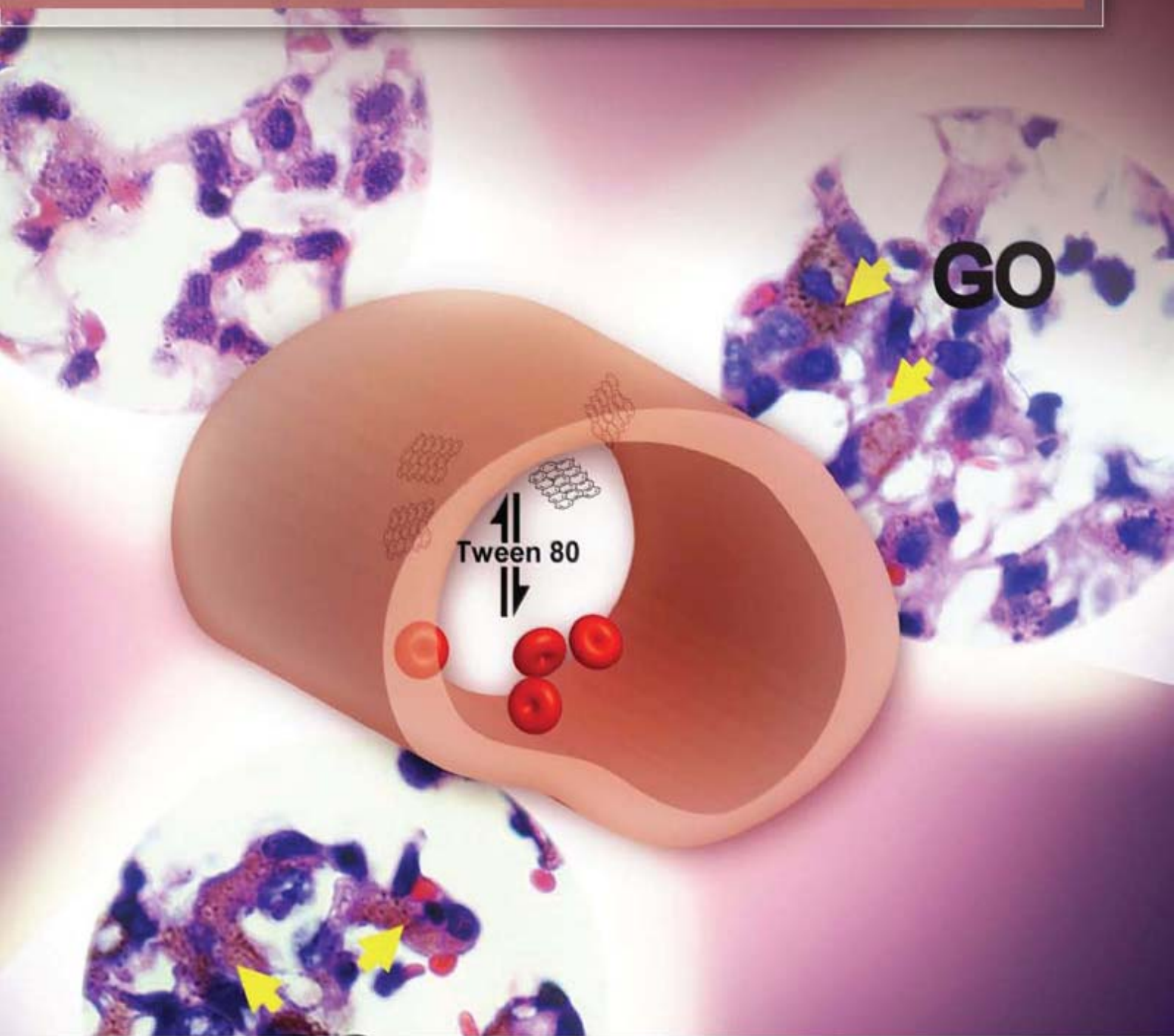


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CONTENTS

Environmental biology

Continuous live cell imaging of cellulose attachment by microbes under anaerobic and thermophilic conditions
using confocal microscopy

Zhi-Wu Wang, Seung-Hwan Lee, James G. Elkins, Yongchao Li, Scott Hamilton-Brehm, Jennifer L. Morrell-Falvey 849

Response of anaerobes to methyl fluoride, 2-bromoethanesulfonate and hydrogen during acetate degradation

Liping Hao, Fan Lü, Lei Li, Liming Shao, Pinjing He 857

Effect of airflow on biodrying of gardening wastes in reactors

F. J. Colomer-Mendoza, L. Herrera-Prats, F. Robles-Martínez, A. Gallardo-Izquierdo, A. B. Piña-Guzmán 865

Environmental health and toxicology

The *ex vivo* and *in vivo* biological performances of graphene oxide and the impact of surfactant on graphene
oxide's biocompatibility (Cover story)

Guangbo Qu, Xiaoyan Wang, Qian Liu, Rui Liu, Nuoya Yin, Juan Ma, Liqun Chen, Jiuyang He, Sijin Liu, Guibin Jiang 873

