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Matrix-bound phosphine, phosphorus fractions and phosphatase activity through sediment profiles in Lake Chaohu, China

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Environmental impact

Phosphorus, the nutrient causing the eutrophication in most of lakes, has been in the forefront of hydrobiological research to explore the mechanism and prevention of eutrophication. Matrix-bound phosphine is an important gaseous link in the P biogeochemical cycle, and reliable detection of this compound in the sediments will improve our understanding of P cycling and their environmental significance in the eutrophic lakes.

Abstract

The distribution patterns of Matrix-bound phosphine (MBP), phosphorus (P) factions and neutral phosphatase activity (NPA) were investigated through the five sediment profiles in Lake Chaohu, China. MBP was found in all the sediment profiles with the concentration range of 1.58–50.34 ng kg^{-1}. The concentrations of MBP exhibited a consistent vertical distribution pattern in all the profiles, and higher MBP concentrations generally occurred in the surface sediments. MBP concentrations showed a significant positive correlation with P fractions, total nitrogen (TN), Cu and Zn under lower levels of inorganic phosphorus (<0.6 g kg^{-1}), organic phosphorus (<0.2 g kg^{-1}), TN (<0.13%), Cu (<25 mg kg^{-1}) and Zn (<150 mg kg^{-1}), but no statistically significant correlations were obtained under higher levels. The multiple stepwise regression model ([MBP]=1.36[NPA]-6.21[pH]-0.06[Zn]+0.75[Cu]+49.86) was obtained between MBP concentrations and environmental variables, and MBP concentrations showed a strong positive correlation with NPA (P<0.0001), indicating that the production of sediment MBP was controlled by the microbially-mediated processes in Lake Chaohu. This model could be used to predict MBP levels in the sediments. Our results indicated that MBP level could not be used as an indicator for the degree of lake eutrophication. The study of sediment MBP, P factions and NPA will improve our understanding of P cycling and their environmental significance in the eutrophic Lake Chaohu.

Key words: Matrix-bound phosphine; Organic phosphorus; Inorganic phosphorus; phosphatase activity; Lake sediment.

Introduction

Phosphorus, the nutrient limiting organic matter production and causing the eutrophication in most of lakes, has been in the forefront of hydrobiological research to explore the mechanism and prevention of eutrophication during the past decades.[1–4] Previous publications on lake nutrients focused almost completely on phosphates in aqueous and solid forms and did not consider the possible presence of volatile phosphorus compounds. Phosphine (PH_3), as a reactive and reduced phosphorus component, has been detected in the natural environment with two different forms: free gaseous phosphine (FGP) and matrix-bound phosphine (MBP).[5–10] MBP, defined as PH_3 bound to condensed environmental samples, can hydrolyze in biological aquatic media to form FGP by acid or alkaline digestion. Since phosphine produced during fermentation is prone to be adsorbed by condensed matrix, the actual amount of phosphine released as free gas form is much less than the total amount of phosphine formed in soils or sediments.[10,11] Therefore a better understanding of the behavior of MBP, as a gaseous carrier of the nutrient phosphorus, is essential to explore whether MBP contributes to a certain extent to the geochemical cycle of phosphorus.

As for the formation mechanism of phosphine in the nature, it has been controversial for years. The point that the production of PH_3 is considered to be associated with microbial activity, has been universally accepted, because all kinds of organic or inorganic phosphorus compounds can be reduced to PH_3 by anaerobic bacteria.[12–16] Non-biological PH_3 formation mechanisms have also been proposed.[17] Many evaluations have showed that environmental factors, such as P fractions, redox condition, metal elements and phosphatase activity (PA), could affect the formation of phosphine in various matrixes including lake sediments.[18–22] In lake ecosystems, phosphine can ultimately be converted to phosphate and hypophosphite, released into the water from the sediments, and thus phosphine might play a considerable role in lake eutrophication.[23–26] In the eutrophic waters, phosphine and its oxides could accelerate the growth of *Microcystis aeruginosa*, and furthermore PH_3, as a highly toxic compound, might induce the death of aquatic organisms at the concentration of above 550 mg m^{-3}.[27] Sediments could be the main sources of phosphine in the eutrophic lakes due to higher P level compared with overlying water.[26] Therefore it is very important to investigate the distribution patterns of phosphine and P fractions in lake sediment profiles, and their possible links with lake eutrophication.

Lake Chaohu, as the fifth largest freshwater lake in China, has been suffering the eutrophication due to a large amount of nutrient (mainly N and P) loading from industrial wastewater, domestic sewage and agricultural fertilizers since the late 1970s.[28–31] To the best of our knowledge, no previous research has been conducted on the occurrence of MBP and its distribution patterns in the sediments of Lake Chaohu. In this study, a total of five sediment cores were collected from Lake Chaohu and the concentrations of MBP, phosphorus fractions, phosphatase activity and other environmental factors were measured in these cores. Our main objectives are: (1) to detect the distribution patterns of MBP, P fractions and phosphatase activity through the sediment depth profiles; (2) to investigate the effects of environmental parameters on the concentrations of sediment MBP; (3) to discuss the effects of MBP on the P-cycle and its environmental significance in Lake Chaohu.

Materials and methods

Study area

Lake Chaohu (117°16′54″–117°51′46″E and 31°25′28″–31°43′28″N; Fig. 1), which is located in the middle and lower reaches of Yangtze River in Anhui Province of China, covers an area of 780 km^2 and has a mean water depth of 3 m.[31] The climate of Lake Chaohu belongs to subtropical monsoon climate, with an annual mean precipitation of 1120 mm and temperature of 15–16 °C.[32] Eight main rivers (Nanfei River, Pai River, etc.), which provide about 90% of the runoff volume from the catchments, feed Lake Chaohu, and the Yuxi River as its outflow is the only channel linking to the Yangtze River. Lake Chaohu is divided into the western lake and eastern lake by Mushan Island. Hefei City (~ 11000 km^2), Feidong County (~ 2200 km^2) and Feixi County (~ 2100 km^2) are distributed around the western lake (ca. 1/3 of area), whereas Chaohu City (~ 2000 km^2) is distributed around the eastern lake (ca. 2/3 of area). Lake Chaohu plays an important role in fishing, industrial and agricultural irrigation water, flood prevention, and drinking water for surrounding cities and counties. Economic development and rapid urbanization in Chaohu Lake catchments have led to the excessive input of the nutrients and contaminants by runoff into the lake. It was recorded that the concentrations of TP, TN and Chl-a in Lake Chaohu were 1.2–4.6 mg L^{-1}, 0.11–0.42 mg L^{-1}, and 1.1–38.2 μg L^{-1}, respectively.[30] The toxic metal contents in the sediments were 9.23–40.97 μg g^{-1} (26.23±8.66 μg g^{-1}) for Cu and 33.20–360.29 μg g^{-1} (153.68±98.37 μg g^{-1}) for Zn.[32,33] According to the New York sediment screening criteria for the metal contamination, the values of the severe effect level are 110 μg g^{-1} for Cu and 270 μg g^{-1} for Zn, and the sediments in Lake Chaohu are severely contaminated in 20% of the area for Zn, but 0% for Cu.[32] In Lake Chaohu, the *cyanobacteria* often bloom, and the macrophytes are not abundant. The water system in the western lake suffers more serious eutrophication than that in the eastern lake.[29]

Sample collection

According to the pollution degree, we collected five sediment cores (CH1, CH2, CH3, CH4 and CH5) from Lake Chaohu in the middle of October, 2010 using a gravity core sediment sampler (Fig. 1). The cores CH1, CH2 and CH3 were located in the heavily polluted western lake while CH4 and CH5 were in the slightly polluted eastern lake. The lengths of these sediment cores were 70 cm, 60 cm, 60 cm, 30 cm and 20 cm, respectively. They had not been disturbed and kept intact at the bottom of the lake. Immediately after collection, all samples were completely sealed and stored in the dark under -20 °C until laboratory analysis. The storage method did not compromise the samples' integrity, and it minimized the effects of MBP concentration in the sediments according to several references and our previous studies.[19–21,34] The sediment cores were sectioned at 2 cm intervals, and then the sediment samples for each section were divided into two portions in sequence. One portion was used to analyze MBP concentrations, whereas the other portion was used to determine phosphorus factions, phosphatase activity, and other physiochemical properties of the sediments. The concentrations of MBP and P fractions, and phosphatase activity in all the samples were measured within one month after the sediment cores were collected.

