

Distribution and ecotoxicological significance of trace element contamination in a ~150 yr record of sediments in Lake Chaohu, Eastern China

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This paper presents the concentrations, vertical profiles and possible sources of selected major and trace elements in a sediment core covering ~150 years of sedimentation in Lake Chaohu, eastern China. Element concentrations were measured by portable X-ray Fluorescence Spectroscopy (XRF) and were used to evaluate possible environmental consequences of the recent industrialization in China. Statistical analyses identify four groups: (1) organic carbon (OC), total nitrogen (TN), Pb, Zn, and As associated with the use of chemical fertilizers and pesticides; (2) Mn, Cr, Ni and Cu from industrial and mining activities; (3) Fe, Rb, K, Co, Ti and Ca influenced by post-depositional processes and land exploitation; and (4) Zr and Sr from the soil. The vertical profiles of elements placed in the first two groups show distinct increases in concentrations above depths of 20 cm (~1978), coincident with the timing of industrialization in China, and the anthropogenic-derived fluxes are higher than the lithogenic-derived fluxes over the last three decades. With the exception of Zr and Sr, association of the measured metals with organic carbon and nitrogen suggests that organic matter may act as a carrier phase. The geoaccumulation index (I_{geo}) reveals increased contamination from elements in the first two groups in recent years. Element concentrations, compared with the Effects Range-Low (ERL) and Effects Range-Median (ERM) levels set by NOAA, suggest that adverse biological effects from Ni contamination are very likely.

1. Introduction

Human activities such as metal mining, smelting, refuse incineration, the burning of fossil fuels and agriculture practices have greatly increased the fluxes of trace metals to the aquatic environment.¹ Sediments are important carriers of trace metals in the hydrological cycle, and aquatic sediments constitute one of the

main sinks for anthropogenic emissions of nutrients, heavy metals and other contaminants, such that lake sediments can provide a valuable archive of the contamination history at a regional scale.^{2,3} Metals enter the terrestrial and aquatic environment by two means: natural processes, including erosion of ore-bearing rocks, wind-blown dust and forest fires; and anthropogenic processes, including atmospheric deposition, entrainment in rivers, and direct discharge and dumping.³ The latter processes have the potential to severely impact the water quality in lakes on a regional scale. To evaluate the contaminant trends and their possible harmful effects on the aquatic ecosystems, historical information on waste types and trends is required.

Significant monitoring of the impacted systems should be developed to provide policy makers with the information

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Environmental impact

Although the history of trace element contamination has been extensively investigated in developed countries, the information is still sparse in China. This paper presents the concentrations, vertical profiles and possible sources of major and trace elements, as well as organic carbon and total nitrogen in a sediment core in Lake Chaohu. Multivariate analyses provide useful information on source contributions, erosion signals, the role of organics in transport of trace elements and the selection of a conservative reference element. The historical variations of trace element concentrations and fluxes show good correlations with the industrialization in China. A pollution assessment shows strong contaminations from arsenic, while a toxicity assessment suggests adverse biological effects are very likely from nickel.

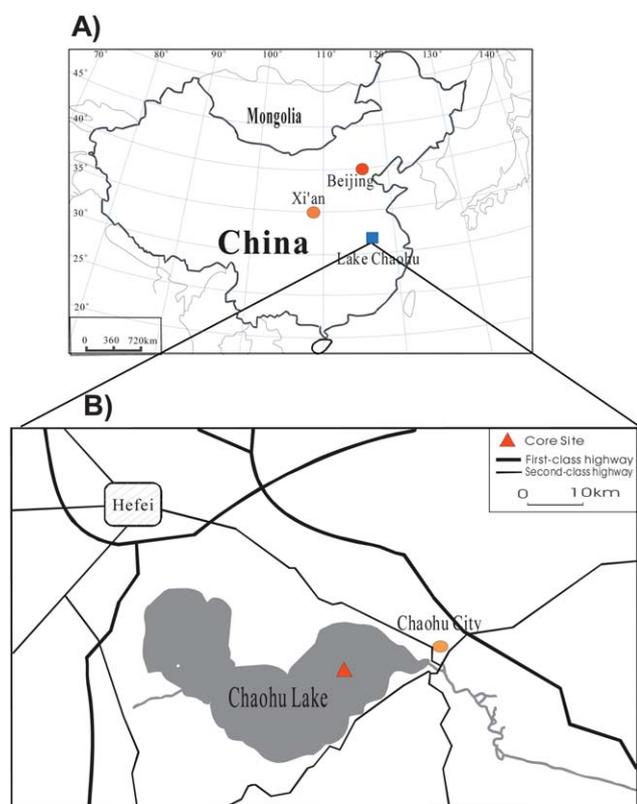


Fig. 1 Locations of A) Lake Chaohu in China and B) sampling site.

necessary to implement effective land management regulation, including for restoration and remediation. The measurement of trace element concentrations in lake sediments not only reflects pollution from atmospheric deposition, but also reveals the past drainage basin or land-use histories.⁴ Carefully dated sediment cores can provide chronologies of contaminant concentrations and a record of the changes in concentrations of chemical indicators in the environment over time. Many studies have clearly shown that lake ecosystems have been contaminated by trace elements from anthropogenic sources for at least the last 200 years in some developed countries.^{2,5–8} Over the last three decades, China has experienced rapid and extensive industrial growth, particularly in the more densely populated eastern areas. This may have resulted in dramatic increases in emissions of pollutants into the atmosphere and, as a consequence, caused an increase in the deposition of these pollutants over wide areas.^{9,10} However, there is relatively sparse information on the contamination history in China,^{11,12} even in eastern China.

Lake Chaohu, the largest lake (756.2 km², see Fig. 1) in the Anhui province, eastern China, is one of the three most

polluted freshwater lakes in China. The lake was well known for its scenic beauty before the 1950s.¹³ However, it is now a hyper-eutrophic freshwater lake. The pronounced ecological changes in this region are due to the substantial discharge of domestic and industrial wastes, along with the rapid and massive changes in industry and shifts in the population and social structure. Following the booming industrial development in the late 1970s, along with increasing population pressures, drainage of industrial and agricultural wastewater into the lake has been increasing.^{14,15} The annual discharge of industrial and domestic wastewater totaled more than 1×10^8 and 0.5×10^8 tons, respectively, and daily discharge of both industrial and domestic wastewater exceeded 5×10^5 tons in 1999.¹⁵ In recent years, large scale algal blooms, dominated by cyanobacteria, occurred throughout most of the year. The deharmonization and deterioration of the lake's ecosystem, the decline in water quality, algal blooms, and the large-scale loss of fish and other aquatic organisms have prompted increased attention to Lake Chaohu and have stimulated efforts for its effective remediation.