Determination of the mechanism of photoinduced toxicity of selected metal oxide nanoparticles (ZnO, CuO, Co₃O₄ and
TiO₂) to *E. coli* bacteria

Thabitha P. Dasari¹, Kavitha Pathakoti², Huey-Min Hwang 882

Joint effects of heavy metal binary mixtures on seed germination, root and shoot growth, bacterial bioluminescence,
and gene mutation

In Chul Kong 889

Atmospheric environment

An online monitoring system for atmospheric nitrous acid (HONO) based on stripping coil and ion chromatography

Peng Cheng, Yafang Cheng, Keding Lu, Hang Su, Qiang Yang, Yikan Zou, Yanran Zhao,

Huabing Dong, Limin Zeng, Yuanhang Zhang 895

Formaldehyde concentration and its influencing factors in residential homes after decoration at Hangzhou, China

Min Guo, Xiaoqiang Pei, Feifei Mo, Jianlei Liu, Xueyou Shen 908

Aquatic environment

Flocculating characteristic of activated sludge flocs: Interaction between Al³⁺ and extracellular polymeric substances

Xiaodong Ruan, Lin Li, Junxin Liu 916

Speciation of organic phosphorus in a sediment profile of Lake Taihu II. Molecular species and their depth attenuation

Shiming Ding, Di Xu, Xiuling Bai, Shuchun Yao, Chengxin Fan, Chaosheng Zhang 925

Adsorption of heavy metal ions from aqueous solution by carboxylated cellulose nanocrystals

Xiaolin Yu, Shengrui Tong, Maofa Ge, Lingyan Wu, Junchao Zuo, Changyan Cao, Weiguo Song 933

Synthesis of mesoporous Cu/Mg/Fe layered double hydroxide and its adsorption performance for arsenate in aqueous solutions

Yanwei Guo, Zhiliang Zhu, Yanling Qiu, Jianfu Zhao 944

Advanced regeneration and fixed-bed study of ammonium and potassium removal from anaerobic digested wastewater
by natural zeolite

Xuejun Guo, Larry Zeng, Xin Jin 954

Eutrophication development and its key regulating factors in a water-supply reservoir in North China	
Liping Wang, Lusan Liu, Binghui Zheng	962
Laboratory-scale column study for remediation of TCE-contaminated aquifers using three-section controlled-release potassium permanganate barriers	
Baoling Yuan, Fei Li, Yanmei Chen, Ming-Lai Fu	971
Influence of Chironomid Larvae on oxygen and nitrogen fluxes across the sediment-water interface (Lake Taihu, China)	
Jingge Shang, Lu Zhang, Chengjun Shi, Chengxin Fan	978
Comparison of different phosphate species adsorption by ferric and alum water treatment residuals	
Sijia Gao, Changhui Wang, Yuansheng Pei	986
Removal efficiency of fluoride by novel Mg-Cr-Cl layered double hydroxide by batch process from water	
Sandip Mandal, Swagatika Tripathy, Tapswani Padhi, Manoj Kumar Sahu, Raj Kishore Patel	993
Determining reference conditions for TN, TP, SD and Chl- <i>a</i> in eastern plain ecoregion lakes, China	
Shouliang Huo, Beidou Xi, Jing Su, Fengyu Zan, Qi Chen, Danfeng Ji, Chunzi Ma	1001
Nitrate in shallow groundwater in typical agricultural and forest ecosystems in China, 2004–2010	
Xinyu Zhang, Zhiwei Xu, Xiaomin Sun, Wenyi Dong, Deborah Ballantine	1007
Influential factors of formation kinetics of flocs produced by water treatment coagulants	
Chunde Wu, Lin Wang, Bing Hu, Jian Ye	1015
 Environmental catalysis and materials	
Characterization and performance of Pt/SBA-15 for low-temperature SCR of NO by C ₃ H ₆	
Xinyong Liu, Zhi Jiang, Mingxia Chen, Jianwei Shi, Wenfeng Shangguan, Yasutake Teraoka	1023
Photo-catalytic decolourisation of toxic dye with N-doped titania: A case study with Acid Blue 25	
Dhruba Chakraborty, Susmita Sen Gupta	1034
Pb(II) removal from water using Fe-coated bamboo charcoal with the assistance of microwaves	
Zengsheng Zhang, Xuejiang Wang, Yin Wang, Siqing Xia, Ling Chen, Yalei Zhang, Jianfu Zhao	1044
 Serial parameter: CN 11-2629/X*1989*m*205*en*P*24*2013-5	



Speciation of organic phosphorus in a sediment profile of Lake Taihu II. Molecular species and their depth attenuation