Determination of MBP

In this study, MBP is defined as the amount of phosphine released from the sediments during an acidic digestion, which releases adsorbed phosphine, metal-phosphine complexes, and inorganic phosphides.[18] Briefly, about one gram of wet sediment was digested in a glass reactor with 5 ml of 0.5 mol L^{-1} H_2SO_4 for 5 min at 100 °C under highly pure N_2 (99.999%).

The liberated phosphine was purged with pure N_2 out of the reactor into a 30 ml syringe and transferred into the gas chromatograph (Varian CP 3800) after enrichment through a capillary cryo-trapping (a Plot-Q capillary column, cooled down with liquid nitrogen). The gas chromatograph was equipped with a capillary 121 column (crosslinked 5% Ph Me Silicone, 25 m×0.2 mm×0.33 μm film thickness, Hewlett Packard) and a pulsed flame photometric detector (PFPD). A standard gas mixture of phosphine in N_2 (10 ppmv) was used as authentic reference. The method has a detection limit of 0.1 ng m^{-3} of phosphine. Each gas sample was measured at least three times with a relative standard deviation of less than 10%.[34]

Analyses of P fractions and NPA

Phosphorus fractions in the sediment were measured as total phosphorus (TP), inorganic phosphorus (IP) and organic phosphorus (OP). TP was analyzed by measuring phosphate using the ammonium molybdate spectrophotometric method after digestion, in which all the samples were dried at room temperature, and then incinerated in a muffle furnace at 550 °C for 2 h, followed by the extraction with 1 mol L^{-1} hydrochloric acid for 16–18 h at room temperature.[35] IP was detected by the same method as TP except the incinerating procedure, and OP was obtained by the difference between TP and IP.[35] The standard reference material (GSD–4 as a standard reference sample drainage sediment supplied by the Chinese Academy of Geological Sciences) were included with every batch of samples to test the validity of the data, and the analytical errors for P fractions are within ±0.5%.

The present study was focused on the characterization of neutral phosphatase activity (NPA) in the sediments since almost all the samples were almost neutral (pH close to 7). NPA was determined using phenyl phosphate disodium (0.115 M).[36] This assay was based on the release and detection of phenol (PN). The 2.5 ml of 0.1 M citric acid buffer and 2.5 ml of substrate were added into 2.5 g of sample and incubated at 37 °C for 24 h. The phenol (PN) in the filtrate was determined using a spectrophotometer at 578 nm, expressed as mg PN kg^{-1} h^{-1}. Every sample was measured three times with a relative standard deviation of less than 10%.

General analysis of sediment characteristics

All the samples were separated from sediment cores and mixed homogeneously for the general analyses. The mean grain size (Mz) of the sediments was determined three times for each sample by using a laser diffraction particle size analyzer (LS I3 320).[37] The pH was determined by ion selection electrode.[22] The pH was determined by ion selection electrode.[22] Total carbon (TC), total nitrogen (TN) and total sulfur (TS) were determined by using a CNS Elemental Analyzer (Vario EL III) with a relative error of 0.1%.[34] For the analyses of other chemical elements including Cu and Zn, the samples digested by multi-acids (HNO_3–HF–$HClO_4$) were analyzed by Inductively Coupled Plasma Optical Emission Spectrometer (Optima 2100DV).[34] Data quality was ensured through the use of duplicates, blanks and standard reference materials (GSD–6 as a standard reference sample drainage sediment and GSS–7 as a geochemical standard reference sample drainage soil supplied by the Chinese Academy of Geological Sciences). The analytical errors for the elements are within ±5% of the certified ones.

Statistical analysis

The mean values and standard deviation (mean±sd) were calculated to facilitate comparisons of the data between the different sediment cores. Differences in the mean concentrations of MBP, P fraction, NPA and other environmental parameters (Mz, pH, TN, TC, TS, Cu and Zn) between both the sediment cores and different depths of each core were tested with Student's *t*-test. The relationships between MBP concentrations and environmental factors were shown by the linear regression analysis, and the multiple stepwise regression analysis was used to identify the main driving factors for the MBP contents. All statistical analyses were preformed using Microsoft Excel 2007, SigmaPlot 12.0 and SPSS 16.0 for Window XP.

Results and discussion

Environmental variables, phosphorus fractions and phosphatase activity through sediment profiles

The grain size (Mz) of the sediments was highly variable with the range of 11.10–34.92 μm in the sediment profiles (Table 1), and the maximum of Mz almost occurred at about 20 cm with the exception of the profile CH1 (Fig. 2). In this study, all the sediment profiles displayed a slight decrease in pH from the bottom to surface sediments ranging between 5.8 and 7.2, and overall pH values were almost neutral. The concentrations of P fractions, especially OP and TP, all showed an increasing trend with sediment depths from the bottom to surface sediments in all the profiles (Fig. 2). High TP and IP concentrations occurred in the sediment profiles with the ranges of 474–1617 μg g^{-1} and 395–1075 μg g^{-1}, respectively, whereas OP concentrations (41–542 μg g^{-1}) were one order of magnitude lower than IP concentrations (Table 1). Overall the mean contents of P fractions in sediment profile CH1 were two to three times higher than those in other sediment profiles (Fig. 3).

Of all the profiles TC, TN, TS, Cu and Zn concentrations also displayed a slight increase trend with depths from the bottom to surface sediments although some fluctuations occurred at the different sediment layers (Fig. 2). TP levels showed significant positive correlations (P<0.01) with TC, TN, Cu, Zn levels when all the data were combined (Fig. 4). In addition, the concentrations of TC, TN, TS, Cu and Zn showed a significant positive correlation with each other, but they significantly negatively correlated with pH values (Table 2). Heavy metals such as Cu and Zn, are regarded as serious contaminants in aquatic ecosystems since they are accumulated in the sediments instead of degradation. Thus Cu and Zn levels can be used as the indicators for anthropogenic sources. It was noted that the mean TC and TN contents in profile CH1 were two or three times higher than those in other profiles, and Cu and Zn contents were also significantly higher in profile CH1 (Fig. 3). As reported in several previous references,[30,34,36] anthropogenic sources, such as discharge of industrial waste water and domestic sewage, and the runoff of agricultural phosphorus fertilization, might increase sediment P, N, Cu and Zn levels in Lake Chaohu. The sediment profile CH1 was closer to the bayou of Nanfei River, a seriously polluted river from Hefei City, indicating that the sediment profile CH1 might be subjected a stronger impact from anthropogenic sources.

Neutral phosphatase activity (NPA) through the sediment profiles showed an inconsistent variation pattern with the range from 0.65 to 1.81 mg PN kg^{-1} h^{-1}. The mean NPA indicated no statistically significant differences between these five sediment profiles (P>0.05, Fig. 3). It was noted that relatively lower NPA, but higher TP, OP, TC, TN, Cu and Zn contents occurred at the surface 20 cm than in deep layer sediments for profiles CH1, CH2 and CH3, which were located in the heavily-polluted western lake, suggesting that high-level pollutants might inhibit NPA in the sediments. A significant negative correlation between NPA and pH indicated that sediment acidification could stimulate the formation of NPA and the related microbial activities involved in P cycles.

