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Research article

# Environmental pollution evaluation and spatiotemporal distribution of different forms of phosphorus in a phosphate mining area in Western Hubei, China

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A R T I C L E I N F O

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A B S T R A C T

Taking the typical phosphate mining area in Western Hubei as the research object, groundwater, surface water, soil and sediment in phosphate mining area were investigated and evaluated comprehensively to clarify the temporal and spatial distribution characteristics of different forms of phosphorus in phosphate mining area and reveal the migration and transformation of phosphorus. Results showed that whether in the dry season or the wet season, total phosphorus levels in groundwater (dry season from November to December 2021, 0.42 mg/L; wet season from August to September 2022, 0.24 mg/L) exceeded the standard index. The total phosphorus was related to seasonal changes and the distribution of phosphate rock. Particulate phosphorus was the main component of total phosphorus in surface water, and sediment phosphorus was one of the sources of phosphorus in surface water. The total phosphorus in surface water was strongly correlated with particulate phosphorus, and the correlation coefficient was 0.984. The main sources of phosphorus in surface water were exogenous input. The sediment had a certain contribution to the phosphorus in the water, but it was not the main factor. The correlation coefficients between sediment total phosphorus and water total phosphorus and particulate phosphorus were 0.349 and 0.346, respectively. The soil total phosphorus content was closely related to phosphate mining activities. The migration and transformation of phosphorus sources were mainly through soil leaching, scouring and mine drainage into surface water, and there may be migration of surface water to groundwater in monitoring wells. The correlation between total phosphorus in soil and groundwater was poor. The high content of total phosphorus in surface soil was not the main source of total phosphorus in groundwater. Rainwater scours the surface soil of the ore yard and the mine entrance, resulting in the loss of soil total phosphorus to the river, and the phosphorus in the soil may indirectly enter the groundwater.

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## 1. Introduction

Phosphorus (P) is an essential macronutrient for biota, but it is also the main factor causing eutrophication of water [1]. Phosphorus exists naturally in various forms of oxidation and can be dissolved or bound (adsorbed) to the soil. Both dissolved phosphorus and particulate-bound phosphorus are affected by rainfall-driven runoff [2]. Once they enter the waters in large quantities, they can cause eutrophication (algae and other plankton rapid reproduction [3]), water dissolved oxygen decreased, water quality deterioration. The natural source of phosphorus is through rock weathering [4], but human mining of phosphate rock makes the phosphorus flux increase by about 8 times compared with natural weathering [5].

The pollution of the surrounding environment in the process of development and utilization of phosphate mines is mainly through the discharge of waste water, waste gas, waste residue, etc. [6]. Mining and ore processing activities produce a large number of tailings and overburden [7]. Mine wastewater mainly comes from concentrators and fertilizer production workshops [8]. Direct discharge of sewage will cause serious pollution to surface water or soil in mining areas [9], especially total phosphorus and heavy metal pollution [10]; mine waste residue can bring out some harmful elements through rainwater leaching, resulting in excessive surface water pollutants [11]; groundwater may also be affected by mining activities because there is a close hydraulic connection between shallow groundwater and surface water [12]. In many mining areas, surface water pollution can be directly observed, but soil and groundwater pollution are usually not directly observed [13]. Groundwater has a long residence time, which usually has a certain buffering capacity for pollution [14,15]. However, the pollution of groundwater can't be found until the pollution becomes serious [16], and the same is true for soil [17]. Once groundwater is contaminated, it will be difficult to recover.

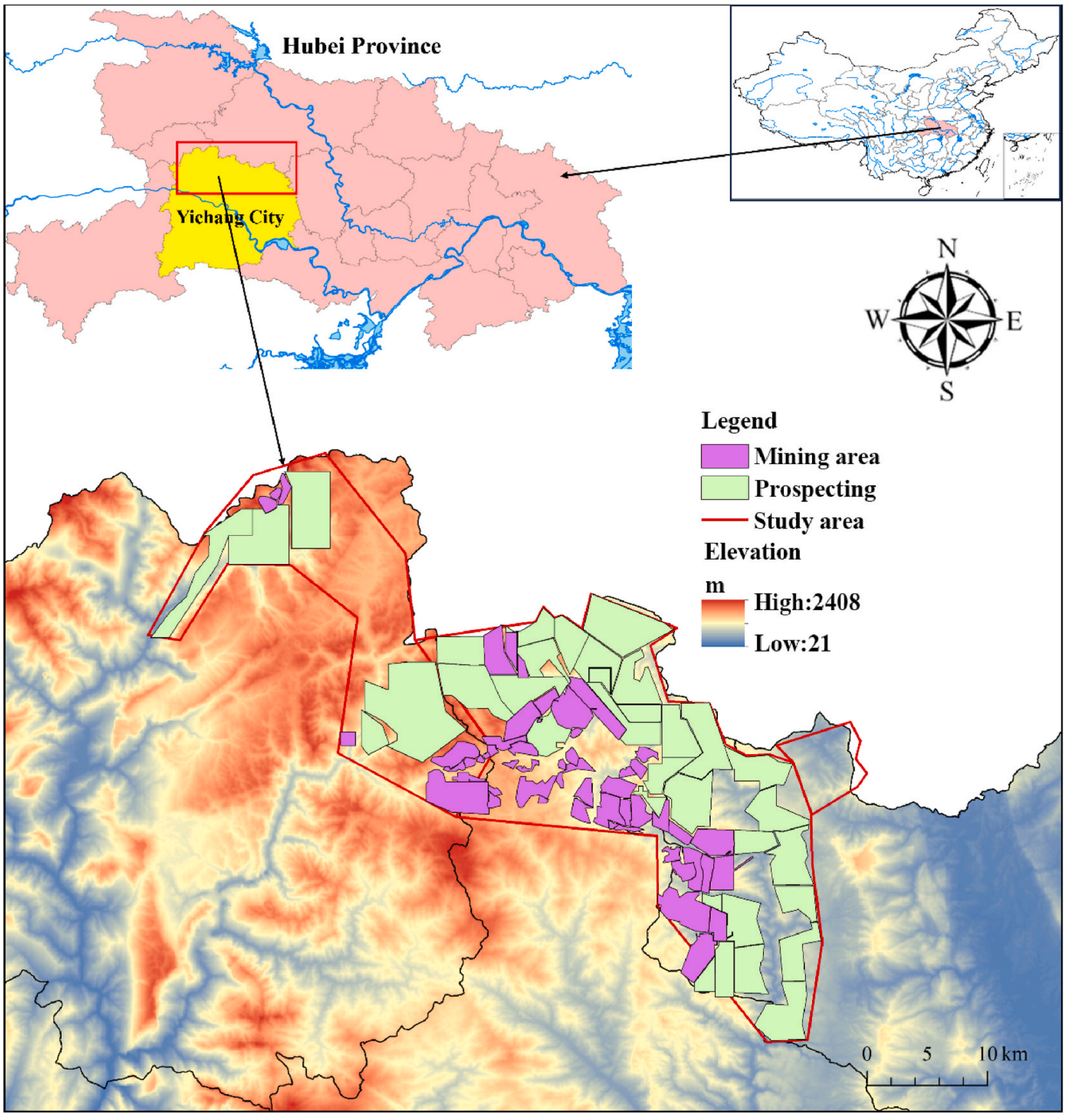



**Fig. 1.** Map of the study area showing the geographical location of phosphate mining area.

The Western Hubei phosphate mining area is the second largest phosphate mining area in China and the largest phosphate base in the Yangtze River Basin. The total identified phosphorus reserves in the phosphate mining area are 4.24 billion tons, and the remaining reserves are 3.93 billion tons. This also leads to the serious problem of total phosphorus in the Yangtze River Economic Belt, and the intensity of pollution control needs to be improved. Mine wastewater contains a large amount of soluble phosphorus, and the pH value changes greatly. Phosphorus in mine water is an important source of water pollution load, which poses a challenge to the self-purification capacity of water and the environmental capacity of the basin [18]. In addition, a large amount of waste rock and waste residue will be produced in the mine activities, most of which are stacked in the slag yard specially built on the surface, and a small part is used for backfilling in the goaf. The leaching water of wastewater, waste liquid and waste residue formed by mining leads to a certain degree of pollution of soil and water environment, which has a negative impact on the local living environment and industrial and agricultural production. The number of phosphate rocks in a phosphate mining area in Western Hubei is huge, and the mining history is long [19].