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Abstract

The understanding of organic phosphorus (P) dynamics in sediments requires information on their species at the molecular level, but such information in sediment profiles is scarce. A sediment profile was selected from a large eutrophic lake, Lake Taihu (China), and organic P species in the sediments were detected using solution phosphorus-31 nuclear magnetic resonance spectroscopy (³¹P NMR) following extraction of the sediments with a mixture of 0.25 mol/L NaOH and 50 mmol/L EDTA (NaOH-EDTA) solution. The results showed that P in the NaOH-EDTA extracts was mainly composed of orthophosphate, orthophosphate monoesters, phospholipids, DNA, and pyrophosphate. Concentrations of the major organic P compound groups and pyrophosphate showed a decreasing trend with the increase of depth. Their half-life times varied from 3 to 27 years, following the order of orthophosphate monoesters > phospholipids ≥ DNA > pyrophosphate. Principal component analysis revealed that the detected organic P species had binding phases similar to those of humic acid-associated organic P (NaOH-NRP_{HA}), a labile organic P pool that tends to transform to recalcitrant organic P pools as the early diagenetic processes proceed. This demonstrated that the depth attenuation of the organic P species could be partly attributed to their increasing immobilization by the sediment solids, while their degradation rates should be significantly lower than what were suggested in previous studies.

Key words: organic phosphorus; sediment; half-life time; ³¹P NMR; Lake Taihu

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Introduction

Organic phosphorus (P) in natural aqueous environments encompasses a wide variety of organic compounds containing both P and carbon. Once organic P deposits on the surface of sediments, it tends to be degraded into small compounds by microbes, and may be released to the overlying water (Huang and Zhang, 2010). Further degradation occurs in anoxic sediments originating from diagenetic decomposition of organic matter. Contrary to the degradation process, immobilization of organic P compounds by sediment solids may occur and likely prevent their degradation (Celi and Barberis, 2005). The occurrence of the degradation and immobilization processes depends on the molecular structures of organic P compounds. Taking the critical role of P in regulating lake trophic status into consideration (Schelske, 2009),

it is important to understand the species of organic P in sediments at the molecular level.

Solution phosphorus-31 nuclear magnetic resonance spectroscopy (³¹P NMR) is currently a direct and powerful tool in the characterization of organic P forms at the molecular level (Cade-Menun, 2005). This technique uses the magnetic resonance of the ³¹P nucleus to identify its chemical forms in solution samples originating from alkaline extraction of P in sediments. Due to the advantage that all P compounds of interest can be detected simultaneously with high resolution without complex preparation (Paytan et al., 2003; Xu et al., 2012), applications of this technique to aquatic systems have advanced rapidly (Ahlgren et al., 2005; Bai et al., 2009; Reitzel et al., 2009). A range of P compounds (or compound classes) have been detected using solution ³¹P NMR in various surface sediments from rivers, lakes, and marine areas, typically including orthophosphate, pyrophosphate, polyphosphate,

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phosphonates, orthophosphate monoesters and orthophosphate diesters (DNA and phospholipids) (Cade-Menun, 2005). However, the changes of organic P species in sediment profiles have only been reported in Lake Erken (Sweden) (Ahlgren et al., 2005; Reitzel et al., 2007), the Baltic Sea (Ahlgren et al., 2006), and an embayment in Helsinki, Finland (Turner and Weckström, 2009).

Lake Taihu is a large, shallow, eutrophic lake in the Changjiang (Yangtze) delta, the most industrialized area in China. This lake has been receiving large inputs of agricultural fertilizers and domestic and industrial wastewater since the early 1980s, leading to the rapid appearance of water eutrophication (Chen et al., 2003). The dynamics of P in sediments and its relationship with water eutrophication have attracted great attention. Most of the previous studies focused on inorganic P in the sediments of Lake Taihu (Zhou et al., 2005; Zhu et al., 2006), while organic P in the sediments has been paid much less attention (Zhang et al., 2008, 2009; Bai et al., 2009). Bai et al. (2009) and Zhang et al. (2009) have reported on organic P species in surface sediments of Lake Taihu using solution ^{31}P NMR measurement. However, little is known about their changes with sediment depth.

In this study, organic P species in a sediment profile of Lake Taihu were detected by solution ^{31}P NMR following extraction of the sediments with an alkaline solution. Their dynamic changes with sediment depth was analyzed and compared to previous reports of other sediments. The mechanisms involved were discussed in combination with data from chemical fractionation of organic P in the sediments.

1 Materials and methods

1.1 Sampling site and sediment collection

The sampling site and sediment collection for this study have been reported elsewhere (Xu et al., 2012). The sampling site was located in the northern part of Meiliang Bay (120.19°E and 31.51°N), which is one of the most eutrophied regions in Lake Taihu. It has a distance of approximately 4 km from the outlet of the River Liangxi. This site is representative of eutrophic and polluted regions in Meiliang Bay.

The sediment samples were collected in November 2007 using a gravity core sampler. Six sediment cores were collected, and each core was sliced into 0.5 cm sections down to 10 cm and 2.5 cm sections down to 15 cm. The sediment samples at the same depths were pooled and homogenized to obtain a representative sample. After transportation to the laboratory, the sediment samples were lyophilized at -80°C , sieved to pass through a 100-mesh sieve and then stored at 4°C until analysis.

