

Responses of organic phosphorus fractionation to environmental conditions and lake evolution

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Supporting information

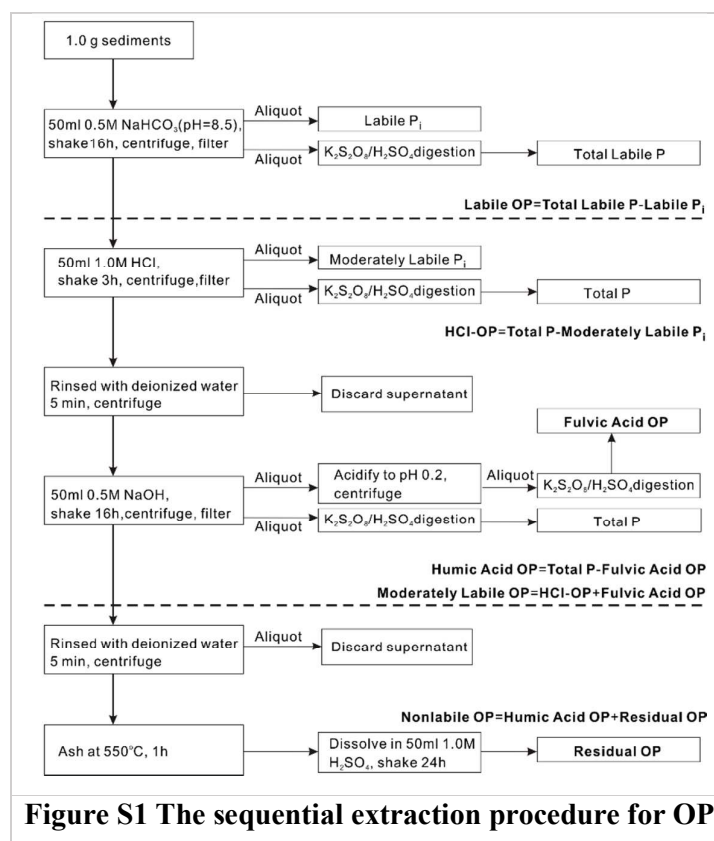
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S1 Material and Methods

S1.1 Organic phosphorus fractionation

The fractionation of the individual organic phosphorus (OP) pools is based on the reactivity with the given extractants. The optimized OP fractionation procedure, detailed in the literature,¹ can be simply summarized as follows: The labile pool is extracted with 0.5M NaHCO₃ at pH 8.5. The moderately labile pool is extracted with 1.0 M HCl (HCl-OP), followed by 0.5 M NaOH. The NaOH extract is acidified with concentrated HCl to separate the nonlabile fraction (humic acid fraction, HAOP) from the moderately labile fraction (fulvic acid fraction, FAOP). Finally, the highly resistant (Residual OP, Re-OP), nonlabile fraction is determined by ashing the residue from the NaOH extraction at 550°C for 1 h, followed by dissolution in 1.0 M H₂SO₄. In all cases, P concentration in the extracts was determined colorimetrically by the phospho-molybdate method of Murphy and Riley.² Acid or alkaline extracts are neutralized prior to P determinations. OP in the extracts is calculated from the difference between total P (TP) and inorganic P (IP). TP in all extracts was measured after an aliquot was digested with K₂S₂O₈ + H₂SO₄.³

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34 Total P (TP) in sediments was measured by treating at 500 °C (2 h), followed by HCl
 35 extraction. Inorganic P (IP) was determined by direct extraction with 1 M HCl (16 h). OP
 36 concentrations in sediments were calculated as the difference between TP and IP (Aspila et al.,
 37 1976). The recovery (%) of OP was measured as the ratio of the OP concentration determined
 38 by extraction to that determined by ignition. The results showed that the recovery of TOP
 39 ranged from 90.25% to 110.93%, with an average of 99.81% (Table S1 and S2), suggesting
 40 that total OP in sediments was satisfactorily extracted with this procedure.

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Table S1 Concentration and recovery of TP, IP and TOP in surface sediments

	Concentration (mg/kg)			Recovery (%)		
	TP	IP	TOP	TP	IP	TOP
HLH1 (n=3)	498.01	427.38	70.63	104.55	104.93	102.39
HLH2 (n=3)	707.39	536.54	170.86	100.93	99.86	104.23
HLH3 (n=3)	654.63	501.11	153.51	98.80	98.89	98.71
HLH5 (n=5)	738.72	549.54	189.18	101.85	100.34	103.36
HLH6 (n=3)	701.66	534.25	167.41	101.80	101.73	102.02
HLH7 (n=3)	821.87	603.24	218.63	96.35	96.44	96.28
HLH9 (n=3)	709.49	531.19	178.31	100.71	100.92	100.34
HLH10 (n=3)	698.37	490.17	208.20	102.89	103.83	101.16
HLH11 (n=3)	823.55	676.27	147.27	99.99	99.93	100.65
HLH12 (n=3)	390.86	312.00	78.86	99.69	99.86	99.71
HLH13 (n=3)	324.84	244.57	80.27	100.19	99.97	100.88
HLH14 (n=5)	563.35	447.28	116.07	97.85	97.39	98.31
HLH15 (n=3)	643.53	525.61	117.93	98.71	98.55	99.45
HLH16 (n=3)	705.83	548.08	157.75	100.43	100.24	101.30
HLH17 (n=3)	750.67	605.17	145.51	96.00	95.53	97.86
HLH19 (n=3)	853.36	645.09	208.27	97.85	98.59	95.82
HLH20 (n=3)	758.25	585.55	172.71	99.74	100.32	98.21
HLH21 (n=5)	703.52	511.17	192.34	97.46	98.82	96.09
HLH22 (n=3)	690.89	535.57	155.32	99.35	99.82	98.39
HLH23 (n=3)	756.61	626.66	129.95	95.16	94.11	100.53
HLH24 (n=3)	440.88	344.05	96.84	98.15	97.96	98.85
HLH25 (n=5)	711.20	609.76	101.44	100.96	100.04	101.88
HLH26 (n=3)	770.53	621.77	148.76	97.43	97.35	98.32
HLH27 (n=5)	832.35	628.78	203.57	98.16	95.76	100.55
HLH28 (n=3)	677.36	525.05	152.31	103.94	103.16	106.67
HLH29 (n=3)	788.12	612.75	175.37	92.58	92.26	93.77
HLH31 (n=3)	404.91	299.13	105.78	100.90	101.14	100.68
HLH32 (n=3)	362.85	230.40	132.46	92.37	90.33	95.80
HLH33 (n=3)	377.69	288.58	89.11	104.83	104.16	107.20