MBP concentrations and its correlation with environmental variables

The MBP was found in all the sediment profiles of Lake Chaohu. The concentrations of MBP exhibited a consistent vertical distribution pattern in almost all the profiles, and high-level MBP occurred in the surface sediments, decreased with depths and then increased again in the bottom sediments (Fig. 2). The mean MBP concentrations of sediment profiles CH1 (18.38±7.10 ng kg^{-1}), CH2 (14.78±3.75 ng kg^{-1}) and CH3 (19.33±3.88 ng kg^{-1}) in the western area of this lake were much lower than those of sediment profiles CH4 (25.65±12.38 ng kg^{-1}) and CH5 (22.54±6.66 ng kg^{-1}) in the eastern area of Lake Chaohu (Fig. 3). Sediment MBP concentrations had no statistical correlation with P fractions, TC, TN, TS and Cu, Zn levels when all the data were combined from these five sediment profiles (Table 2). However, it is interesting that all the data points for MBP and environmental variables can be categorized into two groups (Fig. 5): Group I indicated a good positive correlation between MBP and TP, IP, OP, TN, Cu and Zn under relatively lower levels of TP (<0.7 g kg^{-1}), IP (<0.6 g kg^{-1}), OP (<0.2 g kg^{-1}), TN (<0.13%), Cu (<25mg kg^{-1}) and Zn (<150 mg kg^{-1}); Group II indicated no statistically significant correlation between MBP and these variables under higher levels of P fractions, TN, Cu and Zn in the sediments of Lake Chaohu. The MBP concentrations showed a significant positive correlation (P<0.001) with NPA (Fig. 6a). A significant negative correlation was obtained between MBP and pH (P=0.03) in the sediments (Fig. 6b). We further analyzed the relationships between MBP concentrations and environmental variables using multiple stepwise regression analysis. The following best fitting regression model was obtained:

$$[MBP]=1.36[NPA]-6.21[pH]-0.06[Zn]+0.75[Cu]+49.86$$

$$(r=0.53,\ F=3.15,\ P=0.02,\ n=54)$$

In this model, MBP concentrations were related with NPA, pH, Cu and Zn levels, and the correlation coefficient (r=0.53) is higher than those through simple linear regression analysis. MBP concentrations showed no statistical correlation with Cu and Zn concentration in the sediments (Table 2). Overall MBP concentrations were controlled by NPA and pH in the sediments. According to this model, the regression values of MBP concentrations showed a strong correlation (P=0.02) with their measurement values, suggesting that this model could be used to predict MBP levels in the sediments.

Effects of environmental variables on sediment MBP concentrations

Recent studies have shown that the fine Mz favored high MBP concentrations.[19,20] This mainly results from larger surface areas and higher absorption potentials to phosphine for finer sediments, whereas coarse sediments allow the transfer and oxidation of phosphine due to porous characteristics. In this study, no significant correlation was obtained between MBP and Mz (Table 2), suggesting that sediment grain size might have little impact on MBP preservation in Lake Chaohu. The disturbance from the hydrodynamic effects is also a physical factor affecting the production and depletion of MBP in the sediments.[5,18] The sediment disturbance might change the sedimentation rates, bottom sediment compositions and the anaerobic conditions, and promote phosphine oxidization into phosphate.[5] In shallow Lake Chaohu, the sediment profiles CH1 and CH2 might be subject to strong disturbance from the hydrodynamic effects since they were close to the river inflow. Therefore lower MBP levels occurred in profiles CH1 and CH2 than in other profiles, indicating that the disturbance might have an important effect on the MBP levels in the sediments of Lake Chaohu.

The phosphorus and nitrogen levels are generally regarded as an important index to determine the degree of lake eutrophication.[1,2,36] Generally the internal phosphorus release had been one of the main sources of lake eutrophication besides external input.[32] MBP, as the approach to an internal phosphorus release, can be converted to phosphate into the water or transfer into the atmosphere through the biogeochemical processes.[21] Previous researches revealed that the enhanced inputs of easily decomposable organic substance were in favor of the production of phosphine in the sediments.[19,20] In this study, sediment MBP concentrations showed a positive correlation with the contents of P fractions and N under the relatively lower levels, whereas no statistically significant correlation was obtained under higher levels of P fractions and N (Fig. 5a-d). Therefore the relatively lower-level P and N nutrient loadings might promote the formation of phosphine in the sediments, whereas higher-level P and N did not favor the formation of MBP in Lake Chaohu, indicating that MBP level could not be used as an indicator for the degree of lake eutrophication.

In addition, NPA has an important effect on the decomposition and conversion of soil organic phosphorus and inorganic phosphorus, and it can be an indicator for the microbial activities related to P biogeochemical cycles.[38] The significant positive correlation between MBP concentrations and NPA (Fig. 6a) suggested that the formation of MBP might be associated with microbially-mediated process of both the IP reduction and the OP decomposition in the sediments.[15,16] Multiple regression analysis further indicated that MBP levels in Lake Chaohu sediments might be controlled by the NPA under effects of microbes.

The pH affected the existence of phosphine in the sediments by changing the physicochemical properties of sediments and the activity of microbes responsible for the fate of phosphine. Han et al.[39] claimed that the highest MBP was produced under neutral conditions (pH=6.74), and the lowest was in acidic soil (pH=4.85). Other studies reported that low pH in a certain range accelerated chemical reactions and stimulated the formation of MBP and bacterial activity in the sediments,[22] which was accordance with our results. A significant negative correlation between MBP and pH (P=0.03) showed that sediment acidification was conducive to MBP storage in Lake Chaohu (Fig. 6b). Multiple regression analysis also indicated that sediment acidification favored the preservation of MBP in Lake Chaohu.

Some researchers have found that PH_3 can react with some transition metals such as Cu^{2+}, Pb^{2+}, Zn^{2+}, etc., to form slightly or not soluble metal-phosphides[25] in solutions with H^+, and there were dramatic increases in PH_3 loss.[3] Therefore high levels of trace metals, such as Cu and Zn might have an effect on the MBP distribution in lake sediments. In this study, the increase in MBP concentrations corresponded to low Cu (<25 mg kg^{-1}) and Zn (<150 mg kg^{-1}) levels, and high Cu and Zn levels did not increase the concentration of MBP in the sediments (Fig. 5e, f), suggesting that high heavy metal levels might lead to metal-phosphide formation and the increase in PH_3 loss. According to the multiple regression equation, MBP levels had a positive correlation with Cu but a negative correlation with Zn, and thereby the complex chemistry needs further research in the future.

Generally the fate of phosphine in the sediments was determined by three processes: (i) adsorbed by the sediments as a matrix-bound form; (ii) oxidized by microorganisms, chemical reaction and physical transformation; and (iii) transported as a free gas form. The complex combination of these processes is subsequently controlled by different characteristics of the sedimentary environment.[6,26] In summary, MBP detected in the sediments of Lake Chaohu can be regarded as a relative equilibrium concentration of phosphine between the production and consumption which can be impacted by sediment characteristics, and mediated by microbial processes.

Effect of MBP on the P-cycle and its environmental significance in Lake Chaohu

Recent researches provide an overview of MBP concentrations in different types of sediments at the global scale (Table 3). In this study, MBP concentrations are in the ranges of 1.58–50.34 ng kg^{-1} in the sediment profiles of Lake Chaohu. Our data are comparable to those in the freshwater sediments of Lake Taihu in China,[26] Elster River[11] and Elbe River[40] in Germany, Chinese paddy fields,[41] the ornithogenic sediments in eastern Antarctica and Arctic,[34] and in marine surface sediments of Chinese coastal areas.[19,20,24] although they are one to two orders of magnitude lower than those in the freshwater sediments of Lake Wulongtan,[8] and in marine surface sediments of seriously polluted areas[42] in Chinese Jiaozhou Bay. Furthermore, MBP concentrations in this study are higher than those in ornithogenic sediments of western Antarctica,[43] and estuarine intertidal sediments of Yangtze River.[44] Therefore, MBP is an important reduced phosphorus compounds in the sediments of Lake Chaohu.

Lake Chaohu is characterized with shallow water and the medium eutrophication due to high load of the nutrients. To a certain degree, the load of nutrients such as N and P favors the MBP formation in the sediments under the effects of microbial activity. On the other hand, MBP is a reduced and unstable phosphorus compound, and easily oxidized into phosphate under the aerobic conditions.[11] The shallow water (mean 3 m deep) might accelerate the oxidation and transformation of MBP in the sediments, thus a relatively rapid turnover of MBP might occur in the sediments, and a rapid migration process of PH_3 was possible in the interstitial gas of lake sediments.[21] Therefore MBP might be an important gaseous link in the P biogeochemical cycle in Lake Chaohu. The study of MBP and P fractions in the sediment profiles of Lake Chaohu will improve our understanding of P cycling and its environmental significance under the eutrophic conditions.