The present study was initiated with the following objectives: (1) to reconstruct the pollution history of trace elements and differentiate between natural and anthropogenic inputs; (2) to evaluate the geochemical factors that affect the vertical distribution of trace elements; and (3) to assess the ecological environmental risks posed by the trace elements. These results will aid in directing the environmental management of this region in the future.

2. Materials and method

2.1. Study site

Lake Chaohu (117°16'54"–117°51'46"E, 31°25'28"–31°43'28" N) is among the five most famous freshwater lakes in eastern China, and covers an area of 834 km² with an average water depth of ~3 m. The physical and chemical properties of the modern-day Lake Chaohu are presented in Table 1. The annual average air temperature is ~15–16 °C, and the annual average precipitation is ~1100 mm yr⁻¹. Approximately 33 rivers supply water to the lake, and the amount of sand input is positively related to the precipitation in the drainage area.¹⁴ The major prevailing wind direction is northeasterly in winter and southeasterly in summer. Quaternary clay dominates the recent sediments in the drainage basin, and there are outcrops of Devonian red quartz sandstone and Cretaceous white sandstone along the shore.

2.2. Sampling

A 61 cm long sediment core was taken from the eastern part of Lake Chaohu in the summer of 2006 using a gravity corer

Table 1 Physical and chemical properties of the modern-day Lake Chaohu (after Wang *et al.*¹⁴)

Properties	Values	Properties	Values	Properties	Values
Altitude (m.a.s.l)	23	Mean wind velocity (m s ⁻¹)	4.1	Mineralization (mg L ⁻¹)	72.1
Surface water area (km ²)	834	Annual temperature (°C)	15–16	Total suspended solid (mg L ⁻¹)	40–1000
Catchment area (km ²)	11266	Annual precipitation (mm)	1100	Dissolvable oxygen (mg L ⁻¹)	6.9–12.1
Average depth (m)	3.0	Conductivity (μS cm ⁻¹)	166	Total nitrogen (mg L ⁻¹)	1.68
pH of lake water	7.5–8.2	Total hardness (mg L ⁻¹)	37.2	Total phosphor (mg L ⁻¹)	0.13
Surface run-off (10 ⁸ m ³)	48.5	Total alkalinity (mg L ⁻¹)	56.7	Dissolvable sSolid (mg L ⁻¹)	150

(Fig. 1). Latitude and longitude were determined with a global position system. The core was sectioned at 1.0 cm intervals. The lithology was variable, with gray-yellow silts in the upper 2 cm, dark clay at depths of 3–12 cm, and gray–yellow clay at depths of 13–61 cm. A distinct water–sediment interface and discernible laminations in the core indicated a lack of bioturbation and other post-depositional disturbances of the sediments. The slices were oven dried at 40 °C for approximately 144 h. Samples were partitioned for subsequent analysis of the sediment's chemical and physical properties, and for radioisotope dating.

2.3. Dating

Samples were analyzed for ^{137}Cs , ^{210}Pb and ^{226}Ra by direct gamma counting of 3–6 g of dried sediment using a Canberra HpGe well detector model GCW2022 connected to a multi-channel buffer (Ortec model 919 Spectrum Master; 16,384 channels) and a personal computer running the MAESTRO® multi-channel analyzer emulation software package (Ortec). The activities of ^{137}Cs and ^{210}Pb were determined by monitoring their characteristic emissions at 661 keV and 46.5 keV, respectively. Ra-226 activities were determined from the weighted mean of the daughter nuclides ^{214}Pb at 295 and 352 keV and ^{214}Bi at 609 keV. Corrections to the measured radionuclide counts included background, counting efficiency, geometry, branching ratio, and dry sample mass to obtain activity per dry weight gram. Pb-210 activities were corrected for self-attenuation after Appleby.¹⁶ The excess Pb-210 was calculated by subtracting the Ra-226 from the total ^{210}Pb . Excess ^{210}Pb and ^{137}Cs activities were then decay corrected to the core collection date. Typically, the precision of the measurements was ± 2 –10%, and the background levels were all < 0.05 cpm.

2.4. X-ray fluorescence spectroscopy

Multi-element analysis of the dried sediments, standard reference materials (SRM), and blanks was performed using an Innov-X Alpha series 4000 X-ray fluorescence spectrometer (XRF) (Innov-X Systems, Woburn, MA). SRMs included those from NRCC (BCSS-1 and MESS-1), NIST (2704, 2709, 2710, and 2711) and USGS (MAG-1, SCO-1, SDO-1); blanks consisted of clean SiO_2 powder. Approximately 3 g of the dried sediment and the SRMs selected for dry XRF analysis were packed into sample cups equipped with Mylar polyester supports (Chemplex part Nos. 1330 and 257, respectively). The dry materials were analyzed with the instrument positioned in a sampling test stand supplied by the manufacturer. Analyses were performed using the proprietary soil mode in both the standard protocol and the light element analysis protocol (LEAP), which are included in the manufacturer's software. Fifteen elements (K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Pb, Rb, Sr, and Zr) with uncertainties lower than 10% were used in this study. Additional details regarding calibration and evaluation of instrument performance are published elsewhere.¹⁷ Such a method has also been used in pollution studies by other researchers.^{18–20}

2.5. Total organic carbon (OC) and nitrogen (TN) analysis

OC and TN were determined using a CHNOS elemental analyzer (Vario EL III, German) with acid pretreatment.²¹ Acetanilide

