Recent palaeolimnological change recorded in Lake Xiaolongwan, northeast China: climatic versus anthropogenic forcing

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Abstract

Lake Xiaolongwan, is a closed maar lake located in the Long Gang Volcanic Field, northeast China. Core XLW2 was collected in 2007 from the central region of the lake and provides a palaeoecological reconstruction over the past ca. 130 years (dated using radiometric methods: ^{210}Pb and ^{137}Cs). Diatom floristic changes and catchment productivity (carbon isotope ratios) were analysed on the core. Indicators of atmospheric pollution (XRF and SCP inventories) were also conducted. Results show a marked transition from a dominant benthic assemblage to a planktonic one (increasing P:B ratios) starting after ca. 1940 AD, becoming most prominent after ca. 1980 AD (P:B > 1). Most notable floristic changes result from the increase in the planktonic species *Discostella woltereckii*. These changes are concomitant with increased temperature trends from the region and reconstructed temperature anomalies of the NH. SCP concentrations and flux rates also increase after ca. 1950 AD, with highest values seen at ca. 1980 AD after which values decline. Normalised elemental geochemistry (e.g. Pb/Ti) also show a marked increase after ca. 1970 AD, most likely derived from atmospheric deposition of Pb. The recent increase in *D. woltereckii* precedes anthropogenic contamination (Pb/Ti) at the site and persists after the decline in SCP concentrations. This suggests that the recent increases are driven by increased mean annual temperature trends. These temperature trends may be manifested as earlier (later) ice off (on), a longer growing season and/or increased DOC at Lake Xiaolongwan: conditions for which planktonic species have a more competitive advantage.

Key words: diatoms, carbon isotope ratios, spheroidal carbonaceous particles, pollution, recent climate change, China

1. Introduction

It is now well established that lakes, particularly in heavily polluted regions, have been impacted by anthropogenic contamination over the past ca. 150 years, e.g. through acidification (e.g. O'Dwyer and Taylor, 2010; Battarbee and Bennion, 2011) and heavy metal

pollution (e.g. Thevenon et al., 2011). Many of these studies have focused on the regions of North America and Europe, where ecological thresholds are frequently crossed due to the sheer scale of atmospheric deposition and anthropogenic nutrient loading (e.g. nitrogen hotspots such as the Rocky Mountains, North America, Saros et al., 2003; western North America, western Canada and the Arctic, Holtgrieve et al., 2011). Increasingly, impacts upon lakes in remote regions, including increased mercury (Hg) accumulation in Arctic Canada (Kirk et al., 2011) and Svalbard (Drevnick et al., 2012) and lead (Pb) deposition in European Arctic and alpine lakes (Camarero et al., 2009; Liu et al., 2012) have been detected. Contamination in remote, continental regions such as the Tibetan Plateau have also been reported (e.g. Pb and Hg deposition; Wang et al., 2010; Yang et al., 2010a; persistent organic pesticides (POPs) and polychlorinated biphenyls (PCBs); Yang et al., 2010b), at least some of which may be deposited after long-range transport (Yang et al., 2010a). Atmospheric transport and deposition of Hg has resulted in widespread contamination (Fitzgerald et al., 2005; Lindberg et al., 2007), potentially impacting sensitive ecosystems, as well as yielding concerns over its toxicity (Hylander and Meili, 2005). However, despite such marked pollution (e.g. Wang et al., 2010; Yang et al., 2010a; Yang et al., 2010b), evidence suggests that over the 20th century, in the remote region of the Tibetan Plateau, and in the context of this paper, diatom community changes have been modest. Wischnewski et al (2011) highlight that lake geochemistry changes are more apparent than those of diatom species, with the latter showing only muted changes. This is thought to be most likely a response to localised and/or negative climate feedbacks and highlights that pollution effects do not have a clear, coherent impact upon lakes in this region (Wischnewski et al., 2011).