Conclusion

The present study reveals the existence and distribution patterns of MBP through sediments profiles in Lake Chaohu. The MBP was found in all the sediments with the range from 1.58 to 50.34 ng kg^{-1}. It was found that sediment MBP concentrations showed a positive correlation with the contents of P fractions and N under the relatively lower levels of P fractions and N, whereas no statistically significant correlation was obtained under their higher levels. The MBP concentrations showed a significant positive correlation with NPA (P<0.001), suggesting that the formation of MBP might be associated with microbially-mediated process of both the IP reduction and the OP decomposition in the sediments under anaerobic conditions. Our results indicated that MBP level could not be used as an indicator for the degree of the eutrophication, though sediment MBP contributed to the P geochemical cycle in Lake Chaohu.

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Captions of figures:

Fig 1. Study area and the sampling sites. The five sediment profiles (CH1, CH2, CH3, CH4 and CH5) were collected from Lake Chaohu in the autumn of 2010.

Fig 2. Vertical distribution patterns of MBP, P fractions (TP, IP and OP), NPA and environmental variables (Mz, pH, TN, TC, TS, Cu and Zn) in the five sediment profiles CH1 (Fig. a), CH2 (Fig. b), CH3 (Fig. c), CH4 (Fig. d), and CH5 (Fig. e). Note: MBP, TP, IP, OP and NPA indicated matrix-bound phosphine,total phosphorus, inorganic phosphorus, organic phosphorus and neutral phosphatase activity, respectively. Mz, TC, TN and TS indicated mean grain size, total carbon, total nitrogen and total sulfur, respectively.

Fig 3. Box plots of MBP, P fraction (TP, IP and OP) and environmental variables (Mz, pH, TN, TC, TS, Cu and Zn) in five sediment profiles. The plots show means with the 75th percentile within the box and the 90th percentile within the error bars. The mean concentrations with different superscript letter (a, b or c) indicate significant differences at $P<0.05$ between the sites. Note: MBP, TP, IP, OP and NPA indicated matrix-bound phosphine,total phosphorus, inorganic phosphorus, organic phosphorus and neutral phosphatase activity, respectively. Mz, TC, TN and TS indicated mean grain size, total carbon, total nitrogen and total sulfur, respectively.

Fig 4. Relationships between the concentrations of TP, TN, TC, Cu, Zn in the sediment profiles. Note: r and p represent Spearman's rank correlation coefficient and the significant level between the environmental parameters, respectively. Note: TP and TN indicated total phosphorus and total nitrogen, respectively.

Fig 5. Relationships between MBP concentrations and P fractions, TN and heavy metals Cu and Zn in the profiles of all samples. All these points can be categorized into two groups by the dotted line: Group I with lower levels of these variables indicated the regressing equations; Group II with higher levels of these variables indicated no statistically significant correlation between them.

Note: r and P represent Spearman's rank correlation coefficient and the significant level between MBP and other parameters, respectively. Vertical bars represent the standard error based on three replicates. MBP, TP, IP, OP and TN indicated matrix-bound phosphine,total phosphorus, inorganic phosphorus, organic phosphorus and total nitrogen, respectively.

Fig 6. Relationships between MBP concentrations and NPA and pH with linear variations in the profiles of all samples. Note: r and p represent Spearman's rank correlation coefficient and the significant level between MBP and NPA, pH, respectively. Note: MBP and NPA indicated matrix-bound phosphine and neutral phosphatase activity, respectively.

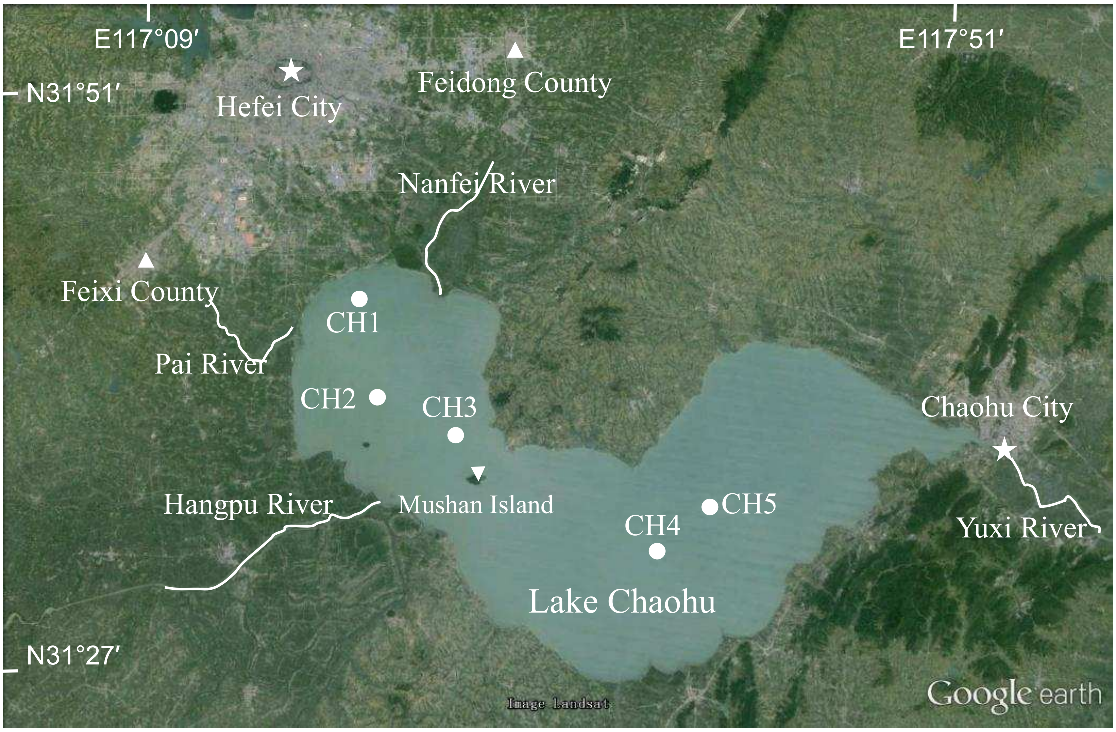
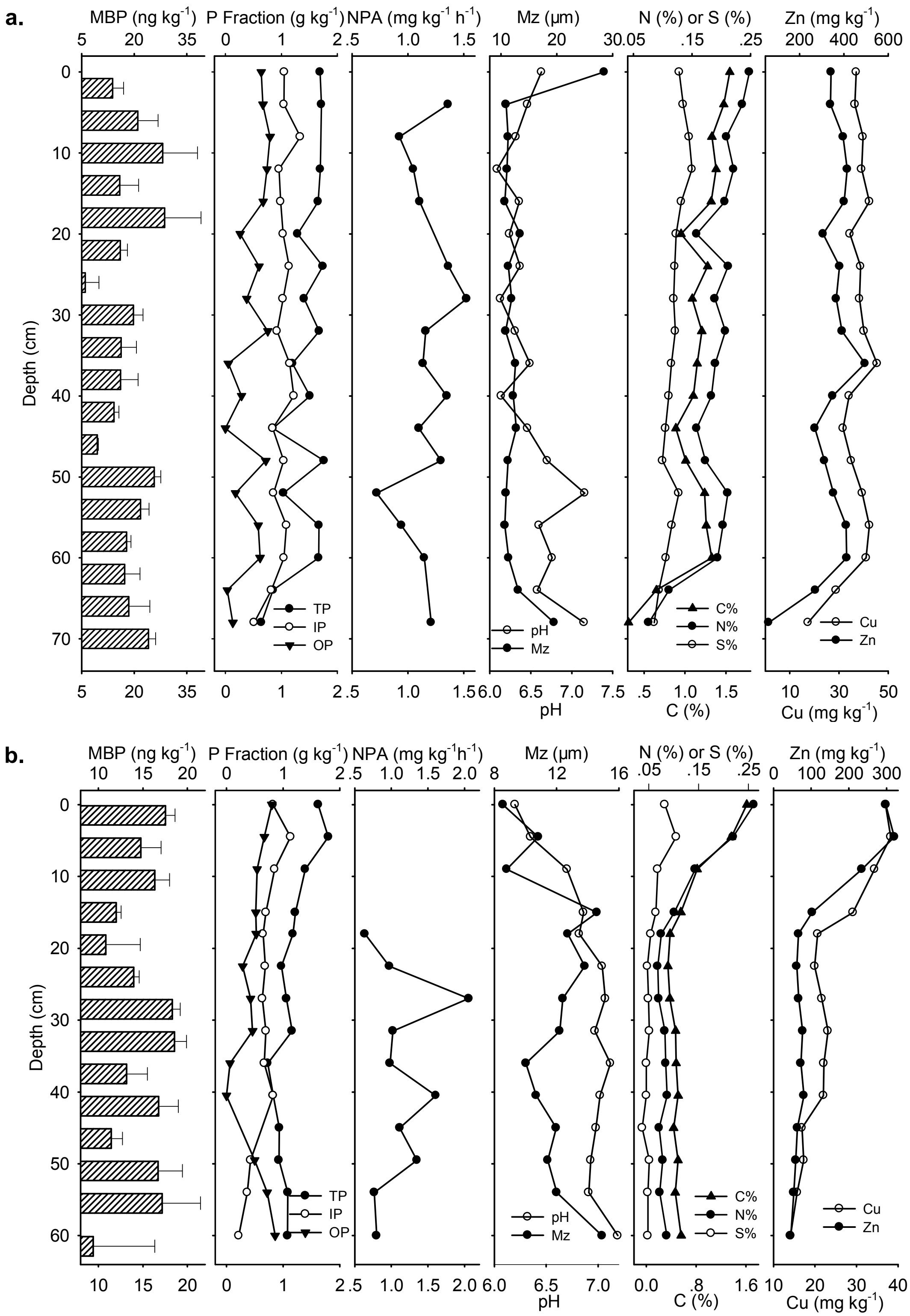

