution. The carbonate content was calculated by the difference amount between the total HCl and the HCl neutralised with NaOH. The ammonium oxalate extractable $\text{Fe}_{\text{ox}}/\text{Al}_{\text{ox}}$ and Mehlich 3 solution extractable Ca/Mg were analysed using inductively coupled plasma atomic emission spectroscopy (ICP-AES, Perkin Elmer, Shelton, USA). The particle size distribution of the sediments was determined using a laser diffraction particle size analyser (Mastersizer 2000, Malvern, UK). For quality control, a standard sample (GBW07427) was used to determine the TP concentrations, and the measured deviation of the standard samples was determined to be less than 5%.

Phosphorus sorption experiments. We used batch experiments to obtain the P sorption isotherms. The amount of 1.0 g of each sample was placed in a screw-cap centrifuge tube (50 mL), along with 20 mL of standard phosphate solution (KH_2PO_4) of various concentrations, including 0.0, 0.5, 1.0, 2.5, 5.0,

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10.0, 15.0, 30.0, 50.0, 75.0, 100.0, 120.0, 160.0, and 240.0 mg/L. The solution was shaken for 24 h at 25 °C to allow the solution to reach equilibrium. The equilibrium P concentration was determined using the continuous flow method after the supernatant was filtered through a 0.45- μ m membrane. The difference between the amount of P added and the equilibrium amount of P was calculated as the amount of P adsorbed onto the soil (Nair and Reddy 2013). The Langmuir model was used to generate the sorption parameters, including the maximum P sorption capacity (S_{\max}) (Bai et al. 2017).

Data analysis. Correlation analysis of the soil S_{\max} and the chemical properties of the soil (electrical conductivity (EC), pH, sand, clay, silt, Fe_{ox} , Al_{ox} , Ca_{M3} , Mg_{M3} , $CaCO_3$, and SOM) was conducted, and the variables that contributed significantly ($P < 0.01$) to S_{\max} were identified. The variables that did not contribute significantly ($P > 0.05$) to S_{\max} were eliminated before the P sorption capacity (PSC) evaluation. After this, stepwise regression modelling (best-subset method) was used to determine the estimated PSC from the selected independent variables according to the significance of the coefficients and the adjusted R^2 ($P < 0.01$ for the model and regression coefficients). Once the PSC prediction was established, the soil specific DPS was calculated using the following equation:

$$DPS = \frac{\text{Olsen} - P}{PSC} \quad (1)$$

The relationship between the WEP and DPS was determined using a split-line model in SAS (SAS Institute 2001), which describes two lines that intersect at a change point (d_0):

$$WEP = \begin{cases} a_0 + b_0 DPS, & DPS \leq d_0 \\ a_1 + b_1 DPS, & DPS > d_0 \end{cases} \quad (2)$$

$$b_0 = \frac{(a_1 - a_0) + b_1 d_0}{d_0} \quad (3)$$

where: a_0 and a_1 – intercepts; b_0 and b_1 – slopes of the two segments; d_0 – DPS value at the threshold (change point).

Using the soil P loss threshold (d_0), the soil SPSC was calculated as follows:

$$SPSC = (d_0 - \text{soil DPS}) \times PSC \quad (4)$$

RESULTS

Soil characteristics. The means, standard deviations, and ranges of the basic physicochemical and P-related properties of the 95 soil samples from the Yellow River Delta are presented in Table 1. Overall, the soils were slightly acidic to alkaline, with a pH range of 5.85–8.57 and an average pH of 7.84. The EC values ranged from 0.1 to 15.7 mS/cm. The carbonate contents ranged from 2 to 178 g/kg. The SOM contents ranged from 2.0% to 12.0%, with an average of 5.3%. The proportions of sand, silt, and clay were highly variable, ranging from 46 to 602, 333 to 844, and 53 to 234 g/kg, respectively. The

Table 1. Basic physical and chemical properties of soil samples from the Yellow River Delta ($n = 95$)

