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Diatom response to heavy metal pollution and nutrient enrichment in an urban lake: evidence from paleolimnology

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Abstract – Diatoms and geochemical stratigraphy were studied in sediment core samples collected from a heavily polluted urban lake (SE China) in order to track the history of eutrophication and heavy metal contamination. The sediment profile covered ca. 60 years (from ca. 1951 to 2011) based on ^{137}Cs and Spheroidal carbonaceous particles (SCP) dating, and encompassed a period of rapid industrial development in this region. Diatoms experienced two visible shifts, including the replacement of benthic and epiphytic taxa by planktonic species (*e.g.*, *Cyclotella meneghiniana* Kützing) in 1972, and the dominance of *Cyclotella atomus* Hustedt and *Nitzschia palea* (Kützing) W. Smith after 1999. Metals (*i.e.*, Cd, Pb and Zn), total phosphorus, total nitrogen and total organic carbon all increased in the past 60 years. Redundancy analysis was used to correlate diatom with chemical change and explained 50.3–60% of total variation in diatom data for three periods (from 1951 to 1999, between 1951 and 2011 and from 1972 to 2011). The combined effects of nutrients and metals were the predominant factor, capturing 29.6–42.8% of the total variance. Nutrients alone accounted for little more variance than did metals alone for the first flora shift about 1972. The further shift after 1999 was more influenced by the sole effect of metals than that of nutrients. Increases in species (*e.g.*, *N. Palea*) able to tolerate both nutrient-related and metal-related stressors were related to persistent nutrient and metal inputs. In addition, climate warming might exacerbate eutrophication and metal contamination in this lake.

Key words: Urban lake / heavy metal pollution / eutrophication / diatom / spheroidal carbonaceous particles

Introduction

In surface freshwater environments, lakes are the interface between terrestrial and riverine ecosystems, rendering them essential resources for life in this planet (MEA, 2005). Among various types of lakes, urban lakes are located in densely populated regions, making an important contribution to recreation, water supply, flood control, mitigation of local climate and other ecosystem functions (Birch and McCaskie, 1999). With stable hydraulic conditions and high levels of public access, urban lakes are generally small, shallow and sensitive to contamination (Schueler and Simpson, 2001). Urban watersheds generally produce higher unit area nutrient loadings from runoff and sewage, compared to other watersheds (Naselli-Flores, 2008). In addition, industrial activities produce large amount of metals that are easily transported to urban lakes by water runoff (Boyle *et al*., 1999; Rose *et al*., 2004; Wu *et al*., 2012). Thus, urban lakes collect and accumulate large amount of nutrients and metals. Many of these chemicals are toxic to organisms and can lead to rearrangement of the biotic structure of urban lake ecosystems (Rai *et al*., 1981; Morin *et al*., 2012). For example, algal communities may be dominated by tolerant species with some diatom taxa forming significant blooms in polluted waters (Rai *et al*., 1981; Morin *et al*., 2008, 2012). Sedimentary records also reveal that the increases of tolerant diatom taxa are generally concurrent with enhanced pollutant inputs (Renberg *et al*., 2001; Cattaneo *et al*., 2004, 2008).

Different from gradual shifts in lake ecosystems over time scales of centuries in the pre-industrial period,

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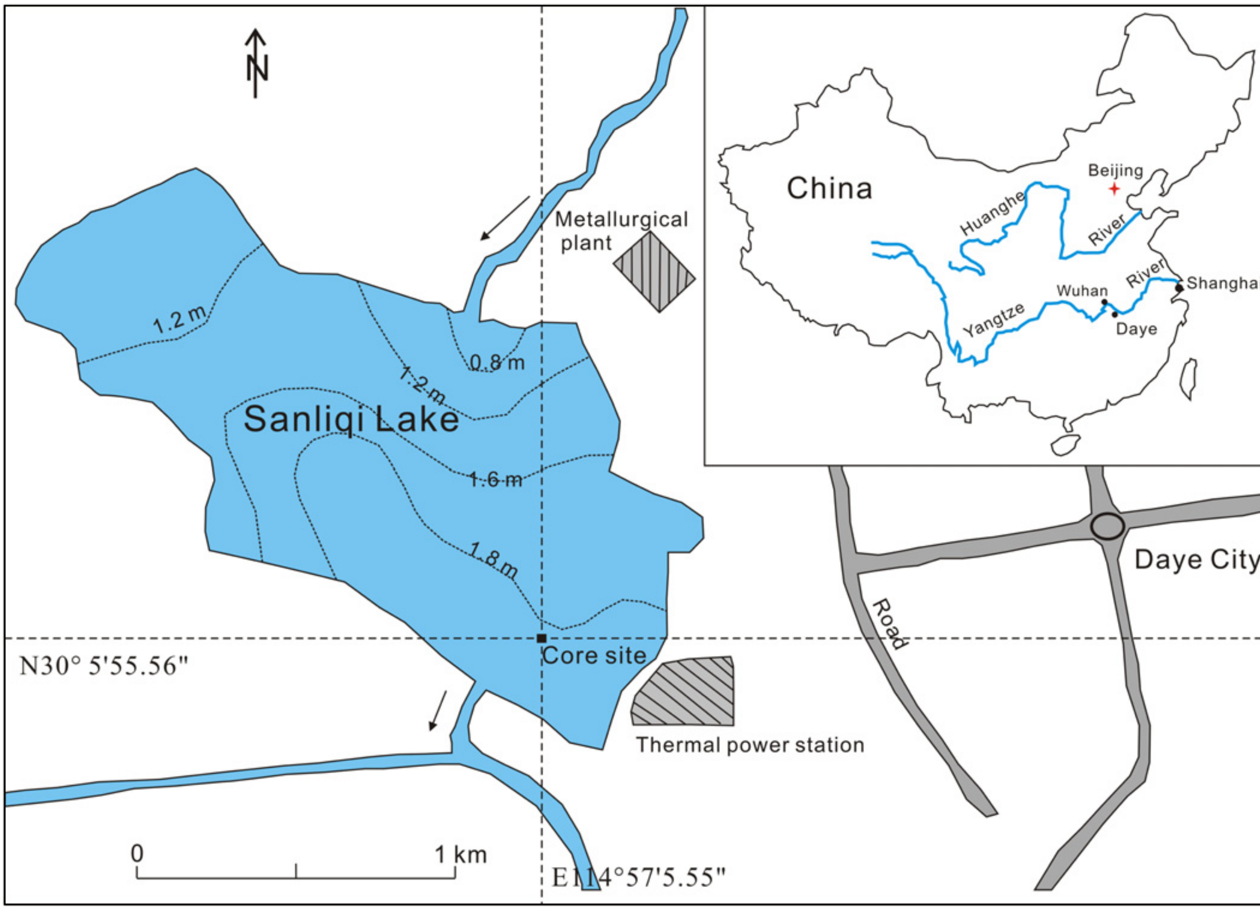