The long-term mining activities have led to different degrees of environmental pollution. However, no systematic pollution investigation and evaluation has been carried out in the past, and the specific pollution situation (pollution degree, pollution range and

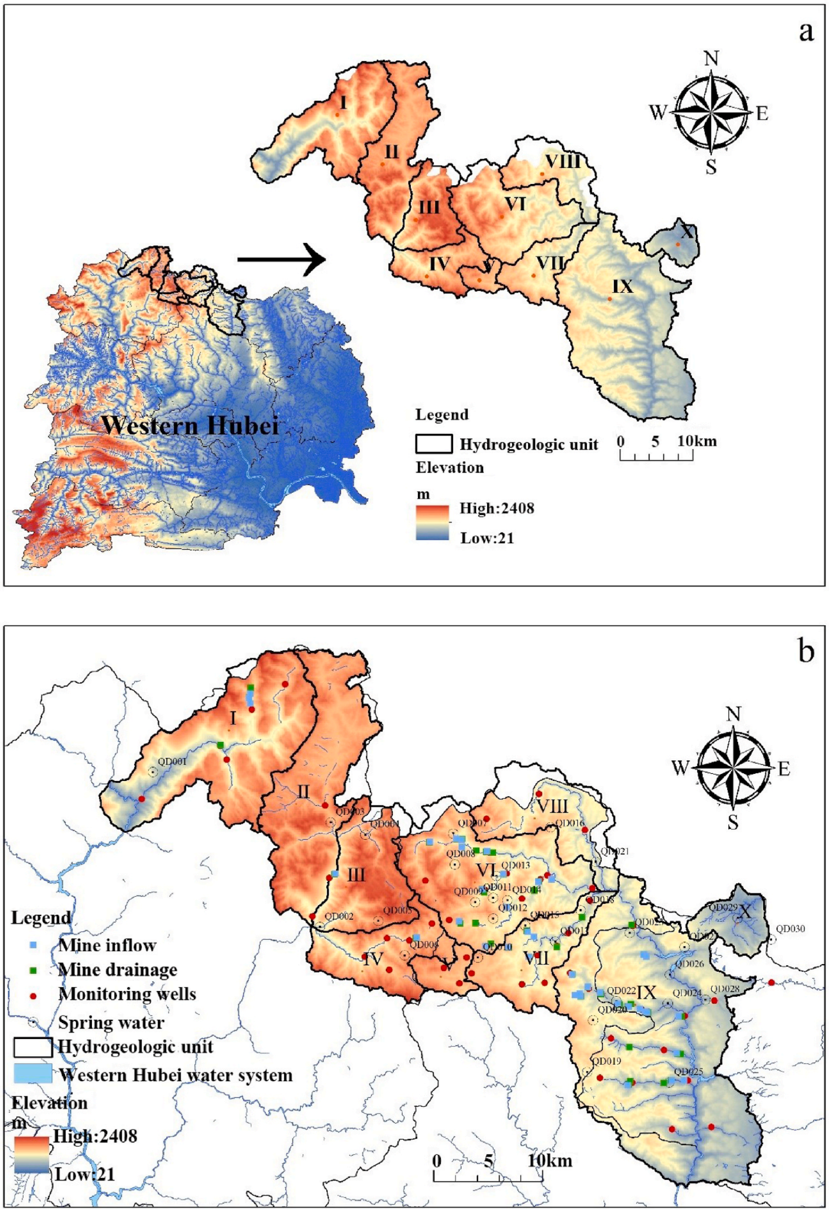



**Fig. 2.** (a) Division of hydrogeological units within the scope of the study; Sampling points distribution of (b) groundwater monitoring points, (c) soil, (d) surface water and sediment.

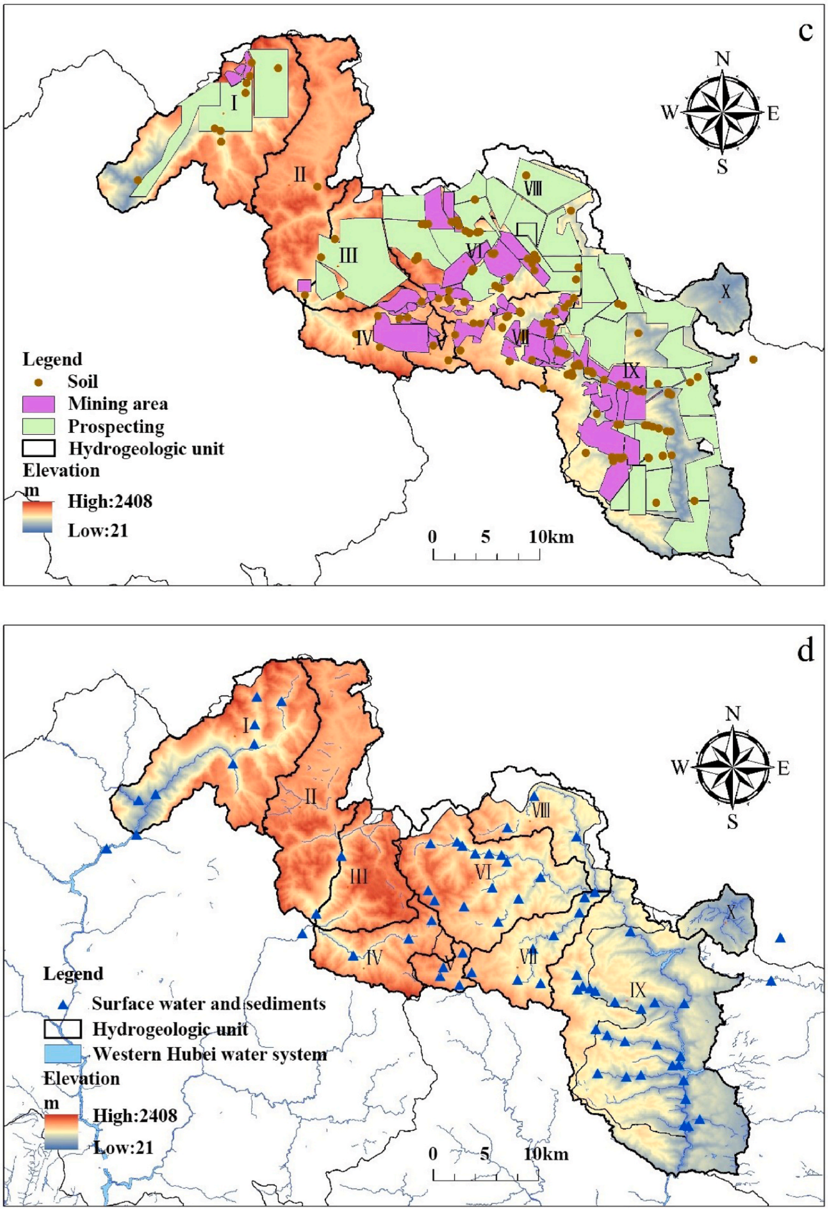



**Fig. 2.** (*continued*).

characteristic pollutants, etc.) is unclear. In this study, it takes a phosphate mining area in Western Hubei as the object, and evaluates the environmental pollution of the area by investigating the current situation of groundwater, surface water, sediment and soil environmental quality in the study area. The pollution history and current situation of the study area were investigated, and potential pollutants were screened. In addition, this work also comprehensively grasps the degree and scope of pollution in the research area, conducts a comprehensive evaluation of environmental pollution in phosphate mining areas, analyzes the deep spatial distribution characteristics of phosphorus, and clarifies the migration and transformation laws of phosphorus sources.

## 2. Materials and methods

### *2.1. Study area*

The topography of the study area is complex and varied, and the elevation difference is large. The altitude is from 35m to 2427m. From west to east, it gradually decreases from mountains, hills and plains. The western mountain area is large, the middle is low mountains and hills, and the east is plain, with an altitude of less than 100m. The lithology is dominated by limestone, purple sandstone, gray-green sandy shale, quartz metamorphic rock and a small amount of volcanic rock, with karst landform and Danxia landform. As shown in Fig. 1, the main mountain range of the phosphate mining area is from west to east, and the ridge line elevation is generally 1100~1886m. The landform belongs to the type of tectonic erosion mid-mountain landform. At present, there are 60 phosphate mines in the phosphate mining area (39 mines in production, 16 closed and abandoned mines, 5 concentrators).

### 2.2. Site description

The division of hydrogeological units within the scope of the study is shown in Fig. 2a. Based on the topography and geomorphology of the study area, the whole investigation division is divided into 10 hydrogeological units with considerable scale and relative independence according to the characteristics of aquifer supplement, diameter and drainage and the distribution of water-containing layers. The main sources of groundwater recharge are atmospheric precipitation and surface water, and the direction of groundwater runoff is northwest and southeast. The main types of groundwater are loose rock pore water and carbonate rock fissure karst water. For key suspected pollution areas with obvious pollution traces and pollution identification, this study established 50 monitoring wells (Fig. 2b). Groundwater sampling points include newly built monitoring wells, springs, mine drainage, and mine inflow. The migration of pollutants in soil and groundwater and potential key areas of concern, and combines with the existing monitoring points in the region were considered to set groundwater points. The sampling depth of groundwater is 0.5m below the surface of the monitoring well, and sampling is conducted during the dry season and the wet season respectively. Considering the pollution sources, distribution of aquifers, and flow direction of groundwater, combined with the diffusion form of pollutants, the soil sampling points are determined by judging the distribution method. One soil sampling point was set at the drainage hole of each mine and 50–100m downstream of the slag storage area. The specific sampling point deployment of soil samples is shown in Fig. 2c. Considering that the phosphate mining area is located in the upper reaches of Huangbai River and Xiangxi River, the surface water points are arranged around these surface water bodies, and a total of 71 surface water monitoring points are arranged (Fig. 2d). Like the groundwater sampling method, according to the surface water flow, the samples were collected in the dry season and the wet season, and the river sediments were collected at the same time.

### 2.3. Sampling

To ensure the accuracy and rationality of the research results, the sampling time of groundwater, surface water, soil, and sediment was consistent. Furthermore, the sampling location of surface water and sediment samples was kept on the same section. The sampling of dry season and wet season samples was completed from November to December 2021 and August to September 2022, respectively.

A total of 329 sets of groundwater samples and 142 sets of surface water samples were collected. The testing indicators included water temperature, pH, electrical conductivity, dissolved oxygen, redox potential, total phosphorus (TP), dissolved total phosphorus (DTP), particulate phosphorus (PP), dissolved phosphate (DP), etc. A total of 221 sets of soil and sediment samples were examined, and the detection indexes included total phosphorus (TP), inorganic phosphorus (IP), organophosphorus (OP), iron and aluminum-bound phosphorus (Fe/Al-P), calcium-bound phosphorus (Ca-P), etc.

