# Chemical speciation of phosphorus in surface sediments from a geological phosphorus-rich watershed, South China

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**Abstract.** In order to clarify the distribution characteristics and potentially environmental effect of phosphorus (P) chemical speciation in river sediments from a typical geological P-rich (GPR) watershed, South China. Forty-eight sediment samples collected from the Huangbai River watershed, Yichang city, Hubei province. The levels of TP in Huangbai River wathershed were remarkably higher than those in most Chinese lakes, reservoirs, and river. The Ca-P and Res-P were the two dominant species that accounted for 78.7% and 13.3% of TP, respectively. Based on the sediment quality guideline (SQGs) and background values of Chinese soil and sediment, the majority of the mean TP concentrations in surface sediments were higher than their background values. The unique distribution pattern of P species in the Huangbai River watershed depends on local environment conditions and P sources. These findings improve our understanding of the eutrophication and P cycle in the GPR watershed.

## 1 Introduction

The problem of eutrophication of water bodies in China is becoming more and more serious. Among the three types of freshwater systems such as rivers, lakes and reservoirs, more eutrophication occurs in lakes and reservoirs because of the slow flow and the slow renewal of these water bodies, but the problem of eutrophication of rivers cannot be taken lightly because once eutrophication occurs in rivers, it will cause greater harm to production and living as well as health. Sediment is an important reservoir of nutrients in rivers and lakes, and the nutrients importing the water bodies will eventually enter the sediment, and under certain conditions, these nutrients will be released into the overlying water again, which in turn impacts the aquatic ecosystem [1]. Phosphorus (P) is the most important limiting factor in freshwater ecosystems, and inorganic P is a key factor in water eutrophication. Therefore, the analysis of inorganic P is important to study the sorption and release of P from sediments and the contribution of eutrophication.

The forms of P in sediments have been extensively studied, and the results show that the relative amounts of each form of P vary in different regions, and not all forms of P in the sediments can be released to the overlying water [2]. Chen et al. [3] investigated the P species in Taihu lake and found the P forms in sediments are distinct in different regions. Tang et al. [4] researched the P distribution in the sediment of the Three Gorges Reservoir and found the release of sediment Bio-P contributed a minority to the water column dissolved P loads. Previous studies mainly focused on lakes, reservoirs, and estuaries. However, there is a lack of research about P species of rivers, especially in the geological P-rich (GPR) watersheds. The bedrock-derived P is a significant feature of GPR watersheds. There are two other features about GPR watersheds: (1) large phosphate deposits and intensive mining activities are found; (2) the content of P is relatively high in rock, soil, and sediment. Mining and other human disturbances lead to severe environmental decay, and P is lost to adjacent water from GPR area.

The Huangbai River is a typical GPR watershed in Yichang, Hubei province, China. Yichang city holds the second largest phosphate reserves in China and there are extremely extensive phosphate mining activities in the upper and middle Huangbai River. Since the last ten years, phosphate rock mining has continuously been booming. However, the natural endowment also poses serious challenges for the environment. Due to extensive mining activities in the watershed, eutrophication has affected the self-purification capacity of the fresh water and this has been a key contributor to algal blooms [5]. Confronted with these challenges, Bao et al [6] investigated the P factions from sediments of deep reservoirs located in the Huangbai River and found different P-forms decreased sharply from upstream to downstream reservoirs, which corresponded with phosphate mining activities in the watershed. However, few studies have focused on the P forms in the sediment of the mainstream or a tributary of Huangbai River.

The objectives of this paper are, therefore, (1) to investigate the concentrations and distribution characteristics of the P forms in the sediments of Huangbai River along the flow direction; (2) to

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determine the degree of P contamination in sediments; (3) explore the reasons for the P pollution.

## 2 Materials and methods

### 2.1 Watershed description

The Huangbai River watershed is located in the middle reaches of the Yangtze River. The Huagnbai River watershed is mostly occupied by forests (89.35%), whereas arable areas account for 7.86% of the land use in the watershed, respectively. Upstream areas of the watershed are mainly composed of forests, whereas downstream areas in the east of the main stream are composed of arable lands. The dominant crop is corn within the watershed.