Fig. 1. Map of the study area and the sampling site (filled square) with the locations of the thermal power station and metallurgical plant (grey-hatched areas).

abrupt and pronounced changes may occur following pollutant inputs in urban lakes (Birch and McCaskie, 1999; Hall *et al*., 1999; Naselli-Flores, 2008), especially in a region undergoing accelerated urbanization such as the middle and lower reaches of the Yangtze River (SE China). This region contains large cities (*e.g*., Shanghai, Nanjing and Wuhan) and it is famous for the abundance of freshwater lakes (Dong *et al*., 2012). For example, there are 138 lakes with surface area >0.1 km^2 in Wuhan City, located in the centre of China (Fig. 1) (Xu *et al*., 2010). Presently, most of these urban lakes are suffering from severe pollution, such as eutrophication and heavy metal contamination (Boyle *et al*., 1999; Rose *et al*., 2004; Yang *et al*., 2008; Wu *et al*., 2012; Chen *et al*., 2013a). During the recent years, attention of scientists and managers has focused on eutrophication following a series of algal blooms in these lakes (Yang *et al*., 2008). Previous studies have focused on the direct effect of nutrients on biotic communities of these lake ecosystems, but the impact of other pollutants (*e.g*., heavy metals) has not yet been considered (Dong *et al*., 2008; Yang *et al*., 2008; Chen *et al*., 2011; Zhang *et al*., 2012; Liu *et al*., 2012a). In fact, nutrient enrichment is often accompanied by increased metal concentrations in urban lakes (Renberg *et al*., 2001; Naselli-Flores, 2008; Liu *et al*., 2012b; Wu *et al*., 2012). Therefore, information about the response of biotic communities to multiple contaminants in urban lakes is urgently required.

To establish an ecosystem management plan for a lake influenced by multiple pollutants, it is essential to understand how, and to what extent, the biotic communities have been altered in response to these multiple stressors (McGowan *et al*., 2005; Chen *et al*., 2013b). This study used sedimentary proxies to evaluate the relative importance of nutrient and heavy metal factors as controls of diatom assemblages in an urban lake (SE, China). Partial and constrained redundancy analysis (RDA) (Hall *et al*., 1999) was used to partition variance in diatom data into categories associated with nutrient, heavy metal and their interaction.

Methods

Study area

Lake Sanliqi is a small (area 2.2 km^2) and shallow (mean depth 1.6 m) lake located in Daye City (Fig. 1), which has been a centre of mining and metallurgy since the 1950s. Several metallurgical plants have operated in the watershed, resulting in contamination of surface waters with high levels of metals (*e.g*., Cd, Mn and Zn)

(Chen *et al.*, 2013a). In addition, the nearby thermal power station was a fly-ash pollution source when it operated between 1980 and 2000. From 2000 to 2009, the average concentrations of total phosphorus (TP) and total nitrogen (TN) in this lake were 295 and 4066 $\mu g.L^{-1}$, respectively (Li and Zhang, 2010). In December 2011, metal concentrations in 12 sampling sites ranged from 8 to 21 $\mu g.L^{-1}$ for Cd, 113 to 375 $\mu g.L^{-1}$ for Mn, 115 to 251 $\mu g.L^{-1}$ for Ni and 52 to 128 $\mu g.L^{-1}$ for Zn (Chen *et al.*, 2013a).

Sampling methods

A sediment core (34 cm in length) was collected in the deepest part of the lake in May 2012 using a modified Kajak gravity corer. The core was immediately sectioned on shore by extruding 1 cm-sections. Subsamples of each slice were allocated for multi-proxy analyses, including magnetic susceptibility, particle size, chemical elements, diatoms, spheroidal carbonaceous particles (SCP) and activity of ^{137}Cs, the latter two measures to help provide a sediment chronology. Samples were stored at 4 °C until analyses.

Analytical methods

^{137}Cs ($t_{1/2} = 30.2$ a) is an anthropogenic radionuclide originating from above-ground nuclear tests, and 90% of the radionuclide releases occurred between 1963 and 1964 (Ritchie and McHenry, 1990). Thus, ^{137}Cs activity depth profiles are often used for sediment core dating (Audry *et al.*, 2004). ^{137}Cs was measured on the short core by EG&G Ortec well-type coaxial low background germanium detectors (HPGe GWL-120-15).