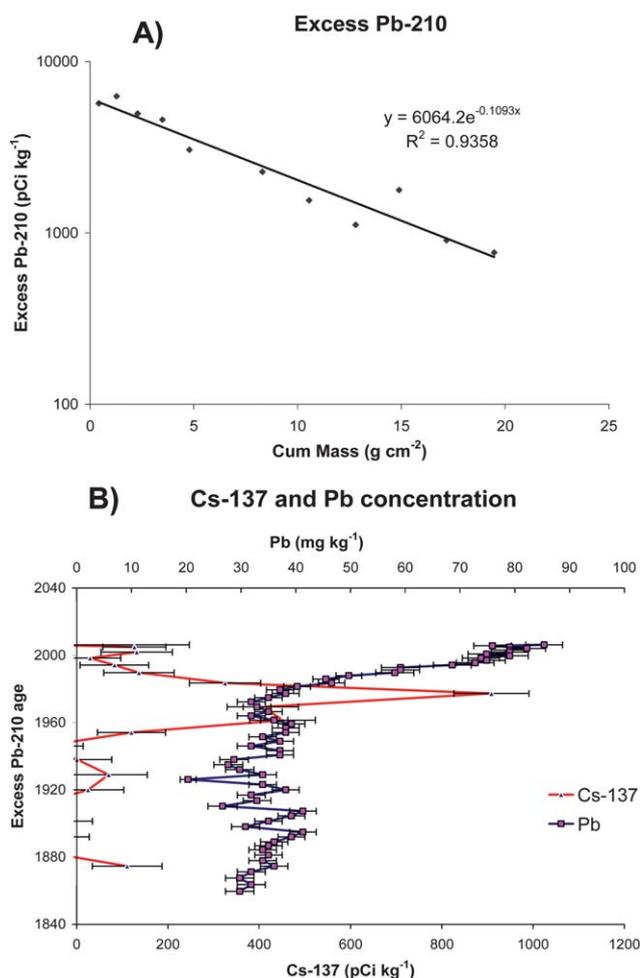


Fig. 2 A) The excess Pb-210 data yield a sediment accumulation rate of $\sim 0.28 \text{ g cm}^{-2} \text{ y}^{-1}$. B) Pb-210 dating is consistent with the initial appearance of Cs-137 and its increase in the 1960s. The Cs-137 max in ~ 1977 could be due to nuclear tests in China, which were ongoing throughout 1980. The Pb profile is also presented to show its increase, beginning in the late 1970s, which is consistent with the timing of industrialization mg kg^{-1} .

standards were performed at the rate of three per group of 20 samples. Duplicates were analyzed at the rate of one per group of 10 samples. The overall analytical precision was estimated as $\pm 3\%$ for OC and $\pm 5\%$ for TN.

2.6. Multivariate analyses

Correlation analysis, principal component analysis (PCA) and cluster analysis (CA) were used in this study. SPSS for Windows, version 11.5 (SPSS Inc, USA) was utilized for the multivariate statistical analysis, and for descriptive analyses.

3. Results and discussion

3.1. Sediment accumulation rates and chronologies

In order to estimate the rate of sediment accumulation, we used the constant flux : constant sedimentation (CFCS) excess Pb-210 model,^{22,23} fitting an exponential curve to the excess ^{210}Pb versus depth in units of cumulative mass (Fig. 2A). Excess ^{210}Pb

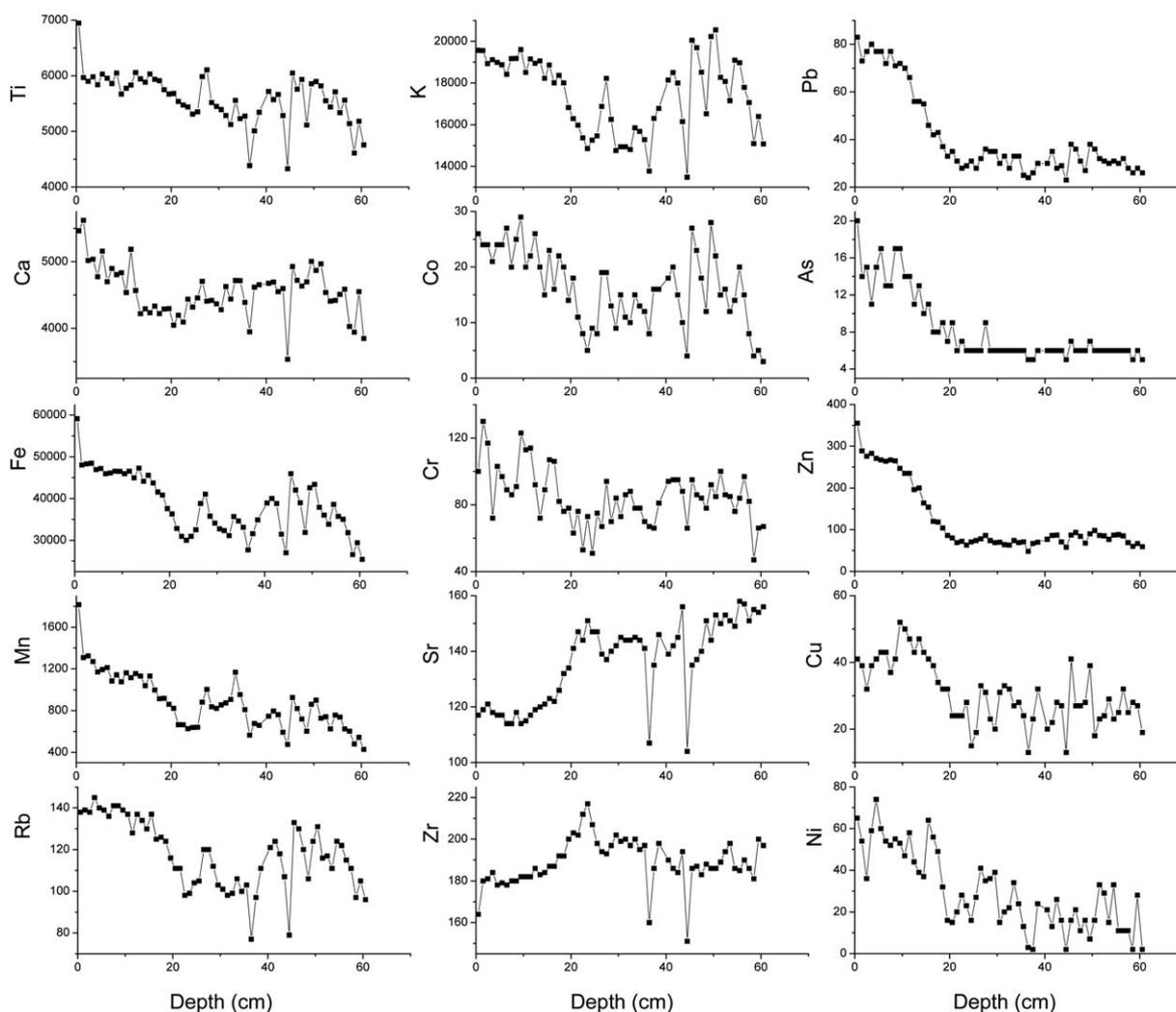


Fig. 3 Vertical profiles of the major and trace elements (mg g^{-1}) in the sediment of Lake Chaohu.

activities ranged between 0 and 8800 pCi/kg. The measured activities exhibited a monotonic decrease in the log of the activity over the length of the down-core record, and model results yielded a sediment accumulation rate (SAR) of $0.28 \text{ g cm}^{-2} \text{ yr}^{-1}$ and a coefficient of determination of 0.93, which we interpret as steady state accumulation and radioactive decay.