1.2 Estimation of sediment age

Sediment age was estimated using dating methods involving ^{210}Pb . The lyophilized sediments were stored in sealed containers to allow radioactive equilibration for 3 weeks. The ^{210}Pb in the sediments was determined using an EG&G Ortec Gamma Spectrometer via gamma emission at 46.5 keV, ^{226}Ra emission at 295 keV and 352-keV gamma rays emitted by its daughter isotope, ^{214}Pb . The activity of excess ^{210}Pb ($^{210}\text{Pb}_{\text{ex}}$) in each sample was obtained by subtracting the ^{226}Ra activity from the activity of total ^{210}Pb . Sediment age was then obtained by exponential fitting of the sediment depth versus activity of $^{210}\text{Pb}_{\text{ex}}$, assuming that the deposition rate was stable (Appleby, 2001).

1.3 Sediment extraction and solution ^{31}P NMR analysis

Organic P in the sediment was extracted using a solution containing 0.25 mol/L NaOH and 50 mmol/L EDTA (NaOH-EDTA) for 16 hr at 20°C . The solid:solution ratio was 1:8 (*m/V*), which produced a concentration of P high enough for ^{31}P NMR analysis (Xu et al., 2012). An aliquot of the extract was used to analyze total P. The remaining solution was concentrated 10 times in a rotary vacuum evaporator at 28°C . The concentrated extracts were stored at -20°C until ^{31}P NMR analysis.

Prior to ^{31}P NMR analysis, all concentrated extracts (0.9 mL for each sample) were centrifuged at 10,000 r/min for 10 min to remove any possible particles. A 0.1 mL of heavy water (D_2O) was added to each solution for signal lock. The ^{31}P NMR spectra were measured at 161.98 MHz on a Bruker AV400 spectrometer equipped with a 5-mm broadband probe using a 45° pulse, a relaxation delay of 2.2 sec and an acquisition time of 0.4 sec. The use of a 45° pulse was to shorten the delay time required (Cade-Menun et al., 2005). The pulse and delay times were similar to those used by Turner and Weckström (2009). The scan time for each sample was approximately 16 hr. Chemical shifts were recorded relative to 85% H_3PO_4 via the signal lock, and the orthophosphate peak for each sample was standardized to 6 ppm in all spectra to simplify comparison of samples (Cade-Menun, 2005). Peak area was quantified through manual integration of significant peaks. The P compounds were identified based on literature (Turner et al., 2003; Cade-Menun et al., 2010; Jørgensen et al., 2011). All spectral processing was carried out using NMR Utility Transform Software for Windows (2000 edition; Acorn NMR, Livermore, USA).

Due to the time-consuming and expensive nature of ^{31}P NMR scans, replicate analyses were not performed. The analytical errors from P extraction and the following ^{31}P NMR analysis were estimated as within 10% for large signals (e.g., orthophosphate, orthophosphate monoesters and DNA) and within 20% for small signals (e.g., phospholipids and polyphosphate) (Ding et al., 2010a, 2010b; Xu et al., 2012).

2 Results and discussion

2.1 Sediment ages

The age of the sediments was obtained by exponential fitting of the sediment depth versus activity of $^{210}\text{Pb}_{\text{ex}}$ (Fig. 1). The exponential equation was $y = 277.6e^{-0.037x}$ ($r = 0.74$, $p = 0.003$), from which an average sedimentation rate of 0.85 cm/yr was obtained. This rate is much higher than 0.33 cm/yr as reported by Zhu et al. (2007) but is close to 0.88 cm/yr reported by Wu et al. (2007) for two sites in the Meiliang Bay. The high sedimentation rate in this site reflects a high input and sedimentation of particles from the River Liangxi. According to this rate, the sediment depth of 15 cm represents a sedimentation period of 18 years.

2.2 Extraction of total P using NaOH-EDTA solution

As shown in Table 1, the concentrations of total P extracted by NaOH-EDTA had a decreasing trend with sediment depth which is similar to that of total P in sediments (Xu et al., 2012). The values decreased from ~440 mg/kg in the uppermost layers to ~240 mg/kg in the deepest layers. The extracted total P accounted for 29%–43% of the total P in the sediments. The recovery rate decreased from 43% to 37% in the upper 2.0 cm, but below this it showed a small fluctuation until a depth of 10.0 cm. After this depth, it decreased sharply from 36% to ~30%.

The single-step NaOH-EDTA extraction used in this study is currently the most common preparation technique for solution ^{31}P NMR analysis of sediment organic P.