Soil property	Unit	Min	Max	Mean	Standard deviation
pH		5.85	8.57	7.84	0.47
Electrical conductivity	(mS/cm)	0.1	15.7	1.4	2.3
Sand		41.9	96.9	74.9	12.6
Silt		2.9	48.9	21.9	10.8
Clay	(%)	0.24	9.43	4.09	1.88
SOM		2.0	12.0	5.3	2.3
$CaCO_3$		0.2	17.8	6.1	3.9
Al_{ox}		6.3	77.0	22.6	11.2
Fe_{ox}		3	101	20	15
Ca_{M3}		93	1 014	423	212
Mg_{M3}	(mmol/kg)	12	110	40	18
Olsen-P		0.05	10.27	1.39	2.08
WEP		0.01	4.84	0.31	0.69
TP		11	192	36	26

SOM – soil organic matter; TP – total phosphorus; WEP – water-extractable phosphorus

Fe_{ox} and Al_{ox} contents were 3–101 mmol/kg and 6.3–77 mmol/kg, respectively. The Mehlich 3 extracted Ca and Mg concentrations of the soils were 93–1 014 mmol/kg and 12–110 mmol/kg, respectively. The soil P levels varied widely from 0 to 4.84 mmol/kg for WEP, from 0.1 to 10.3 mmol/kg for Olsen-P, and from 11 to 192 mmol/kg for TP. Therefore, the soil samples have a wide range of chemical and physical properties and are representative of the major soils in the YRD.

Correlation analysis among variables and PSC determination. As is shown in Table 2, there were significant positive correlations between S_{max} and CaCO₃, SOM, Al_{ox}, Fe_{ox}, Mg_{M3}, Ca_{M3}, and the clay particle proportion (*P* < 0.01). Thus, these variables were included in the subsequent evaluation and PSC determination. In comparison, the soil pH and EC were not significantly correlated with S_{max} (*P* > 0.05), so they were excluded from the PSC evaluation.

Based on the correlation analysis and stepwise regression modelling, CaCO₃ and SOM were identified as the most important variables for calculating the PSC using the following equation:

$$PSC = 0.113 \times SOM + 1.343 \times CaCO_3 \quad (5)$$

This relationship accounted for 85.6% of the PSC variability across the soils studied and demonstrates the influences of CaCO₃ and SOM in soil reactions. The standard errors for CaCO₃ and SOM were 0.261 and 0.021, respectively.

The DPS and P environmental threshold. Based on the PSC data, the DPS value was estimated as follows:

$$DPS = \frac{Olsen - P}{0.113 \times SOM + 1.343 \times CaCO_3} \quad (6)$$

The relationship between the DPS and WEP is shown in Figure 2. The regression below the threshold was:

$$WEP = 2.24, DPS \leq 11.5\% \quad (7)$$

The regression above the threshold was

$$WEP = 164 \times DPS - 16.6, DPS > 11.5\% \quad (8)$$

As a result, the change point (threshold) of the DPS value in this model was determined to be 11.5% (*P* < 0.01). Above DPS = 11.5%, there is a rapid increase in the WEP in the soil, and therefore, the P has a negative impact on the quality of the adjacent water.

SPSC determination and variation from upland to wetland. Based on the DPS threshold, the soil P storage capacity (SPSC) was calculated as follows:

Table 2. Correlations between the maximum adsorption amount of phosphorus in the soil and the basic physical and chemical indicators (*n* = 95)

	pH	EC	CaCO ₃	SOM	Al _{ox}	Fe _{ox}	Ca _{M3}	Mg _{M3}	Sand	Slit	Clay	S _{max}
pH	1											
EC	-0.053	1										
CaCO ₃	0.097	0.452**	1									
SOM	-0.284**	0.43**	0.535**	1								
Al _{ox}	-0.256*	-0.159	0.074	0.553**	1							
Fe _{ox}	-0.355**	0.398**	0.592**	0.560**	0.473**	1						
Ca _{M3}	0.346**	0.365**	0.165	-0.114	-0.444**	-0.006	1					
Mg _{M3}	-0.025	0.416**	0.411**	0.484**	0.118	0.306**	0.204	1				
Sand	0.052	-0.324**	-0.441**	-0.458**	-0.378**	-0.230*	-0.135	-0.426	1			
Slit	-0.051	0.465**	0.500**	0.484**	0.274**	0.488**	0.093	0.506**	-0.719**	1		
Clay	-0.043	0.486**	0.545**	0.537**	0.385**	0.506**	0.034	0.526**	-0.665**	0.929**	1	
S _{max}	0.200	0.211	0.649**	0.596**	0.276**	0.431**	0.242*	0.510**	-0.438**	0.468**	0.526**	1