Deposition ages obtained from the CFCS ^{210}Pb model are consistent with the timing suggested by ^{137}Cs (Fig. 2B) as an indicator of nuclear related activities and the lead distribution profile features as an indicator of industrial activities. The initial appearance of ^{137}Cs is consistent with the onset of nuclear weapons related activities in the early 1950s and increase in the 1960s. The Cs-137 maximum in ~ 1977 could be due to nuclear tests in China, which were ongoing throughout 1980. Pb concentrations also exhibit an increasing trend starting at the end of the 1970s, which is consistent with the timing of industrialization in China.

3.2. Vertical profiles in elements in the sediment core

Vertical profiles of all the elements are shown in Fig. 3. Descriptive statistics of the heavy metal concentrations are also

presented in Table 2. Of all the elements studied, Fe shows the highest mean concentrations (3.8%), followed by K (1.8%), Ti (0.54%) and Ca (0.48%). The ranges of Cr ($23\text{--}151 \text{ mg kg}^{-1}$), Ni ($3\text{--}70 \text{ mg kg}^{-1}$), Cu ($20\text{--}52 \text{ mg kg}^{-1}$), Pb ($27\text{--}85 \text{ mg kg}^{-1}$), and Zn ($61\text{--}339 \text{ mg kg}^{-1}$) are comparable with those in the Liuchahe watershed¹² and in the estuarine regions of Lake Chaohu,¹¹ the only parts of the region with available data, although the average concentrations of Pb and Zn are a little higher in the centre of the lake. The variation coefficient (VC), which is defined as the standard deviation divided by the mean,²⁴ shows that crustal elements (*e.g.* Zr, Ti, Ca, K, Fe, Rb and Sr) have VCs lower than 0.2, while the others have VCs higher than 0.2, indicating that they probably have different sources from the other elements.

Most of these elements, except Sr and Zr, show an increase at $\sim 20 \text{ cm}$ depth (~ 1978), at which point all elements are divided into two parts (Table 2). The ratios of the mean concentrations in the upper part to the lower part are greatest for Ni, followed by Zn, As and Pb. The vertical profiles separate these elements into three groups, based on the similarities of their trends: (1) Fe, Ca, Ti, Mn, Rb, K, Co and Cr; (2) Sr and Zr; and (3) Pb, As, Zn, Cu and Ni. The first group shows a relatively disordered pattern, but with

Table 2 Descriptive statistics of the elements in the sediment core from Lake Chaohu

Element	Average mg kg ⁻¹	Minimum mg kg ⁻¹	Maximum mg kg ⁻¹	Standard deviation	Variation coefficient ^c	Upper ^a average	Lower ^b average	Upper/Lower
K	17 431	13 482	20 546	1796	0.1	18 768	16 762	1.12
Ca	4550	3534	5619	376	0.08	4724	4463	1.06
Ti	5595	4330	6947	443	0.08	5950	5418	1.1
Cr	84.6	46.9	130.4	16.8	0.2	96.9	78.5	1.23
Mn	875.7	427	1815.6	259.7	0.3	1151	738	1.56
Fe	38 500	25 412	59 135	7063	0.18	46 078	34 711	1.33
Co	16.4	2.7	29.3	6.7	0.41	22	13.6	1.62
Ni	29.6	1.8	74.1	18.8	0.66	50.4	18.8	2.68
Cu	30.7	12.6	52.3	9.4	0.3	40.9	25.7	1.59
Zn	123.2	48.4	354.6	81	0.66	219.8	74.9	2.94
As	8.8	4.8	20.4	3.9	0.47	12.9	6	2.15
Rb	117.8	77.5	144.7	16.2	0.14	134.5	109.5	1.23
Sr	136.1	104.1	158.5	14.9	0.11	119.9	144.2	0.83
Zr	189.2	150.7	217	11.3	0.06	183.1	192.2	0.95
Pb	41.6	22.7	83.1	18.1	0.43	63.2	30.7	2.06
TN ^{0%}	0.095	0.052	0.239	0.049	0.51	0.148	0.068	2.17
OC ^{0%}	0.722	0.419	1.695	0.34	0.47	1.103	0.531	2.08

^a Upper part indicates samples from 0 to 20 cm. ^b lower part indicates samples from 21 to 61 cm. ^c the variation coefficient is defined as the standard deviation divided by the mean.

a clear increasing trend in the last three decades, which may be partly associated with the post-depositional demineralization and diffusion (see Sec. 3.4). The second group, Sr and Zr, is opposite to the elements in the first group, which shows decreasing concentrations from the depth of 22 cm. The last group can be subdivided into two subgroups: (A) Pb, As and Zn; and (B) Cu and Ni. Both subgroups show clear patterns, with the lowest element concentrations at the bottom of the core and the highest concentrations at the surface. In particular for Pb, Zn and As, a marked increase in the concentrations occurs at a depth of 20 cm (~1978), which corresponds to the beginning of the reform and opening in China. Thereafter China experienced a rapid industrialization. The elements in the third group very likely have anthropogenic origins, although post-depositional processes might also contribute to observed concentration profiles.²⁵

3.3. Organic matter records and mass accumulation rates

Historical records of the OC and TN concentrations, as well as OC/TN ratios and OC and TN fluxes are presented in Fig. 4. OC and TN concentrations vary in the ranges of 0.419–1.695% and 0.052–0.239%, respectively, which are comparable with sediment values obtained from lakes in other regions of eastern and southern China.^{26,27} The historical variations of OC and TN concentrations show similar trends, with the lowest concentrations at the bottom and the highest concentrations at the surface. The mineralization of organic C to CO₂ may be a contributor to the up-core increase in OC and TN concentrations.²⁸

The origin of sedimentary organic matter from aquatic sources, as opposed to land sources, can be distinguished by the characteristic C/N ratio.²⁸ Generally algae have a C/N ratio between 4 and 10, whereas terrestrial organic matter such as vascular land plants have a C/N greater than 20.²⁹ The OC and TN are positively correlated, and their regression equation is $OC = (6.95 \times TN) + 0.06$ ($R^2 = 0.995$), which suggests the type of organic matter delivered to the lake sediments has remained predominantly algal in origin.