SCPs produced from fossil-fuel combustion can be used to track regional atmospheric pollution history and determine dates in the sediments (Boyle *et al.*, 1999; Rose *et al.*, 2004; Rose, 2008). One feature is that the SCP concentration maximum can be used as a dating marker (Rose, 2008). SCPs in the sediments were extracted using HNO_3, HF and HCl according to Rose (2008). Particles larger than 20 μm were identified and counted using an Olympus BX53 microscope at 400 × magnification. SCP concentrations are expressed as grains per gram dry mass of sediment (grains g DM^{-1}).

Particle-size spectra were determined using a Malvern automated laser-optical particle size analyzer (Mastersizer-2000; Malvern Instruments Ltd, Worcestershire, UK) after removal of organic matter by 10% hydrogen peroxide treatment. Mass-specific low-frequency magnetic susceptibility (χ_{lf}) was measured at 0.47 kHz using a Bartington MS2C sensor. Total organic carbon (TOC) and TN were determined by combustion with an Elemental Analyzer (EA 3000) with reference to standard samples; replicate analyses of well-mixed samples indicate a precision of ±0.1% (1 SD). Concentrations of metals and TP in sediments were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, Profile DV) after digestion with HF–HCl–HNO_3–$HClO_4$ (Liu *et al.*, 2012b).

Diatom samples were treated using hydrogen peroxide and HCl in order to remove all organic and carbonate components (Battarbee *et al.*, 2001). All samples were mounted on microscope slides using the high refraction mountant Naphrax®. Diatoms were identified and counted using an Olympus BX53 microscope with an oil immersion objective (magnification 10 × 100). A minimum of 300 valves were counted in the top 25 cm, but count sums were reduced to 200 and 300 for the bottom samples where preservation was poor. Diatom taxonomy mainly followed Krammer and Lange-Bertalot (1986, 1988, 1991a, 1991b). The taxonomy was corrected to current conventional names based on the Catalogue of Diatom Names (Fourtanier and Kociolek, 2011). Chrysophycean stomatocysts were counted concurrently with diatoms in order to calculate a cyst: valve ratio.

Statistical methods

All numerical analyses of diatoms were based on percentage abundance and included 34 diatom taxa with ≥2% abundance in at least one sample. Diatom zones were identified using the constrained incremental sum of squares (CONISS) facility within the computer program TILIA and TILIAGRAPH (Grimm, 1991). Temporal patterns of diatom community change were explored with detrended correspondence analysis (DCA). The gradient length of DCA axis 1 was 2.19 SD indicating that a linear method (RDA) was suitable for ordination analysis (ter Braak and Šmilauer, 2002).

Partial canonical ordinations were applied to evaluate the relationships between two categories of explanatory variables (*i.e.*, nutrients and heavy metals) and shifts in diatom assemblages. Sedimentary TP, TN and TOC can be selected as indicators of historical nutrient load (Rose *et al.*, 2004; Chen *et al.*, 2013b). Similarly, three common heavy metals (*i.e.*, Cd, Zn and Pb) were selected into the metal category. We found that each variable was significantly correlated with the diatom data ($P < 0.05$), based on a series of RDAs constrained to a single explanatory variable at a time. Then we performed a series of RDAs on each category, sequentially eliminating the explanatory variable with the highest variable inflation factor (VIF) until all VIFs were <10 (Hall *et al.*, 1999). This step eliminated collinearity among variables within each category (ter Braak and Šmilauer, 2002). Thereafter, two-way partitions were performed independently on three time spans (from 1951 to 2011, between 1972 and 2011 and from 1951 to 1999) to investigate how the relative importance of explanatory categories differed during the two major shifts in the diatom flora and the long-term data. Hall *et al.* (1999) have provided further details of variance partitioning procedures. The statistical significance of each block of partitioned variance was assessed using Monte Carlo tests with 499 random permutations. Computations were performed using the