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Table S2 Concentration and recovery of TP, IP and TOP in sediment core

Depth(cm)	Concentrations (mg/kg)			Recovery (%)		
	TP	IP	TOP	TP	IP	TOP
0-2	611.43	350.54	260.89	94.23	94.69	93.62
2-4	628.14	381.08	247.07	91.74	90.87	93.07
4-6	598.19	379.31	218.87	90.37	89.53	91.83
6-8	610.60	374.27	236.33	92.35	93.03	91.29
8-10	570.16	364.50	205.66	101.45	96.24	110.70
10-12	599.82	323.16	276.66	99.26	101.45	96.70
12-14	590.12	345.14	244.97	101.80	97.54	107.79
14-16	605.68	348.01	257.67	97.82	100.37	94.37
16-18	550.18	326.81	223.37	94.28	97.04	90.25
18-20	546.16	346.36	199.80	105.37	107.21	102.18
20-22	598.26	397.57	200.69	98.30	97.76	99.38
22-24	574.14	397.45	176.70	98.99	93.68	110.93
24-26	480.41	331.31	149.11	105.15	103.91	107.92
26-28	451.51	310.03	141.48	96.56	99.24	90.69
28-30	550.10	363.41	186.69	108.97	108.14	110.58
30-32	582.50	390.93	191.56	100.35	97.00	107.20
32-34	581.40	382.74	198.66	101.21	98.37	106.68
34-36	582.22	397.84	184.37	96.46	97.39	94.46
36-38	617.99	384.15	233.84	97.19	100.12	92.39
38-40	649.47	429.90	219.57	96.26	97.03	94.75
40-42	676.63	421.68	254.95	93.91	95.76	90.87
42-44	549.31	360.09	189.23	107.91	108.03	107.67
44-46	685.81	428.54	257.28	92.76	91.85	94.27
46-48	531.07	349.47	181.60	106.92	105.42	109.82
48-50	520.61	322.21	198.40	109.49	109.89	108.85
50-52	621.80	405.63	216.18	96.87	90.13	109.51
52-54	657.88	402.73	255.15	93.61	91.96	96.23
54-56	625.61	388.55	237.05	97.15	93.91	102.45
56-58	566.48	348.41	218.07	101.74	97.46	108.57
59-60	562.44	364.09	198.35	100.69	98.37	104.94
60-62	464.83	348.88	115.95	103.99	105.99	97.95
62-64	517.99	395.19	122.80	92.72	93.02	91.76
64-66	502.13	386.75	115.38	97.76	96.34	102.53
66-68	531.80	392.23	139.57	93.68	91.74	99.14
68-70	576.63	416.84	159.80	90.88	90.79	91.12
70-72	542.90	409.24	133.66	93.18	93.42	92.45
72-74	560.58	415.83	144.75	95.37	95.90	93.86
74-76	531.04	405.32	125.71	95.76	96.05	94.81
76-78	521.06	395.19	125.87	100.32	99.95	101.47
78-80	549.10	412.12	136.98	101.16	100.69	102.56

Furthermore, surface sediments samples from 5 sites (HLH5, HLH14, HLH21, HLH25, HLH27) were selected, capturing the span in levels of different OP fractions, to check the precision of the laboratory methods. Average values and standard deviation (SD) from the analysis of 5 replicate samples for TOP, and for the five fractions determined directly by the OP fractionation procedures are given in Table S3. TOP is determined as the differences between the TP and TIP, which are both relatively large values compared to the OP. Thus the precision in the TOP data was expected to be especially poor, though the average relative standard deviation (RSD) turned out to be 3.3%. This is within the range achieved for the other OP fractions (2.3-4.8%).

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73 **Table S3 Concentration of OP fractions in sediment from HLH (average \pm SD) (mg/kg)**

	LOP	HCl-OP	FAOP	HAOP	ReOP	TOP
HLH5 (n=5)	1.88 \pm 0.05	40.01 \pm 1.23	48.19 \pm 2.20	10.37 \pm 0.54	94.42 \pm 2.75	194.86 \pm 6.31
HLH14 (n=5)	5.00 \pm 0.20	13.28 \pm 0.43	18.98 \pm 0.88	5.71 \pm 0.18	69.92 \pm 2.07	112.89 \pm 3.32
HLH21 (n=5)	11.30 \pm 0.21	15.43 \pm 0.63	40.36 \pm 2.50	18.16 \pm 0.68	98.55 \pm 3.09	183.79 \pm 6.78
HLH25 (n=5)	2.19 \pm 0.03	24.85 \pm 0.76	22.17 \pm 0.66	12.20 \pm 0.49	41.87 \pm 1.60	103.23 \pm 2.90
HLH27 (n=5)	19.03 \pm 0.29	7.02 \pm 0.18	75.50 \pm 4.20	10.46 \pm 0.46	90.92 \pm 3.14	202.93 \pm 8.04

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75 All analytical results are expressed as their average value of three sample replicate
76 measurements. The data were subjected to standard analysis of variance appropriate to a
77 factorial randomized block design. Wherever appropriate, the treatment average were
78 compared at 5% level of significance using least significant difference. The SD's for each OP
79 fraction are given in Table S4. The precision and accuracy of the fractionation procedure have
80 also been described in preceding studies.^{1,4}

81 As can be seen from Table S1-S4, the recovery and SD suggest that OP determination in
82 sediments was satisfactorily extracted with this procedure and the results were relatively
83 accurate for OP concentrations in lake sediments.

