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# Potential pollution and recommended critical levels of phosphorus in paddy soils of the southern Lake Tai area, China

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#### Abstract

The southern Lake Tai area is an important agricultural area distributed with 500,000 ha of paddy soils. Based on the current soil phosphorus status, it is predicted that phosphorus in agricultural runoff from paddy fields is now one of the most dangerous threats to the quality of water in Lake Tai and the application of phosphorus fertilizers should be controlled. Phosphorus adsorption maxima based on the Langmuir equation were calculated for various soil-environmental conditions and the upper limit of accumulative phosphorus application to paddy soils of the area is suggested. © 2003 Elsevier Science B.V. All rights reserved.

Keywords: Phosphorus pollution; Critical level; Agricultural runoff; Paddy soil; Langmuir equation

## 1. Introduction

The increase in amount of phosphorus used together with long-term accumulation in soils would both be expected to result in greater overall losses of phosphorus to aquatic ecosystems (Ahl, 1988; Edwards and Withers, 1998; Fisher et al., 1998). Like western developed countries such as the UK, the USA, Canada, France and Germany, China as a developing country is now paying more attention to the problem of lake eutrophication due to continuous and increasing losses of soil phosphorus by surface runoff.

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In the southern Lake Tai area, rice production and phosphorus fertilizer application have a long history. Paddy soils are the main soil type in the area, up to 500,000 ha. In recent years, the application of phosphorus fertilizers to paddy soils has been increasing in order to enhance the per unit area yield of rice and other crops. In particular, rice, with less phosphorus requirements, is being replaced by rape, legumes, vegetables and other economic crops requiring more phosphorus. Random discharge of wastewater containing phosphorus is also an important source of phosphorus in agricultural soils of the area with the development of rural enterprises such as foodstuff processing plants, poultry breeding yards and phosphorus fertilizer mills. The increasing input of phosphorous into agricultural soils in this area has become an important environmental problem, including the eutrophication of Lake Tai. The aim of the research is to show a relationship between water quality in Lake Tai and local agricultural production according to the current soil phosphorus fertilizers based on phosphorus adsorption experiments.

#### 2. Materials and methods

#### 2.1. Sampling sites

Surface paddy soil samples (0-20 cm) were collected from four representative sites widely distributed in the southern Lake Tai area. In the past, all the sites were used for rice production and have a history of phosphorus fertilizer application. Now economic crops with higher phosphorus requirements have been planted in the sites and thus more phosphorus fertilizers have been applied to the agricultural fields. According to recent investigations, the annual dosage of phosphorus fertilizers is up to 25-35 kg (P) ha<sup>-1</sup> in this area. Correspondingly, more phosphorus is being accumulated in the soil or leached into surface waters.

#### 2.2. Determination of soil phosphorus

# 2.2.1. Total phosphorus (TP)

After the soil samples were air-dried, ground and digested with potassium persulphate and 30% v/v sulphuric acid, TP was measured using the acidic molybdate–ascorbic acid (AMAA) method (He et al., 1998; Zhou et al., 2001).

#### 2.2.2. Chemically extractable phosphorus

According to Olsen et al. (1954), Chang and Jackson (1957), Psenner et al. (1985), Yanishevskii (1996), Sabbe and Dunham (1998), Overman and Scholtz (1999) and Reddy et al. (1999), chemically extractable forms of phosphorus that are closely related to the transport of phosphorus from soils to surface water include water-soluble phosphorus (WSP), readily desorbed phosphorus (RDP), algal available phosphorus (AAP) and NaHCO<sub>3</sub> extractable phosphorus (Olsen-P). Their analytical procedures are described as follows. 2.2.2.1. *WSP.* One gram of soil was placed into bottles with 100 ml of deionized water and then shaken for 2.0 h on a reciprocating shaker at 150 rpm at 25 °C. The suspensions were filtered through 0.45- $\mu$ m pore size membrane filters and the filtrate was analyzed for WSP using the AMAA method.

2.2.2.2. *RDP.* Two grams of soil was placed in bottles, then the samples were shaken for 1.0 h with 50 ml of 0.01 M CaCl<sub>2</sub> solution, in a wet sediment to extracting solution ratio of 1:25. The suspensions were filtered through 0.45- $\mu$ m pore size membrane filters and the filtrates were analyzed for RDP using the AMAA method.

2.2.2.3. AAP. A total of 0.80 g of soil was placed in bottles and 200 ml of 0.1 M NaOH solution added (wet sediment/extracting solution = 1:250), the bottles were covered and the samples were shaken for 4.0 h on a shaker. The suspensions were filtered and the filtrates were analyzed for AAP using the AMAA method.