OC and TN concentrations are bulk values, representing the fraction of organic matter that escaped remineralization during sedimentation, which are influenced by both primary production and subsequent degradation. They integrate the different origins of organic matter, delivery routes, depositional processes, and consequent degrees of preservation.¹⁴ The degradation of organic matter during the early diagenesis can modify elemental compositions and hence the C/N ratios of organic matter. The C/N ratios in this core show a small decrease from 8.8 to 7.1 from the depth of 22 cm to the surface (Fig. 4), which may be associated with the increase in the C/N ratio of algal-derived organic matter during early sedimentation as nitrogen-rich proteins are selectively degraded.²⁸

Similar to their concentrations, the fluxes of OC and TN have increased dramatically over the past three decades. Organic fluxes are diagnostic in the identification of changes in delivery rates of organic matter to lakes. The most refractory parts of organic matter (*i.e.* soot) show similar trends with the OC and TN fluxes,³⁰ which suggests that anthropogenic activities contribute to the increases in OC and TN fluxes from bottom to top. Zhou *et al.*³¹ demonstrated that the values of $\delta^{13}C_{org}$ varied between -21.74‰ and -19.34‰ , decreasing sharply in the top

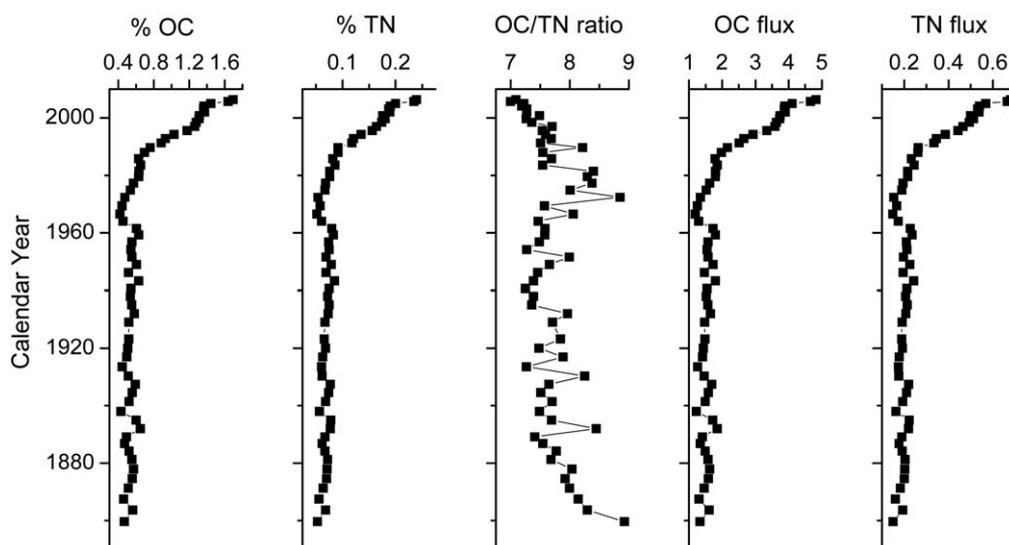


Fig. 4 Historical records of the OC and TN concentrations, as well as OC/TN ratios, and OC and TN fluxes ($\text{mg cm}^{-2} \text{yr}^{-1}$) in sediments of Lake Chaohu, eastern China over the past 150 years.

10 cm, further supporting an algal origin of OC and the intensification of eutrophication in recent years in Lake Chaohu.

3.4. Statistical analyses

Correlation analysis (Table 3) shows that most of the elements studied, except Sr and Zr, are well correlated (generally $P < 0.001$), suggesting that these elements may be controlled by a common factor such as river drainage. It is well established that organic matter contents are important controlling factors in the abundance of trace metals.³² Significant positive correlations of OC (and TN) with most of the elements are also observed, which suggest that the sedimentary organic matter can act as a metal carrier.³ The most noticeable positive correlations between elements are Pb vs. Zn ($r = 0.987$); Zn vs. As ($r = 0.950$) and Pb vs. As ($r = 0.941$). Pb, Zn and As are the three elements which show clear vertical distributions, with lower concentrations at the bottom and higher concentrations at the surface. Zr and Sr are positively correlated with each other, but negatively correlated with other elements, further suggesting their different origins from the other elements.

PCA analysis (Table 4) yields two components, accounting for 79.94% of the total variance. Similar to correlation analysis, all of the elements except Sr and Zr contribute to factor 1, which accounts for 69.31% of the total variance. Factor 2, accounting for 10.63% of the total variance, is dominated by Sr and Zr, which is mainly from soil sources.

Different from the correlation and PCA analyses, which create only two groups, CA analysis using War's method with squared Euclidian distances creates four clusters (Fig. 5): (1) Fe, Rb, K, Co, Ti and Ca; (2) Mn, Ni, Cu and Cr; (3) OC, TN, Pb, Zn, As; and (4) Zr and Sr. This suggests that CA analysis may denote some details of element source appointment.

The first group is dominated by crustal elements. However the vertical profiles of these elements also show an increase in the last three decades, indicating that in addition to increased land exploitation, the metal profiles may also be affected by post-

depositional changes.^{33,34} Elevated concentrations in surface sediments have been well documented in the literature^{33,34} and are thought to be the result of ephemeral surface cycling. Some elements experience changes in oxidation state, and consequent changes in solubility, over the range of redox conditions normally found in lake sediments.^{25,35} Thus, the up-core increase in elements in this group, as well as other elements such as Mn, Ni, Cu and Cr in the third group, may be associated with the post-depositional solubilisation and diffusion into the surface sediments or water column³⁵ (Fig. 3). However, considering that the sediment mass accumulation rate in this lake is high, the influence of post-depositional processes on the metal profiles may be small,²⁵ as increased land exploitation may also be a contributor to the up-core increase in metal concentrations in this group.