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Table S4 Standard derivation of different OP fractions in the sediments (mg/kg)

	LOP	HCl-OP	FAOP	HAOP	ReOP
HLH1 (n=3)	0.12	0.47	0.18	0.36	2.28
HLH2 (n=3)	0.07	2.38	1.72	1.15	2.87
HLH3 (n=3)	0.17	0.74	2.11	0.83	3.11
HLH5 (n=5)	0.05	1.23	2.20	0.54	2.75
HLH6 (n=3)	0.13	0.44	2.19	0.96	4.21
HLH7 (n=3)	0.30	0.99	2.43	0.62	5.42
HLH9 (n=3)	0.15	0.85	1.94	0.96	4.39
HLH10 (n=3)	0.14	1.38	1.90	0.99	5.39
HLH11 (n=3)	0.04	2.47	1.26	0.43	2.61
HLH12 (n=3)	0.08	0.65	0.33	0.06	2.56
HLH13 (n=3)	0.04	0.75	0.23	0.29	2.49
HLH14 (n=5)	0.20	0.43	0.88	0.18	2.07
HLH15 (n=3)	0.05	0.35	1.74	0.61	2.64
HLH16 (n=3)	0.14	0.75	1.88	0.77	3.86
HLH17 (n=3)	0.07	0.27	2.26	0.91	3.06
HLH19 (n=3)	0.37	0.74	2.66	0.62	4.80
HLH20 (n=3)	0.19	1.95	2.02	0.47	3.15
HLH21 (n=5)	0.21	0.63	2.50	0.68	3.09
HLH22 (n=3)	0.33	0.27	1.93	1.14	3.38
HLH23 (n=3)	0.29	1.66	0.87	0.31	2.88
HLH24 (n=3)	0.06	0.66	0.42	0.10	3.28
HLH25 (n=5)	0.03	0.76	0.66	0.49	1.60
HLH26 (n=3)	0.20	2.38	1.21	0.52	2.41
HLH27(n=5)	0.29	0.18	4.20	0.46	3.14
HLH28 (n=3)	0.31	0.11	1.99	0.64	4.52
HLH29 (n=3)	0.27	1.12	2.65	0.88	2.57
HLH31 (n=3)	0.02	0.55	0.35	0.18	3.92
HLH32 (n=3)	0.16	2.08	0.28	0.12	3.26
HLH33 (n=3)	0.36	0.77	0.43	0.10	2.81

94 **S1.2 Other Experiments and methods**

95 Total inorganic carbonate (TIC) in the sediments was measured by volumetric titration
 96 with HCl (1:4, v/v). Organic oxidation by dichromate was applied to measure OM content in
 97 the sediments,^{5,6} and TOC was derived by dividing the OM content by 1.724. Allo-OC was
 98 estimated using a binary model which has previously been successfully applied in Lake
 99 Daihai in Inner Mongolia plateau.⁷ Total nitrogen in the sediments was analyzed by Kjeldahl
 100 method using a BÜCHI B-324 distillation unit. The concentrations of Fe, Al, Ca, Mg, Sr and
 101 Ba in sediments were determined using atomic absorption spectrometer (Perkin Elmer,
 102 AA800). Previous studies had established the depth-age relationship for the core of HL06,
 103 using fallout radionuclide ²¹⁰Pb and ¹³⁷Cs method,⁸ which were performed at the State Key

104 Laboratory of Lake Science and Environment at the Nanjing Institute of Geography &
105 Limnology, Chinese Academy of Science.

106 **S2 Results**

107 **S2.1 Regression models**

108 Organic matter in lacustrine sediments includes detrital terrestrial and aquatic organic
109 materials. There are two general sources: organic matter produced in the aquatic system via
110 photosynthesis (autochthonous), and terrestrial organic matter from the catchment basins
111 delivered via tributaries (allochthonous). Typical autochthonous sources of organic matter are
112 phytoplankton, algae, and macrophytes, while typical allochthonous sources of organic
113 matter are plant detritus, soil organic matter and soil humus. The content of Allo-OC in
114 sediments is mainly controlled by the climate and environmental conditions in the catchment
115 basin. The greater the amount of annual precipitation (MAP), the more surface or sub-lateral
116 runoff and thicker and denser vegetation cover is likely to be found. Both factor lead in turn
117 to a high flux of OM from the terrestrial environment into surface waters and thus to a high
118 amount of allochthonous organic carbon (Allo-OC) in the lake sediments⁷. Hence the content
119 of Allo-OC in lacustrine sediments may reflect the water supply rate to the lake. Likewise, its
120 variations within the sedimentary column may correspond to changes in lake level. This
121 relationship is further enhanced by (1) greater input of nutrients when the water discharge is
122 high⁹ and (2) better conservation of organic matter when the lake level is high, favoring
123 anoxic conditions near or above the water-sediment interface.^{10, 11} Accordingly, levels of
124 Allo-OC in sediments are an index of past environment conditions in the watershed, enabling
125 us to reconstruct historical changes in lake levels.^{7, 11, 12}

126 A significant correlation ($p < 0.0099$) was found between Allo-OC and the lake level of
127 Lake Hulun during the last 50 years (Figure S2(a)). Using this regression model the historical
128 changes in lake level of Lake Hulun were reconstructed according to the variations in the
129 Allo-OC pools in the sediment core. Salinity is a key indicator of changes in water balance,
130 which in turn is related to the lake levels:¹³ A significant correlation ($p < 0.0000$) was thus
131 found between salinity and lake level in Lake Hulun over the past 50 years (Figure S2(b)).
132 Historical changes in salinity could thereby be reconstructed using the regression model
133 according to the above modeled historical lake level. The runoff from the lake basin was
134 reconstructed based on the significant correlation found between HCl-OP and runoff during
135 the last 50 years (Figure S2(c)).