### 2.4. Groundwater quality evaluation

In this study, the groundwater quality in the region was classified and evaluated (single component) and comprehensively evaluated according to the 'Standard for groundwater quality' (GB/T 14848–2017) [20,21]. Due to the absence of a total phosphorus limit in the groundwater quality standards, this study used Class III water from the surface water environmental quality standards as the evaluation criteria. According to the groundwater quality status and human health risks, referring to the water quality requirements of drinking water and industrial and agricultural water, the groundwater quality is divided into I ~ V five categories [22]. Samples with I ~ IV water quality were considered qualified, and samples exceeding the IV standard were considered unqualified. The measured values of groundwater detection indexes in the phosphate mining area are classified and evaluated, and the comprehensive evaluation results are determined based on the evaluation results of single indexes.

**Table 1**
Comprehensive evaluation of groundwater total phosphorus water quality.

| Total phosphorus point | | I | | II | | III | | IV | | V | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | – | % | – | % | – | % | – | % | – | % |
| Monitoring wells | Dry season | 0 | 0.00 | 19 | 38.00 | 11 | 22.00 | 4 | 8.00 | 16 | 32.00 |
| | Wet season | 2 | 4.26 | 24 | 51.06 | 7 | 14.89 | 2 | 4.26 | 12 | 25.53 |
| Spring water | Dry season | 12 | 40.00 | 16 | 53.34 | 1 | 3.33 | 1 | 3.33 | 0 | 0.00 |
| | Wet season | 7 | 23.33 | 21 | 70.00 | 2 | 6.67 | 0 | 0.00 | 0 | 0.00 |
| Mine inflow | Dry season | 2 | 5.00 | 15 | 37.50 | 4 | 10.00 | 1 | 2.50 | 18 | 45.00 |
| | Wet season | 9 | 22.50 | 18 | 45.00 | 7 | 17.50 | 1 | 2.50 | 5 | 12.50 |
| Mine drainage | Dry season | 6 | 13.34 | 20 | 44.44 | 11 | 24.44 | 5 | 11.11 | 3 | 6.67 |
| | Wet season | 8 | 17.39 | 27 | 58.69 | 7 | 15.21 | 4 | 8.70 | 0 | 0.00 |

### 2.5. Surface water quality evaluation

As the main discharge area of phosphate rock drainage and groundwater, the surface river in the study area is also the main source of water for urban residents in the downstream, which is greatly affected by phosphate rock drainage and groundwater. In this study, 142 groups of surface water and river sediments were collected. According to the 'Standard of surface water environment quality' (GB 3838–2002) [23], the single evaluation and comprehensive evaluation of surface water quality in the study area were carried out.

## 3. Results and discussion

### 3.1. Quality evaluation of groundwater total phosphorus

As shown in Table 1, groundwater sampling points include newly built monitoring wells, springs, mine inflow and mine drainage. During the dry season, there were 50 monitoring wells, 16 of which exceeded the standard, accounting for 32.00 %; during the wet season, 47 monitoring wells were monitored, and 12 exceeded the standard, accounting for 25.53 %. The total phosphorus of the

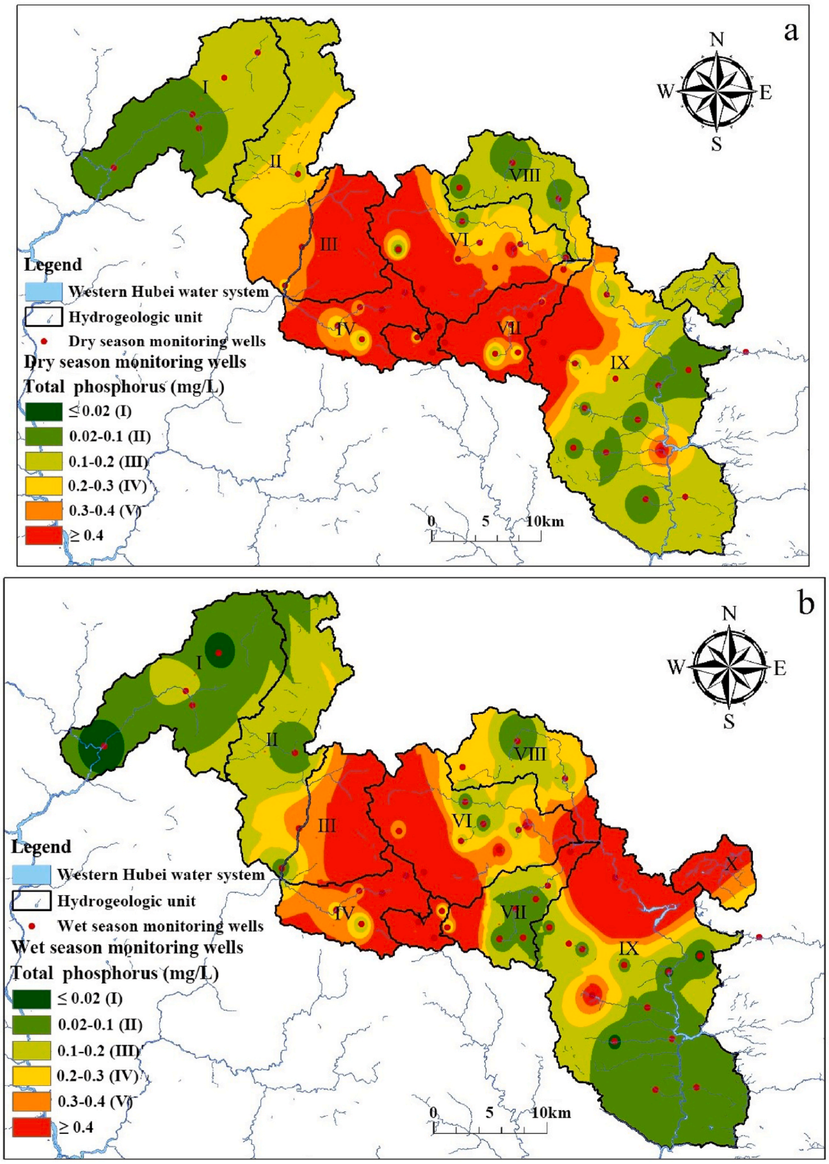



**Fig. 3.** Temporal and spatial distribution of total phosphorus in groundwater: (a) monitoring wells in dry season; (b) monitoring wells in wet season; (c) spring water in dry season; (d) spring water in wet season; (e) mine flow in dry season; (f) mine flow in wet season; (g) mine drainage in dry season; (h) mine drainage in wet season.

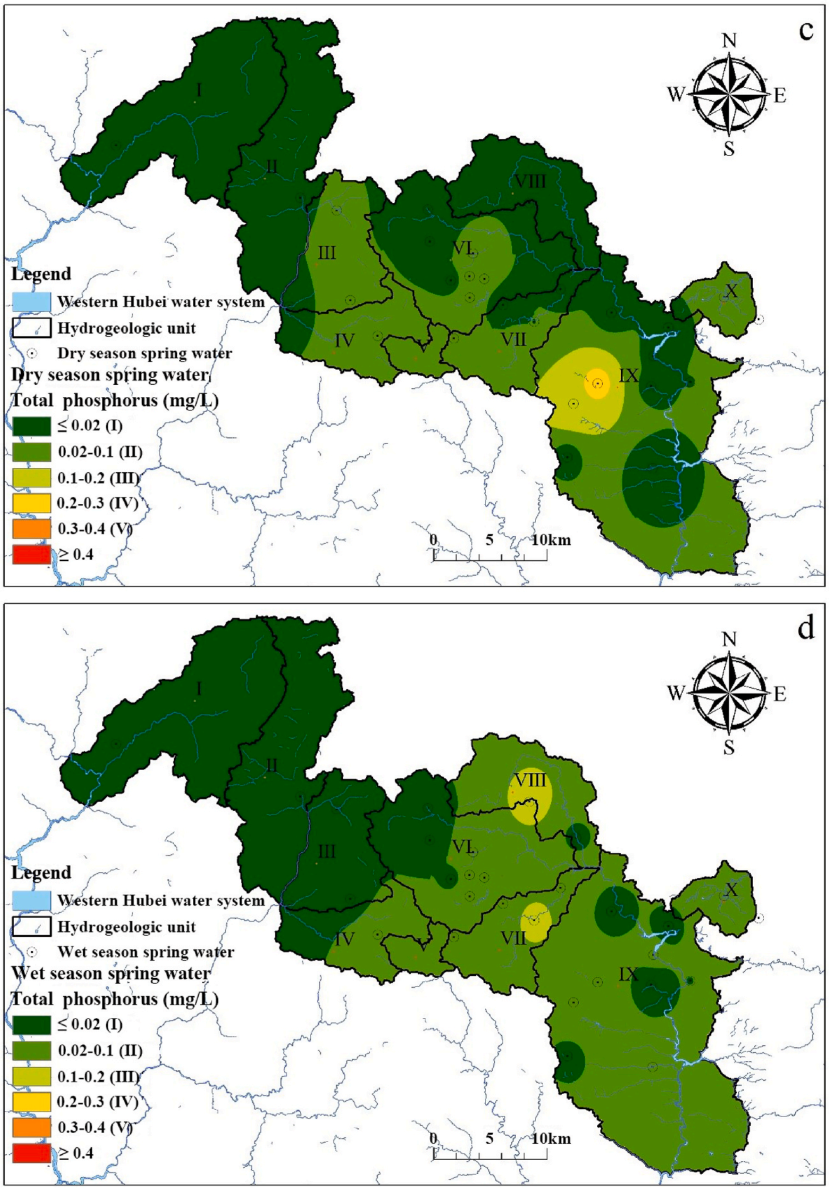



**Fig. 3.** (*continued*).

monitoring wells was better in the wet season than in the dry season. There were more I ~ II water points and fewer IV ~ V water points in the wet season. The II water points increased from 19 (38.00 %) in the dry season to 24 (51.06 %) in the wet season. The IV water and V water points decreased from 4 (8.00 %) and 16 (32.00 %) in the dry season to 2 (4.26 %) and 12 (25.53 %) in the wet season. It is worth mentioning that no matter in the dry season or the wet season, there are no over-standard points in the 30 points of spring water. As for mine inflow and mine drainage, there are 40 and 46 points respectively. There are 18 over standard points of mine inflow in dry season, accounting for 45.00 %; 5 points exceeding the standard in the wet season, accounting for 12.50 %. There are 3 over-standard points of mine drainage in dry season, accounting for 6.67 %; no over-standard point in wet season.