Its use can achieve a greater recovery and diversity of P compared to the use of NaOH due to the chelating ability of EDTA (Cade-Menun and Preston, 1996; Xu et al., 2012). In this study, the recovery rates of total P were within the reported rates based on investigation of 45 different lake sediments and 7 artificial landscape lakes, where most of the recovery rates were less than 50% (Liu et al., 2009; Ding et al., 2010a). These low recovery rates demonstrated that the extraction and associated ^{31}P NMR analysis could only provide molecular information on a portion of organic P in sediments. Larger decreases in extraction rates were reported from NaOH-EDTA extraction of a

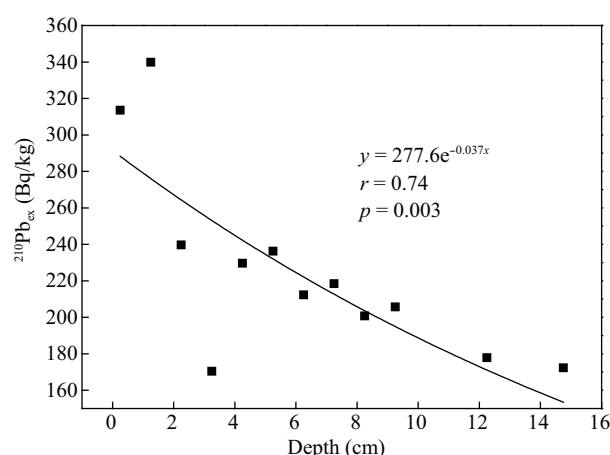


Fig. 1 Concentrations of $^{210}\text{Pb}_{\text{ex}}$ in the sediment profile investigated.

Table 1 Concentrations of individual P fractions and their sum in the sediment profile according to solution ^{31}P NMR analysis

Depth (cm)	Total P ^a (mg/kg)	Extracted total P ^b (%) (mg/kg)	Individual P fraction (mg/kg)						
			Orthophosphate	Orthophosphate monoesters	Phospholipids	DNA	Pyrophosphate	Polyphosphate	Phosphonates
0–0.5	1036	443.8 (42.8)	297.9	79.9	10.14	14.59	27.13	6.74	7.37
0.5–1	1004	425.4 (42.4)	307.0	69.1	8.46	16.11	23.76	n.d.	1.02
1–1.5	1051	427.7 (40.7)	326.4	60.3	9.68	10.20	17.30	3.78	n.d.
1.5–2	1085	399.6 (36.9)	325.1	48.0	8.22	5.59	12.72	n.d.	n.d.
2–2.5	1061	408.3 (38.5)	332.8	51.6	6.13	6.95	10.80	n.d.	n.d.
2.5–3	1008	382.2 (37.9)	314.6	48.1	6.52	5.27	7.73	n.d.	n.d.
3–3.5	994	362.5 (36.5)	308.0	41.4	3.62	6.81	2.65	n.d.	n.d.
3.5–4	946	308.1 (32.6)	250.4	42.4	4.44	5.98	2.94	n.d.	1.89
4–4.5	950	342.3 (36.0)	265.7	53.5	8.25	6.06	8.30	n.d.	0.47
4.5–5	968	327.8 (33.9)	254.8	51.7	9.50	8.52	3.23	n.d.	n.d.
5–5.5	892	301.9 (33.8)	244.6	45.0	4.94	7.43	n.d.	n.d.	n.d.
5.5–6	927	296.9 (32.0)	236.3	44.5	7.38	7.42	1.37	n.d.	n.d.
6–6.5	844	276.8 (32.8)	215.5	43.9	7.49	8.21	n.d.	n.d.	1.70
6.5–7	853	311.6 (36.5)	247.1	47.0	5.25	10.10	2.21	n.d.	n.d.
7–7.5	865	314.0 (36.3)	240.0	54.6	8.97	9.14	1.26	n.d.	n.d.
7.5–8	850	291.6 (34.3)	244.2	33.7	6.44	7.29	n.d.	n.d.	n.d.
8–8.5	814	286.1 (35.1)	224.3	49.8	7.28	4.72	n.d.	n.d.	n.d.
8.5–9	835	298.9 (35.8)	233.5	50.8	7.17	7.46	n.d.	n.d.	n.d.
9–9.5	802	287.0 (35.8)	224.7	50.0	6.35	3.89	2.02	n.d.	n.d.
9.5–10	817	295.9 (36.2)	226.7	47.4	7.37	12.45	1.96	n.d.	n.d.
10–12.5	772	221.2 (28.6)	182.8	35.0	1.44	1.96	n.d.	n.d.	n.d.
12.5–15	792	244.7 (30.9)	195.9	40.8	3.92	4.06	n.d.	n.d.	n.d.

^a Cited from previous publication of Xu et al. (2012); ^b extraction rate based on total P in sediments. n.d.: not detected.