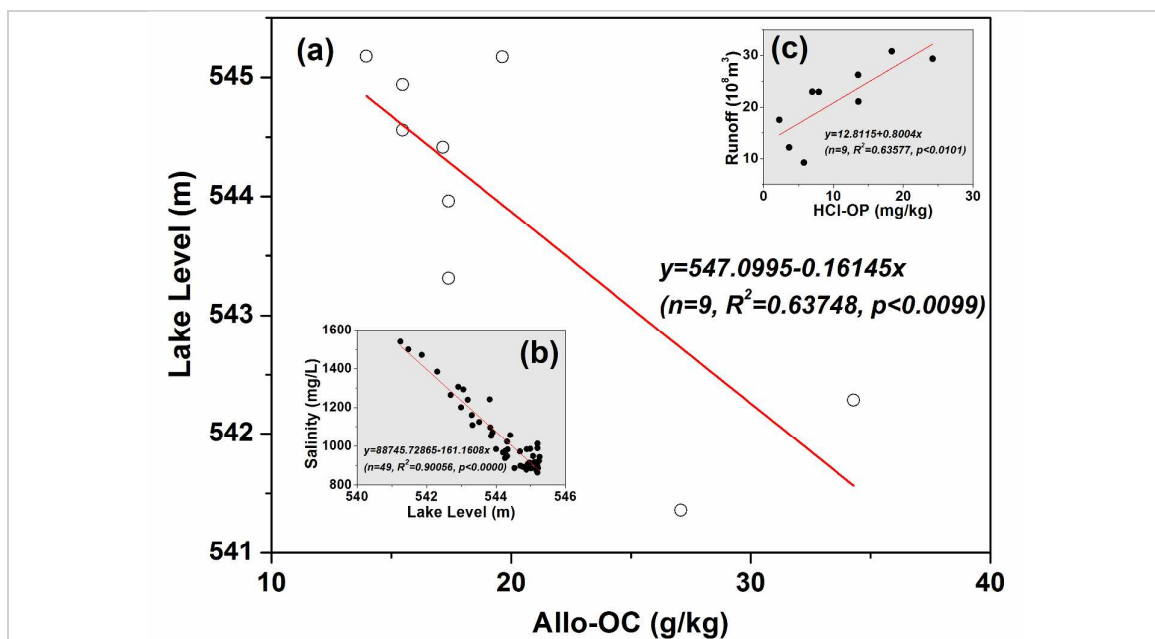


Figure S2 Regression models of (a) Allo-OC and lake level, (b) lake level and salinity, and (c) HCl-OP and runoff

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137 An empirical quadratic function model, linking lake level to lake area, was based on the
 138 large recorded changes in lake surface area during the last 50 years (Figure S3). The axis of
 139 symmetry for the model was $x_{\text{Lake Level}} = 545.75\text{m}$, indicating the maximum lake level of Lake
 140 Hulun. At this lake level the water flow out of Lake Hulun through the Dalanolom River to
 141 the Hailaer River (see Study area) balances the inflow of water from its watershed.

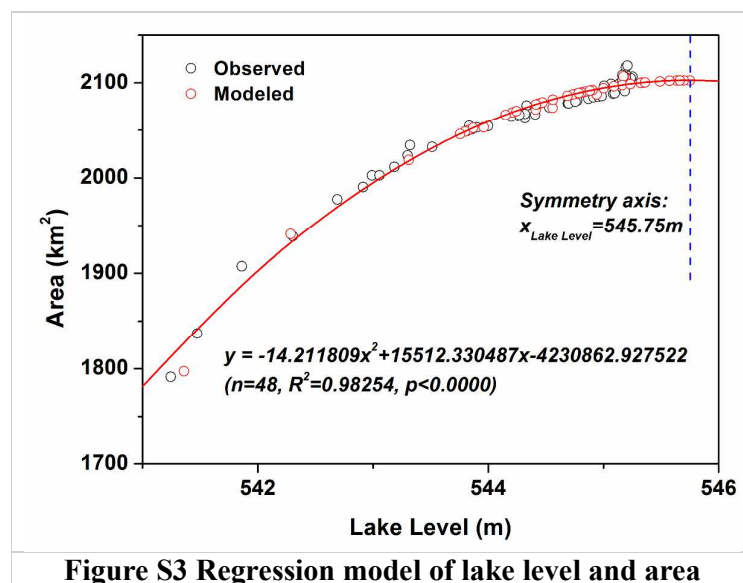


Figure S3 Regression model of lake level and area

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143 S2.2 Redundancy analysis

144 Redundancy analysis (RDA), which is a constraint ordination technique, was applied to

145 understand the relationships between the OP fractions and environmental data. RDA is a
146 linear direct gradient analysis that uses responsive variables (species) and explanatory
147 variables (environmental parameter) in a single integrated analysis. The concentrations and
148 distribution of OP pools in surface sediments from the 13 selected lakes listed in Table S1
149 were used as response variables. The geographical latitude (N), the mean annual temperature
150 (MAT) and the mean annual precipitation (MAP) of the lakes, along with the OM
151 concentration in surface sediments as well as the pH and the total salinity (TS) in overlying
152 water were used as the explanatory parameters. Before the RDA, we tested whether the
153 dataset was based on a linear or unimodal ordination model. Detrended constrained canonical
154 analysis (DCCA) generated a length value for the longest gradient below 3, suggesting it was
155 suitable for linear direct gradient analysis.¹⁴ The forward selection function combined with
156 Monte Carlo permutation tests was used to find the significant environmental parameters
157 ($p < 0.05$) to explain the variation in the two datasets.

158 To interpret the correlations between one of the OP fractions and one of the
159 environmental parameters, Figure 2(a) may be read by projecting the arrow tips of the OP
160 fraction perpendicular to the extended arrow of the environmental parameter (e.g. OM, Lat,
161 MAP). The nearer the projection lies in the direction of the environmental parameter arrow,
162 the higher the correlation. No correlation exists when the projection lies close to the origin of
163 the ordination plot. Projections with opposite directions reveal negative correlations, with
164 increasing strength with increasing parameter loading along the axis.

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166 **S2.3 OP pools in surface sediments**

167 OP levels in surface sediments from Lake Hulun and the other 12 studied lakes were listed in
168 Table S5. As can be seen from Table S5, the concentration ranges of total extracted OP (TOP)
169 were 72.2-210 mg/kg with the means of 146 mg/kg in surface sediments from HLH. The
170 ranges of MLOP and NLOP were 14.7-92.6 and 54.0-133 mg/kg in surface sediments from
171 HLH with the relative contribution of 19-57% and 42-80% to TOP, respectively. The average
172 concentration of LOP found in surface sediments from HLH was 4.54 mg/kg with the
173 average percentages of 3.0%.

