Response of phosphorus fractionation in lake sediments to anthropogenic activities in China

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HIGHLIGHTS

- Ca-P content is related to soil erosion dynamics and geographical location.
- Industrial and domestic effluents lead to changes in Fe/Al–P.
- Fertilizer and livestock breeding cause changes in Hum–P_o and Res–P_o.
- Increases in Fe/Al–P and P_o fractions, essential to internal loads and eutrophication process.

GRAPHICAL ABSTRACT
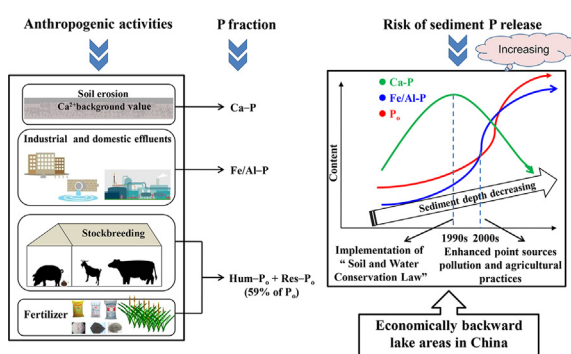
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ABSTRACT

In this study, geochemical fractionation is used to establish the relationship between sediment phosphorus (P) pools and anthropogenic activities based on the dated sediment from a suite of lakes in China. Our extraction results showed that the inorganic P fractions, including Ca-P (46% of TP) and Fe/Al-P (24%), constitute most of the P in sediments. Soil erosion dynamics and geographic location are the dominant factors controlling the historical distribution and partitioning of Ca-P in sediments, while over the last few decades, industrial and domestic effluents were the leading factor controlling Fe/Al-P. The organic P (P_o) fractions, $NaHCO_3$-P_o, HCl-P_o, and Ful-P_o accounted for only 11%, 16% and 12% of P_o on average, respectively, whereas Hum-P_o and Res-P_o made up the dominant P_o fraction (59%) and were the main factors controlling P_o dynamics due to fertilizer and livestock breeding. Thus, the historical fraction of P in the sediment core can be used as an indicator of anthropogenic activities. Ca-P decreased in the top layers of the cores because of the implementation of the Soil and Water Conservation Law in China since 1991. However, Fe/Al-P and P_o continuously increased in the lakes from the economic backward area over the last few decades, which is largely due to enhanced point sources of pollution and an increase in the intensity of agricultural practices. As a potential P source, the massive accumulation of Fe/Al-P and P_o would be released into the overlying water to further facilitate eutrophication via increasing pH and alkaline phosphatase and decreasing in the dissolved oxygen concentration. Therefore, in order to control eutrophication more effectively and efficiently, it is essential that the accumulation of sediment Fe/Al-P and P_o be decreased immediately and domestic wastewater, poultry excreta, and fertilizer loss must be more carefully controlled, especially in economically backward areas.

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1. Introduction

Eutrophication due to excessive phosphorus (P) input is a major global environmental problem that significantly alters water chemistry, disrupts ecological equilibrium, and endangers human health (Carpenter, 2005; Worsfold et al., 2008). Human-induced P loss contributes to lake eutrophication in two major ways, that is, by direct P inputs from anthropogenic activities, the chronic release from enhanced P pools in sediments. The increased P loading due to intensive anthropogenic activities is responsible for accelerating eutrophication worldwide since the 1960s (Yuan et al., 2018). Meanwhile, numerous techniques and strategies for controlling lake eutrophication have been developed since the 1960s. Target activities have included the reduction of external pollution sources (e.g., interception of peripheral pollution, construction of waste water treatment plants, non-point sources control, and wetland treatment technology), internal loading control (sediment dredging, mulching, oxidation, passivation, and biotechnology), ecological restoration (mosaic technology of aquatic plant communities and biomanipulation) and integrated watershed management (Oglesby and Edmondson, 1966; Jin, 2001; Wang and Chu, 2015; Guo et al., 2017; Wang et al., 2019a). Reduction of external P loading is the most basic and primary approach to controlling lake eutrophication (Cavalcante et al., 2018). For many years, emphasis has been placed on the study of the quantitative response of external loading to lake water quality (Liu et al., 2014a) in an effort to improve our understanding of the contribution of external loading to eutrophication. However, the response of external loading due to anthropogenic activities to the availability of P in lake ecosystems remains unclear. Lake eutrophication process and algal bloom are usually closely related to the availability of P (Maykoll et al., 2019). Thus, in order to better understand the effect of anthropogenic activities on lake eutrophication, it is necessary to establish the relationships between anthropogenic activities and the availability of the P in lakes.

The P cycle is an important Earth system process, while intense anthropogenic activities have altered the natural biogeochemical P cycle by reinforcing the transfer of P from the lithosphere into the ecosystems (Yuan et al., 2018). The specific fraction of the different forms of P can is an effective indicator of which anthropogenic activities have altered the origin and availability of P (Rydin, 2000; Zhang and Shan, 2008). Sequential extraction allows for the rapid and simple analysis of the inorganic P (P_i) and organic P (P_o) fractions, so it been applied widely by many scientists (Ruban et al., 1999; Maykoll et al., 2019). The extracted fractions of P_i are usually determined for loosely sorbed (Water/salt-P), potential labile (reductant soluble P and Fe/Al oxide bound-P) and non-labile (calcium-bound P and occluded-P) P_i fractions (Ruttenberg, 1992; Reddy et al., 1995; Jensen et al., 1998; Filippelli and Delaney, 1996). The analytical method of P_o is largely ignored due to P_o is usually treated as a residue and refractory fraction over the past decades (Turner et al., 2005; Ruttenberg, 1992). In recent years, the P_o has been studied by sequential extraction. A sequential extraction method was adapted by Ivanoff et al. (1998) to determine P_o into several fractions associated with environmental sample availability and various physicochemical characteristics. The extracted fractions of P_o were determined for labile (NaHCO$_3$-P_o), the moderate labile (HCl-P_o and Ful-P_o), non-labile (Hum-P_o and Res-P_o) P_o fractions. Sediments are the major pools of P and are essential to the biogeochemical P cycle in lake ecosystems. The preservation of P in sediment cores serves as good archive, which can be used to investigate the past anthropogenic activities and environmental dynamics because of the continuity and high resolution of the sediment layer (Ni et al., 2016). In addition, sediments are potential sources of P that can be released into the overlying water under certain environmental conditions (Filippelli and Delaney, 1996). Thus, in order to more effectively and efficiently guide external loading reduction measures and reduce the risk of eutrophication, we must investigate the effect of anthropogenic activities on the geochemical fractionation of P in sediments and evaluate the subsequent potential effect of P dynamics on lake eutrophication.

Lake eutrophication in China is increasingly disconcerting due to high P loading. According to a 2010 nationwide survey, the area of eutrophic lakes increased by 60 times since the 1980s, and approximately 14,000 km^2 of lakes are at risk of eutrophication (Wang, 2015a; Ni and Wang, 2015). Excessive nutrient loading due to the rapid economic growth in China has accelerated lake eutrophication and caused a dramatic deterioration of water quality since the 1980s, especially in the 1990s (Wang et al., 2016). The tremendous national efforts to reduce nutrient loading in aquatic ecosystems began in the 2000s (Zhou et al., 2017). Overall, the point sources (e.g., industrial and domestic effluents) and non-point sources (NPS) of soil erosion have been significantly improved, while agricultural NPS have remained constant (Huang et al., 2019). Increased investments in external loading management have resulted in large-scale declines in the total phosphorus (TP) concentration of the overlying water in many lakes in recent years (Tong et al., 2017). However, little information is currently available on the dynamics of P fractionation due to changes in external loading. Consequently, the effects of external loading due to anthropogenic activities on lake eutrophication are still poorly understood. Elucidating the relationship between the P fractions and anthropogenic activities is therefore important to understanding the effect of P loading reduction measures on lake eutrophication. Accordingly, the aims of this study are: (1) to establish the relationship between anthropogenic activities and the historical geochemical fractionation of P in sediments, and (2) to assess the potential effect of P dynamics on lake eutrophication due to changes in external P loading, across a suite of lakes in different regions of China in the recent decades.