As shown in Fig. 3a, the points of total phosphorus not exceeding the standard of groundwater monitoring wells in dry season are distributed in hydrogeological units such as I, III, IV, VI, VII, IX, and the total phosphorus concentration range is 0.04–0.29 mg/L. The highest concentration is 0.29 mg/L and located downstream of the phosphate discharge outlet. The total phosphorus exceeding standard points are mainly distributed in V, VI, VII, IX hydrogeological units, and the total phosphorus concentration range is 0.32–3.16 mg/L. As shown in Fig. 3b, the points of total phosphorus not exceeding the standard of groundwater monitoring wells in wet season are mainly distributed in hydrogeological units such as IV, VII and IX, and the total phosphorus concentration range is 0.02–0.30 mg/L. The highest point is located downstream of the concentrator. The total phosphorus exceeding standard points are mainly distributed in IV, V, VII and IX, and the total phosphorus concentration range is 0.31–4.03 mg/L. As shown in Fig. 3c–h, the

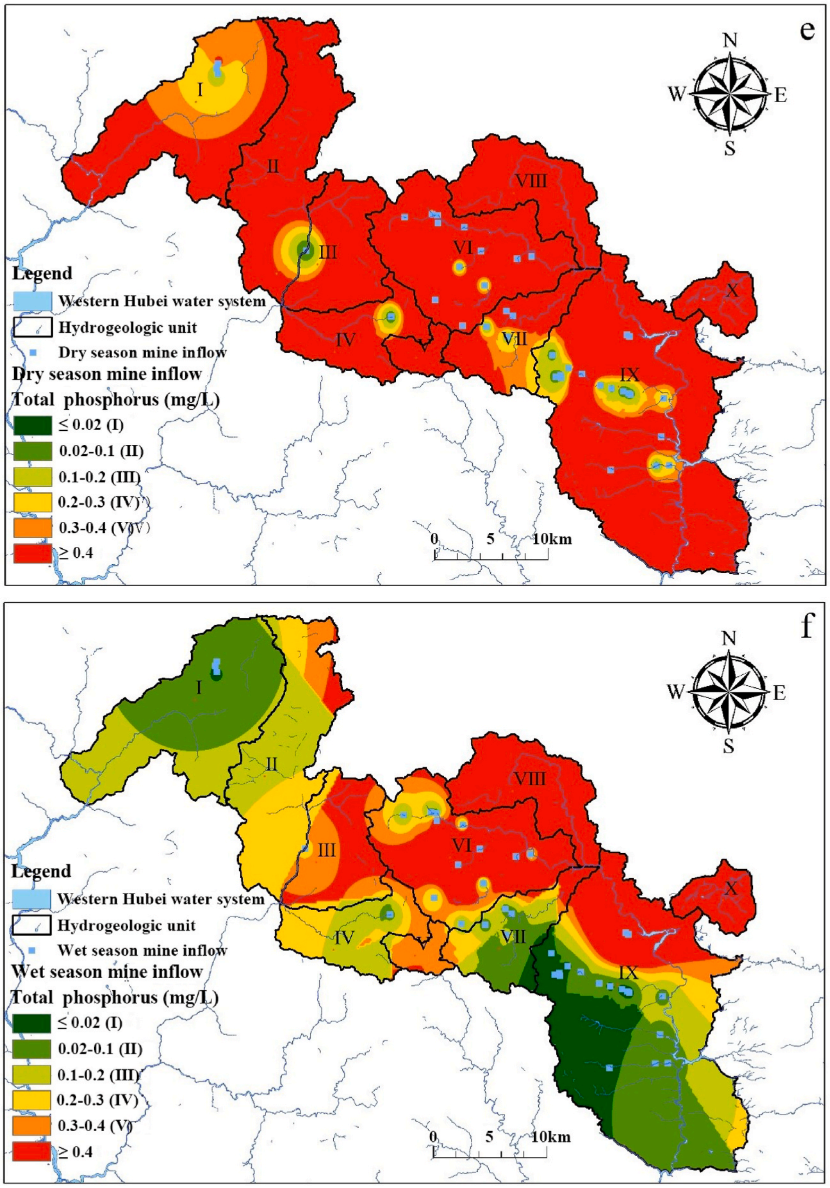
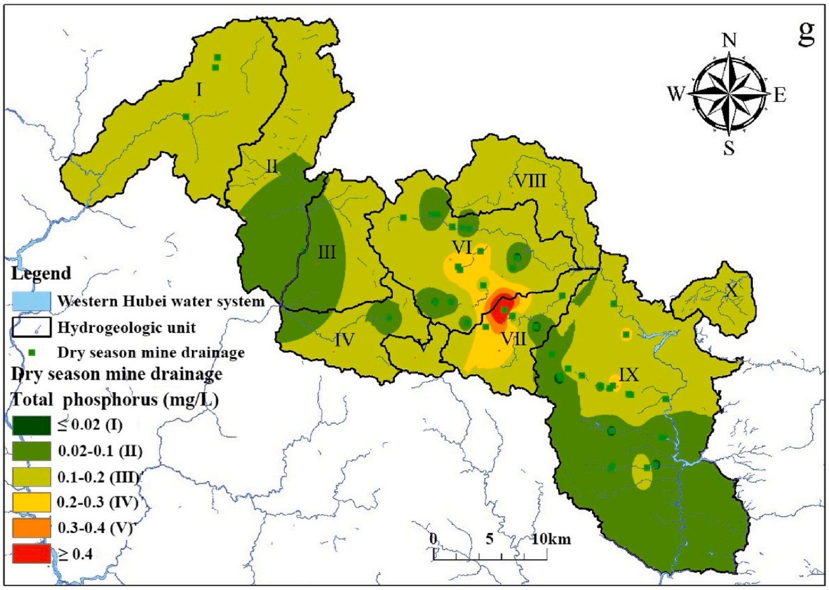



**Fig. 3.** (*continued*).

quality of total phosphorus in spring water does not exceed the standard. Most of the excessive points of mine inflow and mine drainage are located in hydrogeological units such as V, VI, VII and IX.

On the whole, the total phosphorus of groundwater has a lower excessive rate in the wet season, and the monitoring wells and mine inflow have higher phosphorus content. The mine inflow in the dry season is more serious, and the spring water has no phosphorus content exceeding the standard. The influence of phosphate mine activities on groundwater pollution is illustrated. Mine inflow is the water of aquifer seepage or overflow after the roadway is excavated [24]. It is usually mixed with the sediment produced during the operation in the pit [25]. The total phosphorus content in groundwater is high, and it is also the main source of total phosphorus in groundwater in this area. The mine inflow is treated by multistage precipitation and flocculant to form mine drainage and discharged into the external environment [26,27]. Therefore, the concentration of total phosphorus in the mine drainage is greatly reduced compared with the mine inflow. After the groundwater is discharged into the river from the roadway, the surface water interacts with the water body in the process of downstream migration, and enters the groundwater through the fissures of the aquifer [28]. However, the water flow in the aquifer is slow, and the total phosphorus is easy to adsorb sediment and sediment [29]. Therefore, the total phosphorus content observed by the monitoring wells distributed along the river and mine is higher than that of the mine drainage, but lower than that of the groundwater in the roadway. The lowest concentration of total phosphorus in groundwater is spring water. Spring water is generally not affected by phosphate mining. It can usually be used as the background value of regional groundwater.



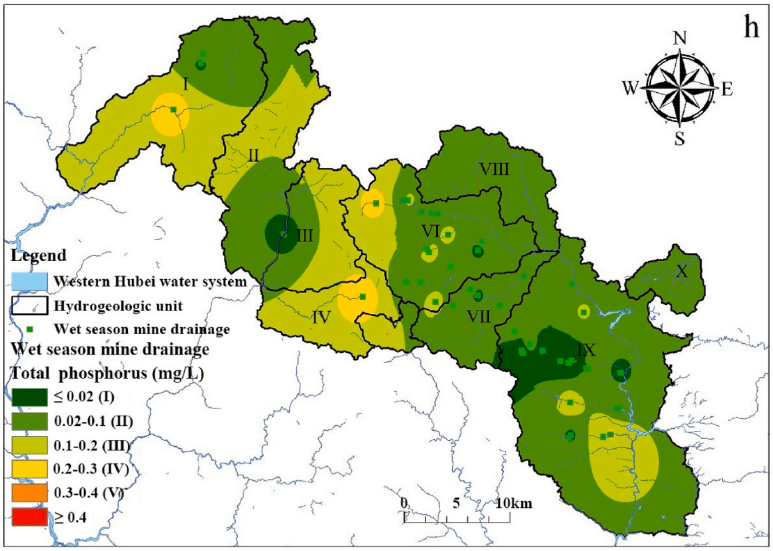




**Fig. 3.** (*continued*).

Therefore, the concentration of total phosphorus is the lowest, and the average value of total phosphorus in spring water is 0.05 mg/L.