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Table S5 OP pools in surface sediments from Lake Hulun and other lakes in China

Lakes		LOP		MLOP				NLOP				MLOP		NLOP		Total Extracted OP mg/kg	TOP Recovery %
				HCl-OP		FAOP		HAOP		Re-OP							
		mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%						
Hulun (n=29)	Min	0.55	0.52	2.34	1.44	4.14	5.12	1.33	1.70	41.87	32.36	14.67	19.26	54.07	41.55	72.15	93.77-107.20
	Max	19.03	9.38	54.86	37.03	75.50	37.27	24.60	16.00	112.16	76.67	92.59	56.70	132.65	80.22	210.42	
	Mean	4.54	3.04	22.49	15.97	34.90	22.05	12.28	8.10	72.05	50.83	57.39	38.03	84.33	58.94	146.26	
Qilu	QL1	16.64	4.80	43.54	12.56	21.34	6.16	12.63	3.64	252.53	72.84	64.88	18.71	265.16	76.49	346.68	100.33-109.31
	QL3	9.01	2.54	48.66	13.74	21.24	6.00	7.50	2.12	267.68	75.60	69.90	19.74	275.18	77.71	354.09	
	QL5	8.28	2.80	51.99	17.59	13.58	4.60	9.52	3.22	212.12	71.79	65.57	22.19	221.64	75.01	295.49	
Erhai		8.70	3.76	15.30	6.61	57.20	24.73	17.80	7.70	132.30	57.20	72.50	31.34	150.10	64.89	231.30	98.9
Hongfeng		18.30	5.96	52.30	17.02	44.00	14.32	28.50	9.27	164.20	53.43	96.30	31.34	192.70	62.71	307.30	101.1
Chenghai	CH3	2.02	1.44	15.66	11.20	48.87	34.94	16.39	11.72	56.93	40.70	64.53	46.14	73.32	52.42	139.87	100.91-105.03
	CH5	3.03	2.01	12.63	8.37	44.68	29.61	32.63	21.63	57.92	38.39	57.31	37.98	90.55	60.01	150.89	
Baihua		17.50	4.27	123.40	30.14	47.30	11.55	35.50	8.67	185.70	45.36	170.70	41.70	221.20	54.03	409.40	96.7
Lugu	L2	34.76	8.85	47.60	12.11	11.84	3.01	58.67	14.93	240.10	61.10	59.44	15.13	298.77	76.03	392.97	84.71-100.36
	L8	43.16	11.43	57.12	15.12	42.61	11.28	35.51	9.40	199.26	52.76	99.73	26.41	234.77	62.16	377.66	
Taihu	Gonghu bay	8.60	5.97	41.10	28.54	27.00	18.75	23.90	16.60	43.40	30.14	68.10	47.29	67.30	46.74	144.00	99.5
	Meiliang bay	11.00	5.63	63.90	32.69	29.60	15.14	21.30	10.90	69.70	35.65	93.50	47.83	91.00	46.55	195.50	100.3
	Yuantouzhu bay	9.30	6.02	42.60	27.55	30.50	19.73	26.00	16.82	46.20	29.88	73.10	47.28	72.20	46.70	154.60	94.3
Chaohu	C1	16.18	7.96	41.75	20.54	47.01	23.13	13.22	6.50	85.10	41.87	88.76	43.67	98.32	48.37	203.26	97.89-99.01
	C14	13.83	8.70	65.21	41.03	17.40	10.95	16.39	10.31	46.12	29.02	82.61	51.97	62.51	39.33	158.95	
Qinghai	Q4	4.87	2.80	24.72	14.22	24.15	13.89	48.33	27.80	71.78	41.29	48.87	28.11	120.11	69.09	173.85	94.48-99.56
	Q7	11.20	6.08	17.22	9.35	18.94	10.28	52.65	28.59	84.16	45.70	36.16	19.63	136.81	74.28	184.17	
Wuliangsuhai		2.53	1.94	28.27	21.72	29.72	22.84	12.42	9.54	57.21	43.95	58.00	44.56	69.63	53.50	130.16	92.83-105.51
Jingpo		5.50	2.27	98.00	40.45	60.00	24.77	37.50	15.48	41.25	17.03	158.00	65.22	78.75	32.51	242.25	104.27
Wudalianchi		43.00	9.93	155.50	35.91	100.00	23.09	20.75	4.79	113.75	26.27	255.50	59.01	134.50	31.06	433.00	97.43

Data sources: Data of OP fractions in Lake Qilu, Chenghai, Lugu, Chaohu, Qinghai, Wudalianchi and Jingpo from Hou et al,⁴ OP fractions in Lake Erhai, Hongfeng, Baihua and Taihu (bays of Gonghu, Meiliang and Yuantouzhu) from Zhang et al,¹ OP fractions in Lake Hulun and Wuliangsuhai were determined in this work.