EC – electrical conductivity; SOM – soil organic matter; S_{max} – maximum P sorption capacity; **P* < 0.05; ***P* < 0.01

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$$\text{SPSC} = (11.5\% - \text{soil DPS}) \times (0.113 \times \text{SOM} + 1.343 \times \text{CaCO}_3) \quad (9)$$

The SPSC values of the vegetable fields (-94.7 ± 79.1 mg/kg), cereal fields (6.3 ± 33.4 mg/kg), cotton fields (16.4 ± 24.9 mg/kg), barren soil (26.8 ± 8.3 mg/kg), tidal wetlands (49.3 ± 16.3 mg/kg), and restored wetlands (76.3 ± 26.1 mg/kg) in the Yellow River Delta were calculated (Figure 3) using this equation. Thus, vegetable cultivation significantly decreased the SPSC, while the restored wetland had the highest SPSC value in the watersheds from upland to wetland.

DISCUSSIONS

Environmental phosphorus loss threshold. The determination of the P loss threshold is the most important part of the SPSC calculation. In this study, an environmental P loss threshold (DPS = 11.5%) was identified for the Yellow River Delta. The DPS has been suggested to be an effective indicator of the P loss potential. However, previous studies have reported that the P loss threshold of the DPS is greatly variable, so comparisons should be made with great caution because these different studies used different methods to calculate the DPS (Nair and Harris 2004, Butler and Coale 2005, Nelson et al. 2005). According to the linear correlation between the DPS and WEP (or Olsen-P), a DPS threshold of 11.5% is equivalent to WEP and Olsen-P threshold values of 10.5 and 44.8 mg/kg, respectively. The WEP and Olsen-P threshold values are consistent with those

reported in previous studies. For example, Xue et al. (2014) reported WEP and Olsen-P threshold values of 8.8 and 49.2 mg/kg, respectively, for slightly to strongly calcareous soils in China. Bai et al. (2013) observed that the critical soil Olsen-P ranged from 40 to 52 mg/kg in two neutral and calcareous soils in China. Similar Olsen-P thresholds ranging from 40 to 55 mg/kg have also been reported for calcareous soils in the Minnesota River Basin (Fang et al. 2002). Thus, our P loss threshold is consistent with those reported in previous studies.

Based on the threshold DPS, the SPSC was calculated to assess the remaining soil P storage capacity, and the zero SPSC was defined as the threshold value below which the P loss risk increases precipitously. The SPSC was used to directly estimate the amount of P that a soil can store before the soil exceeds the DPS threshold value. Utilising the concept of the SPSC, we can calculate the amount of P that can be loaded into the soil before that soil becomes a P source. According to the SPSC and the P load, we can predict the safe lifespan of an application site, which is more important for wetland and farmland management (Nair and Harris 2014). Therefore, it is important to extend the concept of the SPSC from acidic soils to alkaline soils, and the usage of this concept deserves further investigation.