In the past three decades, accompanied by the increase of the population in this area, the clearing of woodland and wildland for cultivation has led to large water loss and soil erosion.¹⁴ The cleared area accounts for 69% of the total cultivated land area.¹⁴ Temporal Rb/Sr ratio variations (Fig. 6), which have been widely used as a chemical weathering indicator,³⁶ show similar patterns to these crustal elements (Fig. 3) and are well correlated with the elements of this group ($P < 0.001$, not shown). Therefore, the increased run-off from the land may be another contributor to the increase in concentrations of the crustal elements in recent decades.

The second group is comprised of Mn, Ni, Cu and Cr, and they also show an up-core increase in concentrations. While we cannot rule out some influence from post-depositional processes,²⁵ the distinct increase in elements of this group occurred in ~ 1978 , coincident with the industrialization in China, suggesting that industrial and mine sources may contribute to this group. There were over 2000 factories in the villages and towns surrounding Lake Chaohu in the 1990s.¹⁴ These small factories used old equipment with no technology controls and environmental oversight, probably resulting in the heavy metal contamination in this group. In addition, there are many mines around the lake, extracting limestone, manganese,

Table 3 Pearson's correlation matrix (2-tailed) for the metal concentrations (Values significant at the $P < 0.001$ level are expressed in bold)

Element	K	Ca	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Rb	Sr	Zr	Pb	TN
K	0.64															
Ca	0.783	0.635														
Ti	0.643	0.625	0.547													
Cr	0.594	0.636	0.785	0.588												
Mn	0.854	0.675	0.889	0.679	0.897											
Fe	0.856	0.656	0.779	0.648	0.753	0.885										
Co	0.523	0.51	0.713	0.545	0.8	0.775	0.584									
Ni	0.598	0.467	0.624	0.597	0.715	0.745	0.679	0.705								
Cu	0.62	0.61	0.641	0.59	0.855	0.85	0.681	0.799	0.733							
Zn	0.579	0.53	0.658	0.59	0.849	0.833	0.684	0.798	0.766	0.95						
As	0.918	0.626	0.851	0.652	0.755	0.929	0.854	0.738	0.735	0.794	0.754					
Rb	-0.305	-0.199	-0.328	-0.402	-0.648	-0.623	-0.513	-0.604	-0.553	-0.726	-0.719	-0.462				
Sr	-0.347	-0.17	-0.067	-0.334	-0.335	-0.419	-0.365	-0.187	-0.229	-0.49	-0.426	-0.287	0.659			
Zr	0.619	0.608	0.647	0.596	0.859	0.853	0.696	0.816	0.762	0.987	0.941	0.808	-0.73	-0.437		
Pb	0.543	0.654	0.581	0.583	0.854	0.797	0.648	0.753	0.663	0.971	0.911	0.717	-0.713	-0.495	0.96	
TN	0.553	0.63	0.581	0.576	0.85	0.8	0.655	0.749	0.68	0.977	0.922	0.727	-0.723	-0.496	0.967	
OC																0.997

Table 4 Rotated component matrix with principle component analysis (PCA) for sediment samples from Lake Chaohu. (PCA loadings >0.5 are shown in bold)

Element	Components		Communities
	1	2	
K	0.816	0.373	0.806
Ca	0.731	0.278	0.612
Ti	0.839	0.383	0.851
Cr	0.732	0.124	0.551
Mn	0.907	-0.112	0.835
Fe	0.971	0.068	0.948
Co	0.869	0.205	0.798
Ni	0.822	-0.142	0.695
Cu	0.805	-0.031	0.648
Zn	0.92	-0.322	0.95
As	0.898	-0.302	0.897
Rb	0.925	0.214	0.902
Sr	-0.636	0.643	0.818
Zr	-0.4	0.578	0.493
Pb	0.925	-0.295	0.943
TN	0.884	-0.365	0.915
OC	0.887	-0.371	0.925
Initial Eigenvalues	11.78	1.81	
% of variance	69.31	10.63	
Cumulative %	69.31	79.94	

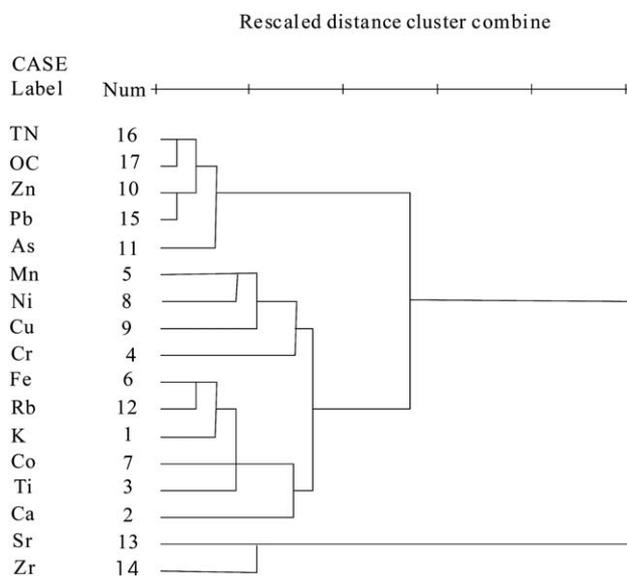


Fig. 5 Hierarchical dendrogram for the major and trace elements, TN and OC obtained by the hierarchical clustering method. The distances reflect the degree of correlation between different elements.

copper, zinc, and clay,¹⁴ which discharge Mn, Ni, Cu and Cr into the lake through Mn oxides.³⁷ Furthermore, the cities surrounding the lake produce huge amounts of industrial wastewater. It was reported that about 9197.9×10^4 and 1891.8×10^4 of industrial wastewater from Hefei city and Chaohu city, respectively, was discharged into Lake Chao in 1999.¹⁵ Non-point chemical industries have been suggested as the main sources polluting Lake Chaohu.³⁸

Concentrations of the elements in the third group also show abrupt increases after 1978 (Fig. 3). This group may be mainly associated with the use of chemical fertilizers and pesticides.^{39,40}

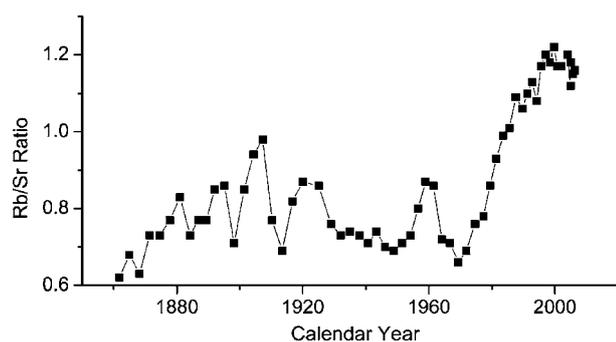


Fig. 6 Historical variations of the Rb/Sr ratio, which indicate the rate of physical erosion.