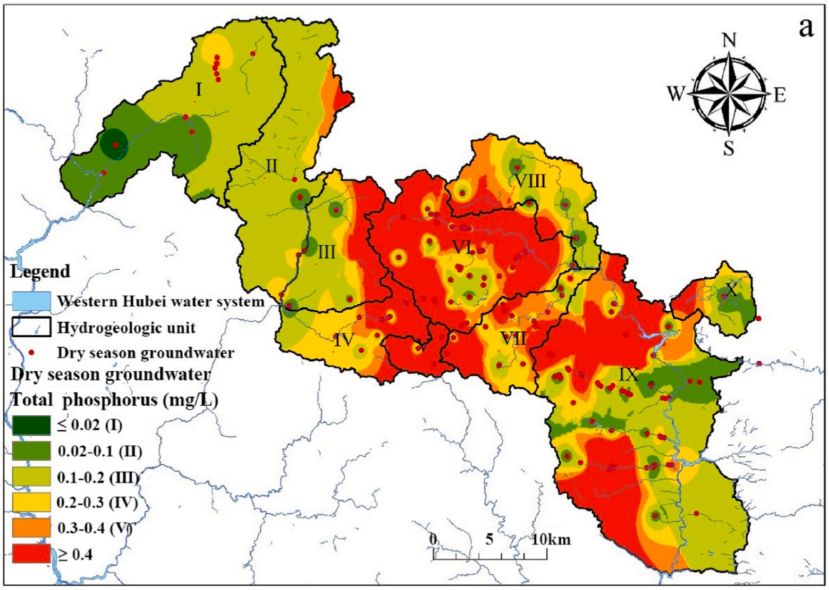
### *3.2. Quality evaluation of surface water total phosphorus*

The surface water in the dry season and the wet season was sampled and analyzed. The average value of total phosphorus concentration in 71 groups of water samples was 0.09 mg/L, ranging from 0 to 1.62 mg/L; the average pH was 8.38, ranging from 7.73 to 8.72. The coefficient of variation is between 0 and 8 (the coefficient of variation can reflect the dispersion of each index and the influence of human activities on the chemical composition of water. The higher the coefficient of variation, the stronger the influence of human activities on the water environment [30,31]). During wet season, the pH of surface water ranged from 7.15 to 9.46, with an average of 8.35. Total phosphorus level was between 0.02 and 0.38 mg/L, the average was 0.09 mg/L. During wet season and dry season, the over standard rates of total phosphorus were 5.63 % and 7.04 % respectively.

Comparing the main monitoring indexes of surface water in dry season and wet season, the average values of the main indexes are not much different. In the wet season, the dissolved oxygen and redox potential were higher, and the turbidity and suspended solids were lower, which was consistent with the characteristics of high temperature and large water volume in the wet season [32]. The range of each index is different. The maximum value of total phosphorus concentration decreases obviously in the wet season, and the proportion of particulate phosphorus in total phosphorus is relatively high. This is due to the large precipitation in the wet season and the increase of river flow. Under the same input of phosphorus source, the maximum phosphorus concentration in river water decreases obviously. In addition, the different mining frequency of phosphate rock in different months will also lead to the difference of phosphorus content in surface water. The total phosphorus at downstream monitoring points of phosphate ore have exceeded the standard, indicating that the phosphate rock activity was related to the excessive total phosphorus.

### 3.3. Spatiotemporal distribution of total phosphorus

The total phosphorus (TP) concentration in groundwater in the study area during the dry season ranged from 0 to 5.44 mg/L, with an average of 0.42 mg/L; the TP concentration in groundwater during the wet season ranged from 0.01 to 6.14 mg/L, with an average of 0.24 mg/L. Due to the differences in study areas and land use patterns, the concentration of total phosphorus in groundwater of Sihu Basin in Jianghan Plain is higher in dry season than in wet season, and the results of this study are consistent with those of Liu et al. [33]. As shown in Fig. 4a, the areas with higher TP content in groundwater during the dry season are distributed in the central and southern parts of the survey area. The distribution of phosphate rock enterprises in this area is dense. The sites with higher TP content



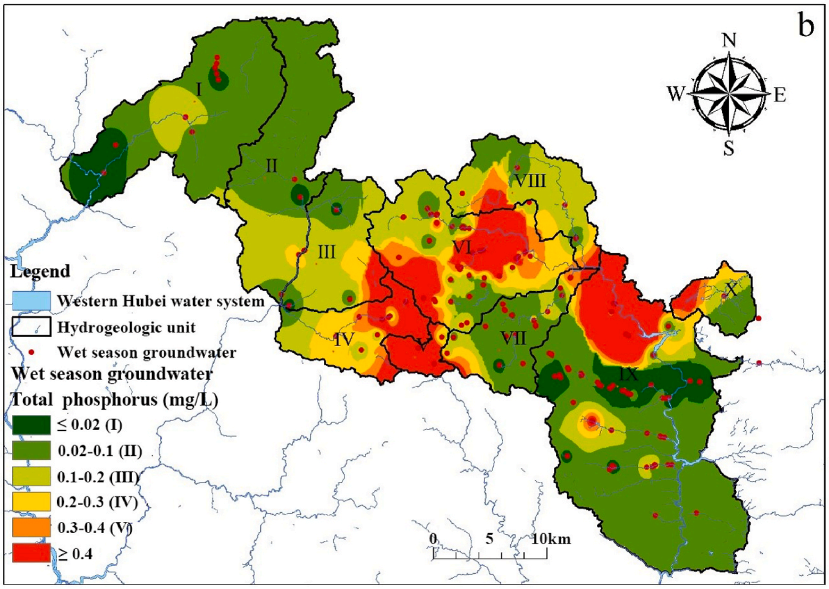




**Fig. 4.** The spatiotemporal distribution of total phosphorus in the study area: (a) groundwater in dry season; (b) groundwater in wet season; (c) surface water in dry season; (d) surface water in wet season; (e) soil; (f) watershed sediments.

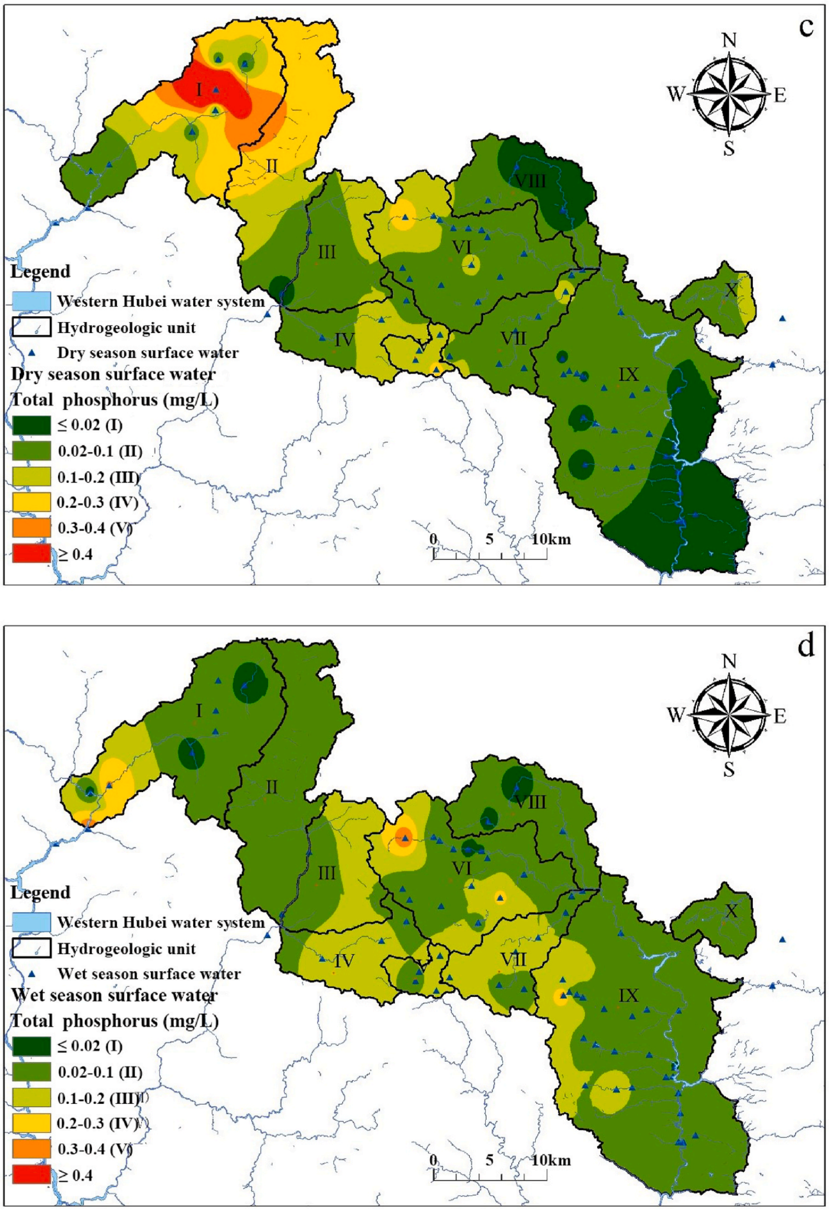
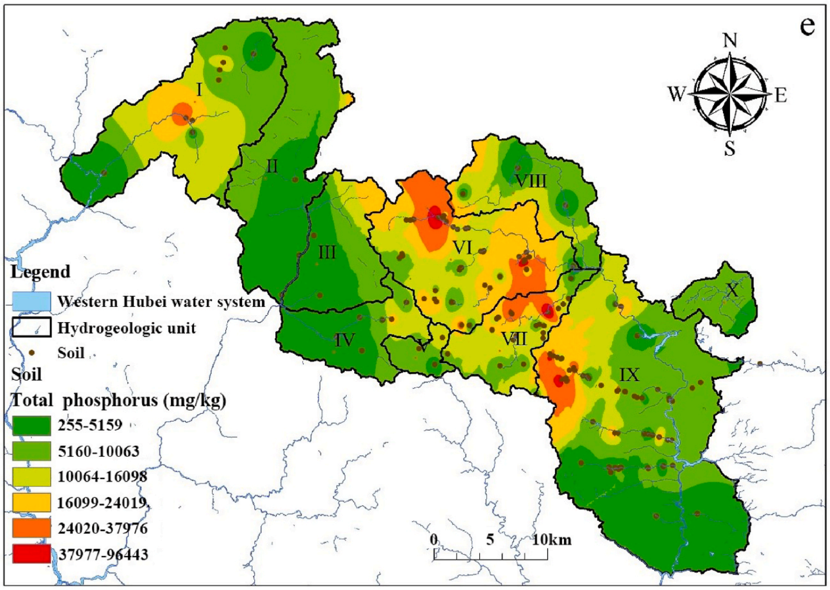