The 20th century global air temperature rise, north of 60^{o}N is well documented with warming in the order of 1.5^{o}C being observed in the periods between ca. 1915 and 1940 AD and from the late 1960s until 2010 AD (e.g. Moritz et al., 2002; Jones and Moberg, 2003; Mann et al., 2008; Manabe et al., 2011). Indeed, in the context of the past ca. 150 years, temperature rise over the past two to three decades has been particularly prominent (Jansen et al., 2007). This recent warming, and subsequent increases in the length of the ice-free season, has been found to affect algal assemblages in circum-Arctic lakes and ponds (Smol et al., 2005) as well as alpine and temperate lakes (Rühland et al., 2008). Similar ecosystem responses have also been shown from sites in northeastern China, based on analyses of regional time-series data, where the length of the spring season has increased by more than 10 days and the summer season by up to 40 days, over the period 1951 to 2000 AD (Dong et al., 2010; Liu et al., 2010).

Rühland et al. (2008) provide a coherent picture that climate-driven, taxon-specific changes, especially increases in planktonic diatoms such as *Discostella* taxa (previously named *Cyclotella*) are now evident across large regions of the Northern Hemisphere (NH), representing a wide spectrum of non-acidified/non-enriched lake ecosystems. Many of these

lake ecosystems have crossed ecological thresholds with changing climate initiated in the 19th century in Arctic and alpine regions (e.g. Wolfe and Perren, 2001), but which typically only occurred in the mid-20th century in lakes from mid-latitude regions of North America. In Arctic regions, rapid changes in algal populations have also been shown to occur since the latter part of the 20th century (e.g. Wolfe and Perren, 2001). However, it is important to highlight that evidence of 20th century warming is not spatially coherent across the Arctic (e.g. northern Québec; Laing et al., 2002). In particular regions of northern Labrador, in the Canadian Arctic, these trends have not been found. For example, at Saglek Lake-15, Paterson et al (2003) highlight that minimal evidence of 20th century warming exists, compared with other regions of the Arctic and sub-Arctic. They discuss that only muted changes are seen in diatom and chrysophte assemblages, at both Saglek Lake-15 (reference site) and neighbouring Saglek Lake-2, with the latter also documenting high values of PCB contamination since the mid-20th century. Paterson et al (2003) further outline that recent warming documented across the Arctic, is most likely driving diatom regime shifts (e.g. increase in planktonic *Discostella* species) rather than long distance transport of pollutants, documented in lake sediments from other regions of the Arctic and sub-Arctic, outside of northern Labrador and northern Québec (Finney et al., 2004). This argument is being increasingly supported (e.g Rühland et al., 2003a; Smol et al., 2005; Rühland et al., 2008). In northeast China, similar diatom floristic changes have now been identified, where abundances in *Discostella pseudostelligera* increased in tandem with records of increased summer temperatures (Wang et al., 2012), which result in longer lake thermal stratification periods (and weaker wind driven mixing) in summer months (Sorvari et al., 2002; Rühland et al., 2003a). Contemporary monitoring at Lake Tahoe shows that with intensified lake stratification, abundances of small celled phytoplankton (namely the genus *Discostella*) increased due to their competitive advantage over larger sized cells (e.g. *Stephanodiscus*), which is believed to be a result of their ability to survive in more nutrient deplete conditions following reduced lake mixing and/or as a result of reduced lake water clarity, as these valves have a lower sinking velocity (Winder and Hunter, 2008; Winder et al., 2009). Other evidence has shown that benthic assemblages decline as a response to reduced periods of lake ice cover duration, another response to increasing trends in mean annual temperatures (e.g. Lotter and Bigler, 2000).

As well as causing problems of aquatic contamination, fossil fuel combustion has made a significant contribution to global warming over the past century (Oreskes, 2004). Direct interactions between pollutants and climate change are also increasingly being recognised. Indeed, there is also a strong relationship between 20th century climate trends and byproducts of anthropogenic combustion (e.g. nitrogen, sulphur and heavy metal deposition) (Curtis et al., 2009; Pla et al., 2009). For example, in parts of the Tibetan Plateau, You et al. (2009) describe the clear weakened effect in diurnal temperature ranges (important in regulating precipitation and circulation) due to anthropogenic emissions. In northeast China, Yu et al. (2011) investigated atmospheric deposition in response to industrialisation, and in particular

the role that deposited pollutants may play in influencing sensitive ecosystems. Instrumental data from regions affected by the East Asian Summer Monsoon (EASM) document considerable decadal variability during the second part of the 20th century, displayed as persistent moisture anomalies (Li et al., 2009). In order to aid in the discussions of forcing factors triggering this change (e.g. natural versus anthropogenic), particularly in regions where data are sparse, this study provides a detailed investigation of recent floristic changes in diatom species composition from a small, remote crater lake in northeast China. The analysis of pollutants (trace metals and spheroidal carbonaceous particle (SCPs)) as well as lake and catchment productivity (as measured by $\delta^{13}C$), enable a detailed discussion of environmental change over the past ca. 150 years.