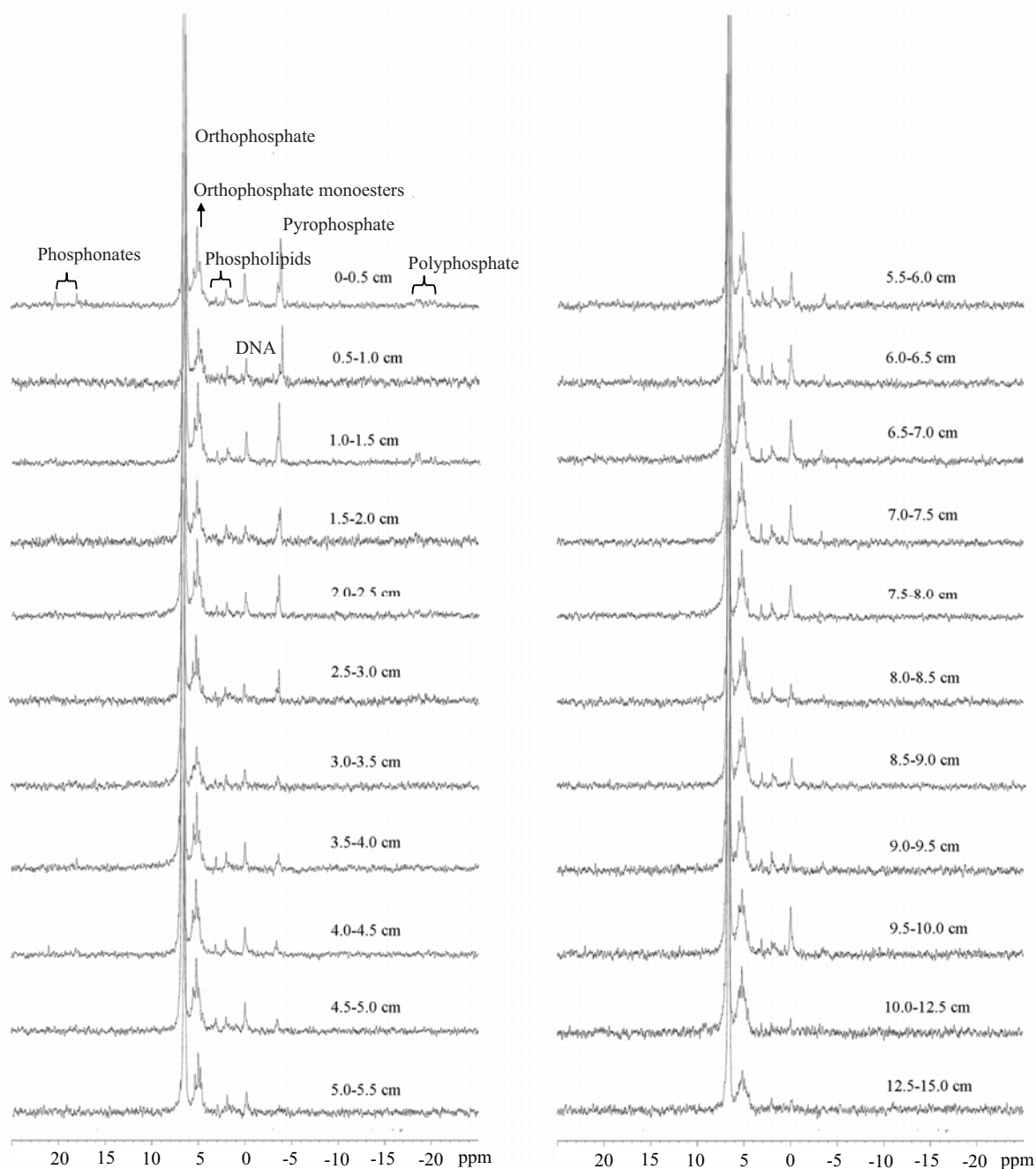


Fig. 2 ^{31}P NMR spectra of NaOH-EDTA extracts from the sediment profile investigated.

sediment profile in the Baltic Sea (Ahlgren et al., 2006), and NaOH extractions of two sediment profiles in Lake Erken (Ahlgren et al., 2005). Since an extraction with an alkaline solution (e.g., 0.1 mol/L NaOH) could recover the labile P fraction (especially labile organic P fractions) in sediments (Rydin, 2000), the decrease in extraction rates reflected the fact that P in the sediments became increasingly recalcitrant as the early diagenetic processes proceeded. This change agreed with the transformation of organic P from labile to recalcitrant forms as revealed

previously (Xu et al., 2012).

2.3 Organic P species in sediments

Results from ^{31}P NMR analyses are listed in **Table 1** and **Fig. 2**. The results showed that P in the extracts was composed of orthophosphate (6 to 7 ppm), orthophosphate monoesters (4 to 6 ppm), phospholipids (1 to 3 ppm), DNA (0 ppm), pyrophosphate (−3.5 to −4.5 ppm), polyphosphate (−17 to −19 ppm) and phosphonates (18 to 20 ppm). Polyphosphate and phosphonates were only detected in a

few sediment layers. Orthophosphate was the dominant fraction (on average 79%) of all P compound groups detected, followed by orthophosphate monoesters (15%), DNA (2.3%), pyrophosphate (2.1%) and phospholipids (2.0%).

The diversity of P compound groups determined by ^{31}P NMR was in accordance with a previous report on surface sediments (1 cm) in Lake Taihu (Bai et al., 2009). Orthophosphate monoesters constitute a dominant part of organic P detected. Jørgensen et al. (2011) identified that this P group was mainly composed of *myo*-inositol hexakisphosphate, *scyllo*-inositol hexakisphosphate, α -glycerophosphate and β -glycerophosphate, but the latter two compounds were most likely degradation products of phospholipids caused by the alkaline extraction. Inositol hexakisphosphates were found to be highly stable in the sediment profile. Taking their stability into consideration, *myo*-inositol hexakisphosphate has been recommended as a paleo-indicator to reflect historical changes in P inputs to water bodies in brackish sediments (Turner and Weckström, 2009).