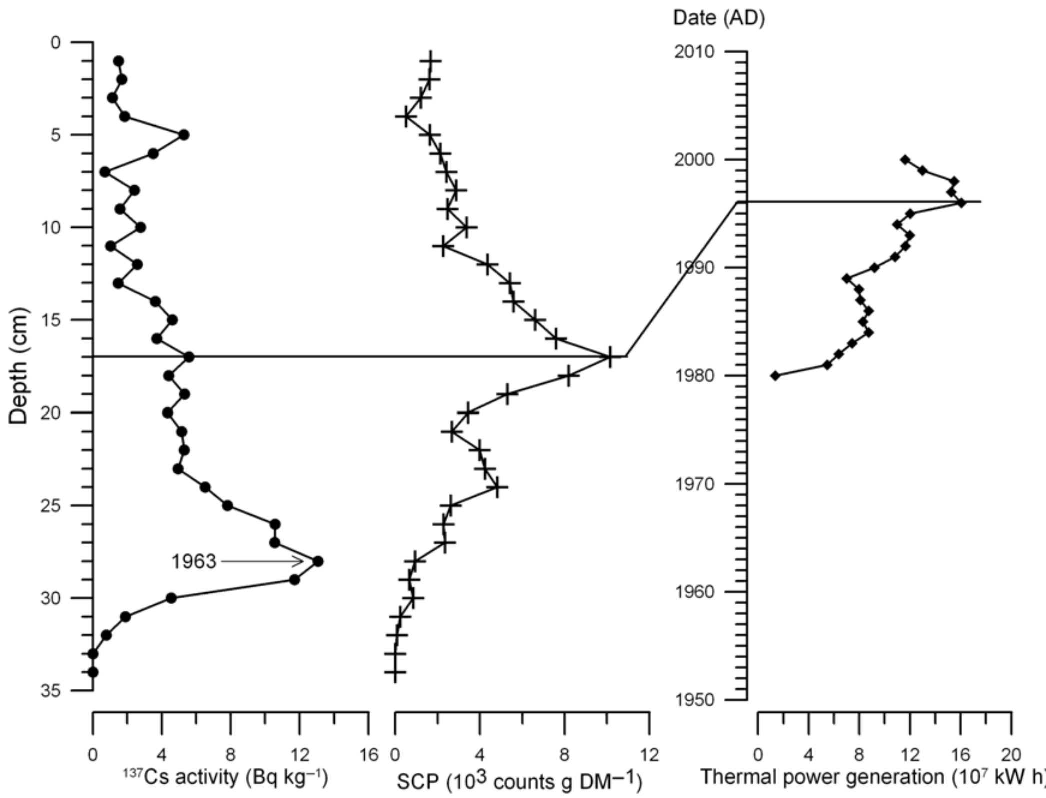

Fig. 2. ^{137}Cs activity and SCP profiles for the sediment core in Sanliqi Lake. Power generation of the thermal power station is also shown (Data source: Daye Statistical Bureau).

computer program CANOCO 4.5 (ter Braak and Šmilauer, 2002).

Results

Chronology

^{137}Cs was firstly detected at 32 cm depth, and the major peak occurred at 28 cm depth with corresponding activity of 13 Bq.kg^{-1}. Subsequently, the values declined (Fig. 2). Thus, this ^{137}Cs peak is assigned to the maximum atmospheric global fallout that corresponds to 1963 (Ritchie and McHenry, 1990; Audry *et al.*, 2004).

SCP in Sanliqi Lake was firstly detected at 32 cm depth, and then two peaks were observed in the profile, including one small peak at 24 cm depth and the sharpest peak at 17 cm depth (Fig. 2). The maximum concentration was followed by a decline to the sediment surface. A similar trend was observed between SCP concentrations and thermal power generation (Fig. 2). It is deduced that the sharpest peak at 17 cm depth is concomitant with the maximum power generation in 1996.

Mean sedimentation rates were estimated using the ^{137}Cs peak of 1963 and the SCPs peak of 1996 by dividing the sediment depth where the peaks were located by the proper time elapsed. The age of each sampling interval was established by linear interpolation or extrapolation between two adjacent ages. Thus, mean sedimentation rates of 1.13 cm.a^{-1} were calculated between 1996 and 2011 and 0.33 cm.a^{-1} between 1963 and 1996. Mean sedimentation rate for sediments below 28 cm followed the rate calculated for the 1963–1996 period. We propose that the high sedimentation rates after 1996 should be attributed to enhanced industrial waste discharge since then.

Biotic community

105 diatom species belong to 38 genera were identified in the sediment core from Sanliqi Lake (Supplementary Material Appendix 1), and 34 main species were shown in the diatom diagram (Fig. 3). Cluster analysis identified three major zones in the diatom assemblages. Correspondingly, the first two DCA axes captured 53.7% of variance in diatom data and distinguished three distinct periods with broadly different diatom assemblages (Fig. 4). Zone I (32–25 cm; 1951–1972) was dominated by *Aulacoseira granulata* (Ehrenberg) Simonsen and epiphytic and benthic taxa. The abundance of *A. granulata* fluctuated between 14 and 47%, with mean value about 33%. The total percentages of epiphytic and benthic diatoms ranged from 32 to 44%, mainly including *Gyrosigma acuminatum* (Kützing) Rabenhorst, *Pinnularia* sp., *Hantzschia amphioxys* (Ehrenberg) Grunow in Cleve and Grunow, *Luticola mutica* (Kützing) Mann in Round, Crawford and Mann, *Gomphonema* sp., *Eunotia minor*

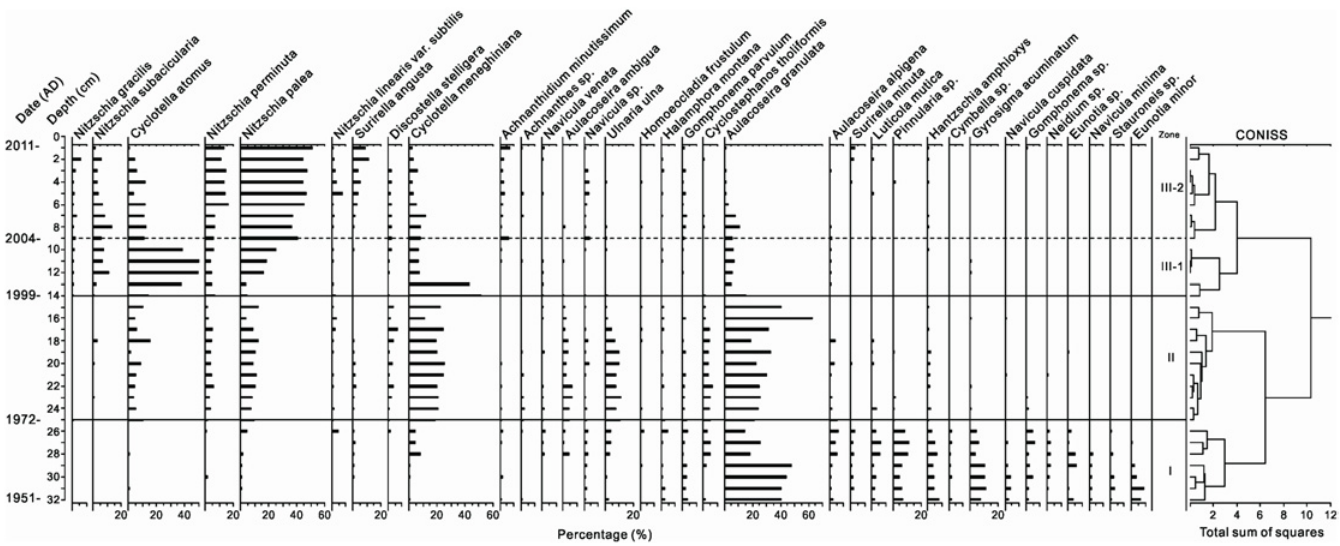

Fig. 3. Diagram showing diatom taxa with $\geq 2\%$ abundance in at least one sample. Zonation is based on constrained incremental sum of squares.