2. Regional setting

Lake Xiaolongwan is one of eight maar lakes present in the Long Gang Volcanic Field (LGVF), Jilin Province, NE China (Figure 1). Mean annual temperature for the region (between 1999-2001), based on the data from Changchun (Figure 1) is +5.9°C, with temperatures falling below a mean monthly value of 0°C from November to the end of March. Highest mean monthly temperatures are in July (+25.5°C) and lowest in January (−16.7°C). Total mean annual precipitation for the years 1999-2001 inclusive was 444 mm and more than 65% of this rain falls during the monsoon period (June to August). The geology of the lake region is mostly composed of alkali basaltic rocks of Quaternary age (Liu et al., 2009). Lake Xiaolongwan is the smallest of the eight lakes (maximum water depth 16.2 m in August 2007, area of 0.1 km^2) and is a closed basin. The lake in August 2007 had a pH of 6.7, dissolved organic carbon (DOC) of 12.3 mg l^1 and surface water temperature of 22.3°C. The catchment of Lake Xiaolongwan is covered with broadleaf (predominantly *Betula costata*) and mixed conifer vegetation. The lake is dimictic with overturn in spring (April-May) and autumn (late September to October) and a period of ice cover between November and April when regional temperatures are lowest. Stratification occurs between May and mid-September. These limnological characteristics are very sensitive to the climate of the region, making it a suitable location for investigating climate (and anthropogenic) forcing over the 20th century.

3. Materials and methods

3.1. Field methodology

On 18th August 2007 core XLW2 was collected from the central region of Lake Xiaolongwan (42°17'59.8"N and 126°21'34.3"E) using an UWITEC-gravity corer. A Plastimo hand-held Echo Sounder II was used to locate the deepest position for coring, 16.2 m. Surface sediments were carefully sampled from the core using a syringe and transferred into labelled Whirlpack bags. Core XLW2 was extruded in the field: at every 0.5 cm until 20 cm and thereafter every 1 cm to the base at 64 cm. These sediments were very soft with a high

water content and account for the long sediment record collected by the gravity corer. Samples were then stored in a dark and cool (<4 °C) environment until later analyses. Only the upper 19 cm form the basis of this study because of its well-constrained chronology.

3.2. Analytical methods

3.2.1. Chronology

Radiometric techniques (^{210}Pb and ^{137}Cs) were used to date sediments from the XLW2 core. Sediment samples were dated by non-destructive gamma spectrometry (Appleby and Oldfield, 1992) at the Centre for Environmental Research, University of Sussex, UK. Ten core sub-samples were counted for at least eight hours on a Canberra well-type ultra-low background HPGe gamma ray spectrometer to determine the activities of ^{137}Cs, ^{210}Pb and other gamma emitters. The constant rate of supply (CRS) (Appleby and Oldfield, 1978) model was used here in order to generate an age model for the XLW2 record.

3.2.2. Diatom sample preparation

A total of 20 samples (0 to 19 cm) were analysed within core XLW2. Approximately 0.1 g of wet sediment was digested in 5 ml 5% H_2O_2 using the water bath technique (Battarbee et al., 2001). Diatom counting was conducted using a Zeiss light microscope at x1000 magnification under oil immersion and phase contrast.

A minimum of 300 valves were counted per slide. Diatom floras such as Krammer and Lange-Bertalot (1986; 1988; 1991b; 1991a), Lange-Bertalot and Metzeltin (1996), Lange-Bertalot and Genkal (1999), and Vyverman (1991) were used for identification. In addition, Krammer (1992), Lange-Bertalot (2001) and Lange-Bertalot and Moser (1994) for the identification of the species *Pinnularia, Navicula* and *Brachysira* respectively. Haworth and Hurley (1986) was used to aid the identification of *D. woltereckii*. For the distinction between the species *Punctastriata discoidea* and the newly identified *Punctastriata glubokoensis*, both Williams et al. (2009) and Flower (2005) were used. Diatom planktonic: benthic (P:B) ratios were calculated by grouping species based on contemporary sampling at the site. Other ratios of *D. woltereckii: Fragilariaceae* benthic and Planktonic: *Fragilariaceae* benthic taxa, were also calculated.