Soil phosphorus storage capacity along the watershed from the upland area to the wetlands. Along with the continuous system from the upland area to the wetlands, we found that the SPSC sequence was as follows: vegetable fields < cereal fields/cotton fields/tidal wetland < restored wetlands. On the

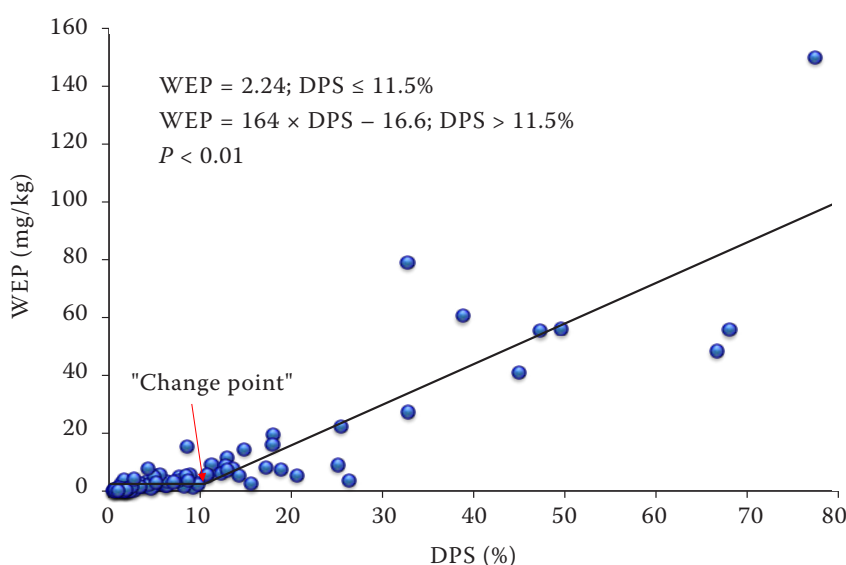


Figure 2. Relationship between the degree of phosphorus saturation (DPS) and the concentration of water-extractable phosphorus (WEP) for all 95 soil samples using the split-line models

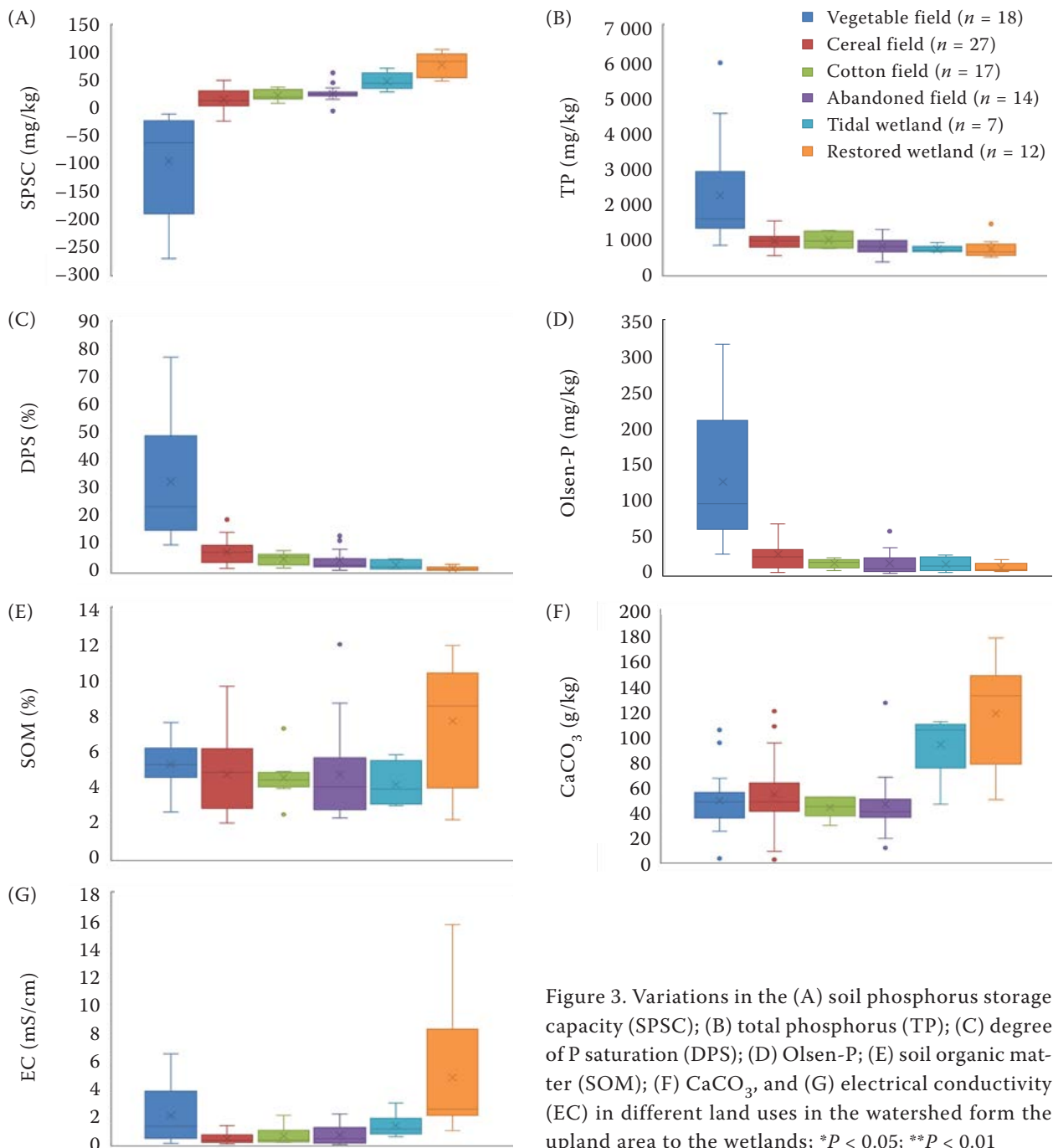
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Figure 3. Variations in the (A) soil phosphorus storage capacity (SPSC); (B) total phosphorus (TP); (C) degree of P saturation (DPS); (D) Olsen-P; (E) soil organic matter (SOM); (F) CaCO₃ and (G) electrical conductivity (EC) in different land uses in the watershed from the upland area to the wetlands; * $P < 0.05$; ** $P < 0.01$