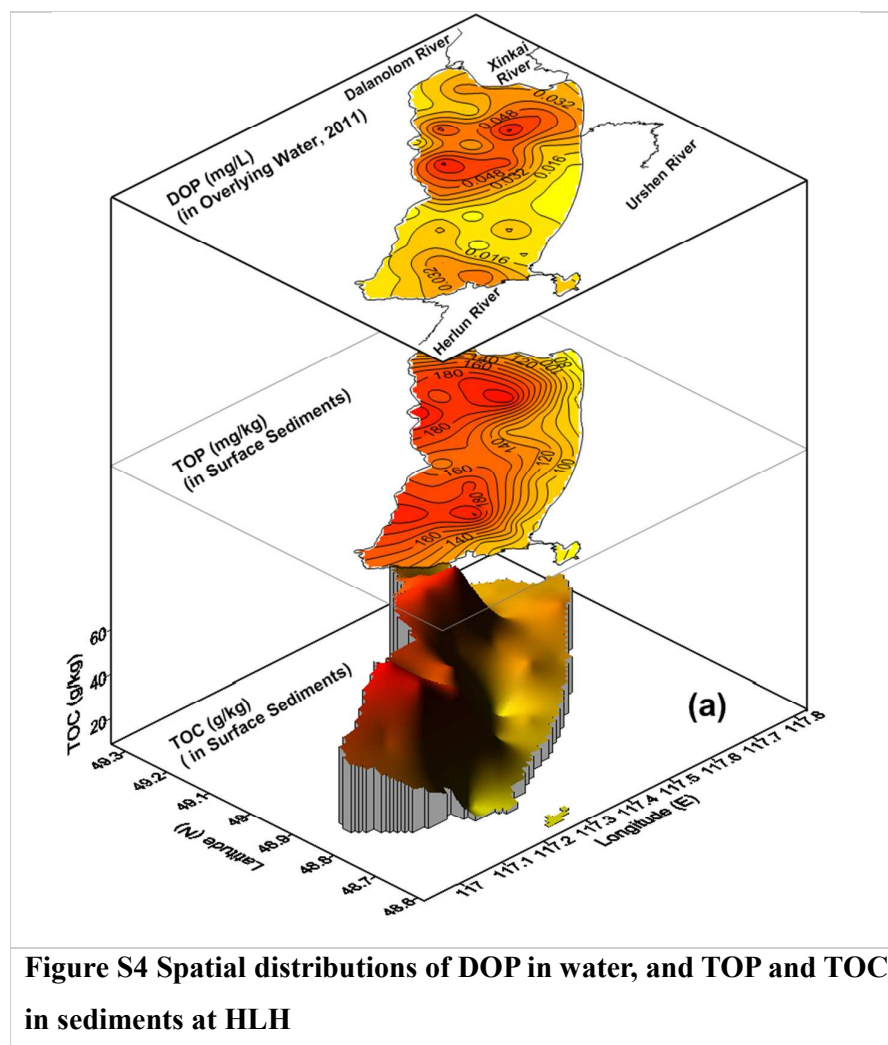
S3 Discussion

3.1 Spatial distribution of OP

The spatial distribution of TOC and TOP in the HLH surface sediments showed clear decreasing trends from the west to the east lake districts (Figure S4). Geomorphologically, the relatively hilly terrains protected by only a semi-arid grassland with less than 40% vegetation cover on the west bank of HLH allow for enhanced soil erosion during rainy season. As a result, a large import of suspended matter, associated OM and nutrients from the HLH west bank are anticipated. This loading of eroded organic matter and nutrients, transported during periods of overland flow, is believed to be one of the main nutrient sources of HLH. Furthermore, the prevailing wind direction is from the 150 km long northwestern shore line to the southeast. The amounts of loess and dry grass deposited into HLH are estimated to be 6.44×10^4 t and 3350 t each year. Previous studies have documented that silty clay is the dominating particle size found in the sediments on the northwest lake bottom, while it is mainly sandy deposit on the south and east lake bottom.¹⁵ Therefore, on the one hand, there are more inputs of loess and dry grass driven by the prevailing wind in the west lake districts; on the other hand, the inputs will be conserved effectively due to the finer grain size in these lake districts. The decreasing trends of TOC and TOP from west to east in the surface sediments from HLH is thus likely due to the combined effect of larger influx of eroded soil material and loess along with dry grass in the west than in the east.

Actually, dissolved OP (DOP) constitutes a major fraction of dissolved phosphorus in surface waters, comprising up to 75% of total dissolved P (TDP).¹⁶⁻¹⁸ This fraction is believed to represent an important potential reservoir for the more bioavailable inorganic phosphorous. Over the past decades, DOP has therefore been increasingly recognized as a critical driver for aquatic biological production and thus ecosystem structure and function.^{19, 20} DOP in water above the sediment in HLH accounted for as much as 24-54% of TDP, implying that this fraction may play an major role as a potential P source for the primary producers.^{21, 22} The level of P levels in water column is mainly governed by the balance between allochthonous P inputs from the watershed and internal loading from the sediments on the one side and assimilation followed by sedimentation and adsorption across the interface of water-sediments, as well as runoff on the other. The spatial distribution pattern of DOP differs from the TOC and TOP (Figure S4). The highest DOP levels were found in areas close to the lake inlets, suggesting that the main sources of DOP to the lake is allochthonous, through the main tributary streams, rather than internal cycling from the sediments. Also the midwestern

214 part of the lake had elevated levels of DOP. DOP in aquatic environments may come from the
 215 secretions and excretions of living bacteria, plants, and animals or from the decomposition of
 216 dead organisms.²³ The elevated DOP levels in the Midwest can thus be explained by the
 217 measured higher biomass levels of phytoplankton in this part of the lake than in the
 218 southeast.²⁴ Therefore, both terrestrial inputs and biological factors are found to jointly
 219 govern the distribution pattern of DOP in overlying water from HLH.
 220



221

222 3.2 Impacts of Fe, Al and Ca

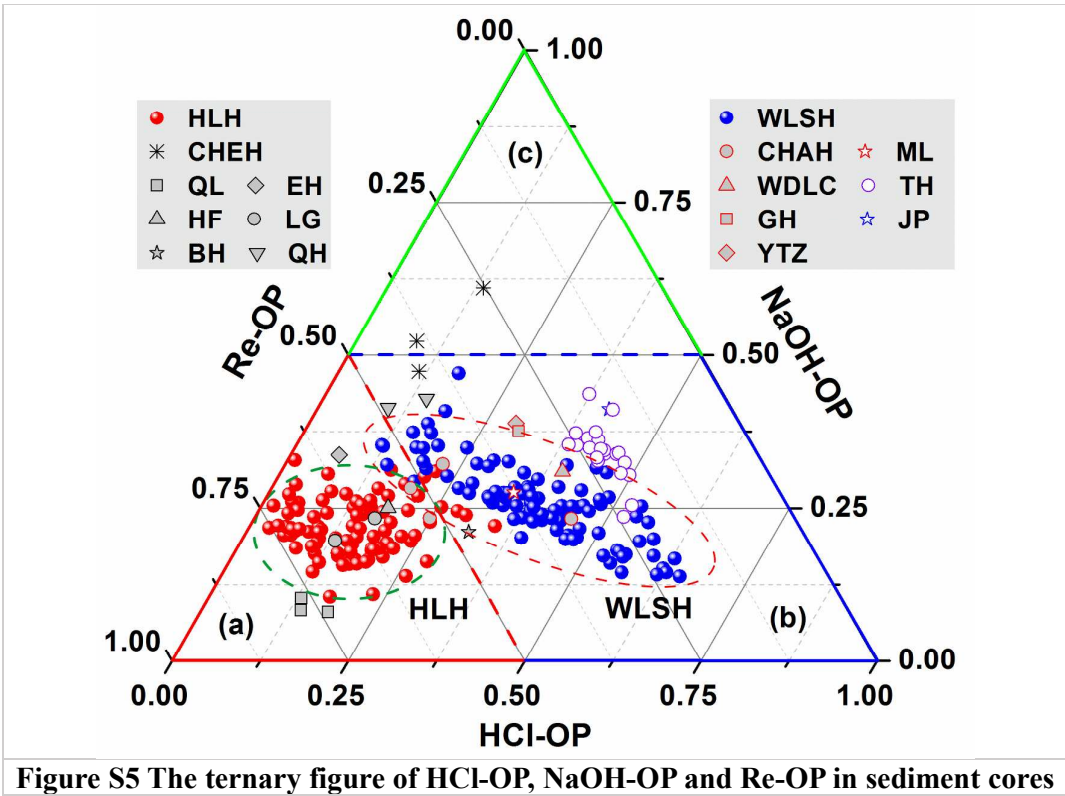
223 P extracted by 1.0 M HCl includes P bound to oxides/hydroxides of Fe and Al.^{25, 26}
 224 Accordingly, acid extractable OP (HCl-OP) are derived principally from the adsorption of OP
 225 to Fe/Al oxides and hydroxides or from the formation of OP salts co-precipitated with
 226 calcium ions.²⁷ Ferric oxide can strongly adsorb OP on their surfaces in soils²⁸ and
 227 sediments,²⁹ even can play a governing role in most acidic soils and sediments. According to