2. Materials and methods

2.1. Study area

Freshwater lakes are widely distributed throughout the Eastern Plains, Northern Plains and the Yun-Gui Plateau of China. As critical water sources, they have sustained China's civilization and socioeconomic progress. The Wuliangsu Lake (WLSH), Yanghe Reservoir (YHR), Taihu Lake (TH), and Erhai Lake (EH) were selected as the research subjects of this study (Fig.1). The WLSH (40°36′–41°03′N, 108°43′–108°57′E), which is located on the Northern Plain, is a typical oxbow lake and an important international wetland formed by the diversion of the Yellow River. This lake has experienced severe eutrophication due to agricultural activities since the 1990s. The YHR (39°58′–40°01′N, 119°08′–119°14′E), which is located on the Northern Plains, is a medium-to-large artificial reservoir built in 1963. The lake has suffered severe water quality degradation coinciding with the rapid development of sweet potato planting in the upper reaches of the watershed since the 1990s. The TH (30°56′–31°33′N, 119°54′–120°36′E) on the Eastern Plains provides significant services to over 60 million people, including drinking water, water for industrial and agricultural uses, fish production and flood mitigation. The water quality has continuously deteriorated and caused tremendous socioeconomic implications since the 1990s. In recent year, controlling the external loadings has gradually improved the water quality. The EH (25°35′–25°58′N, 100° 05′–100°17′E) on the Yun–Gui Plateau is facing a transition from a mesotrophic to eutrophic status because of the agricultural intensification, soil erosion, and pollution from tourism in the upper reaches in recent years.
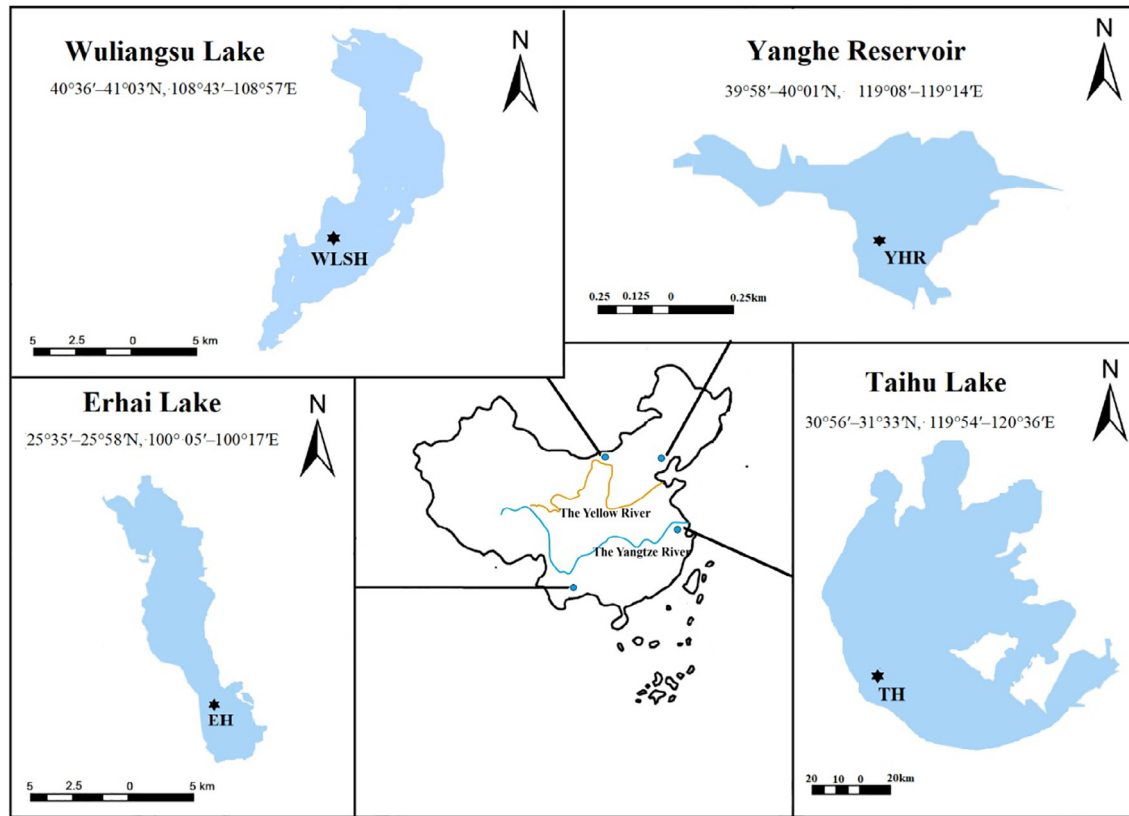
Fig. 1. Locations of the four selected lakes in China and sampling sites in Wuliangsu Lake (WLSH), the Yanghe Reservoir (YHR), Erhai Lake (EH), and Taihu Lake (TH).

Table 1
Basic Characteristics of the 4 different lakes. Lake area (LA), drainage area (DA), hydraulic residence time (HRT), mean depth (D_{mean}), sampling depth (D_s), sediment TN, TP and OM (TN_s, TP_s, OM_s), water TN and TP (TN_w, TP_w), algal biomass (AB), algal density (AD), climatic condition and soil type.

Lake	La km²	DA km²	HRT day	D_{mean} m	D_s m	TN_s mg kg⁻¹	TP_s mg kg⁻¹	OM_s %	TN_w mg L⁻¹	TP_w mg L⁻¹	AB mg L⁻¹	AD ind L⁻¹	Trophic status	Climatic condition	Soil type
WLSH	293	11,800	180	0.7	0.8	1280	750	3.23	2.35	0.11	26.3	3.3×10^7	Eutrophic	Mesothermal monsoon	Saline-alkali soil
YHR	14	755	/	5.7	4.9	1783	1112	2.39	3.6	0.06	10.9	1.1×10^{10}	Eutrophic	Warm temperate monsoon	Cinnamon soil
TH	2445	36,900	309	5.1	2.6	819	487	1.02	2.7	0.08	5.85	1.6×10^7	Eutrophic	Subtropical monsoon,	Red and brown Soil
EH	256	2565	670	10.5	8.2	4207	903	5.2	0.54	0.025	12.4	3.46×10^7	Mesotrophic	Subtropical monsoon	Calcareous and red soil

The TH watershed covers 0.38% of the total area of the national territory, but it contributes over 11.6% of the national GDP. Domestic wastewater and agricultural pollution are the main source of P loading in the TH. They contribute 60% and 28% of the total external loading, respectively. In contrast, the economic situation in the WLUS, YHR, and EH watersheds are different those of the TH. The P loading in these areas are due to agricultural intensification, with fertilizer and livestock loss contributing 74.6%, 96.4% and 65.2% of the P loading in the WLSH, YHR, and EH, respectively (Dong et al., 2011; Chen et al., 2018a; Zhang and Chen, 2010; Chen, 2014). The detailed information on the basic background along these selected lakes is presented in Table 1.

2.2. Sample collection

Four sediment cores were collected in September 2014 (EH, WLSH) and September 2015 (TH, YHR) using a core sampler (HL-CN, Xihuayi Technology, Beijing, China). The depths of the cores were 30 cm with 2 cm increments. These sampling sites were less influenced by direct anthropogenic activities (e.g., aquaculture, dredging) and hydrodynamic conditions and no macrophytes growth was observed, which reduced the impact on the historical distribution and fractionation of P in the sediments. Prior to analysis, the samples were immediately stored in sterile sealable plastic bags, lyophilized, and passed through a 100-mesh sieve to ensure homogeneity prior to analysis.