landscape scale, our observations suggest that the restored wetlands are the highland for P storage between the upland area and the wetlands. Therefore, the wetlands (especially the restored wetlands) can buffer the impact of P on the aquatic ecosystems by sequestering the excess P in the watershed as it migrates from the upland area (Hongthanat et al. 2011). The SPSC value did not vary significantly although a slightly increasing trend was observed from tidal wetlands to the abandoned fields to the cotton

fields to the cereal fields. In contrast, the negative SPSC values of the vegetable fields indicate that the vegetable fields cannot retain additional P and act as a P source to the adjacent water. The significant decrease in the SPSC values of the vegetable fields may be due to the significant input of P fertilisers (Fischer et al. 2018). Therefore, the application of P fertiliser to vegetable fields should be stopped immediately to protect the adjacent water bodies. As a result, it is strongly recommended that the restored

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wetlands be utilised for more P storage, while the application of P fertiliser to the vegetable fields should be stopped and amendment measures should be taken to decrease the P loss at the landscape scale. For the YRD soils, the tidal wetland soils act as the parent material, and the other land-use types were developed on the tidal wetlands. The tidal wetlands were created on newly formed land as a result of the large amount of sediment carried by the river from the upland area and deposited in the delta (Yu et al. 2015). In general, the tidal wetlands are characterised by a higher EC and CaCO₃ content and lower SOM and TP contents (Figure 3). With natural soil development, the soil undergoes desalination and organic matter accumulation during the reclamation of the tidal wetlands (Figure 3). Consequently, the soil's physicochemical properties tend to improve, and the P sorption increases during the reclamation of the tidal wetlands (Yin et al. 2017). However, human alternations of the soil properties also occur during this process. For example, the TP, Olsen-P, and DPS generally slightly increase from the tidal wetlands to the cereal fields and they abruptly increase from the cereal fields to the vegetable fields because of the significant input of P fertiliser into the vegetable fields (Figure 3). From the tidal wetlands to the restored wetlands, the natural soil development significantly increased the SPSC value. However, the P fertiliser input significantly decreased the SPSC values from the tidal wetlands to the vegetable fields. As a result, the SPSC values were complicated by the natural soil development and human fertiliser application during the reclamation of the tidal wetlands.

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