3.2.3. Organic isotope geochemistry

Sediment subsamples were prepared for organic geochemical analyses (^{13}C/^{12}C, %Total Organic Carbon (TOC) and %Total Nitrogen (TN)) to determine possible sources of organic matter within the lake sediments (Leng and Marshall, 2004). Bulk organic carbon samples were prepared by placing 2 g of wet sediment in 5 ml of 5% HCl overnight in order to remove carbonates. A resolution of every 0.5 cm was selected between 0-20 cm after which every 1 cm was sampled to the base of the core. Samples were washed four times with de-ionised

water through Whatman 41 filter papers using manifolds and dried overnight at 40^{o}C. Bulk sediment samples were ground to a fine powder using a marble pestle and mortar, $^{13}C/^{12}C$ analyses were performed by combustion using a Carlo Erba NA1500 on-line to a VG TripleTrap and Optima dual-inlet mass spectrometer at NERC Isotope Geosciences Laboratory (NIGL). Carbon isotope composition ($\delta^{13}C_{organic}$) was calculated to the Vienna Pee Dee Belemnite (VPDB) scale using within-run laboratory standards calibrated against NBS-18 and NBS-19. %TOC and %TN, from which weight C/N is calculated, were determined simultaneously by reference to an Acetanilide standard. Replicate analyses of well-mixed samples for both $\delta^{13}C$ and C/N were conducted in order to obtain a precision of +/– 0.1‰ and 0.1 respectively

3.2.4. X-ray fluorescence (XRF) spectrometry analysis

Up to 2 g of accurately weighed (4 decimal places) freeze dried sediment was finely ground and compressed into 25 mm deep polythene sample pots for XRF analysis. A total of 50 samples were analysed throughout the 64 cm core, although only the upper 19 cm are presented within this study. Samples were analysed using a Spectro Xlab 2000 energy dispersive X-ray fluorescence spectrometer. Certified reference material (Buffalo River Sediment: reference material 8704) was run every 6th sample.

In order to determine the anthropogenic component of trace elements in the sediments, the data were normalised to titanium (a conservative geochemical element) as follows (e.g. here for Pb):

$$Pb_{a(x)} = Pb_{total(x)} - (TiO_{2(x)}/TiO_{2(b)})(Pb_{b})$$

Norton and Kahl (1987); where $_{a}$ = anthropogenic, $_{(x)}$ is sample depth and $_{b}$ = background. This method is appropriate when total element concentrations are firmly bound in mineral lattices. Although for elements such as Cu, Ni and Pb, the labile fraction is generally greater and reduces the value of the method (Boyle, 2001). Its use permits discussion of anthropogenic contamination in the recent sediments of Lake Xiaolongwan.

3.2.5. Spheroidal Carbonaceous Particle (SCP) Analysis

Spheroidal carbonaceous particle (SCP) analysis followed the procedure described in Rose (1994). Sequential treatments using nitric, hydrofluoric and hydrochloric acids removed organic, siliceous and carbonate fractions respectively. A known fraction of the resulting suspension was then evaporated onto a coverslip and the number of SCPs counted using a light microscope at x400 magnification. The criteria for SCP identification followed Rose (2008). Sediment SCP concentrations were calculated in units of ‘number of particles per gram dry mass

of sediment (or soil)' (gDM^{-1}). Analytical blanks and SCP reference material (Rose, 2008) were included in each batch of sample digestions. Reference concentrations agreed closely with expected values, while no SCPs were observed in the blanks. The detection limit and accuracy for the technique are typically ca.100 gDM^{-1} and ca. ± 45 gDM^{-1} respectively.

3.2.6. Multivariate statistics

Detrended correspondence analysis (DCA) was undertaken on diatom relative abundances > 2% in order establish the magnitude of species turnover along the first axis (i.e. the gradient length of the dataset). Relative abundance data were square root transformed in order to stabilise species variance and rare species were down-weighted. The DCA axis 1 gradient length was relatively short (1.952) so trends in diatom assemblage data were subsequently investigated using the linear ordination technique of Principal Components Analysis (PCA) (Lepš and Šmilauer, 2003). The number of significant PCA axes was determined using a broken stick model (Jolliffe, 1986).