2.3. Analytical methods

2.3.1. TP, P_i, and P_o

The TP, inorganic P (P_i) and P_o contents of the sediments were analyzed using the standard measures technology (SMT) producer (Ruban et al., 1999). Briefly, after the sediment was combusted at 500 °C for 2 h, the TP was extracted by immersion in HCl (1 mol L⁻¹) for 16 h. The P_i was directly extracted by immersion in HCl (1 mol L⁻¹) for 16 h. The extracts were then identified as
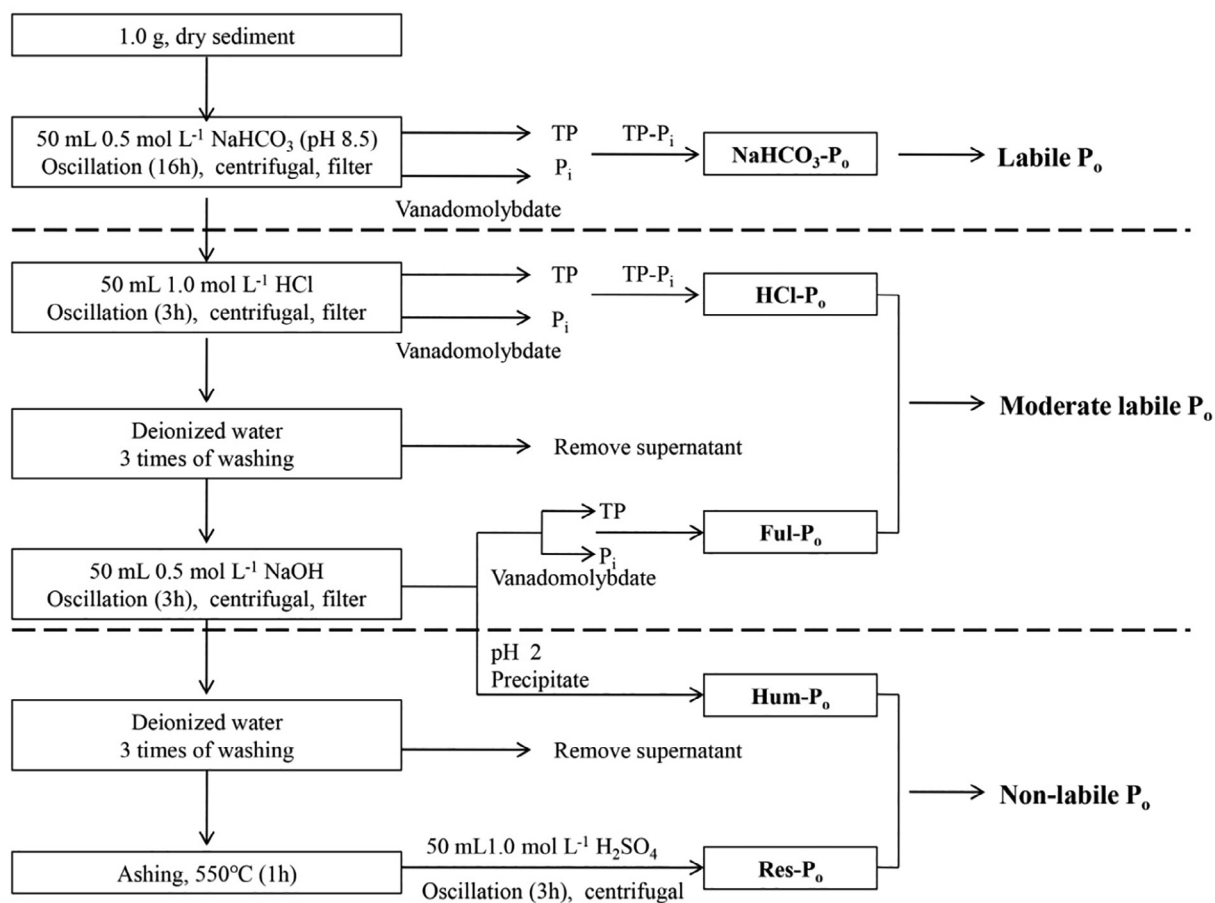
Fig. 2. Modified sequential extraction scheme of the P_o fractions in the sediment.

orthophosphate spectrophotometrically using the vanadomolybdate method. The P_o content was defined as the difference between TP and P_i.

2.3.2. P_i and P_o fractionation scheme

The P_i fractions analyzed using the SMT procedure included moderately labile (Fe/Al-P) and nonlabile (Ca-P) P_i forms. Point two grams of dry sediment and 20 mL of NaOH (1 mol L^{-1}) were mixed in a centrifuge tube at room temperature. The mixture was oscillated for 16 h, and then it was centrifuged at 10,000g for 10 min. The supernatant was filtered through a 0.45-μm fiberglass membrane, and then 4 mL of HCl (3.5 mol L^{-1}) was added. The mixture was stirred, allowed to settle for 16 h, and centrifuged at 8000g for 10 min (Fe/Al-P). The residue from the previous step was mixed with 12 mL of NaCl (1 mol L^{-1}), centrifuged, filtered, then 20 mL HCl (1molL^{-1}) was added into the supernatant, oscillated, centrifuged and filter (Ca-P). The extracts were then determined spectrophotometrically as orthophosphate using the vanadomolybdate method.

The P_o fractions were sequentially extracted from the sediment using a five-step process adapted from the sequential extraction procedure developed by Ivanoff et al. (1998) (Fig. 2). The P_o was operationally divided into five fractions, i.e., the NaHCO$_3$-P_o, HCl-P_o, fulvic acid-associated P (Ful-P_o), humic acid-associated P (Hum-P_o), and Res-P_o fractions. The P_o fractions extracted were the labile (NaHCO$_3$-P_o, extracted using 0.5 M NaHCO$_3$), the moderate labile (HCl-P_o, extracted using 1 M HCl; Ful-P_o, extracted using 0.5 M NaOH), and non-labile (Hum-P_o, extracted using 0.5 M NaOH, the difference between NaOH-P_o and Ful-P_o; Res-P_o, ashing,

and then, extracted using 1.0 M H$_2$SO$_4$) P_o fractions. In each extraction step, TP and P_i were spectrophotometrically identified as orthophosphate using the vanadomolybdate method.

2.3.3. Loss loading of P due to agricultural NPS

Fertilizer and livestock breeding are the major sources of P loading from agricultural NPS in China. Therefore, P fertilizer and P loss from livestock farming were selected as the major indices to reflect the amount of agricultural NPS. Annual P fertilizer applications were calculated using the watershed usage data obtained from the Chinese agricultural statistics (1980–2015) and the local rural statistical yearbook.

P fertilizer usage (kg hm^{-2}) = total P fertilization amount/crop acreage.

The annual loss of P from livestock farming (1980–2015) was calculated from the fecal and urine production using the following equations (Wu, 2005):

$$\text{Fecal P production (ton)} = (\text{number of cattle} \times 21.02 \\ + \text{number of pig} \times 6.5 + \text{number of sheep} \times 2.34)/1000;$$

$$\text{Urine P production (ton)} = (\text{number of cattle} \times 1.35 \\ + \text{number of pig} \times 0.77 + \text{number of sheep} \times 0.08)/1000.$$