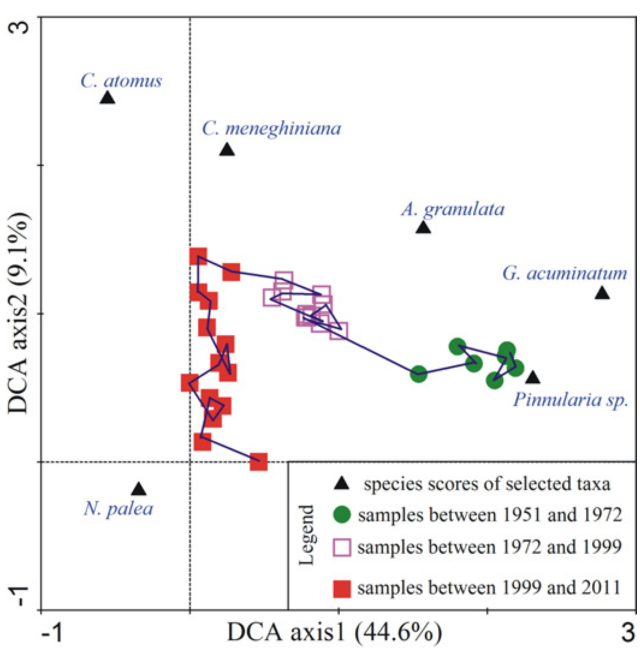

Fig. 4. Detrended correspondence analysis (DCA) ordination of sample scores and selected species scores from diatom data.

(Kützing) Grunow in Van Heurck. Zone II (25–14 cm; 1972–1999) was co-dominated by *A. granulata* and *Cyclotella meneghiniana* Kützing with their average percentages of 30 and 21%, respectively. Prominent increases occurred in *Cyclotella atomus* Hustedt, *Nitzschia perminuta* (Grunow in Van Heurck) M. Peragallo, *Nitzschia palea* (Kützing) W. Smith, albeit in low relative abundances. Conversely, epiphytic and benthic taxa were almost absent, except for few abundances of *Ulnaria ulna* (C.L. Nitzsch) Compère, *Navicula* sp., *Gomphonema parvulum* (Kützing) Kützing. The tight cluster of assemblages in this zone suggested that species composition was stable (Fig. 4). Zone III (14–0 cm; 1999–2011) was split into two subzones. *A. granulata* was rapidly replaced by the genus of *Cyclotella* and *Nitzschia*. In Zone III-1, a brief shift with high abundance of *C. meneghiniana* was observed before the dominance of *C. atomus*. *N. palea* increased gradually in Zone III-1 and replaced the dominance of *C. atomus* in Zone III-2. Concurrently, obvious increases in *N. perminuta*, *Surirella angusta* Kützing and *Achnanthidium minutissimum* (Kützing) Czarnecki were observed in the surface samples. The uppermost samples were far from the basal samples, suggesting that the present-day diatom communities remain distinctly different from assemblages from 1951 to 1972. The ratio of cyst and valve was above 1 before 1972, and then shrinking to near zero (Fig. 5).

Geochemical indicators, magnetic susceptibility and grain size

Geochemical indicators showed similar upward trends over time (Fig. 5). In Zones I and II (from 32 up to 14 cm), the concentrations increased by 151.5-fold for Cd, 17.6-fold for Pb, 14-fold for Zn, 1.6-fold for TP, 2.2-fold for TN and 4-fold for TOC. In Zone III (from 14 cm up to surface), geochemical indicators showed different trends, with steady increases in Cd, Zn, TP and TN, a fluctuating level in TOC and a decline in Pb. The concentrations of the surface sample reached 1793 $mg.kg^{-1}$ (Cd), 709 $mg.kg^{-1}$ (Pb), 9708 $mg.kg^{-1}$ (Zn), 2077 $mg.kg^{-1}$ (TP), 6.27 $mg.g^{-1}$ (TN) and 51.8 $mg.g^{-1}$ (TOC). The metal concentrations were much higher than the threshold effect levels of toxicity (*e.g.*, 1992-fold, 18.8-fold and 79-fold higher for Cd, Pb and Zn, respectively; see Fig. 5) (cf. MacDonald *et al.*, 2000). The ratio of TOC and TN increased twofold from the bottom to 18 cm depth, and then decreased.