Manure was the main fertilizer in the Chaohu catchment prior to the 1980s,¹⁴ before the switch to chemical fertilizers that has introduced substantial C, N, and P into Lake Chao and has long been suggested as the main factor for eutrophication in the lake.³¹ The annual usage of chemical fertilizers and pesticides are reported as 547.4 and 23.3 kg km⁻², respectively,⁴¹ which are much higher than their corresponding typical amounts used in China (225 and 14.0 kg km⁻², respectively). It is estimated that about 6869 tons of nitrogen and 376 tons of phosphorous were discharged into Lake Chaohu every year during the 1990s.¹⁴ The usage of chemical fertilizers and pesticides, which contain metals as common impurities, can also contribute to the increase of As, Zn and Pb concentrations.^{42–44}

The last group, comprising Sr and Zr, is thought to be mainly from soil sources,⁴⁵ and shows very different vertical profiles from the other elements (Fig. 3). The variation coefficient (Table 2) of Zr is the lowest of all the elements, and Zr is therefore selected as a conservative reference element in this study.

3.5. Estimates of anthropogenic versus lithogenic metal accumulation rate

Taking Zr as a lithogenic trace element supplied by weathering, the estimation of the “lithogenic” fluxes of trace elements with anthropogenic origins can be calculated based on:^{9,45–47}

$$[M_{\text{flux}}]_{\text{lithogenic}} = (Zr_{\text{con}} \times [B_{\text{con}}/Zr_{\text{ref}}]_{\text{background}}) \times \text{mass accumulation rate} \quad (1)$$

Then the excess, anthropogenic fluxes can be calculated by subtracting the lithogenic component from the total flux:^{9,45–47}

$$[M_{\text{flux}}]_{\text{total}} = [M_{\text{con}}] \times \text{mass accumulation rate} \quad (2)$$

$$[M_{\text{flux}}]_{\text{anthropogenic}} = [M_{\text{flux}}]_{\text{total}} - [M_{\text{flux}}]_{\text{lithogenic}} \quad (3)$$

Where $[M_{\text{flux}}]_{\text{total}}$, $[M_{\text{flux}}]_{\text{lithogenic}}$ and $[M_{\text{flux}}]_{\text{anthropogenic}}$ are total, lithogenic and excess anthropogenic fluxes, respectively; B_{con} is the content of the examined element in the upper continental crust (UCC);⁴⁸ sediment mass accumulation rate is 0.284 g cm⁻² a⁻¹ of this core.

Since all these crustal elements have anthropogenic fluxes close to zero, only elements with anthropogenic origins, which include elements in the second and third groups in CA analysis, were calculated with lithogenic and anthropogenic metal fluxes. The

results show that all the elements had lithogenic fluxes with small variations in the past 150 years (Fig. 7). Distinct increases in the anthropogenic fluxes occurred for all the elements studied in the 1970s. Before the 1970s the anthropogenic fluxes for all the elements except As approached their corresponding lithogenic fluxes despite fluctuations observed for Cu, Ni, Mn and Cr. As presented higher anthropogenic fluxes than its lithogenic fluxes over the past 150 years. After the late 1970s, all elements showed a progressive increase in their anthropogenic fluxes, with anthropogenic fluxes exceeding their corresponding lithogenic fluxes. The maximum anthropogenic fluxes of Zn, As and Pb occurred in recent year, reaching 90.6, 5.4 and 20.3 μg cm⁻² a⁻¹, which were about 8.9, 13.8 and 6.1 times higher, respectively, than their corresponding lithogenic fluxes. The fluxes of anthropogenic-derived Pb in the last three decades are far higher than those reported in rural and remote areas of China such as in the Daihai⁹ and Qinghai Lake regions,¹⁰ but are comparable with those in the industrialized regions in Europe^{49,50} and North America.⁵¹

3.6. Pollution assessment

The geoaccumulation index (I_{geo}) was originally defined by ref. 52 as a quantitative measure of the metal pollution in aquatic sediments, and is divided into six contamination categories (Table 5). I_{geo} can be calculated using the equation $I_{\text{geo}} = \log_2 (M_{\text{con}}/(1.5 \times B_{\text{con}}))$, where M_{con} is the concentration of the examined element in the sediment, and B_{con} is the content of the examined element in the UCC⁴⁸ [here UCC values were selected as the baseline].

Boxplots of I_{geo} values for the metals in the sediment core of Lake Chaohu are presented in Fig. 8. The overall pattern of the I_{geo} values for the different elements is similar to their corresponding concentration profiles (not shown here). K, Ca, Rb, Fe, Co, Ni, Sr and Zr have mean I_{geo} values generally lower than zero, indicating a non-contamination status for these elements. Ti, Cr, Mn, Cu, Pb and Zn have mean I_{geo} values in the range of 0 to 1, indicating that these elements have probably been contaminated. The mean I_{geo} value of As is between 1 and 2, implying moderate contamination. The maximum I_{geo} values are between 0 and 1 for Ti, Fe and Co; between 1 and 2 for Cr, Mn, Ni, Cu and Pb; and between 2 and 3 for As and Zn. Since all these elements exhibit high concentrations and I_{geo} values at the surface of the core, this indicates increasing contamination in recent years, and especially for As and Zn, which show moderate to strong contamination.