**Fig. 4.** (*continued*).

in groundwater during the wet season were mainly distributed in the middle of the survey area (Fig. 4b). During the on-site investigation, it was learned that although some phosphate rocks had not carried out mining activities for the time being, there were a large number of phosphate rocks stacked in the adjacent yard and large vehicles were carrying out transshipment work. A large number of cracks have appeared on the ground due to the driving of heavy vehicles. Therefore, it can be inferred that the location of the water after the leaching of the ore flowing through the fracture through the monitoring well leads to a higher TP concentration at these points. From the average content, the TP content in the four types of groundwater is mine inflow > monitoring well > mine drainage > spring water.

Fig. 4c and d give the spatiotemporal of TP in surface water during the dry and wet seasons in the study area. In the dry season, there were 1 point belonging to inferior V class, accounting for 1.41 %, 4 points belonging to IV class, accounting for 5.63 %, and 9 points belonging to III class, accounting for 12.68 %. In the wet season, there were 4 points belonging to class V, accounting for 5.63 %, 1 point belonging to class IV, accounting for 1.41 %, and 10 points belonging to class III, accounting for 14.08 %. The TP in surface water is mainly distributed in the downstream of phosphate mining area, phosphate rock drainage outlet and other places.

As shown in Fig. 4e, the highest TP content in all soil samples is located in phosphorus mine, which is shut down; the minimum value appears is located in the phosphorus-free area. The distribution of TP content is not uniform, and there is no obvious rule to



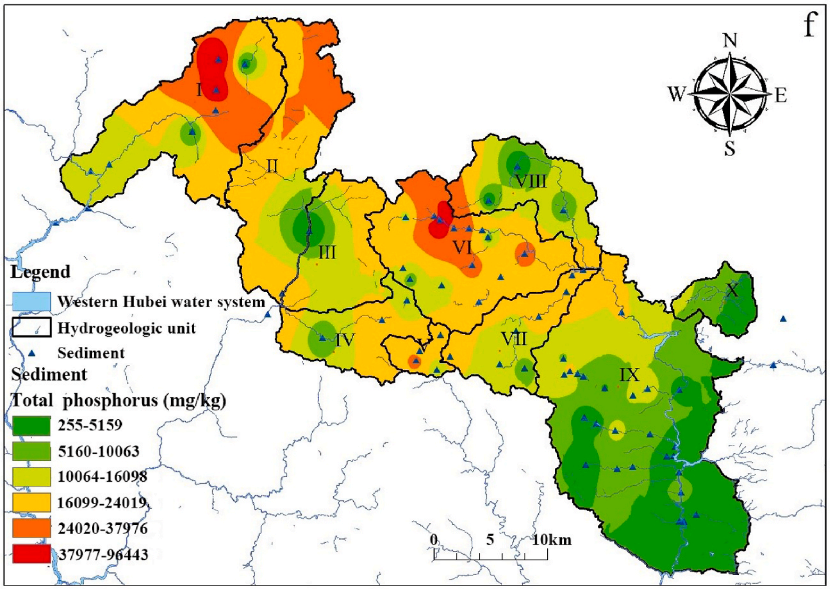




**Fig. 4.** (*continued*).

follow. The sites with high soil TP content in the survey area have a high degree of coincidence with the mining area. The soil TP content in the non-mining area and the east bank of Huangbai River is low. The average content of TP in soil was ranked as pithead > yard > borehole. The borehole is mainly distributed along the groundwater discharge. The surface soil is the quaternary loose layer above the bedrock, and the TP in the soil is the lowest.

In Fig. 4f, sediment samples were collected from surface water during the dry season. Heavy metals and organic matter in surface water did not exceed the standard, and only the impact of phosphorus in sediments on the surface water environment was considered. The TP content of sediment samples ranged from 222 to 82500 mg/kg, with an average of 13993.11 mg/kg. The maximum value was located in the phosphate rock drainage outlet, and the minimum value appeared in the non-phosphorus area. This was close to the distribution law of TP in surface water in dry season, and the distribution of phosphate rock enterprises in this area is also less, which was less affected by phosphate rock mining.

### *3.4. Spatiotemporal distribution of different forms of phosphorus in soil and sediment*

The content of various forms of phosphorus in different types of soil in the study area is shown in Fig. 5. The content of inorganic

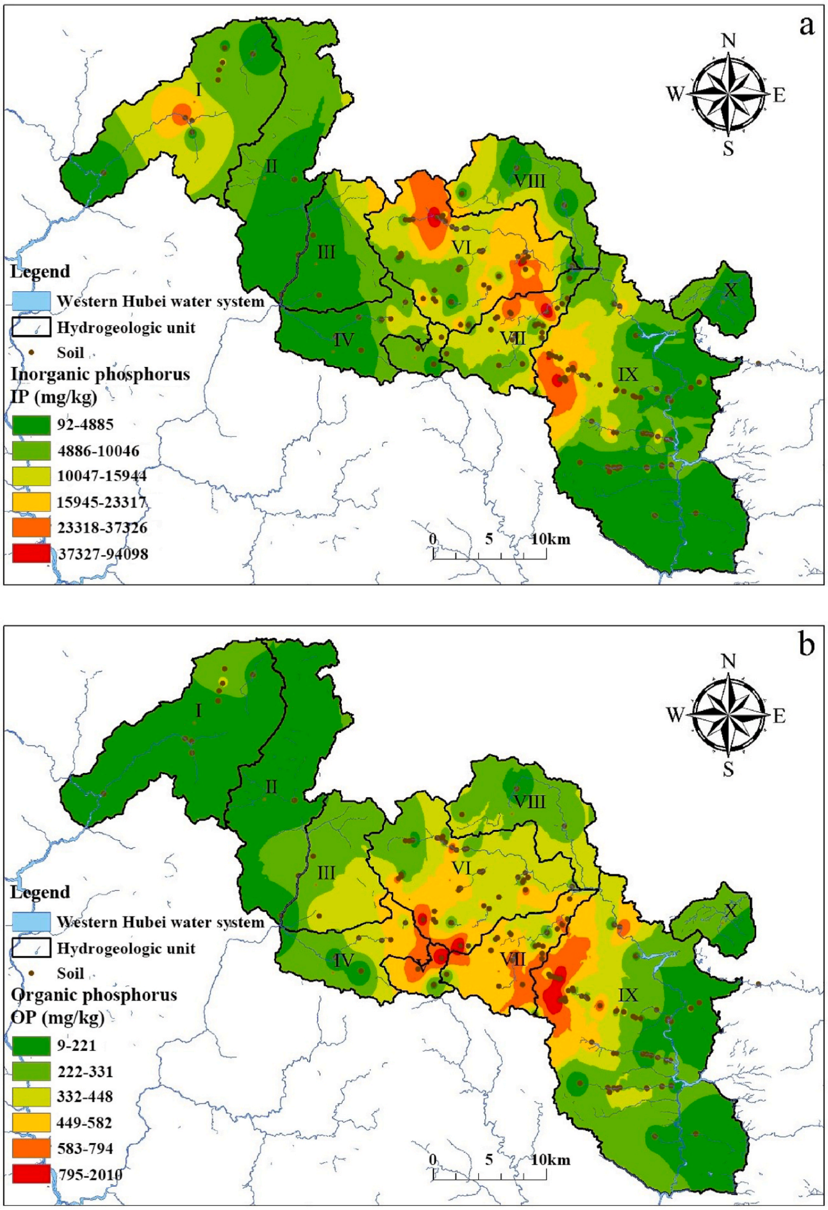



**Fig. 5.** Distribution of (a) inorganic phosphorus, (b) organic phosphorus in surface soil of study area; distribution of (c) inorganic phosphorus, (d) organic phosphorus in watershed sediments of study area.