E117°09′
E117°51′
N31°51′
N31°27′
Hefei City
Feidong County
Nanfei River
Feixi County
Pai River
CH1
CH2
CH3
Chaohu City
Mushan Island
Hangpu River
CH4
CH5
Yuxi River
Lake Chaohu
Google earth

Fig. 1.


a.
MBP (ng kg-1)
P Fraction (g kg-1)
NPA (mg kg-1 h-1)
Mz (µm)
N (%) or S (%)
Zn (mg kg-1)
Depth (cm)
TP
IP
OP
pH
Mz
C%
N%
S%
Cu
Zn
pH
C (%)
Cu (mg kg-1)
b.
MBP (ng kg-1)
P Fraction (g kg-1)
NPA (mg kg-1h-1)
Mz (µm)
N (%) or S (%)
Zn (mg kg-1)
Depth (cm)
TP
IP
OP
pH
Mz
C%
N%
S%
Cu
Zn
pH
C (%)
Cu (mg kg-1)

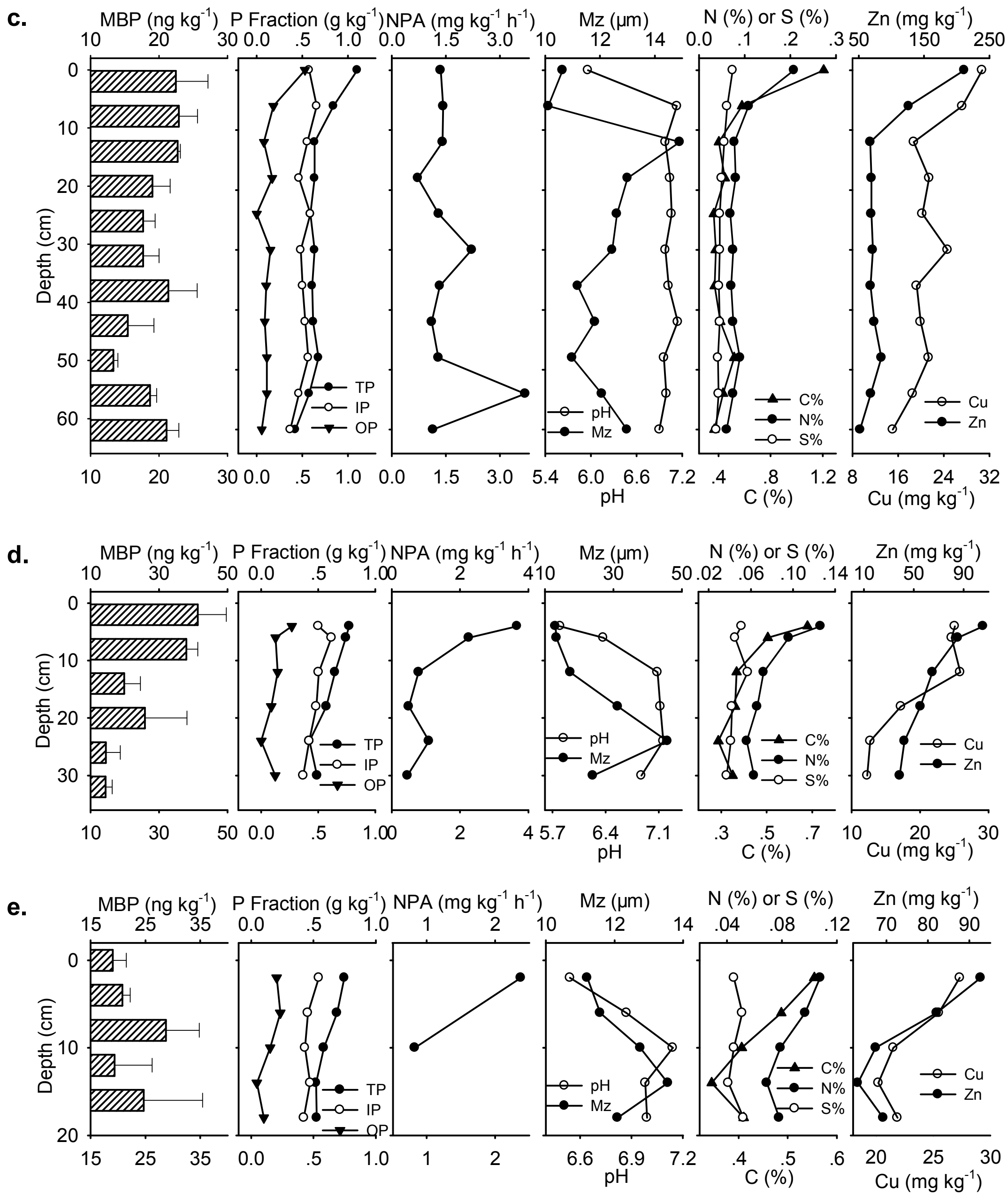

c.
MBP (ng kg-1)
P Fraction (g kg-1)
NPA (mg kg-1 h-1)
Mz (μm)
N (%) or S (%)
Zn (mg kg-1)
Depth (cm)
TP
IP
OP
pH
Mz
C%
N%
S%
Cu
Zn
pH
C (%)
Cu (mg kg-1)
d.
MBP (ng kg-1)
P Fraction (g kg-1)
NPA (mg kg-1 h-1)
Mz (μm)
N (%) or S (%)
Zn (mg kg-1)
Depth (cm)
pH
C (%)
Cu (mg kg-1)
e.
MBP (ng kg-1)
P Fraction (g kg-1)
NPA (mg kg-1 h-1)
Mz (μm)
N (%) or S (%)
Zn (mg kg-1)
Depth (cm)
pH
C (%)
Cu (mg kg-1)

Fig. 2.