3.7. Toxicity assessment

The sediment quality guide proposed by ref. 53 is most widely used to assess the toxicity of sediments. This approach is based on the relation between the measured concentrations of chemicals and the observed biological effects, such as mortality, growth or reproduction of living organisms. The Effects Range-Low (ERL) and Effects Range-Median (ERM) concentrations are considered. The ERLs were suggested to represent concentrations below which biological effects are rarely observed, while the incidence effects increased to 20% to 30% for most trace elements when the concentrations exceed ERL values but are lower than the ERM values. When concentrations exceed the ERM values, the

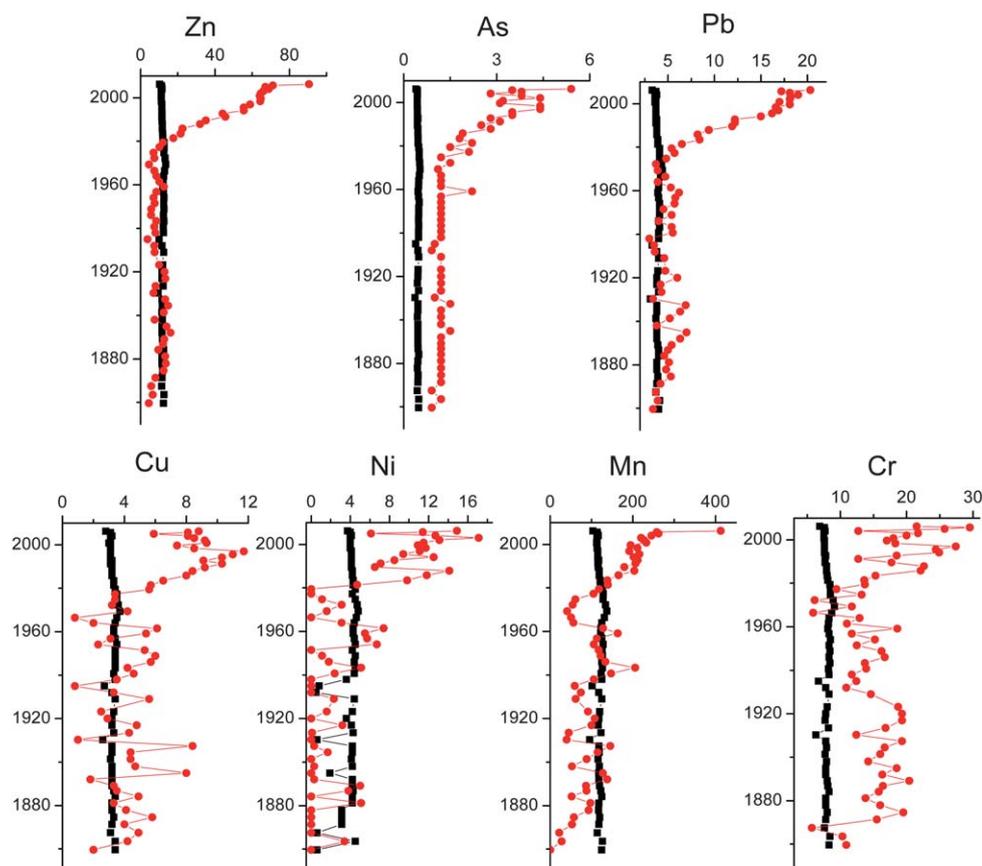


Fig. 7 Comparison of lithogenic (dark squares) versus anthropogenic (red cycles) fluxes ($\mu\text{g cm}^{-2} \text{a}^{-1}$) for trace metals with anthropogenic sources estimated from multivariate statistical analyses.

Table 5 Contamination categories based on I_{geo} values⁵²

I_{geo}	I_{geo} class	Description of sediment quality
>5	6	Extremely contaminated
4–5	5	Strongly to extremely strongly contaminated
3–4	4	Strongly contaminated
2–3	3	Moderately to strongly contaminated
1–2	2	Moderately contaminated
0–1	1	Uncontaminated to moderately contaminated
<0	0	Uncontaminated

incidence of adverse effects increased to 60% to 90% for most trace metals.⁵³ To estimate the possible environmental consequences of the analyzed metals, we compared our results with the US NOAA sediment quality guidelines. For most of the elements compared, including Cr, Cu, Zn, As and Pb, the concentrations in the upper part of the core are between the ERL and ERM levels, indicating that adverse biological effects are possible. The concentrations of Ni in the upper 10 cm (56.4 mg kg^{-1} in average) exceeded the ERM values, indicating that it is very likely that adverse biological effects will occur. Since there is no indication of any imminent decrease in these metal concentrations, it is likely that this contamination will pose a health risk for local residents who still consume fish from the lake.

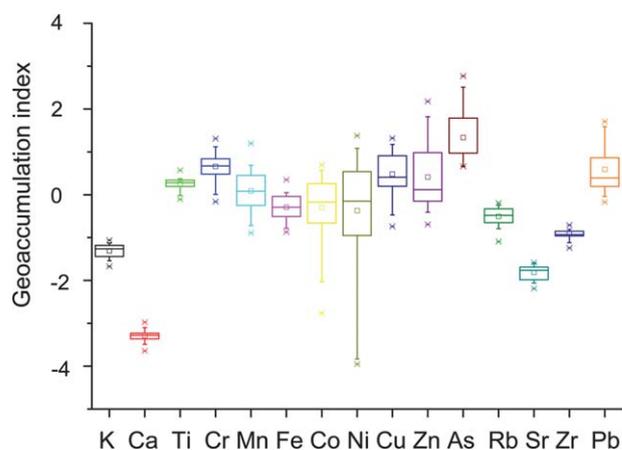


Fig. 8 Boxplot of the geoaccumulation index (I_{geo}) values for the metals in the sediment core from Lake Chaohu. The boxplot essentially divides the normalized I_{geo} into quartiles. The middle line inside the box represents the median; the boxes mark the 25th and 75th percentiles; the horizontal lines outside the box mark the 5th and 95th percentiles.

4. Conclusion

This study presents a historical record of metal accumulation in a sediment core extracted from Lake Chaohu in eastern China. It is evident that the intensification of human influence after 1978 coincident with the reform and opening of China, significantly

affected metal accumulations in lake sediments. Initial analysis demonstrates that for trace element contaminations there are important historical signatures in this developed region in China. In addition to increased levels of pollutants due to increasing anthropogenic inputs in recent decades, intensified land exploitation during this period has also moderately increased crustal element concentrations *via* river run-off. Although the major pollutant in Chaohu Lake is As, the element Ni may be very likely to induce adverse biological effects. Decreasing waste drainage into the lake and reducing the impacts of industrial activities and land exploitation in the Chaohu catchment are therefore of critical importance.

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