2.2.2.4. Olsen-P. A total of 2.50 g of the samples were placed in bottles and the samples were shaken for 0.5 h with 50 ml of 0.5 M NaHCO<sub>3</sub> solution (pH 8.5, wet sediment/extracting solution = 1:20). The suspensions were filtered through 0.45- $\mu$ m pore size membrane filters and the filtrates were analyzed for Olsen-P using the AMAA method.

#### 2.3. Phosphorus adsorption experiments

Before the adsorption experiment, the four paddy soil samples were homogeneously mixed into one paddy soil sample. Samples of the mixed paddy soil were heated at 105 °C for 2, 5 and 10 min. The three heated samples had final organic matter content of 1.47%, 0.64% and 0.21%, respectively.

The adsorption experiment was carried out according to Nair et al. (1984). This mainly involves addition of six  $KH_2PO_4$  solutions (0, 5, 10, 15, 20 and 30 mg (P)  $1^{-1}$  in 0.01 M CaCl<sub>2</sub> solution) to the homogenized paddy soil samples at five soil/solution ratios (w/ v=1:10, 1:25, 1:50, 1:100, 1:150) under varying pH (regulated by adding diluted HCl and NaOH solution) conditions. The solutions were equilibrated for 24 h at 5, 15, 25 (room temperature) and 35 °C in a shaker and filtered through 0.45-µm filter paper.

The phosphorus adsorption maximum was determined by use of the linearized form of the Langmuir equation (Olsen and Watanabe, 1957):

$$\frac{C}{x/m} = \frac{1}{kb} + \frac{C}{b} \tag{1}$$

Where x/m is the amount of phosphorus adsorbed per unit weight of soil, *C* is the concentration of phosphorus in the solution at equilibrium, *b* is the phosphorus adsorption maximum and *k* is a constant presumably related to binding strength of phosphorus on the soil.

In theory, since

$$Q = x/m \tag{2}$$

In other words, Q is the amount of phosphorus adsorbed per unit weight of soil. Then Eq. (1) can be changed into

$$C/Q = (1/b)C + 1/(kb)$$
(3)

# 2.4. Maximum phosphorus fertilizer application

Adsorption of phosphorus by soils is finite. Some of phosphorus adsorbed on soils during phosphorus adsorption processes can be also desorbed and released into surface waters when environmental conditions change. In particular, the release of soil phosphorus becomes a dominant process and will threaten the health of aquatic ecosystems after the maximum phosphorus adsorption level is reached. In addition, excess phosphorus application is wasteful in terms of agricultural production. Thus, suggestions of maximum phosphorus fertilizer application levels can be useful to both agricultural production and environmental protection, based on long-term agricultural and environmental practice.

Maximum phosphorus fertilizer application levels can be in theory calculated according to following formula:

$$F_p = 1.0 \times 10^{-6} \delta b \tag{4}$$

Where  $\delta$  is soil weight of plough layer (kg ha<sup>-1</sup>) and  $F_p$  is the upper limit of accumulative phosphorus application (kg ha<sup>-1</sup>) that is in practice equal to the sum of maximum annual phosphorus application to agricultural soils over a long period of time (m, more than 50 years), namely

$$F_{\rm p} = \sum_{T=1}^{\rm m} \rm NP_{\rm max} \tag{5}$$

Where *T* is time (years) of phosphorus application, and NP<sub>max</sub> is the maximum annual phosphorus application rate (kg ha<sup>-1</sup>). When  $F_p$  is given, the maximum annual phosphorus application rate can be calculated according to following formula:

$$NP_{max} = F_p/T \tag{6}$$

# 3. Results and discussion

## 3.1. Current soil phosphorus status and transport

Basic characteristics of these surface paddy soils and their TP are listed in Table 1. Given the soil pH, soil clay and organic matter contents, these soils are suitable for the growth of rice and other economic crops. In particular, the TP in all the paddy soils had been enriched and accumulated compared with the previous relevant analytical data and the TP (0.044%) in the original mother matters of the tested soil.

Compared with TP, RDP in the surface paddy soils was relatively low (Table 2), only accounting for 0.53 % of TP. However, according to the results from some researches

Sampling site	Soil clay (%)	Organic matter (%)	pH	TP (%)
1	51.3	2.61	6.5	0.092
2	44.7	2.44	5.8	0.078
3	46.9	2.48	6.1	0.082
4	48.3	2.33	6.4	0.085
Average	47.8	2.47	6.2	0.084

Table 1 Basic characteristics of paddy soils and their TP

(MAFF (UK Ministry of Agriculture Fisheries and Food), 1991; Dobermann et al., 1998; Gibson, 1998; Heckrath et al., 1995), phosphorus in paddy soil can meet the needs for the growth of rice when Olsen-P>20 mg kg<sup>-1</sup>. The Olsen-P in all the surface paddy soils from the southern Lake Tai area have four times as much as the minimum Olsen-P level for rice growth. Some of the excess phosphorus that is not required for rice production may be discharged into Lake Tai.