our previous work, the average concentrations of Fe-P and Al-P were 1.54 and 2.04 mg/kg in sediment cores from HLH, respectively; while the pools of Fe-P and Al-P were much higher in the sediments from Lake WLSH, i.e. 11.10 and 7.15 mg/kg, respectively.³⁰ Therefore, both Fe-P and Al-P significantly correlated with HCl-OP and MLOP in the WLSH sediment cores, respectively; while no significant correlations were found in HLH. It suggested that Fe and Al oxyhydroxides play a more important role in OP accumulation and fractionation in Lake WLSH than in Lake Hulun³⁰ due to that the amount of iron oxide in the substrate governs the extent of OP adsorption.^{31, 32}

Calcium (Ca) is usually more abundant than Fe and Al in aquatic environment. This is why P extracted by HCl in sediments is mainly found to be bound to Ca (mainly apatite).^{25, 26} P bound to Ca is fractionated to ACa-P (authigenic carbonate fluorapatite + biogenic apatite + CaCO₃-associated P) and De-P (detrital apatite P).³³ Calcium ions and its minerals can also complex with OP in soils or sediments^{34, 35} For instance, precipitation of calcium salts with calcite occurs at even very low concentrations of *myo*-inositol hexakisphosphate³⁶ due to the simultaneous occurrence of adsorption and precipitation of insoluble calcium-phytate.³⁷ This may explain why the OP content is positively correlated to the calcium content.³⁴ As can be seen from Figure S5, the samples from WLSH and HLH were clustered in each their groups. Almost all of the points of Re-OP and HCl-OP in HLH sediment cores were found in the ranges of 50-70% and ~25%, respectively. As for HLH, Re-OP and HCl-OP in the ranges of 20-50% and 12-60%, respectively.³⁰ Furthermore, as well as HLH, the points of QL (Lake Qilu),⁴ EH (Lake Erhai),¹ HF (Lake Hongfeng)¹ and LG (Lake Lugu)⁴ presented in Area (a) (Figure S5). Comparatively, most lakes in Southwestern China Plateau were far away from local cities, where weathering and erosion were the main processes in the carbonate watershed.³⁸ It indicated that calcium ions and their minerals played a key role in regulating OP fractionations in these lakes due to co-precipitation with calcite.^{30, 39}

As can be seen from Figure S5, as well as WLSH, the points standing for Lake Chaohu (CHAH),⁴⁰⁻⁴² Lake Gonghu (GH),⁴³ Lake Taihu (TH),^{40, 42} Lake Meiliang (ML),⁴³ Lake Yuantouzhu (YTZ),^{44, 45} Lake Jingpo (JP) and Lake Wudalianchi (WDLC)⁴⁶ distributed in Area (b) (Figure S5). These lakes including WLSH shared the same characteristics that excess nutrients, especially P, were input by wastewater discharge and agricultural runoff from the neighboring cities, which subsequently enhanced the association and adsorption of P on Fe/Al oxyhydroxides.⁴⁰ Previous publications showed that the fraction of P bound to Al and Fe oxyhydroxides was a major fraction, even the dominant fraction, in sediments from CHAH,⁴⁰⁻⁴² GH,⁴³ TH,^{40, 42-45} JP and WDLC.⁴⁶ In light of the OP extraction scheme, HCl-OP

262 includes OP fractions adsorbed to Fe and Al oxyhydroxides or OP salts co-precipitated with
 263 calcium ions. As a result of the mentioned above, it suggested that OP fractionations were
 264 jointly regulated by Ca, Fe and Al and their minerals in sediments (Figure S5).³⁰



265 **Figure S5 The ternary figure of HCl-OP, NaOH-OP and Re-OP in sediment cores**

266 The vertical distribution of TP and TOC in the core of HLH15 is shown in Figure S6.

267 Significant correlations between TOP and TP were found both in the surface sediments and in

268 the sediment core from Lake Hulun (Figure S7). Mean annual temperature (MAT) and ratios

269 of E/P (evaporation/precipitation) and their trends in the Lake Hulun basin from 1960's till

270 present are depicted in Figure S8.