Detrended canonical correspondence analysis (DCCA) was undertaken upon the complete data set (with square root transformion and detrending by segments) in order to investigate species turnover (a measure of the total diatom floristic change), with the diatom data constrained using dates obtained from the age model (Birks, 2007). In order to establish the significance of turnover (standard deviation (SD) units) from the Lake Xiaolongwan core, it was compared with turnover established for a number of unimpacted, references sites (sensu Smol et al., 2005). Smol et al (2005) detail that diatom turnover (beta diversity) > 1 SD unit at circumpolar lakes, can be used to indicate sites where taxonomic change is greater than that measured at unimpacted temperate lakes (e.g. reference sites). As reference sites were not sampled as part of this project, the SD value of > 1 presented by Smol et al (2005) is applied to gauge the significance of compositional turnover at Lake Xiaolongwan. We believe this is appropriate in the context of this paper, as the average time interval analysed by Smol et al (2005) is comparable (ca. 150 years) and identical multivariate methods were applied. Diatom zones were delimited by optimal partitioning (OPTIMAL) using the program Zone v. 1.2 (Juggins, 1992) (Birks and Gordon, 1985).

4. Results

4.1. Core chronology

The chronology of the core was calculated using the CRS model (based on a constant flux of ^{210}Pb) and corrected by the ^{137}Cs concentration peak at 8.5 cm (Figure 2) which was assigned the date 1963, associated with peak atmospheric nuclear weapons testing. There are two decreases in ^{210}Pb activity between 8.5 and 3 cm and after 1.5 cm. The first event corresponds with an increased mineral component and lower %TOC, and the later event after ca. 2000 AD, corresponds with increased geochemical elements (e.g. Si and Al). As such, both may be reflecting a dilution of the sediments with increased catchment in-wash. The resulting age-depth model is shown in Figure 2 with the start of the chronology (1892 ± 22) at

16.5 cm. The sediment accumulation rates are also displayed, and show an increase over the last ca. 30 years. This chronology is used in all subsequent stratigraphic analyses.

4.2. Diatoms results from XLW2

Diatom preservation was good with little frustule dissolution and a total of 55 species were identified. Three zones were delimited using optimal partitioning and applied to the diatom stratigraphy. Zone 1 is dominated by a benthic assemblage (P:B ratios close to 0) (Figure 3). At the beginning of the record, after ca. 1885 AD, there was a mixed floristic assemblage of *Staurosira construens* var *venter*, *Punctastriata discoidea* and *Achnanthidium minutissimum.* This assemblage persisted for the duration of Zone 1, with *P. discoidea* and *S. construens* var *venter* decreasing after ca. 1920 AD. PCA axis 1 scores show an increasing trend throughout this zone.

The start of Zone 2 is marked by the first notable appearance of planktonic diatoms, with a distinct increase in both *Discostella woltereckii* (ca. 5 to 35%) and P:B ratios. *S. construens* var *venter* and *P. discoidea* fluctuate between 15-30% and 10-30% respectively. *A. minutissimum* and *T. flocculosa* fluctuate between ca. 10 and 15% and 0 to 10% respectively. PCA axis 1 scores are greater than in Zone 1, remaining close to 0 for the entirety of Zone 2.

After ca. 1985 AD (Zone 3) planktonic assemblages increase further. However at ca. 1985 AD there is a short lived increase in the abundance of *Fragilaria delicatissima,* to ca. 45%, concomitant with a decrease in *D. woltereckii*, following which, this planktonic species returns and dominates. At ca. 1985 AD, abundances of *S. construens* var *venter* and *P. discoidea* further decline along with *T. flocculosa.* The floristic assemblage at this time, and for the first time in the record, is dominated by a planktonic composition of *D. woltereckii, F. nanoides,* and *F. delicatissima*. Benthic assemblages of *A. minutissimum* and *Brachysira neoexilis* were also present, with the latter having its first sustained period of appearance in the core after ca. 1990 AD. After 1995 AD abundances of *Encyonopsis descripta* increase and remain between ca. 5-10% until the top of the core while *T. flocculosa* increases to 3-6%. P:B ratios increase during Zone 3, fluctuating between 1.3 and 2 as does the ratio of *D. woltereckii: Fragilariaceae* benthic taxa. PCA axis 1 scores also increase steadily to values close to 2.