There is no doubt that WSP can be easily transported with water flow. And this fractionation of soil phosphorus is usually transported into surface waters by runoff. WSP in all paddy soil surface layers was quite high, up to 1000 times more than the TP (36.5 µg  $1^{-1}$ , n=4) in water of the southern Lake Tai. Thus, soil phosphorus in agricultural runoff is likely to be a major source of phosphorus in Lake Tai.

Noticeably, AAP in the surface of paddy soils was higher than other kinds of chemically extractable phosphorus, and approaches the level of AAP in phosphorus– surplus soils of western developed countries such as the UK, the USA and Canada (Gibson, 1997; Edwards and Withers, 1998; Reddy et al., 1998; Sabbe and Dunham, 1998; Stout et al., 1998). It is evident that mobile phosphorus in the paddy soils of the southern Lake Tai area is at a high level although the associated TP values are not very high. We believe that the cause of the water quality deterioration of Lake Tai is due in large part to the phosphorus in agricultural runoff. This conclusion has been supported by our further work (Zhou et al., 2001).

## 3.2. Adsorption of phosphorus on soils

Adsorption of phosphorus by soils is a physicochemical and ecological process related to the initial concentration of phosphorus in soil solution. Under the normal environmental

Sampling site	WSP (mg $kg^{-1}$ )	AAP (mg kg <sup><math>-1</math></sup> )	RDP (mg kg <sup><math>-1</math></sup> )	Olsen-P (mg kg <sup>-1</sup> )
1	44.32	187.23	5.64	99.32
2	28.43	145.73	3.30	73.23
3	36.75	157.38	4.41	84.07
4	39.17	166.21	4.56	88.34
Average	37.17	164.14	4.48	86.24

Table 2 Chemical fractionations of phosphorus in paddy soils (based on air-dry weight)

Parameters	Tested conditions	Remarks
TP (%)	0.084	mixed paddy soil sample
Organic matter (%)	2.47	mixed paddy soil sample
Clay content (%)	47.8	mixed paddy soil sample
pH	6.2	mixed paddy soil sample
Temperature	25 °C	room temperature
Soil/solution ratio	1:25	×.

Table 3 Normal conditions of the adsorption experiments

conditions (Table 3), adsorption of phosphorus on the (mixed) paddy soil could be quantified as follows:

$$C/Q = 2.1921C + 4.0688$$
 ( $R^2 = 0.9657$ ,  $n = 24$ ,  $p < 0.005$ ) (7)

Where *p* is the level of statistical significance, *R* is the correlation coefficient and *n* is the number of tested samples. It can be calculated according to Eq. (7) that the mean phosphorus adsorption maximum (PSM) that in theory amounts to the phosphorus adsorption maximum (*b*) of paddy soil in the area was equal to 456.2 mg kg<sup>-1</sup>.

In fact, PSM of paddy soils systematically changes when adsorption conditions related to soil characteristics and agricultural production are varied. Four clear trends were primarily observed for phosphorus adsorption.

First, phosphorus adsorption was negatively correlated with tested water temperature (Fig. 1, level of significance p = 0.05). For example, mean phosphorus adsorption on the soil was 483.1 mg kg<sup>-1</sup> when water temperature was 5 °C. When water temperature was increased to 35 °C, mean phosphorus adsorption on the soil was reduced to 338.7 mg kg<sup>-1</sup>. In other words, soil phosphorus adsorption capacity in the summer is lower than in the winter. In practice, phosphorus fertilizers are usually applied to rice fields and other agricultural soils in the hot season. Thus, PSM should be modified according to the adsorption results under high temperature conditions.



Fig. 1. The relationship between PSM and water temperature ( $^{\circ}$ C). When water temperature was being varied, other conditions including soil pH (6.2), organic matter levels (2.47%) and the ratio of water to soil (25:1) were held constant.



Fig. 2. The relationship between PSM and levels of organic matter in the soil. When levels of organic matter were being varied, other soil conditions including soil pH (6.2), room temperature (25  $^{\circ}$ C) and the ratio of water to soil (25:1) were held constant.

Second, when the content of organic matter in the soil is lowered, the phosphorus adsorption capacity is significantly less (Fig. 2, p = 0.025). For example, mean phosphorus adsorption on the soil containing 0.21% of organic matter was low, only 328.4 mg kg<sup>-1</sup>. On the contrary, mean phosphorus adsorption on the soil containing 0.64 % of organic matter was high, up to 398.7 mg kg<sup>-1</sup>. With agricultural production, organic matter in paddy soils decreases with time. In some paddy soils of the area, organic matter is very low, only 0.1–0.2%. Thus, the determination of PSM should also consider levels of organic matter in agricultural soils.