2.3.4. Core chronology

The sediment cores were dated by analyzing the ^{137}Cs and ^{210}Pb of each layer of sediment. The sediment core locations in this study are similar to those described by Ni et al. (2011), Wang et al.
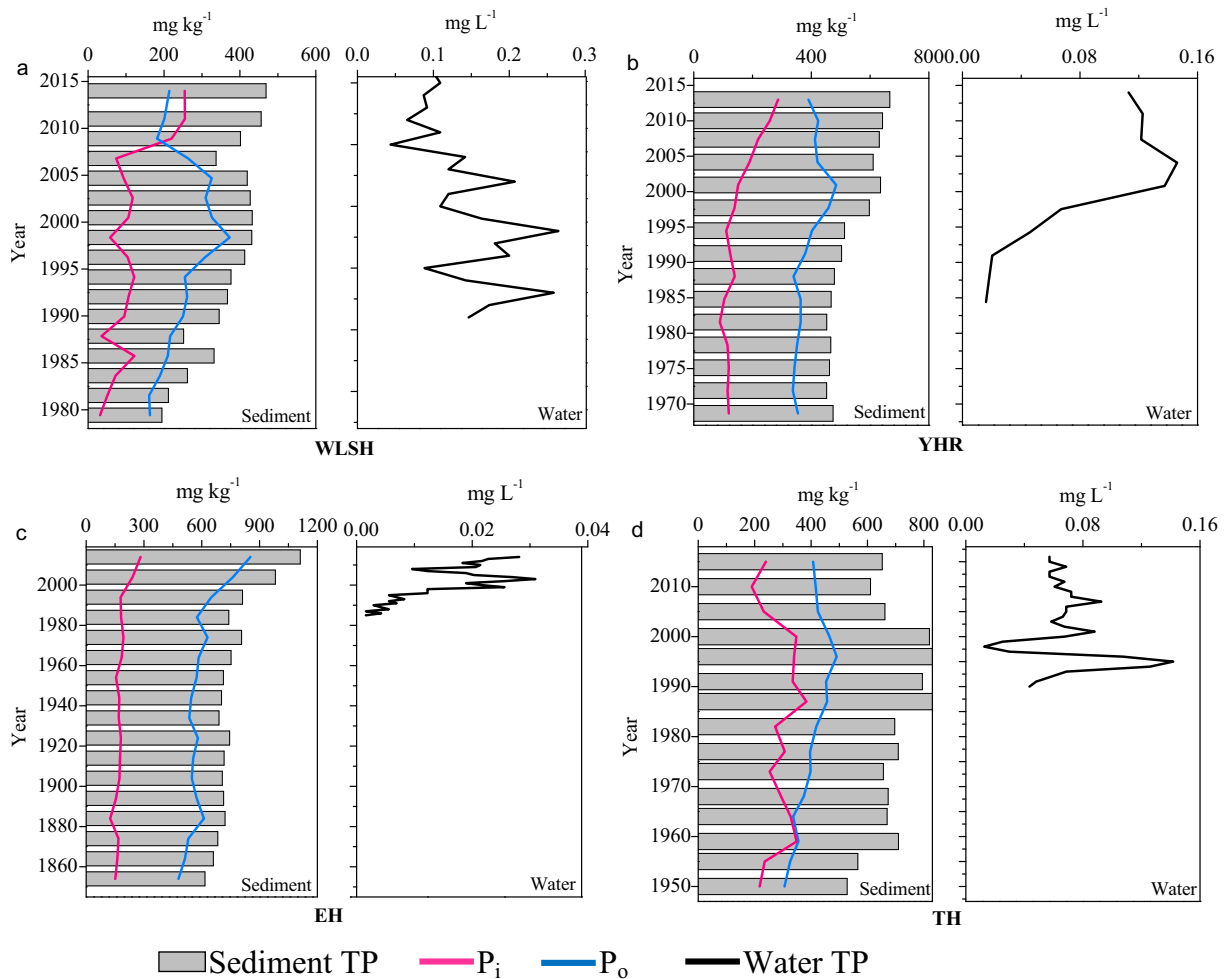
Fig. 3. Trends in the TP, P_i and P_o contents of sediment cores, and the corresponding TP concentration of the overlying water in the WLSH, YHR, EH, and TH over the last few decades (water quality data was provided by the local Environmental Protection Bureau).

(2015), Ni et al. (2015) and Zhang (2013). The sedimentation rates of the WLSH, YHR, EH, and TH were 0.95, 0.62, 0.20, and 0.44 cm yr^{-1}, respectively.

2.4. Data analysis and quality control

The data was analyzed and presented using SPASS 18 (IBM, New York, USA) and Origin 8.5 (OriginLab, Northampton, Massachusetts, USA). Spiked samples, duplicate field samples, and analytical blanks were used to control the data quality. Triplicate measurements of each sample were conducted and their arithmetic mean values were reported. For the TP, P_i, and P_o fraction analysis, the precision was approximately 10% with a confidence level of 95%.

3. Results

The TP, P_i, and P_o concentrations were plotted versus sample age for the four lakes (Fig. 3). The mean concentration of TP increased steadily with time since the 1980s in the WLS, YHR, and EH sediments. In contrast, TP continuously decreased in the TH sediments since the 1990s. The P_i fraction, including Ca-P and Fe/Al-P, accounted for 43–87% of the TP (70%, average), and it can be divided into three stages in the WUSH, YHS, and TH: a stable phase before the 1990s, a clear increasing phase from the 1990s to

the 2000s, and a stable or decreasing period after the 2000s. The P_i concentrations in the EH have increased since the 1990s. The Ca-P (P bound to calcium) is recognized to be nonbioavailable and difficult to release (Cavalcante et al., 2018), was the dominant P_i fraction in the sediments (accounting for 24–93% of P_i, 71% on average), and it accounted for relatively high percentages in the WLSH, YHR, and EH (Figs. 4a–c). The Ca-P fraction was similar with P_i in the four sediment cores. The Fe/Al-P (Fe and Al oxyhydroxide bound P) is a moderately labile P, which can be released when anoxic conditions prevail in the sediment-water interface (Ting and Appan, 1996), accounted for 7–76% of the P_i in the sediment cores, but had a relatively low ratio in the WLSH (6.6%). This fraction continuously increased in the YHR and EH, particularly after the 1990s and 1950s. In the TH, a clear inflection appears in the 2000s, before Fe/Al-P began steadily increasing. Then, it gradually decreased. In the WLSH, the Fe/Al-P content remained relatively stable over the last decades (Fig. 4d).

The P_o fraction, including NaHCO$_3$-P_o, HCl-P_o, Ful-P_o, Hum-P_o, and Res-P_o, accounted for 13–57% of the TP, and it has increased steadily in the WLSH, YHR, and EH since the 2000s (Fig. 5a–c). In the TH, a clear inflection appeared in the 2000s, before P_o began steadily increasing. Then, it gradually decreased, similar to the trend of the TP of the sediments (Fig. 5d). NaHCO$_3$-P_o, which mainly consisted of phospholipids, nucleic acids, and phosphosaccharides and is easily affected by mineralization and decomposition (Zhu et al., 2013), accounted for 5–27% (average, 12%) of the
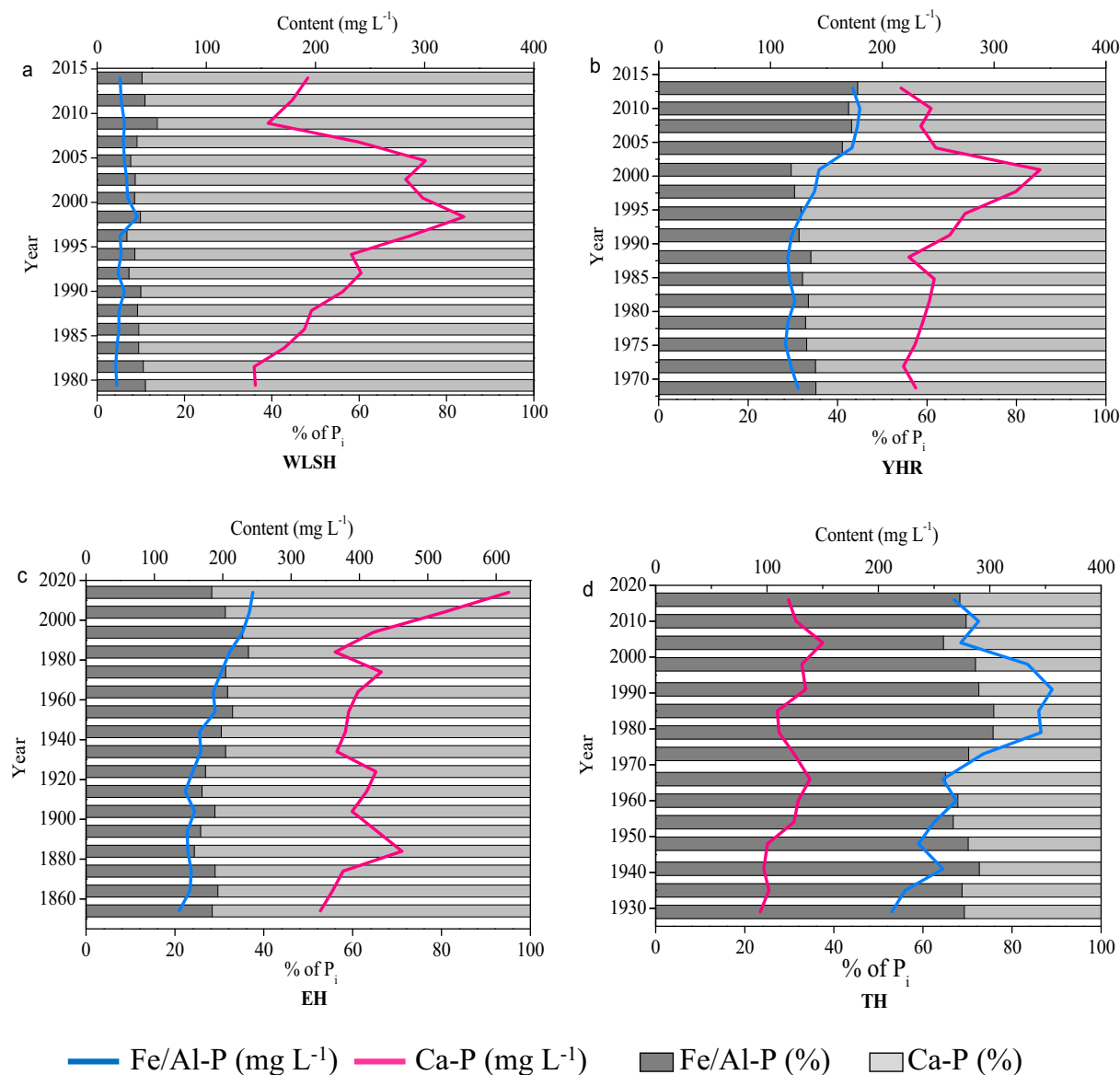
Fig. 4. Temporal contents of the P_i fractions (including Fe/Al-P and Ca-P), and the Fe/Al-P and Ca-P percentage in P_i from the WLSH, YHR, TH and EH sediment cores.