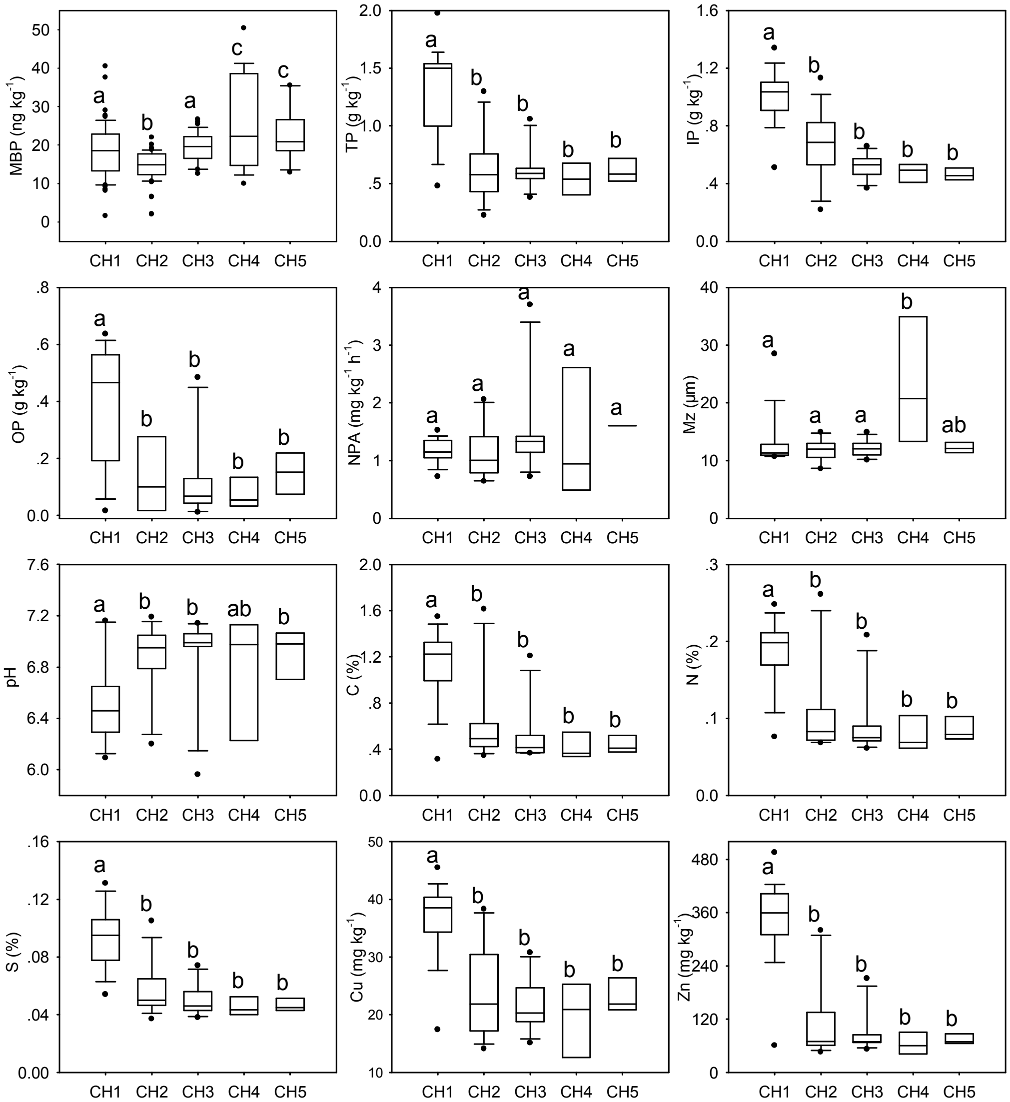
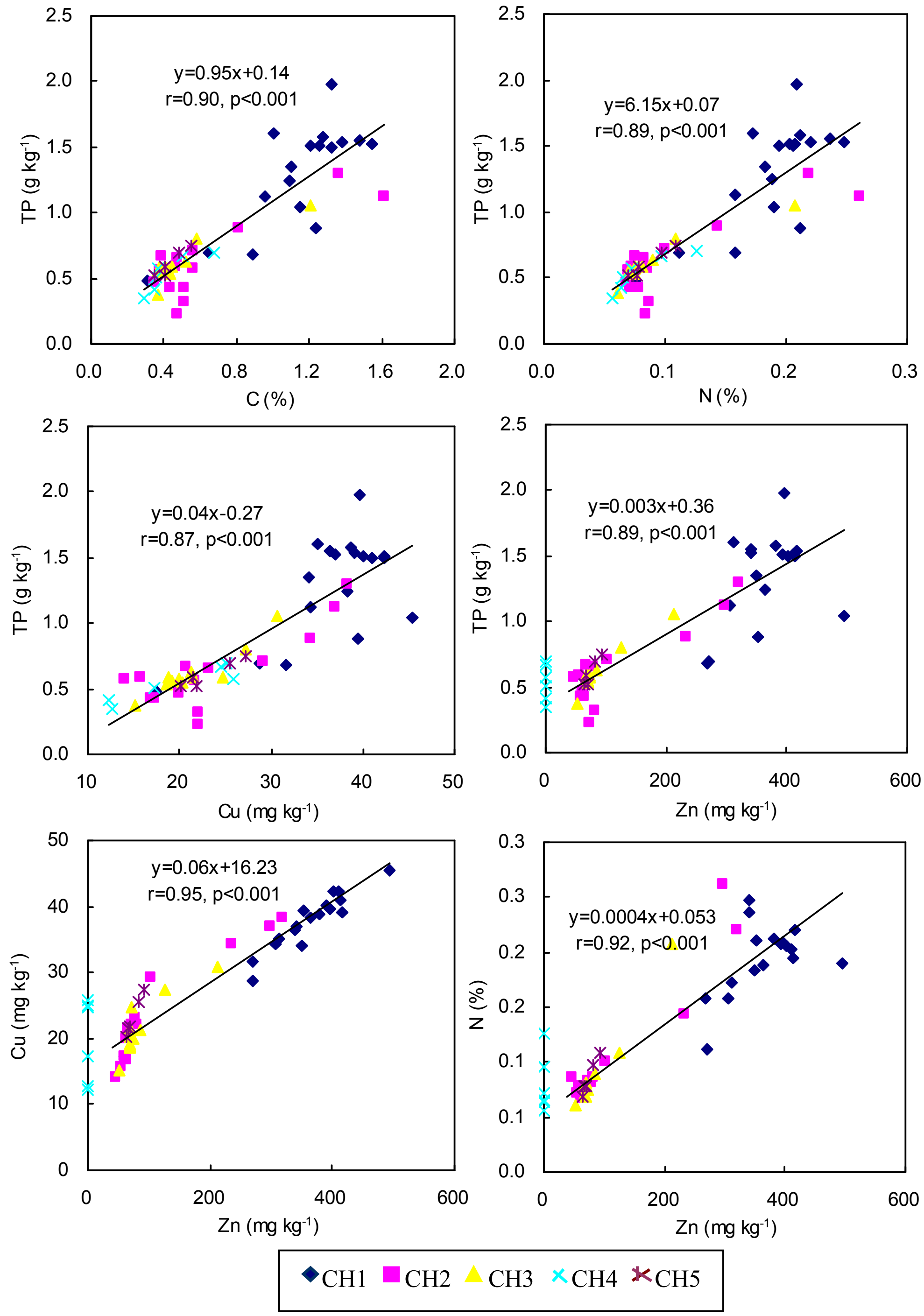

MBP (ng kg-1)
TP (g kg-1)
IP (g kg-1)
OP (g kg-1)
NPA (mg kg-1 h-1)
Mz (μm)
pH
C (%)
N (%)
S (%)
Cu (mg kg-1)
Zn (mg kg-1)
CH1 CH2 CH3 CH4 CH5

Fig. 3.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r=0.90, p<0.001
TP (g kg-1)
C (%)
y=6.15x+0.07
r=0.89, p<0.001
N (%)
y=0.04x-0.27
r=0.87, p<0.001
Cu (mg kg-1)
y=0.003x+0.36
r=0.89, p<0.001
Zn (mg kg-1)
y=0.06x+16.23
r=0.95, p<0.001
y=0.0004x+0.053
r=0.92, p<0.001
CH1 CH2 CH3 CH4 CH5

Fig. 4.