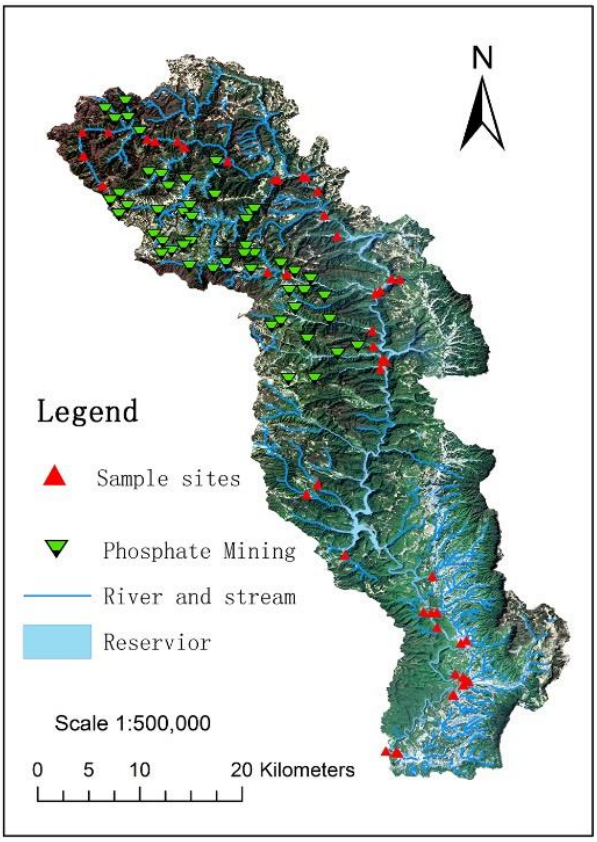


**Fig. 1.** Map of Jianxi watershed with sampling sites

There are four enchained reservoirs: Xuanmiaoguan(XMG), Tianfumiao(TFM), Xibeikou(XBK), and Shangjiahe(SJH), built by dams in the upstream, upper-middle stream, midstream and downstream areas of the watershed, respectively (Figure 1). There were 45 phosphate mining sites in the catchment of XMG and TFM reservoirs; there were 11 phosphate mining sites in the catchment of XBK reservoirs; the catchment area of SJH reservoir had no mining sites [5]. The phosphate mining sites are primarily distributed in the northwest of the watershed. Phosphatic rocks are widely distributed in the Neoprotozoic Ediacaran Doushantuo Formation, and generally dolostones occur as their host rocks [6]. Doushantuo phosphorite is mostly composed of francolite [7].

### 2.2 Sample collection and treatment

Forty-eight river sediment samples were collected during the period from May to June in 2019. There were 17 sampling stations in the upstream, 15 sites in the midstream, and 17 sites in the downstream. Each sediment sample with depths from 0 to 10 cm was mixed, and they were collected from each station consisted of three composite samples. After sampling, the samples were stored in plastic containers. After transportation to the laboratory, the samples were frozen at -20 °C until analysis. Prior to analysis, the sediment samples were dried in vacuum freeze drier and homogenised, then ground to pass through a 100-mesh sieve.

### 2.3 Chemical analysis

Sediment samples were analysed with total phosphorus (TP) determined by molybdate colorimetric method with perchloric acid digestion. The TN concentration in surface sediments were determined by the semi-micro Kjeldahl method. The pH value was determined by the electrode method. The organic matter (OM) in the sediments was measured after treatment with $K_2Cr_2O_7/H_2SO_4$. The major elements (Ca, Al, Fe, Mn and Si) were determined using X-ray fluorescence spectrometer.

A sequential extraction method [8] was used to obtain the chemical P fractions. In this method, TP in sediments was divided into inorganic P (IP) and organic P (OP). The IP forms were divided into exchangeable or loosely absorbed P (Ex-P), reduced P (BD-P), metal oxide bound P (NaOH-P), calcium-bound phosphorus (Ca-P), and residue P(Res-p).

### 2.4 Assessment of the sediment contamination

The assessment of surface sediment contamination by TP was based on the Chinese sediment background, Chinese soil background, and sediment quality guideline (SQGs) published by the Ministry of Environment and Energy, Ontario, Canada.