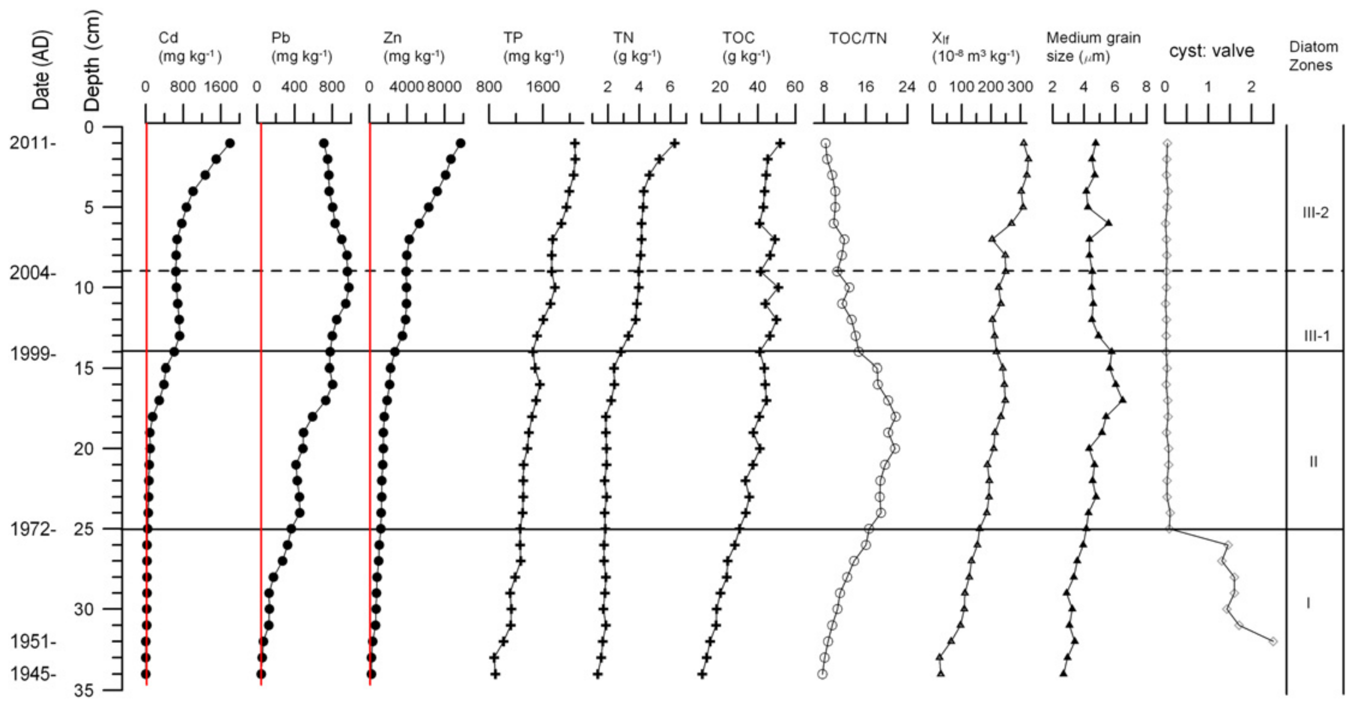

Fig. 5. Heavy metal, nutrient element concentrations, magnetic susceptibility, medium grain size (MD) and the ratio of cysts and valves profiles for the sediment core in Sanliqi Lake. The red lines on the heavy metal profiles show the threshold effect levels of toxicity according to the reference (MacDonald *et al*., 2000).

χ_{lf} increased gradually in the profile, except for a small trough at 7 cm depth, and significant correlations were observed between χ_{lf} and each geochemical proxy (Table 1). Sediments were characterized by fine particles, with a mean medium grain size (MD) of 4.4 μm for the whole core. Medium grain size increased from 34 to 17 cm, and it showed a declined trend from 17 cm to the surface sample.

Variance partitioning

The sole effects of nutrients and metals all explained significant ($P < 0.05$) amounts of variance in the three time-series diatom data, except for the unique effect of metals in the timespan from 1951 to 1999. Variance partitioning revealed that 50.3–60% of the total variation in diatom assemblages was correlated with nutrient and heavy metal parameters (Fig. 6). Comparison of the partitions in different timespans permitted identification of how the relative importance of each category of variables varied through time. In the time series from 1951 to 2011, the unique effect of metals and that of nutrients explained equal variance (5.1%) in diatom data. The sole effect of metals (12.2%) accounted for more variance than did that of nutrients (8.5%) in diatom data between 1972 and 2011. For the timespan from 1951 to 1999, nutrients alone accounted for little more variance (9.9%) than did that of metals (8.6%). In each timespan, most variance in diatom data was attributed to their combined effects (29.6–42.8%).

Discussion

Diatom response to nutrient enrichment

The diatom flora experienced two main shifts occurring in 1972 and 1999, respectively. Around 1972, the predominance of planktonic species (*e.g.*, *C. meneghiniana* and *C. atomus*) replaced the prevalent epiphytic and benthic taxa, which are commonly associated with the development of macrophytes in shallow lakes (Yang *et al*., 2008; Liu *et al*., 2012a). For example, *G. acuminatum* is more abundance in lakes with extensive macrophyte cover than lakes with sparse macrophyte cover (Liu *et al*., 2012a) and so epiphytic and benthic species are taken to indicate that Sanliqi Lake was macrophyte-dominated before the 1970s. The marked increases in *C. meneghiniana* and *C. atomus*, both of which have high phosphorus requirements (Dong *et al*., 2008; Yang *et al*., 2008), coincided with the absence of epiphytic and benthic taxa after 1972. These diatom flora shifts were contemporaneous with increases in sedimentary TP, TN and TOC. Generally, C/N is 4–10 for algae and other non-vascular aquatic plants, whereas C/N is ≥20 for vascular land plants (Meyers and Ishiwatari, 1993). Therefore, the elevated C/N ratio between 1972 and 1999 (ratios between 16 and 22) reflected an increase in terrestrial sources of organic matter during this period. Meanwhile, the increase in medium grain size should be varied with enhanced terrestrial erosion in the watershed (Liu *et al*., 2012b). In addition, the sole effect of nutrients explained the significant variance in diatom data. Hence, these evidences

Table 1. Pearson Correlation matrix of sediment properties in Sanliqi Lake.