phosphorus (IP) in the surface soil of the phosphate mining area was 18.00–105000.00 mg/kg, with an average value of 11782.15 mg/kg. It can be seen from Fig. 5a that the change trend of IP and TP is similar. The TP content of soil was higher near the mine, and the TP content of soil was lower in the less mining and non-mining areas. The average proportion of IP to TP in the phosphate mining area is 77.64 %, indicating that the phosphorus in the soil of the study area is mainly IP. Organic phosphorus (OP) was considered to be partially available for biological use and related to human activities [34]. It was mainly derived from agricultural non-point sources, with a content of 8.25–2690.00 mg/kg and an average of 393.56 mg/kg. The spatial distribution of OP content in the study area is shown in Fig. 5b. The average proportion of OP to TP in all samples is 9.5 %. In addition, calcium-bound phosphorus (Ca-P), also known as apatite phosphorus, is derived from clastic rocks or native authigenic, and is considered to be biologically unavailable phosphorus. Its content was 3.53–93000 mg/kg, with an average value of 10291.73 mg/kg. Soil IP was mainly composed of Ca-P, and the higher Ca-P was usually related to the phosphate rock in the process of phosphate rock mining. The soil in this study area is mainly Quaternary loose sediments. Phosphorus ore usually occurs in the phosphorus-containing layer, and there is a bare phosphorus layer, but the distribution is less. The main reason is the high background Ca-P content of regional soils due to weathering of

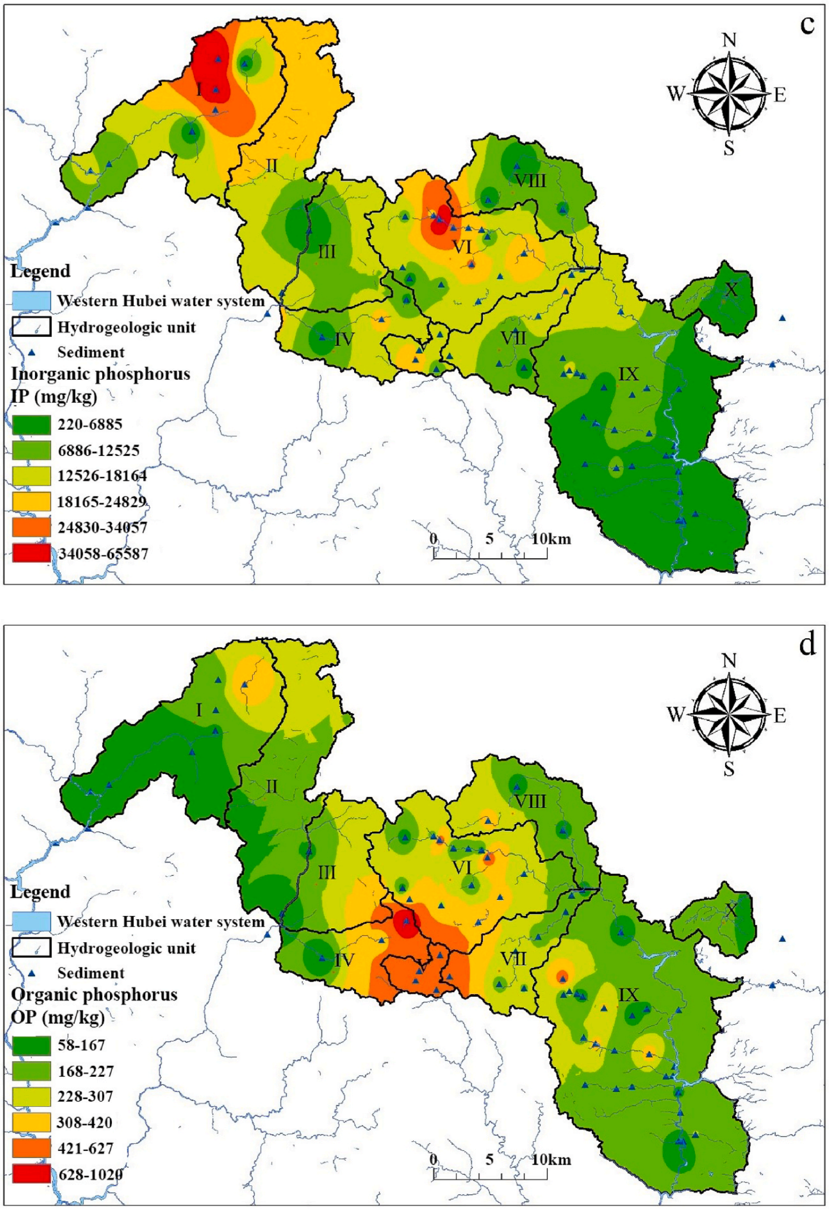



**Fig. 5.** (*continued*).

phosphorus-bearing strata, dumping of slag and ore transport processes, which is also the main reason for the high TP content. Iron/aluminum bound phosphorus (Fe/Al-P) refers to the phosphorus wrapped by Al, Fe, Mn oxides and their hydrates. Under certain conditions, the phosphorus adsorbed on the surface of Fe and Al compounds is released through the replacement of hydroxyl groups. Fe/Al-P is considered to be a phosphorus that can be used by organisms and is related to human activities. It mainly comes from

**Table 2**
Content of various forms of phosphorus in sediments of the study area.

| Test items | TP (mg/kg) | IP (mg/kg) | OP (mg/kg) | Fe/Al-P (mg/kg) | Fe/Al-P/TP | Ca-P (mg/kg) | Ca-P/TP |
|---|---|---|---|---|---|---|---|
| maximum value | 82500.00 | 66100.00 | 1020.00 | 862.00 | 54.95 % | 56400.00 | 99.62 % |
| minimum value | 222.00 | 94.90 | 57.50 | 14.90 | 0.07 % | 92.30 | 8.45 % |
| average value | 13993.11 | 11965.48 | 244.93 | 173.52 | 3.37 % | 10611.91 | 70.00 % |
| deviation | 13385.98 | 11884.73 | 159.29 | 164.88 | 7.04 % | 10552.47 | 19.93 % |

industrial wastewater and domestic sewage. The content of Fe/Al-P is much lower than that of Ca-P, this is because industrial wastewater is mainly discharged from the mine pit, and discharged to the river after drainage treatment. The living area of the mining area is more dispersed, and the domestic sewage is discharged through the pipe network. The contribution of soil Fe/Al-P is small, which is in line with the characteristics of low Fe/Al-P content. The proportion of Fe/Al-P in total phosphorus is small, far less than that of Ca-P, and the change of content and proportion is far less than that of Ca-P.

The content of various forms of phosphorus in the sediments of the study area is shown in Table 2. Liu et al. [35] showed that the highest TP content in the sediment of Anning phosphate mining area in Yunnan Province was 48115.5 mg/kg, with an average of 6224.1 mg/kg, which was much lower than the TP content in the sediment of a certain phosphate mining area in western Hubei Province. Compared with other rivers and lakes in China [36–39], the TP content in the sediment in this study area was also at a relatively high level. The distribution of IP in the sediments of the study basin is shown in Fig. 5c, the content is 94.9–66100 mg/kg, the average value is 11965.48 mg/kg, and the maximum value is located downstream of the phosphate rock drainage outlet; the minimum value is similar to the TP distribution. The average proportion of IP in sediments accounted for 80 % of TP, indicating that the phosphorus in sediments of the study basin was mainly IP. As shown in Fig. 5d, the content of OP in the sediments of the study area was 57.5–1020 mg/kg, with an average of 244.93 mg/kg. The average proportion of OP to TP in all samples was 6 %. The Ca-P content of sediments in the study area was 92.3–56400 mg/kg, with an average of 10611.91 mg/kg. Ca-P is a relatively stable form of phosphorus in sediment. There is mainly apatite phosphorus combined with carbonate phosphorus and a small amount of organic phosphorus which can be acid-digested. It is mainly derived from various calcium phosphate minerals and is difficult to be utilized. The high proportion of Ca-P in sediment TP indicated that the bioavailable phosphorus content in sediment was very low. The higher Ca-P is mainly due to the weathering of phosphorus-containing strata, soil and ore washed by rainwater. Fe/Al-P content was much lower than Ca-P and accounted for a small proportion of TP.

### *3.5. Migration and transformation law of phosphorus source*

From the distribution of phosphorus forms, the ratio of dissolved phosphorus to TP is calculated as I (%). In the dry season, as shown in Table 3, the I in more than two-thirds of groundwater points is less than 25 %, that is, phosphorus in groundwater mainly exists in the form of particulate phosphorus. Among them, all monitoring wells $I<50$ %, and more than 90 % of the monitoring wells $I<25$ %, indicating that particulate phosphorus is the main form of TP in monitoring wells. More than half of the spring water, mine inflow, and mine drainage $I<25$ %, but there are still some points $I>50$ % or even>75 %, which indicates that most of the spring water, mine inflow, and mine drainage in the form of phosphorus is dominated by particulate phosphorus, and a small part is dominated by dissolved phosphorus. Similar to the dry season, more than three-fifths of groundwater $I<25$ % during the wet season, that is to say, most of the phosphorus in groundwater also exists in the form of particulate phosphorus, and a small part mainly exists in the form of dissolved phosphorus.

The correlation analysis of TP in soil and groundwater are shown in Fig. 6, the correlation coefficient between the $R^2$ is 0.006. The correlation between the two is poor, indicating that the high content of TP in surface soil is not the main source of TP in groundwater. This is because the bedrock fissure in the groundwater and soil correlation is small, the TP in the soil through the leaching or desorption into the groundwater. The soil samples at the mine pit mouth are collected at the exit of the air shaft or ore transportation roadway. The average TP content of the soil near the hole is the highest. According to the different management methods of the enterprise, the ore is transported to the ore bin by rail transportation, crawler transportation, and dust-free transportation. In the absence of anti-seepage measures, the dust in the transportation process is scattered near the mine pit mouth, resulting in a higher TP content in the surrounding soil. Although this part of the soil TP is difficult to infiltrate into the groundwater through precipitation, there is rain washing the surface soil, resulting in the loss of soil TP to the river. The soil samples in the yard are collected near the temporary stacking area of ore and slag. There are usually walls near the yard, and the permeability of the soil layer is weak. Hence, the possibility of TP leaching or scouring into groundwater is weak, but the ore stacking method is extensive. The soil around the yard also has a high TP content due to the stacking of ore and slag.