Third, phosphorus adsorption capacity decreases with an increase in water/soil ratios. For example, mean phosphorus adsorption on the soil was 461.3 mg kg<sup>-1</sup> when the ratio of water (v) to soil (w) was 10. When the ratio of water (v) to soil (w) was increased to 50, mean phosphorus adsorption on the soil decreased to 444.6 mg kg<sup>-1</sup>. This situation could be related to agricultural irrigation/drainage or floods (Fig. 3, p = 0.005). In other words, agricultural irrigation/drainage and floods are disadvantageous to the adsorption of phosphorus on the soil because it can result in the release of soil phosphorus into water



Fig. 3. PSM at various solution:soil ratios. When the ratio of water to soil was being varied, other soil conditions including soil pH (6.2), room temperature (25 °C) and organic matter levels (2.47%) were held constant.

(Beck and Sanchez, 1996; Olila et al., 1997). Some of the released phosphorus can be discharged into Lake Tai by way of agricultural drainage or surface runoff. Thus, PSM should also take into consideration the status of agricultural irrigation/drainage and precipitation/flooding in the area.

Fourth, the phosphorus adsorption capacity of the soil is positively related to soil pH (Fig. 4, p = 0.05), although the influence of soil pH on phosphorus adsorption is not clear in terms of the results of the adsorption experiments. An increase in soil pH is commonly associated with an increased adsorption of phosphorus in paddy soil, although pH values of paddy soils in this area are lower than 7.0 in most circumstances. Some attention should be given to soil pH when phosphorus fertilizers are applied to rice fields.

#### 3.3. Maximum phosphorus application

It was estimated that the soil weight of the plough layer (0-20 cm) of paddy soils in the area is about  $1.98 \times 10^6 \text{ kg ha}^{-1}$ . We infer from Eq. (4) that the upper limit of accumulative phosphorus application  $(F_p)$  under normal environmental conditions would be 903.3 kg ha<sup>-1</sup>. If the annual phosphorus application rate is  $25-35 \text{ kg ha}^{-1}$ , the highest accumulative limit will be reached in 25-36 years. In other words, all the phosphorus fertilizers applied to paddy soils subsequently will not be adsorbed and all applied phosphorus will thus be lost after 25-36 years.

However, the above  $F_p$  value would be not applicable under some soil-environmental conditions. For example, organic matter (OM%) in some paddy soils of the area is often very low. We can thus calculate according to the equation in Fig. 2 and Eq. (4) that  $F_p$  was equal to 676.4 kg ha<sup>-1</sup> if the organic matter in paddy soils of the area was completely exhausted or close to zero. Moreover, water temperature in rice fields of the area can be as high as 38 °C. Under such conditions, the upper limit of accumulative application of phosphorus fertilizers should not exceed 705.9 kg ha<sup>-1</sup>. In addition, agricultural irrigation and drainage are both frequent in rice fields of the area. In some years, heavy rainfall floods rice fields in the area. In order to avoid surplus phosphorus in agricultural runoff



Fig. 4. The relationship between PSM and soil pH. When soil pH was being varied, other soil conditions including soil organic matter levels (2.47%), soil pH (6.2), room temperature (25  $^{\circ}$ C) and the ratio of water to soil (25:1) were held constant.

due to the frequent irrigation/drainage and heavy rainfall, the upper limit of accumulative application of phosphorus fertilizers to the soil should be not exceed 682.9 kg ha<sup>-1</sup>. In this area, the lowest soil pH is 3.0, corresponding to an  $F_p$  of 820.3 kg ha<sup>-1</sup>.

We conclude that all the excess phosphorus applied to similar paddy soils in this area most likely will enter Lake Tai if the accumulative application of phosphorus fertilizers is higher than the limiting value of 676.4 kg ha<sup>-1</sup>. Based on the current annual application rate of phosphorus fertilizers, the increment in the phosphorus adsorption on paddy soils in the area likely will be zero after 19–27 years when paddy soils are saturated with phosphorus. Thus, the zero application of phosphorus fertilizers should be adopted in agricultural production after 19–27 years.

If we can ensure that there is no environmental problem from phosphorus application in 50 years (T= 50) and assume that the leaching of phosphorus applied to soil is zero, it was shown by a calculation based on the formula (6) that the maximum annual phosphorus application rate (NP<sub>max</sub>) is only 13.5 kg ha<sup>-1</sup>. The current annual phosphorus application rate is obviously higher than the value of NP<sub>max</sub>. At the least, it is necessary to decrease the application of phosphorus fertilizers at the present. Otherwise, phosphorus pollution will affect agricultural production and result in other adverse eco-environmental effects in the area.

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