P_o in the four sediment cores. It exhibited an increasing trend in the four sediment cores. The HCl–P_o, which represents moderate P_o consisting of P bound to phytic acid, calcium, or magnesium (Ahlgren et al., 2005), accounted for 4–37% (average, 17%) of the P_o. It exhibited little dependence on depth in the sediment cores. The Ful-P_o, which represented moderate labile P_o in the sediments (Reddy et al., 1995), accounts for 4–26% (average, 12%) of the P_o in the four sediment cores. This fraction has steadily increased since the 2000s, and 1980s in the WLSH, YHR, TH, and EH sediment cores. The Hum-P_o, which consists of inositol five phosphate and inositol hexaphosphate (phytic acid) and it is refractory (Dou, 2010), accounted for 0.3–24% (average, 7.4%) of the P_o. Similar to Ful-P_o, Hum-P_o has also increased since the 2000s, and 1980s in the WLSH, YHR, TH, and EH sediment cores. The Res-P_o, which consists of phytic acid bound P and provides resistance to biodegradation (Bowman and Cole, 1978), accounted for 27–74% (average, 51%) of the P_o, and exhibited a similar increasing trend with P_o in the four sediment cores.

The relationship between P and its geochemical fractions was analyzed using the Pearson correlation (Table 2). Fe/Al-P,

NaHCO$_3$-P_o, Ful-P_o, and Hum-P_o were positively correlated with TP in all of the lake sediments cores. Ca-P was positively correlated with TP except in the YHR, and Res–P_o was positively correlated with TP, except in the TH. HCl-P_o was only positively correlated with TP in the WLSH. Furthermore, Ca-P and Fe/Al-P were both positively correlated with the P_i contents of the sediment (Fig. 6). The correlation coefficients of Ca-P with P_i were higher than with Fe/Al-P in the WLSH, YHR, and EH. Res-P_o was significantly correlated with the P_o content of the sediments (Fig. 7).

4. Discussion

4.1. Relationships between external loadings and records of sediment P fractions

The four selected lakes have high spatial heterogeneity at the landscape scale and experience significantly different anthropogenic activities. Thus, the sedimentation processes of the P fractions in the sediments can be interpreted using the anthropogenic activities and the locations. This study identified a strong response
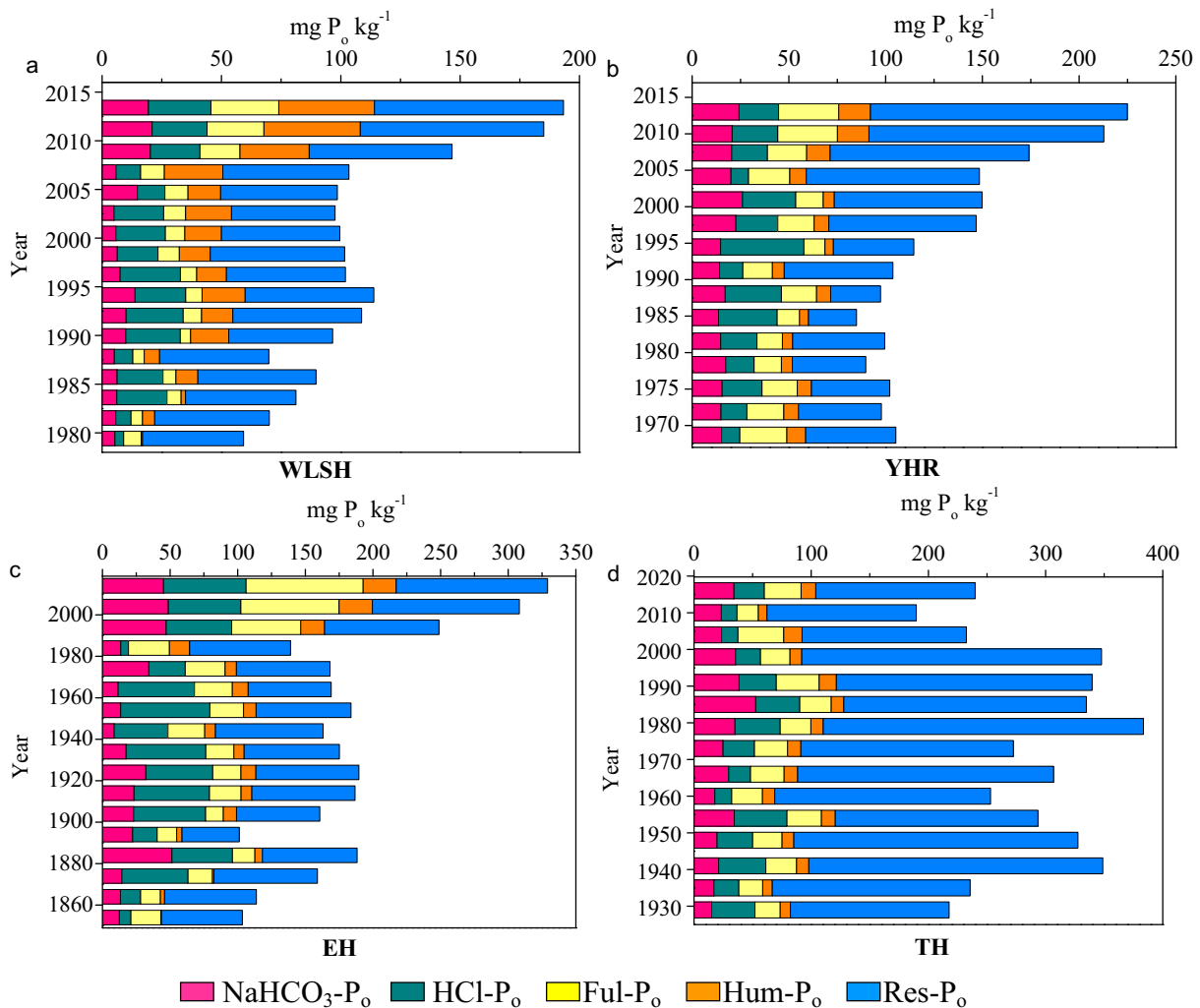
Fig. 5. Temporal distribution of the P_o fractions, including NaHCO3-P_o, HCl-P_o, Ful-P_o, Hum-P_o and Res-P_o in the four sediment cores from the WLSH, YHR, EH and TH.

in the historical records of the sediment P fractions to anthropogenic activities over the last few decades.