The Chinese soil background values of TP are calculated as 520 mg/kg [9]. The Chinese sediment background value of TP is counted as 615 mg/kg [9]. Three levels of sediment contamination are specified by the SQGs which can result in different potential effects (the severe effect level, the lowest effect level, and the no effect level) [10]. For example, according to the SQGs, sediments that have nutrient concentrations below or at the lowest effect level (TP concentration of 600 mg/kg) can be regarded as sediments that are unpolluted. Sediment concentrations that vary between the lowest effect level and the severe effect level (TP concentration of 2000 mg/kg) can be viewed to be moderately polluted, and concentrations at or above the severe effect level point out that the sediments are heavily polluted [11].

### 2.5 Statistical analysis

The raw data were processed using Microsoft Excel 2013(Microsoft, Redmond, Washington, USA). The descriptive statistical analysis and Pearson correlation were conducted using SPSS19.0 statistical software. The charts were prepared using Origin 9.0 (Origin Lab Corporation, Northampton, MA, USA).

## 3 Results and discussion

### 3.1 Basic physicochemical characteristics of river sediments

The basic physicochemical characteristics in sediments of Huangbai River is shown in Table1. pH of the sample varied from 7.51 to 8.06 with an average value of 7.71. The concentrations of TP, TN, and OM were 0.401-35.195 mg/g, 0.162-3.134 mg/g, and 0.33-4.26%, respectively. The TP concentrations were far higher than Dianchi lake [1], Erhai lake [2], Taihu lake [3], and Three Gorges Reservoir [4]. The enriched P in surface sediments were the result of natural and anthropogenic inputs [5]. From the distribution results, the mean content of OM in the downstream was higher than those of the other regions. The mean value of TP in sediments was in the order of high to low in the following sub-watersheds: upstream > midstream > downstream. On the contrary, the orders of sub-watersheds for the mean value of TN contents were downstream > midstream > upstream. Similarly, the orders for the mean value of $SiO_2$ contents were downstream > midstream > upstream. The difference in the concentrations of the same element in the river sediments from the various regions showed the variation of element accumulation sources. Indeed, the distributions of elements in river sediments are relate to the geological conditions, geography and land features, and human activities.

**Table 1**. Distributions of nutrient elements in sediments.

| Regions | Items | Max | Min | Mean | STD |
|---|---|---|---|---|---|
| The whole watershed | OM-% | 4.26 | 0.33 | 1.55 | 1.08 |
| | TN-mg/g | 3.134 | 0.162 | 0.886 | 0.630 |
| | TP-mg/g | 35.195 | 0.401 | 7.858 | 9.246 |
| Upstream | OM-% | 3.64 | 0.60 | 1.35 | 0.81 |
| | TN-mg/g | 1.594 | 0.215 | 0.720 | 0.425 |
| | TP-mg/g | 29.378 | 0.565 | 12.252 | 9.197 |
| Midstream | OM-% | 3.74 | 0.33 | 1.16 | 0.89 |
| | TN-mg/g | 1.900 | 0.162 | 0.711 | 0.526 |
| | TP-mg/g | 35.195 | 0.401 | 10.565 | 10.689 |
| Downstream | OM-% | 4.26 | 0.38 | 2.10 | 1.28 |
| | TN-mg/g | 3.134 | 0.193 | 1.198 | 0.772 |
| | TP-mg/g | 2.045 | 0.640 | 1.196 | 0.401 |

### 3.2 P species in the sediments

In the whole watershed, IP exhibited a higher content, ranging from 0.259 to 28.722 mg/g, accounting for 67-99%. In comparison, OP ranged from 0 mg/g to 0.288 mg/g, with the average value of 0.039 mg/g. The concentration Ex-P ranged from 0.003 to 0.178 mg/g and comprised 1.1% of TP on average, which was approximate to BD-P and NaOH-P. Res-P ranged from 0 mg/g to 3.538 mg/g and accounted for 13.3% of TP on average, which was significantly higher than the concentrations of the former four P forms. Ca-P varied from 0.233 mg/g to 34.576 mg/g and accounted for 34.5%-99.1% of TP, and was the most abundant among all P forms.