271

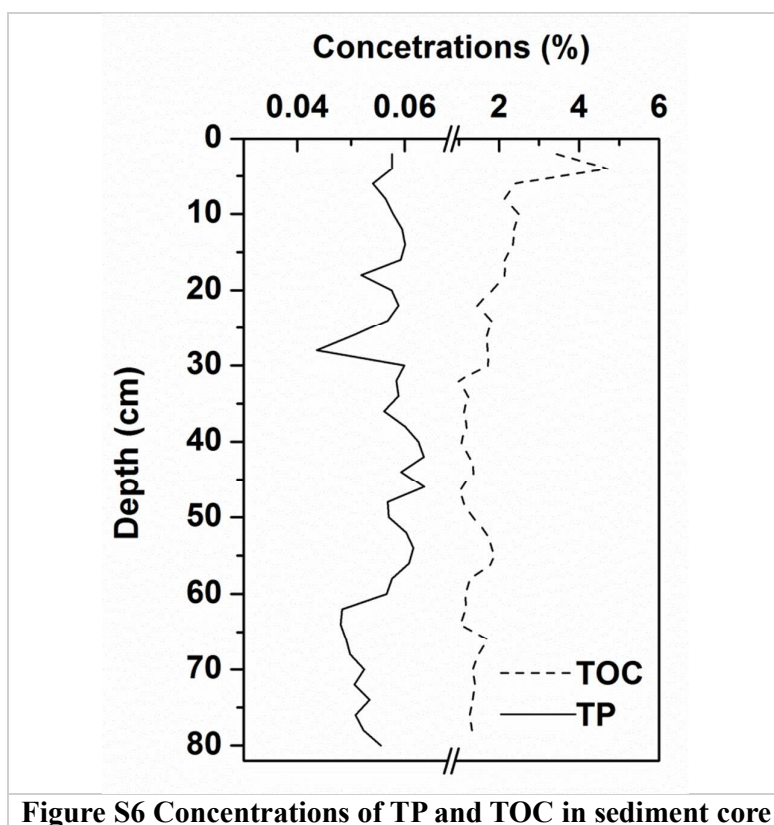


Figure S6 Concentrations of TP and TOC in sediment core

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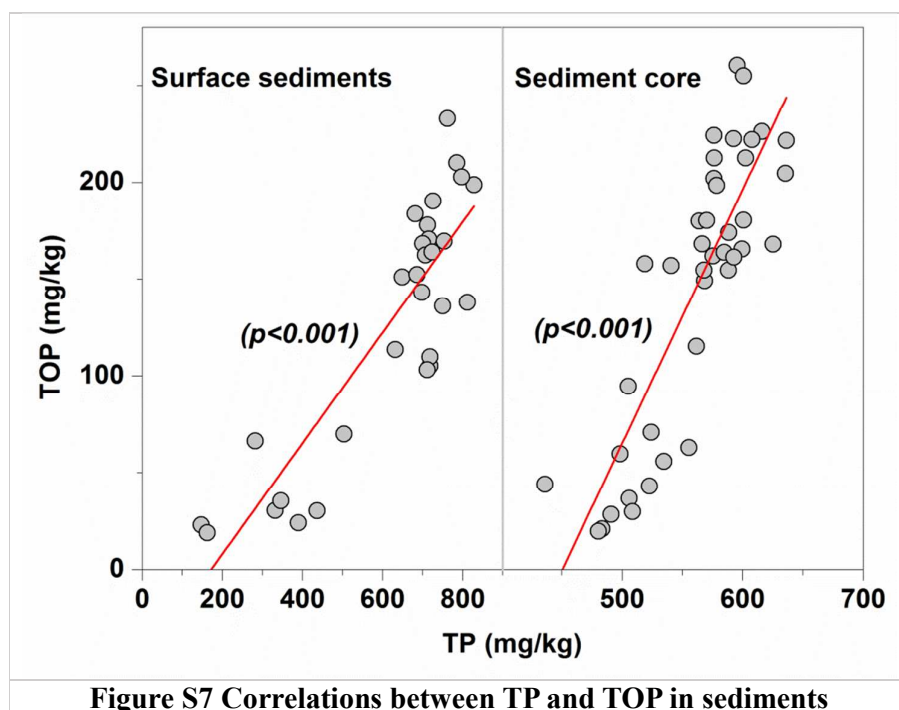


Figure S7 Correlations between TP and TOP in sediments

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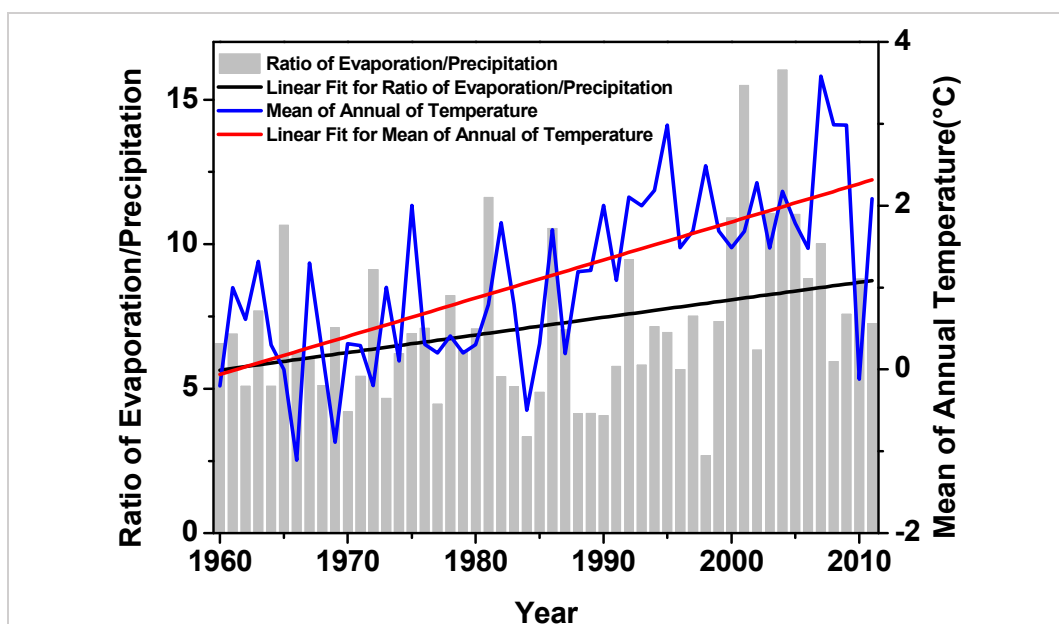


Figure S8 Changes of MAT and E/P ratio in the basin of Lake Hulun from 1960's

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