The Ca-P contents of the dominant P_i fractions in the sediments from the WLSH, YHR and EH, were the primary factor controlling P_i (Fig. 4a–c). The widely distributed carbonate apatite in the soil in northern and southwestern China is an important factor, which enhances the accumulation of Ca-P in the WLSH, YHR, and EH. This is because Ca-P is usually closely related to endogenous element accumulation in carbonates that from rock debris and soils in watersheds (Cao et al., 2017). In comparison, acidic soils are widely distributed through southeastern China, and the rainy climate further accelerates their eluviation, causing the Ca^{2+}, K^+, and Mg^{2+} contents of the soil to decrease accordingly. In the TH, which is watershed located in the plains, the area experiencing soil erosion accounts for only 3.9% of the basin's land area (Zhang et al., 2016). Thus, lower Ca-P contents and ratios were observed in the TH and did not significantly change with sediment depth (Fig. 4c). The Ca-P content continuously increased in the WLSH, YHR, and EH sediments before the 1990s, which is likely almost entirely due to enhanced soil erosion since new China was founded in 1949. Scarcity of available cultivated land and steady increases in population and food demands have resulted in a dramatic increase in vegetation destruction and land reclamation. The area of cultivated land in China increased from 1.0×10^8 hm^2 in 1950 to 1.34×10^8 hm^2 in 1980 (34% increases), while the associated soil erosion area increased from 1.53×10^6 km^2 to 1.79×10^6 km^2 (17% increases), respectively (Fang et al., 2008). As a result, a large amount of carbonate apatite was lost to the lakes, enhancing the accumulation of Ca-P in the sediments. After the 1990s, Ca-P was decreased. An important reason for the decrease in Ca-P during this stage was the initiation of the Soil and Water Conservation Law of the People's Republic of China in 1991. The area of soil erosion decreased by 29% and 25% from the late 1990s to 2010 in the WLSH and YHR watersheds, respectively (Tan et al., 2014; Li, 2011; Luo and Zang, 2014). These schemes alleviated the loss of calcium and P from the lakes and inhibited the increase in the Ca-P contents of the sediments. However, there was a dramatic increase in the Ca-P content in the EH, which attributed to the increase in land reclamation and inadequate water and soil management and conservation (Wang et al., 2015).

Industrial and domestic wastewaters are usually rich in Fe/Al bound P (Ruban, 2001). It is found that industrial, urban and rural domestic wastewater accounted for 60% and 8% of the P loading in the TH (Sheng et al., 2002). Thus, higher levels and ratios of Fe/Al-P were observed in the TH (Fig. 4d). In general, the variations in the Fe/Al-P contents of the Fe/Al-P in TH core were in a relatively stable to slightly increasing stage before the 1980s, in an increasing stage in the 1980s to 2000s, and then, in a decreasing stage after the 2000s. The period of slight increase indicates that Fe/Al-P is mainly controlled by natural processes, with smaller anthropogenic input

Table 2
Relationship between P and its geochemical fractions of sediments cores from the WLSH, YHR, TH and EH.

WLSH

	Ca-P	Fe/A-P	NaHCO$_3$-P$_o$	HCl-P$_o$	Ful-P$_o$	Hum-P$_o$	Res-P$_o$
Hum-P$_o$							0.86
Ful-P$_o$						0.89	0.93
HCl-P$_o$					0.39	0.52	0.46
NaHCO$_3$-P$_o$				0.44	0.80	0.79	0.79
Fe/A-P			0.04	0.18	0.07	0.23	0.06
Ca-P		0.74	-0.21	0.26	-0.17	0.09	-0.14
TP	0.60	0.59	0.55	0.52	0.59	0.74	0.59

YHR

	Ca-P	Fe/A-P	NaHCO$_3$-P$_o$	HCl-P$_o$	Ful-P$_o$	Hum-P$_o$	Res-P$_o$
Hum-P$_o$							0.85
Ful-P$_o$						0.96	0.76
HCl-P$_o$					0.35	0.23	0.17
NaHCO$_3$-P$_o$				0.02	0.46	0.51	0.76
Fe/A-P			0.70	-0.10	0.67	0.78	0.94
Ca-P		0.04	0.47	0.33	0.36	-0.35	0.07
TP	0.35	0.91	0.89	0.04	0.57	0.67	0.92

TH

	Ca-P	Fe/A-P	NaHCO$_3$-P$_o$	HCl-P$_o$	Ful-P$_o$	Hum-P$_o$	Res-P$_o$
Hum-P$_o$							0.18
Ful-P$_o$						0.97	0.17
HCl-P$_o$					0.09	0.08	0.36
NaHCO$_3$-P$_o$				0.34	0.35	0.35	0.29
Fe/A-P			0.77	0.05	0.32	0.31	0.42
Ca-P		0.36	0.26	-0.58	0.65	0.64	-0.21
TP	0.65	0.80	0.58	0.18	0.52	0.51	0.21

EH

	Ca-P	Fe/A-P	NaHCO$_3$-P$_o$	HCl-P$_o$	Ful-P$_o$	Hum-P$_o$	Res-P$_o$
Hum-P$_o$							0.79
Ful-P$_o$						0.89	0.97
HCl-P$_o$					0.31	0.39	0.43
NaHCO$_3$-P$_o$				0.29	0.59	0.58	0.55
Fe/A-P			0.50	0.26	0.88	0.91	0.74
Ca-P		0.63	0.77	0.39	0.82	0.73	0.71
TP	0.94	0.84	0.68	0.37	0.94	0.89	0.81

Red color represents significant at the 0.01 level.

Blue color represents significant at the 0.05 level.

Red color represents significant at the 0.01 level.
Blue color represents significant at the 0.05 level.

before the 1980s. The dramatic increase in Fe/Al-P in the 1980s–2000s period, suggests that industrial and domestic wastewater input was amplified in this period because of rapid urbanization and industrialization in the TH watershed after the Reform and Opening–up in 1978. The population, urbanization rate and industrial output in the watershed increased by 0.25, 0.87, and 12.9 times from 1980 to 2000, respectively (Jin et al., 2006). A large amount of unprocessed industrial and domestic wastewater has been released into the TH due to urbanization and industrialization, enhancing the accumulation of Fe/Al-P in the sediment. Despite the increase in urbanization and industrialization, a decreasing in the Fe/Al-P in the sediment occurred after the 2000s, a direct cause of this decrease in Fe/Al-P was the implementation of the "Zero O' clock Action" in 1999 (Huang et al., 2002). These stringent wastewater discharge standards resulted in a historic low in P loading from industrial and domestic effluents. The Fe/Al-P in the YHR core was relatively stable before the 1990s, and then, it began to increase (Fig. 4b). These trends are closely related to the development processes used in the starch processing industry in the upper reaches since 1990s (Ni et al., 2015). The

Fe/Al-P in the EH core was relatively stable before the 1950s, and then, it began to increase (Fig. 4c). This is because the EH watershed is a national scenic region and an important transportation hub in southwestern China. Since the founding of the People's Republic in 1949, population and tourism have increases rapidly in this watershed (Wang et al., 1999; Wang, 2015b), leading to a large amount of Fe, Al, and P loading in the EH from domestic wastewater. In comparison, Fe/Al-P in the WLSH core was the lowest and remained a relatively stable (Fig. 4a) because it was less affected by industrial and domestic effluents. Overall, the accumulation of Fe/Al-P is closely related to industrial and domestic effluents, suggesting that the Fe/Al-P content of sediment could be an effective indicator of industrial and domestic P loading.