In the different regions of the whole watershed, the average contents of Ca-P followed the order: upstream (11.029 mg/g) > upstream (9.984 mg/g)> downstream (0.755 mg/g). Similarly, the orders for BD-P, Ex-P, and Res-P. In comparison, the average contents of NaOH-P and OP followed the orders: downstream > upstream > midstream. These differences are controlled by various factors such as bacterial activity, human disturbances, acidity, redox potential, geological background, and other relevant environmental conditions.

The average concentration of bioavailable P (BAP=Ex-P + BD-P + NaOH-P + OP) in the sediments of the upper reaches of the watershed was 0.22 mg/g, which was higher than that in the midstream(0.15 mg/g) and close to downstream (0.20 mg/g). The average BAP/TP ratio followed the order: downstream (19.2%) > upstream (5.8%)> upstream (19.2%). In summary, the average contents of BAP and the ratio of BAP/TP in sediments from the downstream were higher. Therefore, the sediments in the downstream of the watershed exhibited highest risks of P release.

### 3.3 Pollution risk of P from the sediments

The TP contents in surface sediments of Huangbai River were compared with Chinese soil background values, Chinese sediment background values, and SQGs (Table 2). The result showed that the TP concentrations in surface sediments from most of sampling sites were higher than Chinese soil background and Chines sediment background. According to the SQGs, a small part of the sediment samples in upstream, midstream, and downstream showed the TP concentrations were lower than the lowest effect level. However, a vast majority of the sediment samples showed TP concentrations were higher than the severe effect level, and 75% of samples in the upstream of the watershed exceeded this level, implying that these sediments might be heavily contaminated and probably giving rise to adverse health effects on sediment-dwelling organisms [10].

**Table 2.** Comparison of TP concentrations in surface sediments from Huangbai River and sediment quality guidelines (SQGs) (%).

| Pollution Assessment | The whole watershed | Upstream | Midstream | Downstream |
|---|---|---|---|---|
| Samples>soil background value* | 97.9 | 100 | 93.3 | 100 |
| Samples>sediment background value* | 93.9 | 93.8 | 93.3 | 100 |
| Samples<lowest effect level** | 4.1 | 6.3 | 6.7 | 0 |
| Samples between lowest effect level and severe effect level** | 43.8 | 18.7 | 26.6 | 94.1 |
| Samples>severe effect level** | 52.1 | 75 | 66.7 | 5.9 |

* Soil background value (Chi and Yan 2007)

** Ontario sediment quality guidelines (Persaud et al. 1993)

The results of assessment showed that the P pollution level is serious. There are many reasons for the serious P pollution in river sediments. Firstly, due to the continuous influence of large-scale phosphate mining on fresh water ecosystem, TP concentrations in the sediments greatly increased in the upper reaches of the watershed. Secondly, Natural source (Bedrock-derived P) is one potential source of P loss which is easily overlooked. Abundant phosphate resources have been recognized and explored in the upper reaches of the Huangbai River watershed. Larger the proportion of the exposed areas of phosphate-bearing formations are, the higher the risk level of the P loss has. Thirdly, agricultural non-point source pollution caused by unreasonable fertilizer application also contributes to the increase of P loads of water bodies and sediment, especially there are concentrated distribution of arable lands in the downstream of the watershed.

## 4 Conclusions

The study elucidated P forms in surface sediments sourced from a typical GPR watershed (Huangbai River), South China. The levels of TP in Huangbai River wathershed were remarkably higher than those in most Chinese lakes, reservoirs, and river. Some conclusions could be drawn as follows:

(1) The TP content ranged 0.401 mg/g -35.195 mg/g, and IP accounted for 67%-99% of TP on average in the whole watershed. The mean value of TP in sediments was in the order of high to low in the following sub-watersheds: upstream > midstream > downstream.

(2) The Ca-P and Res-P were the two dominant species that accounted for 78.7% and 13.3% of TP, respectively. The average contents of BAP and the ratio of BAP/TP in sediments from the downstream were higher. Therefore, the sediments in the downstream of the watershed exhibited highest risks of P release.

(3) Based on the sediment quality guideline (SQGs) and background values of Chinese soil and sediment, the majority of the mean TP concentrations in surface sediments were higher than their background values.

(4) Natural source (Bedrock-derived P from Doushantuo Formation) and anthropogenic (Phosphate mining disturbance, agricultural non-point source pollution) contribute to the P pollution in the river sediments.
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