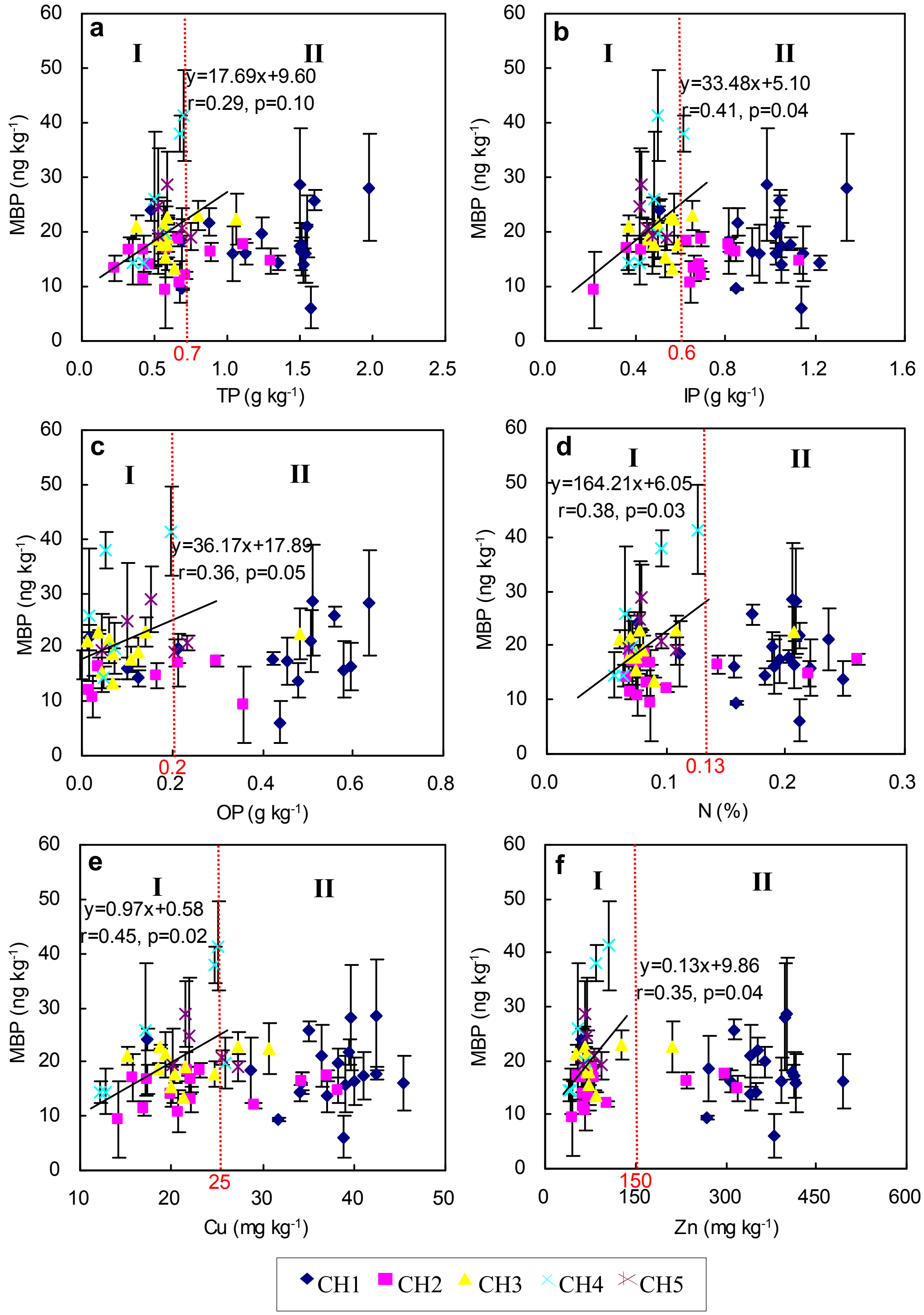
a
I
II
y=17.69x+9.60
r=0.29, p=0.10
0.7
MBP (ng kg-1)
TP (g kg-1)
b
I
II
y=33.48x+5.10
r=0.41, p=0.04
0.6
IP (g kg-1)
c
I
II
y=36.17x+17.89
r=0.36, p=0.05
0.2
OP (g kg-1)
d
I
II
y=164.21x+6.05
r=0.38, p=0.03
0.13
N (%)
e
I
II
y=0.97x+0.58
r=0.45, p=0.02
25
Cu (mg kg-1)
f
I
II
y=0.13x+9.86
r=0.35, p=0.04
150
Zn (mg kg-1)
CH1 CH2 CH3 CH4 CH5

Fig. 5.

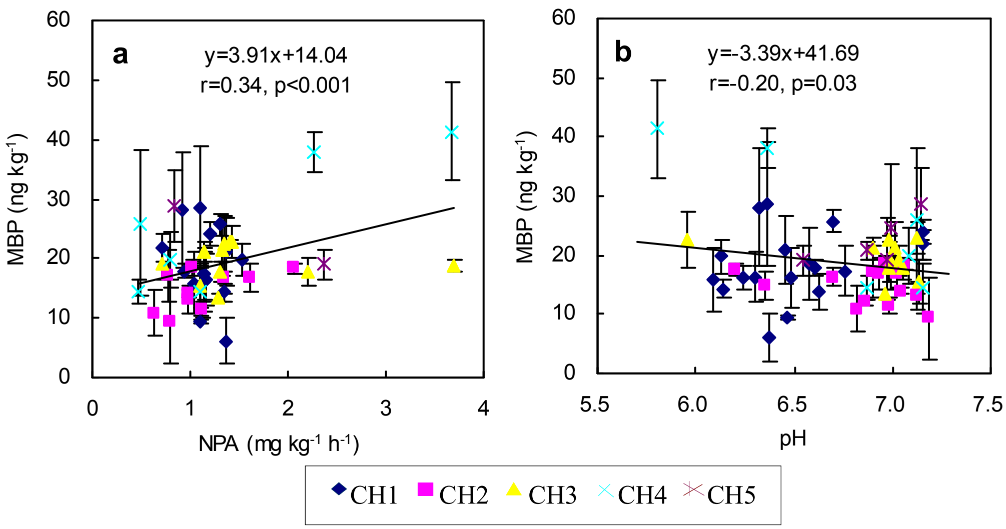
a
y=3.91x+14.04
r=0.34, p<0.001
MBP (ng kg-1)
NPA (mg kg-1 h-1)
b
y=-3.39x+41.69
r=-0.20, p=0.03
MBP (ng kg-1)
pH
CH1 CH2 CH3 CH4 CH5

Fig. 6.

Table 1. The mean concentrations of MBP, P fractions and physicochemical characteristics (mean (sd)) of the sediment profiles in Lake Chaohu.

Sediment profiles	Depth (cm)	MBP (ng kg^{-1})	TP (g kg^{-1})	IP (g kg^{-1})	OP (g kg^{-1})	NPA (mg kg^{-1} h^{-1})	pH	Mz (μm)	TC (%)	TN (%)	TS (%)	Cu (mg kg^{-1})	Zn (mg kg^{-1})
CH1	0~20	21.52a	1.62a	1.08a	0.54a	1.11a	6.4a	14.5a	1.41a	0.22a	0.12a	38.92a	378.61a
		(8.88)	(0.20)	(0.15)	(0.06)	(0.18)	(0.2)	(7.8)	(0.10)	(0.02)	(0.01)	(2.36	(35.66)
	20~40	14.86b	1.30ab	1.05a	0.34a	1.30a	6.3a	12.0a	1.14b	0.19b	0.10b	39.40a	387.72a
		(6.00)	(0.24)	(0.09)	(0.22)	(0.18)	(0.1)	(1.0)	(0.12)	(0.02)	(0.00)	(4.00)	(68.43)
	40~60	17.82a	1.20ab	1.01a	0.28a	1.08a	6.6ab	11.6a	1.10b	0.19b	0.08b	36.50a	338.65a
		(6.00)	(0.40)	(0.16)	(0.25)	(0.26)	(0.4)	(0.9)	(0.16)	(0.02)	(0.01)	(4.32)	(52.33)
	60~70	19.97a	0.89b	0.79a	0.16a	1.18a	6.8b	14.6a	0.76b	0.13b	0.06b	29.09a	247.78a
		(4.95)	(0.54)	(0.27)	(0.00)	(0.04)	(0.3)	(4.3)	(0.52)	(0.06)	(0.01)	(11.82)	(177.14)
	0~70	18.38	1.29	1.00	0.30	1.16	6.5	13.0	1.14	0.19	0.09	36.74	348.23
		(7.10)	(0.40)	(0.18)	(0.20)	(0.20)	(0.3)	(4.4)	(0.30)	(0.04)	(0.02)	(6.30)	(90.97)
CH2	0~20	14.29a	0.94a	0.83a	0.11a	0.64a	6.6a	11.1a	0.95a	0.16a	0.08a	31.90a	204.34a
		(3.23)	(0.27)	(0.19)	(0.12)	(0.00)	(0.3)	(2.6)	(0.53)	(0.08)	(0.02)	(7.18)	(114.38)
	20~40	16.00a	0.68ab	0.67ab	0.06a	1.26a	7.0b	12.1a	0.42a	0.08a	0.05b	21.71b	69.75ab
		(2.84)	(0.18)	(0.03)	(0.02)	(0.53)	(0.1)	(1.6)	(0.07)	(0.01)	(0.00)	(1.34)	(6.92)
	40~60	14.30a	0.47b	0.46b	0.09a	1.13a	7.0b	12.2a	0.50a	0.08a	0.05b	17.21c	60.68b
		(4.76)	(0.11)	(0.26)	(0.08)	(0.36)	(0.1)	(1.6)	(0.05)	(0.01)	(0.00)	(2.99)	(12.87)
	0~60	14.78	0.64	0.67	0.10	1.13	6.9	11.8	0.63	0.11	0.06	23.74	114.58
		(3.75)	(0.30)	(0.23)	(0.15)	(0.43)	(0.3)	(1.9)	(0.38)	(0.06)	(0.02)	(7.89)	(94.45)
CH3	0~20	21.79a	0.76a	0.56a	0.20a	1.23a	6.8a	12.2a	0.66a	0.12a	0.06a	24.57a	118.69a
		(3.06)	(0.22)	(0.08)	(0.19)	(0.34)	(0.6)	(2.2)	(0.37)	(0.06)	(0.01)	(5.44)	(67.58)