Both phospholipids and DNA belong to the group orthophosphate diesters. This P group is much less stable than that in orthophosphate monoesters because its P–O bond is easily broken. Its lower charge density also reduced its binding affinity with sediment solids and caused it to be less resistant to microbiological degradation (Leytem et al., 2002). Polyphosphates and phosphonates were rarely detected in the sediments, which was attributed to their low abundances (Bai et al., 2010). The two P compound groups were also scarcely detected in other lakes in China (Zhang et al., 2009; Ding et al., 2010a).

2.4 Changes of organic P species with sediment depth

Concentrations of the major organic P compound groups, including orthophosphate monoesters, phospholipids and DNA, showed a decreasing trend with the increase of depth in the upper 2 cm layers (Table 1). Concentration of pyrophosphate had a sharper decrease in the upper 3.5 cm layers. The depth attenuations of these P compound groups have been observed in sediments of Lake Erken (Ahlgren et al., 2005; Reitzel et al., 2007) and the Baltic Sea (Ahlgren et al., 2006).

The attenuation rate of a P compound in sediments can be described using its half-life time (Ahlgren et al., 2005). The half-life time is determined by plotting the concentration of the P compound versus sediment age. Their relationship is fitted using an exponential regression curve. The half-life time is then calculated using $\tau = \ln 2/k$, while k (yr^{-1}) is the rate constant in the exponential equation of the regression curve.

The half-life times of the major P compound groups detected in this study were estimated using the method mentioned above. They varied from 3 to 27 years, following the order of orthophosphate monoesters > phos-

Table 2 Half-life time (yr) of P compound groups comparison

Species	Lake Taihu ^a		Lake Erken ^b	Baltic Sea ^c
	Time	<i>p</i> -Value		
Orthophosphate monoesters	27	< 0.01	23	16
Phospholipids	14	< 0.01	21 ^d	5
DNA	12	< 0.01		8
Pyrophosphate	3	< 0.001	13	3

^a From this study; ^b from Ahlgren et al., 2005; ^c from Ahlgren et al., 2006; ^d calculated based on orthophosphate diesters.

pholipids \geq DNA > pyrophosphate (Table 2). This order was similar to those detected in sediments of Lake Erken and the Baltic Sea (Ahlgren et al., 2005, 2006). The half-life time of pyrophosphate found in this study was the same as that in the Baltic Sea. Both were much shorter than that in Lake Erken. The half-life time of orthophosphate monoesters in Lake Taihu was longer than those in Lake Erken and the Baltic Sea, while those of orthophosphate diesters were intermediate between them. Taking the possibly large differences of the three benthic environments into consideration, the half-life times of each P compound group in these sediments were still comparable.

2.5 Relationship between ^{31}P NMR-detected organic P species and fractionated organic P forms

To understand the relationship between organic P fractions measured at the solid-bound and molecular levels in the sediments, principal component analysis (PCA) was performed on the concentrations of each P fraction detected by ^{31}P NMR and chemical fractionation techniques (Xu et al., 2012). Three principal components (PC1, PC2 and PC3) were extracted and accounted for 82% of the total variation (Fig. 3). Both orthophosphate and the major bound forms of inorganic P (NaOH-RP and HCl-RP, referring to organic matter- and reactive metal oxide-bound inorganic P, respectively) were largely controlled by PC1 and could be combined into a group. This behavior reflected the fact that the two bound RP forms were mostly orthophosphate. Orthophosphate monoesters, phospholipids and DNA were controlled by both PC1 and PC2, and could be combined into another group. This group represented the variation in organic P fractions.

Fulvic acid- and humic acid-associated organic P (abbreviated as NaOH-NRP_{FA} and NaOH-NRP_{HA} respectively) were adjacent to the orthophosphate and organic P groups, respectively, in the component plot, demonstrating that the two bound organic forms were dominated by orthophosphate and organic P compounds. This result was in accordance with the findings of Reitzel et al. (2006, 2007) based on solution ^{31}P NMR analyses of the sediments of Lake Erken. The authors found that the precipitate from NaOH extracts of the sediments was primarily composed of organic P compounds, whereas the supernatant contained a much higher proportion of orthophosphate. This reflected an error of the fractionation technique in

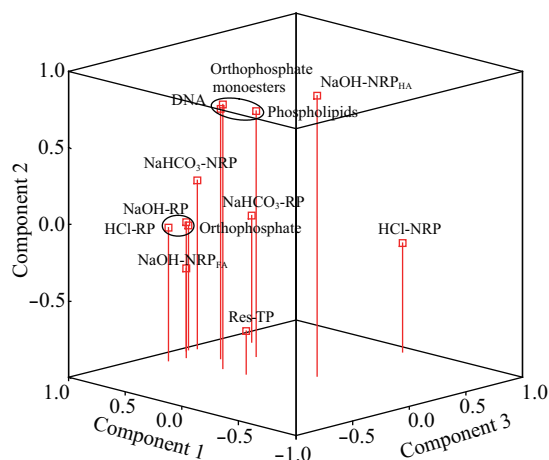


Fig. 3 Principal component analysis (PCA) of the individual P fractions measured by chemical fractionation and solution ^{31}P NMR.