	Cd	Pb	Zn	TP	TN	TOC	χ_{lf}	MD	SCP
Cd	1								
Pb	0.701**	1							
Zn	0.980**	0.676**	1						
TP	0.910**	0.851**	0.939**	1					
TN	0.971**	0.748**	0.962**	0.927**	1				
TOC	0.705**	0.939**	0.691**	0.849**	0.724**	1			
χ_{lf}	0.788**	0.844**	0.824**	0.937**	0.770**	0.891**	1		
MD	0.339*	0.703**	0.305	0.506**	0.284	0.748**	0.697**	1	
SCP	– 0.067	0.422*	– 0.123	0.099	– 0.131	0.496**	0.351*	0.833**	1

**Correlation is significant at the 0.01 level (two-tailed test).
*Correlation is significant at the 0.05 level (two-tailed test).

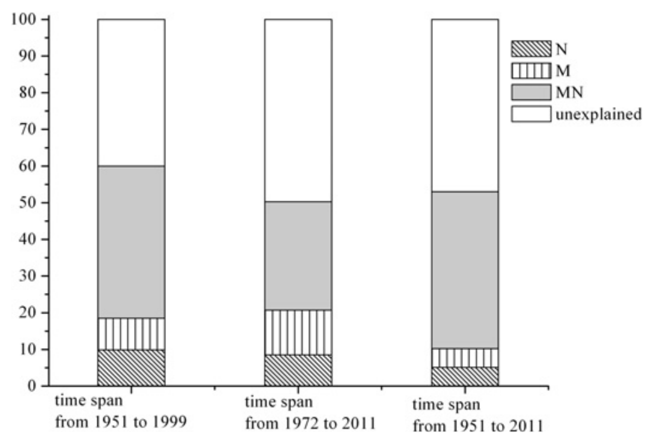

Fig. 6. Effects of nutrient alone (N), metal alone (M), the joint effects of nutrient and metal (MN) on diatom assemblages from Sanliqi Lake determined using variance partitioning analyses in three time series (from 1951 to 1999, from 1972 to 2011 and from 1951 to 2011).

suggested that terrestrial nutrient inputs might trigger regime shift of the lake in the 1970s. Similarly, pronounced increases in nutrient-tolerant taxa (*e.g.*, *C. meneghiniana*) were also observed in several diatom and chironomid profiles in the Yangtze floodplain lakes around the 1970s (Dong *et al.*, 2008; Yang *et al.*, 2008; Chen *et al.*, 2011; Zhang *et al.*, 2012; Liu *et al.*, 2012a). The marked shifts in biotic communities reflected the deterioration of these aquatic ecosystems during the 1970s in this region, resulting from enhanced anthropogenic nutrient inputs (*e.g.*, fertilizer usage and urban sewage).

A. granulata is generally associated with mesoeutrophic, well-mixed and turbid waters, which are often shallow (O'Farrell *et al.*, 2001). Continued nutrient enrichment would cause the replacement of *A. granulata* by nutrient-tolerant species. Between 1999 and 2004, the predominance of eutrophic species (*i.e.*, *C. meneghiniana* and *C. atomus*) was indicative of further eutrophication in Sanliqi Lake, and the lower C/N ratios (ratios between 10 and 15) implied increased contribution of algae (Meyers and Ishiwatari, 1993). After 2004 *N. palea* dominated the diatom assemblages. This genus is adapted to eutrophic conditions in the Yangtze floodplain lakes (Yang *et al.*, 2008), but has a lower TP optimum than *C. meneghiniana* and *C. atomus* (Yang *et al.*, 2008). Therefore, this floristic change does not appear to be caused by increased nutrient inputs, and is most likely associated with another stressor.

Diatom response to heavy metal contamination

N. palea is known to tolerate heavy metals, and it is often designated as a characteristic species in streams and lakes with heavy metal contamination (Morin *et al.*, 2008, 2012; Chen *et al.*, 2013a). In laboratory experimental conditions, Duong *et al.* (2010) detected that increased Cd concentration resulted in a highly significant development of *N. palea*. Between 1972 and 1999, the obvious increase in *N. palea* was concurrent with elevated heavy metal concentrations. In addition, the two dominant species (*i.e.*, *C. meneghiniana* and *A. granulata*) have been observed in heavy metal polluted waters (Morin *et al.*, 2008; Li *et al.*, 2011). Diatom succession can be reasonably related to the expansion of industrial activities during this period. This interpretation is reinforced by strong correlations between χ_{lf} and Cd, Pb and Zn because χ_{lf} in lake sediments can provide evidence for past industrial activities (*e.g.*, smelting) (Rose *et al.*, 2004). High SCP concentrations during this period also reflected enhanced industrial activities (Boyle *et al.*, 1999). In addition, the increased sedimentation rate since 1996 might be suggestive of the influx of heavy metals.

In Zone III-1 (from 1999 to 2004), the diatom assemblages were characterized by high abundances of *C. meneghinian* and *C. atomus*. These two species are tolerant to both eutrophication and heavy metal pollution (Cattaneo *et al.*, 2008; Yang *et al.*, 2008) and high metal concentrations may have created an environmental competitive exclusion scenario where metal-sensitive species could not develop. Thus, taxa co-tolerant to metals and nutrients, dominated the flora. Cd, Pb and Zn concentrations in sediments from Sanliqi Lake are much higher than the threshold levels of toxicity of 0.99, 35.8 and 121 $mg.kg^{-1}$ for Cd, Pb and Zn, respectively (MacDonald *et al.*, 2000). In addition, sediment resuspension due to wind-driven waves in shallow lakes can remobilize deposited particulate heavy metals, which may then become available to biota (Kalnejais *et al.*, 2007). Finally, intense metal inputs resulted in the bloom of metal-tolerant species, such as *N. palea*. Owing to the increasing and persistent metal stress, the demise of sensitive species and the succession towards other more tolerant taxa were observed in other fossil diatom profiles (Ruggiu *et al.*, 1998; Cattaneo *et al.*, 2004, 2008).