	20~40	18.94ab	0.57a	0.52a	0.04a	1.62a	7.0a	12.1a	0.37a	0.07a	0.04a	24.41a	69.57a
		(3.14)	(0.02)	(0.06)	(0.08)	(0.52)	(0.0)	(0.8)	(0.01)	(0.00)	(0.00)	(2.88)	(1.75)
	40~60	17.16b	0.53a	0.48a	0.05a	1.81a	7.0a	12.0a	0.43a	0.08a	0.04a	18.76a	68.78a
		(3.61)	(0.11)	(0.09)	(0.03)	(1.26)	(0.1)	(0.8)	(0.06)	(0.01)	(0.00)	(2.69)	(13.59)
	0~60	19.33	0.62	0.52	0.10	1.54	6.9	12.1	0.50	0.09	0.05	21.60	87.51
		(3.88)	(0.17)	(0.08)	(0.14)	(0.80)	(0.3)	(1.4)	(0.24)	(0.04)	(0.01)	(4.41)	(45.14)
CH4	0~20	31.26a	0.61a	0.53a	0.08a	1.80a	6.6a	18.8a	0.48a	0.09a	0.05a	23.20a	77.92a
		(11.39)	(0.09)	(0.06)	(0.08)	(1.46)	(0.6)	(8.6)	(0.15)	(0.03)	(0.01)	(4.02)	(22.39)
	20~30	14.44a	0.48b	0.40a	0.05a	0.78a	7.0a	34.9a	0.32a	0.06a	0.04a	12.52b	40.67b
		(2.95)	(0.05)	(0.04)	(0.00)	(0.45)	(0.2)	(15.4)	(0.04)	(0.01)	(0.00)	(0.33)	(2.69)
	0~30	25.65	0.54	0.48	0.05	1.46	6.7	24.2	0.42	0.08	0.04	19.64	65.50
		(12.38)	(0.14)	(0.08)	(0.08)	(1.26)	(0.5)	(12.7)	(0.14)	(0.03)	(0.01)	(6.34)	(25.92)
CH5	0~20	22.54	0.61	0.46	0.15	1.60	6.9	12.2	0.44	0.09	0.05	23.28	74.91
		(6.66)	(0.10)	(0.05)	(0.08)	(1.09)	(0.2)	(0.9)	(0.08)	(0.02)	(0.00)	(2.99)	(12.18)

Note: The data in the parentheses indicate standard deviation of the mean. The mean concentrations with different superscript letter (a, b or c) indicate significant difference at $P<0.05$. MBP: matrix-bound phosphine, TP: total phosphorus, IP: inorganic phosphorus, OP: organic phosphorus, NPA: neutral phosphatase activity, Mz: mean grain size, TC: total carbon, TN: total nitrogen, TS: total sulfur.

Table 2. Correlations between MBP, P fractions, NPA and environmental factors in the sediment profiles of Lake Chaohu, China.

Variables	MBP	TP	IP	OP	NPA	Mz	pH	TC	TN	TS	Cu	Zn
MBP	1	0.04	-0.12	0.05	0.34**	-0.04	-0.20*	-0.05	-0.02	-0.04	0.01	-0.06
TP		1	0.85**	0.85**	-0.07	-0.22	-0.67**	0.90**	0.89**	0.89**	0.87**	0.89**
IP			1	0.58**	-0.09	-0.25	-0.60**	0.82**	0.82**	0.85**	0.89**	0.90**
OP				1	-0.09	-0.23	-0.57**	0.77**	0.76**	0.71**	0.68**	0.74**
NPA					1	-0.19	-0.30*	-0.07	-0.04	-0.16	-0.02	-0.11
Mz						1	0.26*	-0.24	-0.24	-0.20	-0.35**	-0.24
pH							1	-0.71**	-0.73**	-0.64**	-0.66**	-0.67**
TC								1	0.99**	0.91**	0.90**	0.92**
TN									1	0.91**	0.91**	0.92**
TS										1	0.88**	0.91**
Cu											1	0.95**
Zn												1

Note: * and ** indicate significant correlation at the 0.05 and 0.01 level, respectively. The data of the five profiles were analyzed to obtain their correlation coefficient. MBP: matrix-bound phosphine, TP: total phosphorus, IP: inorganic phosphorus, OP: organic phosphorus, NPA: neutral phosphatase activity, Mz: mean grain size, TC: total carbon, TN: total nitrogen, TS: total sulfur.

Table 3. An overview of MBP concentrations in aquatic sediments.

Sample type	Location	MBP concentration range	References
Freshwater sediments			
Freshwater lake sediments	Chaohu, China	1.58–50.34 ng kg^{-1}	This study
Freshwater lake sediments	Taihu Lake, China	5.39–919 ng kg^{-1}	Geng et al. (2005)
Freshwater lake sediments	Taihu, China	5.4–919.2 ng kg^{-1}	Niu et al. (2004)
Freshwater river subsurface sediments	Elbe river, Hamburg harbor, German	0.2–56.6 ng kg^{-1}	Gassmann and Schorn (1993)
Freshwater river sediments	Elster river, Germany	4–1140 ng kg^{-1}	Glindemann et al. (2005)
Wetland soils	Beijing paddy field sediments	1.7–12.6 ng kg^{-1}	Liu et al. (1999)
Wetland soils	paddy fields in Jiangsu Province, China	20.8–502 ng kg^{-1}	Han et al. (2011)
Freshwater river subsurface sediments	Wulongtan in Nanjing, China	335 ± 85ng kg^{-1}	Han et al. (2003)
Ornithogenic lake sediments	Y_2 lake in Ardley Island, western Antarctica	0.29–3.04 ng kg^{-1}	Zhu et al. (2006)
Ornithogenic lake sediments	Mochou lake on Millor Peninsula, eastern Antarctica	8.66 ± 1.38 μg kg^{-1}	Zhu et al. (2011)
Ornithogenic lake sediments	Lake Solvatnet in the Bird Sanctuary, Arctic	11.77 ± 6.25 μg kg^{-1}	Zhu et al. (2011)
Lake sediments	Lake Illawarra, New South Wales, Australia	142–1813 ng kg^{-1},	Song et al. (2011)
Marine sediments			
Estuarine intertidal sediments	Yangtze Estuary, China	0.51–3.25 ng kg^{-1}	Hou et al. (2009)
Surface sediments	Yellow sea	0.19–38.24 ng kg^{-1}	Li et al. (2010)
Surface sediments	The coast of China	0.89–25.86 ng kg^{-1}	Feng et al. (2008)
Surface sediments	Changjing River Estuary	1.93–94.86 ng kg^{-1}	Feng et al. (2008)
Marine sediments in coastal areas	Jiaozhou Bay, China	124–685 ng kg^{-1}	Yu and Song (2003)
Marine sediments in coastal areas	Southwest Yellow Sea	0.69–179 ng kg^{-1}	Hong et al. (2010)