The P$_o$ increased dramatically in the agricultural lakes area, in the 2000s in the WLSH and YHR and in the 1980s in the EH (Fig. 5). This suggests that the P$_o$ is most likely primarily derived from agricultural activities. Recent agricultural intensification has facilitated P loading from fertilizers and livestock breeding in agricultural area. Fig. 8 presents an overview of the application of P fertilizer, the P loss from livestock farming, and the sum of Hum-P$_o$
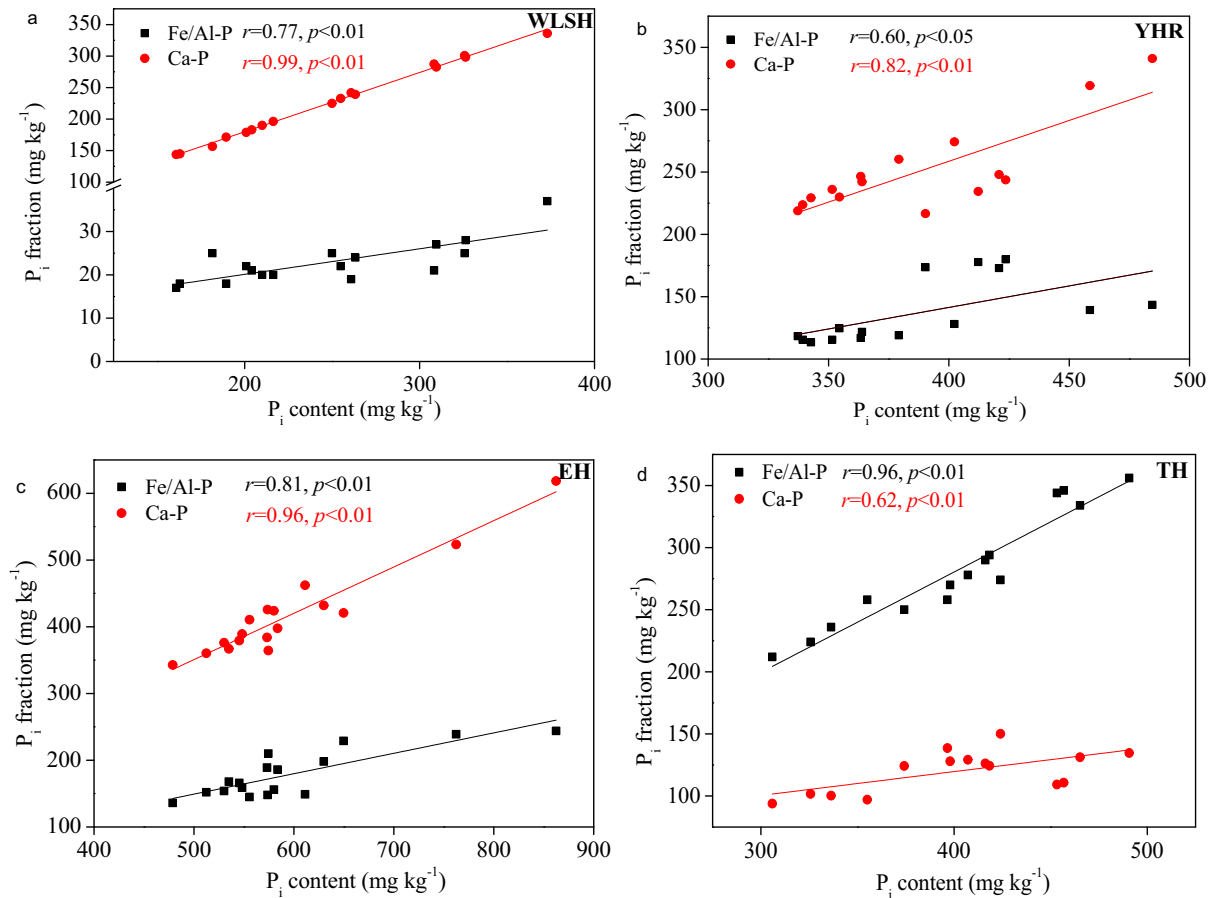
Fig. 6. Pearson correlation coefficients of the relationships between the P_i contents and P_i fractions of the sediment cores from the WLSH ($n = 17$), YHR ($n = 15$), EH ($n = 17$), and TH ($n = 15$).

and Res-P_o of the sediment cores in the four lake watersheds over time. The annual average P fertilizer usage reached 100 kg hm^{-1} in cultivated land in China, which is nearly 2.6 and 2.5 times higher the level used in the USA and the European Union during the same period, respectively (Liu et al., 2014b). After such a prolonged period of intense fertilization, most of the P fertilizer exists as monoester P (phytate P) in the soil (Turner et al., 2003; Copetti et al., 2019). Monitoring revealed that only 10–15% of the P can absorbed by the farmland soil, while the rest is lost to runoff and/or subsurface flow (Zhang and Shan, 2008). Furthermore, livestock manure production reached 6 billion tons in 2015, but more than 60% of this manure is randomly discharged without being treated. Researchers have pointed out that phytate P is the primary form in which P is stored in indigestible P bearing materials, for example, legumes, triticeae, cereals, and the indigestible excrement of non–ruminant animals (Waldrip et al., 2015; Ravindran et al., 1994; Lantzsch et al., 1992). In lake ecosystems, phytate P usually constitutes the largest part of the Hum-P_o and Res-P_o (Ni et al., 2016). In the last few decades, the sum of Hum-P_o and Res-P_o in the sediment cores exhibited a similar trend to that of the application of P fertilizer and the P loss from livestock farming. Correlation analysis revealed that Hum-P_o and Res-P_o are positively correlated with P_o in the WLSH, YHR, and EH (Fig. 7), and Hum-P_o and Res-P_o are the major P_o fractions. This explains the enhanced accumulation of P_o in sediments from agricultural lakes area during the last few decades, because of the rapid increase in fertilizer use and livestock breeding, which add large amounts of phytate P to the watersheds. In contrast, there has been a significantly decrease in Hum-P_o and Res-P_o in the TH since the 2000s, which was caused by the decrease in P emissions from fertilizer and livestock breeding due to the development of modern ecological agriculture. It is implied that fertilizer application and livestock breeding are the main factors controlling the accumulation of P_o in the sediments.

4.2. Possible effect of P dynamics on lake eutrophication

The changes in the increasing trends in the TP concentration of the overlying water in the WLSH, YHR, and TH demonstrate the fine scale effect of external loading in last few decades (Fig. 3). However, the TP accumulation in sediments has continuously increased over the last few decades, suggesting that these massive P reserves may be released and continue to enter the overlying water for a long time, even after the external P loading has decreased. The P_i content at the top of the cores gradually stabilized or even decreased with increasing depth in the WLSH, YHR, and TH. However, the P_i contents remain higher than the baseline values before the intense anthropogenic activities began. In terms of the P_i fractions, Ca-P has decreased recently, but released from the sediment with difficulty, while Fe/Al-P is a potential labile P source that could be released into overlying water under anaerobic conditions (Cavalcante et al., 2018). In the YHR and EH, Fe/Al-P increased each year or remained stable due to a lack of valid control on industrial and domestic effluent loadings. With the intensification of water pollution, the pH increased and the DO concentration decreased, which further enhanced the release of Fe/Al-P from the sediments (Wang et al., 2019b; Chen et al., 2018b).
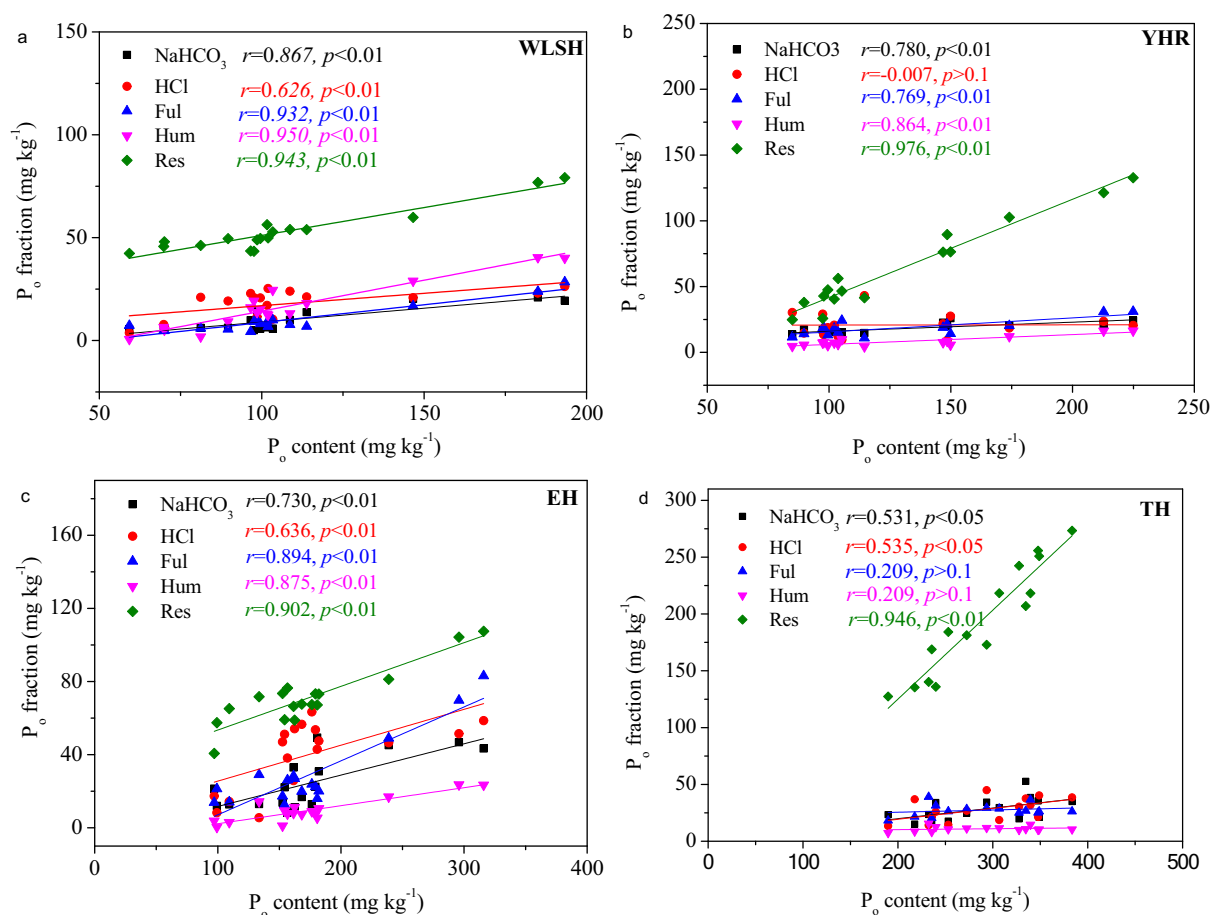
Fig. 7. Pearson correlation coefficients of the relationships between the P_o contents and P_o fractions of the sediment cores from the WLSH (n = 17), YHR (n = 15), EH (n = 17), and TH (n = 15).