differentiating organic P pools in sediments. The defined $\text{NaOH-NRP}_{\text{FA}}$ should be rich in other P species, such as polyphosphate and some inorganic phosphates associated with organic macromolecules and mineral colloids (Turner et al., 2006). HCl-NRP and residual organic P (Res-TP) exhibited very different variations from the above two groups, demonstrating that the two bound forms of organic P had different sources compared to the ^{31}P NMR-detected fractions.

2.6 Mechanisms involved in the depth attenuation of organic P species

The depth attenuation of organic P species in sediment profiles was generally attributed to their degradation during early diagenetic processes (Ahlgren et al., 2005, 2006; Reitzel et al., 2007). However, the information from ^{31}P NMR measurement was limited to a portion of organic P extracted from sediments as mentioned earlier. Since the behaviors of organic P compounds in sediments are simultaneously controlled by degradation and immobilization processes, a better understanding of organic P in sediments requires the dynamical information at the solid-bound and molecular levels.

In this study, the PCA showed that the composition of $\text{NaOH-NRP}_{\text{HA}}$ was dominated by organic P compounds. Since both the $\text{NaOH-NRP}_{\text{HA}}$ and the ^{31}P NMR-detected organic P fractions were extracted by alkaline solutions (0.5 mol/L NaOH and 0.25 mol/L NaOH-50 mmol/L EDTA, respectively), they should have similar binding phases in sediments. Consequently, the measurements with ^{31}P NMR provided the organic P species information for the $\text{NaOH-NRP}_{\text{HA}}$ pool. Since a previous study on the same sediment profile has revealed consistent transformations of organic P from the labile $\text{NaOH-NRP}_{\text{HA}}$ pool to the recalcitrant HCl-NRP and Res-TP pools (Xu et al., 2012), transfers of organic P compounds should have occurred among these binding phases, enabling them to be im-

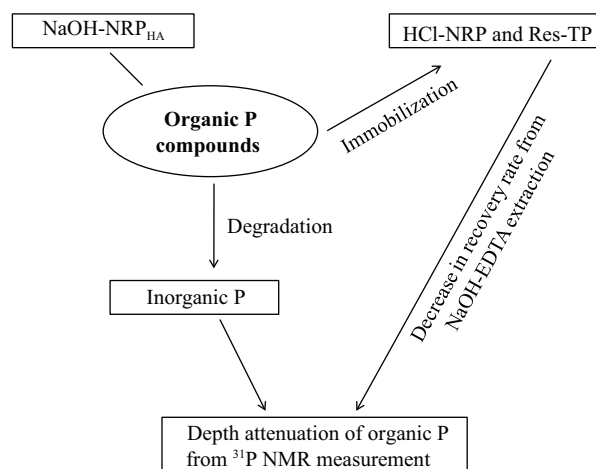


Fig. 4 A schematic of the mechanisms involved in the depth attenuation of organic P species in sediments detected by solution ^{31}P NMR.

mobilized increasingly in sediments. This immobilization process made the organic P compounds more recalcitrant in sediments and resulted in the decrease in recovery rate of total P from the NaOH-EDTA extraction (**Table 2**). This hypothesis was strongly supported by the major decreases in the concentrations of organic P species and the recovery rate of NaOH-EDTA extraction at the same depths (0–2 cm and 10–15 cm) (**Table 1**). Consequently, the depth attenuation of the ^{31}P NMR-detected organic P species was to a considerable extent attributed to their increasing immobilization by the sediment solids, while the degradation rates of these organic P species in sediments should be significantly lower than what were suggested in previous studies (**Fig. 4**).

3 Conclusions

A single-step NaOH-EDTA extraction recovered 29%–43% of the total P in the sediments. The recovery rate had a decreasing trend with sediment depth. The solution ^{31}P NMR analyses showed that P in the NaOH-EDTA extracts was composed of orthophosphate, orthophosphate monoesters, phospholipids, DNA, pyrophosphate, polyphosphate and phosphonates. Concentrations of the major organic P compound groups and pyrophosphate showed a decreasing trend with increasing depth. Their half-life times varied from 3 to 27 years, following the order orthophosphate monoesters > phospholipids \geq DNA > pyrophosphate. The PCA showed that the ^{31}P NMR-detected organic P fractions had binding phases in sediments similar to those of $\text{NaOH-NRP}_{\text{HA}}$. Taking the transformation of $\text{NaOH-NRP}_{\text{HA}}$ to the recalcitrant HCl-NRP and Res-TP pools into consideration, the depth attenuation of the organic P species was to a considerable extent attributed to their increasing immobilization by the sediment solids.

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