As shown in Table 4, the TP in the soil of the study area is mainly IP. The correlation coefficients between TP, IP and Ca-P are 0.997 and 0.980, respectively, which are strongly correlated. The contents of TP, IP and Ca-P in soil are consistent. Science soil Ca-P is a part of IP and TP, and its content is much higher than that of other phosphorus forms [40]. The correlation analysis showed that Ca-P was the main source of TP and IP, and the increase of TP and IP content mainly came from Ca-P. In addition, because the soil is mainly distributed in non-agricultural areas, it is less affected by agricultural non-point sources, and the OP content is low. IP is mainly composed of Ca-P and Fe/Al-P, and the correlation coefficient between IP and Ca-P is 0.981, which has a strong correlation. In theory, the sum of Ca-P and Fe/Al-P in soil is equal to IP, yet, due to the high extraction efficiency of Ca-P and Fe/Al-P, the sum of Ca-P and Fe/Al-P at some sites is higher than IP in fact. From the spatial distribution of different forms of phosphorus, it can be seen that the distribution of TP, IP and Ca-P is similar. It is intuitively shown that the content around the phosphate rock area is relatively high, followed by the content along the coast of the mining area, and the content of the area with exploration rights has not been mined and the content of the non-phosphate rock occurrence area is relatively low. The content of OP and Fe/Al-P is low and the distribution is different. This is due to the fact that OP and Fe/Al-P are distributed in areas with more human activities and agricultural planting. While considering the contribution of agricultural cultivation to soil phosphorus, it is also important to take measures to prevent pollution sources such as phosphate mining activities, ore disorderly stacking, and ore transportation.

The content of various forms of phosphorus in surface water in the study area is shown in Table 5. The results of the correlation analysis between sediment phosphorus and surface water phosphorus at the same point showed that TP was strongly correlated with IP and Ca-P (Table 6). There was a significant positive correlation between sediment total phosphorus and Ca-P, and the correlation

**Table 3**
The ratio of dissolved phosphorus to TP in groundwater in the study area (I).

| dissolved phosphorus/TP(I, %) | | 0~25 | 25~50 | 50~75 | 75~100 |
|---|---|---|---|---|---|
| Dry season | Groundwater | 110 | 12 | 15 | 29 |
| | Monitoring wells | 46 | 4 | 0 | 0 |
| | Spring water | 15 | 2 | 8 | 5 |
| | Mine inflow | 25 | 2 | 2 | 11 |
| | Mine drainage | 24 | 4 | 5 | 13 |
| Wet season | Groundwater | 100 | 35 | 21 | 7 |
| | Monitoring wells | 30 | 8 | 8 | 1 |
| | Spring water | 16 | 6 | 6 | 2 |
| | Mine inflow | 27 | 9 | 1 | 3 |
| | Mine drainage | 27 | 12 | 6 | 1 |

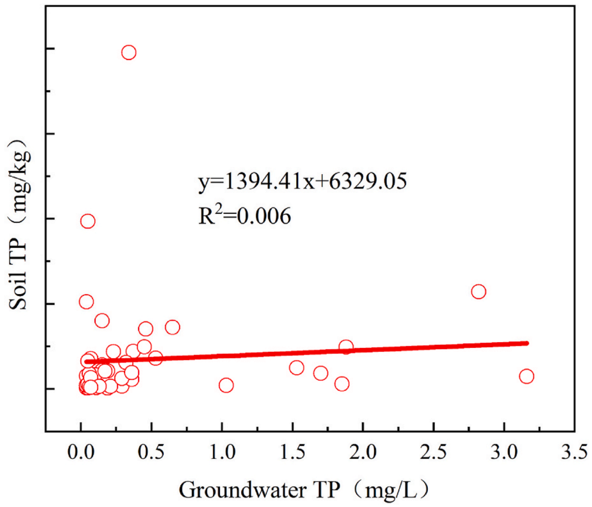



**Fig. 6.** Correlation diagram of total phosphorus in surface soil and groundwater in phosphate mining area.

**Table 4**
The correlation between soil total phosphorus and various forms of phosphorus in the study area.

| | TP | IP | OP | Fe/Al-P | Ca-P |
|---|---|---|---|---|---|
| TP | 1 | 0.997** | 0.331** | 0.092 | 0.980** |
| IP | – | 1 | 0.325** | 0.063 | 0.981** |
| OP | – | – | 1 | 0.238** | 0.290** |
| Fe/Al-P | – | – | – | 1 | 0.057 |
| Ca-P | – | – | – | – | 1 |

Note: **At the 0.01 level (double tail), the correlation is significant.

**Table 5**
The content of different forms of phosphorus in surface water in the study area.

| Indexes | | Unit | Maximum | Minimum | Average | Deviation | Coefficient of variation |
|---|---|---|---|---|---|---|---|
| Dry season | TP | mg/L | 1.62 | 0.00 | 0.09 | 0.19 | 2.17 |
| | DTP | | 0.20 | 0.00 | 0.03 | 0.03 | 1.24 |
| | PP | | 1.57 | 0.00 | 0.07 | 0.19 | 2.80 |
| | DP | | 0.19 | 0.00 | 0.02 | 0.03 | 1.47 |
| Wet season | TP | mg/L | 0.38 | 0.02 | 0.09 | 0.08 | 0.84 |
| | DTP | | 0.18 | 0.00 | 0.04 | 0.03 | 0.87 |
| | PP | | 0.35 | 0.00 | 0.05 | 0.07 | 1.24 |
| | DP | | 0.18 | 0.00 | 0.02 | 0.03 | 1.26 |

**Table 6**
Correlation analysis of different phosphorus forms in sediment and water.

| | | sediment | | | | | water | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | TP | IP | OP | Fe/Al-P | Ca-P | TP | DTP | PP | DP |
| **sediment** | TP | 1 | 0.993** | 0.139 | 0.158 | 0.975** | 0.349** | 0.073 | 0.346* | 0.050 |
| | IP | | 1 | 0.101 | 0.151 | 0.977** | 0.379** | 0.075 | 0.376** | 0.050 |
| | OP | | | 1 | 0.552** | 0.099 | 0.007 | 0.243* | −0.038 | 0.292* |
| | Fe/Al-P | | | | 1 | 0.173 | 0.082 | 0.384** | 0.013 | 0.412** |
| | Ca-P | | | | | 1 | 0.403** | 0.086 | 0.399** | 0.058 |
| **water** | TP | | | | | | 1 | 0.241* | 0.984** | 0.249* |
| | DTP | | | | | | | 1 | 0.062 | 0.931** |
| | PP | | | | | | | | 1 | 0.083 |
| | DP | | | | | | | | | 1 |

Note: *At the 0.05 level (double tail), the correlation is significant.
**At the 0.01 level (double tail), the correlation is significant.

coefficient was 0.975. The result showed that Ca-P was the main component of TP, which was basically consistent with the research results of Liu et al. in the Anning phosphate mining area [35]. The TP in sediments was moderately correlated with the TP and particulate phosphorus in surface water, and the correlation coefficients were 0.349 and 0.346, respectively. Sediments have a certain contribution to phosphorus in surface water, but they are not the main factors. The TP in surface water is strongly correlated with particulate phosphorus, and the correlation coefficient is 0.984. Particle phosphorus is the main component of TP in surface water. The main sources of phosphorus in surface water are exogenous inputs (including mine drainage and agricultural non-point sources) and the part of phosphorus in sediments suspended in water under disturbance.

## 4. Conclusion

(1) The total phosphorus content in groundwater is high, and the phosphorus in groundwater is related to seasonal changes and the distribution of phosphate rock. The total phosphorus level in groundwater decreased from 0.42 mg/L in dry season to 0.24 mg/L in wet season. The total phosphorus concentration of surface water was 0.00–1.62 mg/L in dry season and 0.02–0.38 mg/L in wet season, and the location of high phosphorus content is closely related to the distribution of phosphate rock.

(2) The total phosphorus in surface water is strongly correlated with particulate phosphorus, and the correlation coefficient is 0.984. The main sources of phosphorus in surface water are exogenous input. The sediment has a certain contribution to the phosphorus in the water, but it is not the main factor.

(3)The soil total phosphorus content is high in areas with frequent phosphate mining activities, and the total phosphorus is low in non-phosphorus areas. The distribution of TP, IP and Ca-P is similar, which intuitively shows that the content of non-mining areas with prospecting rights and non-phosphorus ore occurrence areas is relatively low. The contents of OP and Fe/Al-P are low and the distribution is different. OP and Fe/Al-P are obviously distributed in living areas and agricultural planting areas.

(4)The migration and transformation of phosphorus sources are mainly through soil leaching, scouring and mine drainage into surface water, and there will be migration of surface water to groundwater in monitoring wells. The correlation between total phosphorus in soil and groundwater is poor. The high content of total phosphorus in surface soil is not the main source of total phosphorus in groundwater.

## CRediT authorship contribution statement

**Lei Kou:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Junwei Zhang:** Writing – review & editing, Data curation, Conceptualization. **Liyue Huang:** Writing – review & editing, Methodology, Formal analysis. **Guanyu Chen:** Writing – review & editing, Data curation. **Shupeng Jiang:** Investigation, Methodology. **Ding Han:** Writing – review & editing, Resources. **Dayuan Jiang:** Writing – review & editing, Supervision, Funding acquisition.

## Data availability statement

Data is contained within the article.

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## Declaration of competing interest

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