The significant increase in P_o in the top layer indicates that, as an important component of P, the large additions of P_o to the sediment allows for the formation of orthophosphate through enzymatic degradation, causing deterioration of the water quality and accelerated eutrophication. In terms of the forms of P_o, $NaHCO_3$–P_o, Ful-P_o, Hum-P_o and Res-P_o all have maximum values in the surface layer in agricultural lake areas. The $NaHCO_3$-P_o and Ful-P_o, which represent the labile and moderately labile P_o, respectively, are easily degradation and released into the overlying water (Lu et al., 2016). Phytate P constitutes the largest part of Hum-P_o and Res-P_o (Ni et al., 2016), and it is usually considered to be relatively refractory since inositol phosphates can adsorb onto metal ions to form stable, insoluble Fe_4–phytate (Jørgensen et al., 2011). However, the presence of phytate P allows for possible degradation by phytase hydrolysis (Zhu et al., 2013). Agricultural intensification increases the amount of phytase in the soil (Suzumura and Kamatani, 1995). This additional phytase in the soils can be transported into the lakes (Cheng and Lim, 2006). Correlation analysis indicates that theses P_o fractions are positively correlated with P_o, suggesting that the increasing amounts of P_o in the sediments can be mineralized to use the available P and facilitate lake eutrophication.

The lake water quality in China has improved due to a shift in P loading since the 2000s, but the eutrophication problems have not been eradicated (Huang et al., 2019). Our analysis suggests that prevention of soil erosion has prevented the accumulation of Ca-P in sediments since the 1990s. The continued increases in the Fe/Al-P contents of the sediments in the YHR and EH indicate that

despite the fact that the national industrial, urban, and rural domestic P loading to lakes has been significantly reduced since the 2000s (Tong et al., 2017; Zhou et al., 2017), China need to take further action to control industrial and domestic P loading in economically backward area. In addition, the increasing P_o in WLSU, YHR and EH since the 2000s, indicates that the control effectiveness of the agricultural NPS is still unsatisfactory in agricultural lake areas. Despite the fact that efforts to control the agricultural NPS in China began in the 2000s, reducing P loading remain a challenge in China. Therefore, strengthening industrial, domestic and agricultural P loads control, optimization and adjustment of key environmental conditions, and continuing concern about the release dynamics of Fe/Al-P and P_o accumulated in sediment should be the focus of our future efforts to control lake eutrophication, especially in economically backward areas of China.

5. Conclusions

Geochemical fractionation of P was used to establish the relationship between the sediment P pool and anthropogenic activities over the last few decades. The results of our extractions indicated that the inorganic P fractions, including Ca-P (46% of TP) and Fe/Al–P (24%), constitute the majority of P in lake sediments. Soil erosion dynamics and geographic location were the dominant drivers of the historical distribution and partitioning of Ca-P in sediments, while industrial and domestic effluents were the primary factors controlling the change in Fe/Al-P over the last few decades. The
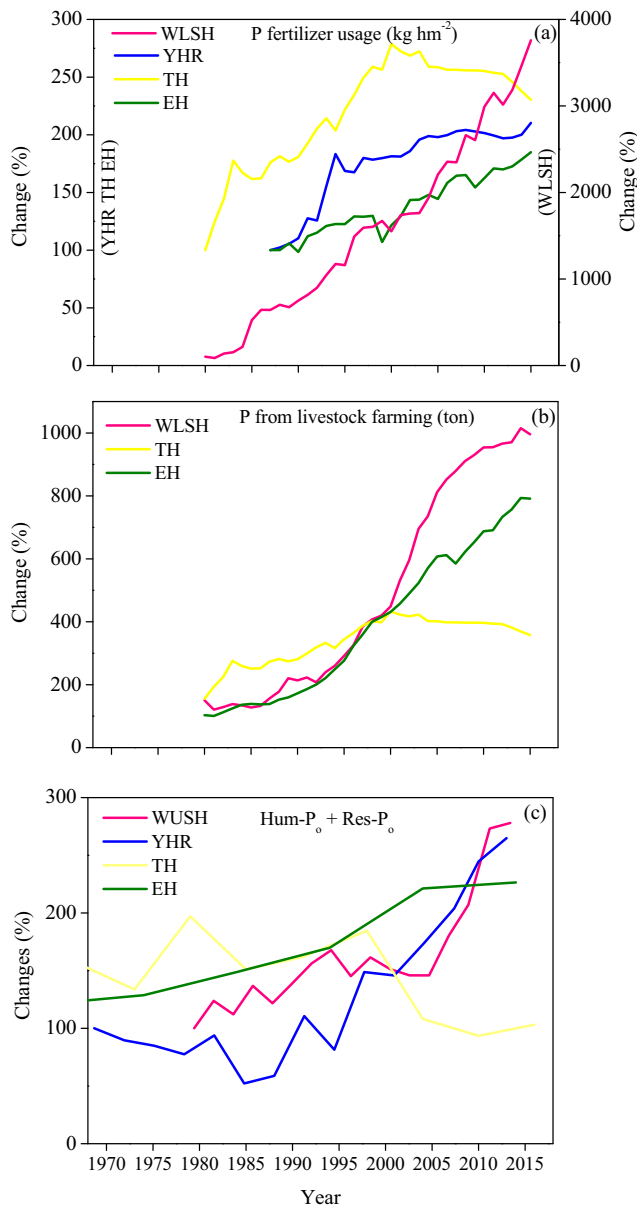
Fig. 8. Changes in the historical (a) usage of P fertilizers and (b) P loss from livestock framing in the watersheds, and (c) the sum of the Hum-P_o and Res-P_o contents in dated sediment from the WULS, YHR, TH, and EH over the last few decades.

organic P (P_o) fractions, $NaHCO_3$ -P_o, HCl-P_o, and Ful-P_o account for only 11%, 16% and 12% of the P_o on average, respectively. Whereas Hum-P_o and Res-P_o are the dominant P_o fractions (59%) and are the main factors controlling the changes in Po due to fertilizer application and livestock breeding. Thus, the historical P fraction in sediment cores can be used as an indicator of anthropogenic activities.

This study also assessed the potential eutrophication risk from sediment P due to changes in the external P loadings. Our results indicated that Ca-P declined in the top layers of the sediment cores because of the implementation of the Soil and Water Conservation Law in China in 1991. However, Fe/Al-P and P_o continued to increase in agricultural lake areas over the last few decades, which are largely attributed to the enhancement of point sources of pollution and agricultural intensification. As a potential P source, the massive amount of Fe/Al-PP and P_o that have accumulated in the sediments maybe released into the overlying water, which would

further facilitate eutrophication via increases in pH and alkaline phosphatase and decreases in the DO concentration. Therefore, further efforts control external P loading, especially in economically backward areas, should include the reduction of industrial and domestic pollution and agricultural NPS.

Declaration of competing interest

The authors declare that they have no conflict of interests.

Acknowledgements

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