Since 2004, the increases of Cd and Zn concentrations in sediments reflected clearly enhanced heavy metal inputs. Nevertheless, Pb concentrations showed a slight decline simultaneously with the Cd and Zn increases. The different patterns in the metals could be attributed to two reasons. Firstly, Pb concentrations declined due to the removal of lead from gasoline. Secondly, emissions from power generation are an important source of Pb in sediments (Boyle *et al.*, 1999), as verified by a significant correlation between SCP and Pb. Therefore, lower Pb concentrations may be attributed to reduced emissions from power generation, as supported by the decreased SCP levels during this period.

The relative effects of eutrophication and metal contamination

The combined effects of nutrients and heavy metals captured a major part of the total variance, indicating that a large proportion of diatom assemblage change was impossible to assign to the sole effect of nutrients or that of metals. However, the results reflect potentially interesting interactions between nutrients and metals. For example, both *A. minutissimum* and *N. palea* in this core are described as metal tolerant in a number of studies (Ruggiu *et al.*, 1998; Cattaneo *et al.*, 2004, 2008; Morin *et al.*, 2008, 2012). On the other hand, *A. minutissimum* is usually adapted to oligotrophic waters (Cattaneo *et al.*, 2004; Morin *et al.*, 2012). Nutrient enrichment should prohibit the development of *A. minutissimum*, but favour the growth of *N. palea* in the metal-polluted waters. The dominant species should be co-tolerant to metals and nutrients. The phenomena of multiple tolerance and co-tolerance have been reported in some algae (Rai *et al.*, 1981). In fact, high nutrient loading would protect some algae from metal toxicity (Guasch *et al.*, 2004).

In addition, chrysophycean algae are more sensitive to both eutrophication and metal contamination than diatoms (Cattaneo *et al.*, 2008). The sharp decline in the ratio of cysts to valves in the 1970s suggested that the synchronous increases in nutrients and metals should extend the tolerant limits of Chrysophyta.

In heavily impacted lake ecosystems, cultural eutrophication is always accompanied by other perturbations, such as increased metal concentrations (Rose *et al.*, 2004; Wu *et al.*, 2012; Chen *et al.*, 2013a). The simultaneous disturbances make it difficult to isolate their sole effects (Cattaneo *et al.*, 2008). Variance partition analyses with moving time windows provide a clue to distinguish the unique effects of multiple stressors. In this study, nutrients accounted for little more variance than did metals for the first shift in diatom assemblages around 1972. In the early period, diatoms may have been nutrient limited and therefore more responsive to nutrients than to metals. For the time series between 1972 and 2011, diatom assemblages were more influenced by the sole effect of metals than that of nutrients. This suggested that persistent metal pollution select for species able to tolerate extreme metal stress (Morin *et al.*, 2012). The dominance of *N. palea*, a species with extreme metal tolerance (Morin *et al.*, 2008; Duong *et al.*, 2010; Chen *et al.*, 2013a), coincided with the further increases in Cd and Zn since 2004.

Potential impact from climate change

Meteorological data show that the annual mean air temperature has increased by more than 1 °C in the Yangtze River Basin since the 1950s (Yang *et al.*, 2009). In shallow lakes, climate warming usually stimulates nutrient release from sediments (Schindler, 2006). So, we deduced that rising temperature would indirectly benefit the development of nutrient-tolerant species. Combined with meteorological data and sedimentary records in Chaohu Lake (SE China), Chen *et al.* (2013b) revealed that annual mean air temperature was a significant factor influencing diatom succession, probably via increasing sediment nutrient release. In addition, rising temperature can increase water-extractable metal fractions, and then strength metal mobility and bioavailability (Adekunle, 2009). Therefore, climate warming might exacerbate eutrophication and metal contamination in these shallow urban lakes.

Conclusions

Severe conditions of contamination were reflected by the enhanced inputs of metals and nutrients (*e.g.*, Cd, up to 1793 $mg.kg^{-1}$ in the surface sediments; Zn, up to 9708 $mg.kg^{-1}$ and TP, up to 2077 $mg.kg^{-1}$) in Sanliqi Lake (SE China). Diatom communities were characterized by *A. granulata*, and epiphytic and benthic taxa before 1972. Subsequently, the blooms of planktonic taxa (*e.g.*, *C. meneghiniana*) replaced epiphytic and benthic taxa. After 1999, diatom assemblages were dominated by the species co-tolerant to nutrients and metals (*e.g.*, *C. atomus* and *N. palea*). Variance partition analyses with moving time window can distinguish the effects of multiple stressors in heavily impacted ecosystems. In this study, diatom flora shifts were mainly mediated by the combined effects of nutrients and metals. The sole effect of nutrients explained little more variance than did that of metals for the first floristic change around 1972, while the unique impact of metals was more important than that of nutrients for the second flora shift around 1999. In addition, climate warming might enhance eutrophication and heavy metal pollution, probably *via* increasing nutrient and metal release from sediments. Therefore, remediation efforts should be undertaken to reduce the severity and amount of nutrient and metal inputs.

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