4.3. Bulk organic isotope geochemistry

For the duration of the record, %TOC varies between 18 and 40% (Figure 4). After ca. 1940 AD, there is a small increase in values until ca. 1960 AD. A later increasing trend is seen in Zone 3 with a peak in values occurring at ca. 1990 AD. C/N oscillates between ca. 11 and 16. There is a declining trend in values until ca. 1965 AD. During this period values are greater than 12 (mixed macrophyte source of carbon) until ca. 1920 AD after which they decline to < 12. These lower values are maintained for Zone 2 and most of Zone 3, increasing at ca. 1990 AD and in surface samples. $\delta^{13}C$ has a small range of values over the XLW2 record, between

–30 and –27‰. Increases in values occur between ca. 1900 to 1945 AD (to ca. –27‰) and later between ca. 1945 and ca. 1970 AD (to ca. –27‰), after which values declined towards the top of the core.

4.4. XRF analyses

Selected elements show an increasing trend after ca. 1925 AD, with Fe increasing to ca. 4% and Pb to 50 μg g^{-1}, although changes in Ti are minimal over this period (<0.1%) (Figure 4). The higher values in Fe and Pb continue during Zone 2, when Ti begins to decline after ca. 1970 AD. Within Zone 3 concentrations of Pb increase further to 165 μg g^{-1} at ca. 2000 AD while %Ti continues to decline towards the top of the record. Contamination indices (Pb/Ti, Zn/Ti, Cu/Ti and Ni/Ti) show little variation throughout Zone 1 with values close to 1. After ca. 1970 AD, ratios of Cu, Zn and Pb enrichment increase and reach peak values at ca. 2000 AD (Zone 3). However, despite this, values for Cu/Ti, Zn/Ti and Ni/Ti all remain close to 1. Pb/Ti, by contrast reaches a peak enrichment of >3.0.

4.5. Spheroidal carbonaceous particles (SCPs)

The first presence of SCPs is detected in ca. 1910 AD and concentrations increase slowly to ca. 1955 after which they increase rapidly to a peak in ca. 1980 AD when concentrations exceed 13,500 (gDM^{-1}) (Figure 4). After this date, concentrations decline towards the surface sediments. SCP fluxes (Figure 5) also show an increasing trend after ca. 1920 AD to a peak of 300 $cm^{-2}yr^{-1}$ in ca. 1980 AD. Fluxes decrease from this time to the top of the core (2007 AD).

4.6. Multivariate statistics

Broken stick analysis reveals that the first two PCA axes are significant and together explain 45% of species data. Axis 1 sample scores summarise the principal floristic change (30.8%), and these are plotted alongside other proxy data in Figures 3 and 5. As discussed in Section 3.2.6, the value of 1 beta diversity (SD) unit, identified by Smol et al (2005) as being a significant level above which species beta diversity has changed at unimpacted, temperate sites has been applied to this study (in the absence of its own independent reference sites). DCCA shows that diatom compositional turnover was significant (1.78 standard deviation (SD) units; Table 1).

5. Discussion

This study provides a reconstruction of palaeolimnological changes from Lake Xiaolongwan over the past ca. 130 years. We focus on this period because we can securely date the upper sediments using radiometric dating, and these place any changes seen in the core into an historical context.

5.1. Evidence of human impact

There is documented evidence for anthropogenic disturbance to the LGVF (over the past ca. 150 years at Lake Sihailongwan), based on pollen reconstructions (Mingram et al., 2004; Li et al., In review). In the catchment of Lake Sihailongwan (location on Figure 1b), there has been increased evidence of human induced forest thinning, based on total pollen counts (Mingram et al., 2004). Furthermore, during the past ca. 70 years there has been an indication of agricultural activity within the region. Pollen analyses conducted on cores from Lake Erlongwan (ca. 1 km from Lake Xiaolongwan: Figure 1b) also show support for these vegetation trends over the late Holocene (ibid.). In particular, human induced vegetation changes are seen during the 1930s at this site (changing vegetation to a deciduous forest with mixed shrub and grassland) as a result of Japanese occupation in the region, which prompted the selective felling of *Pinus koraiensis* (Liu, 1989; Li et al., In review). Charcoal deposits in Lake Erlongwan sediments, further highlight human induced forest clearance, although these have declined since ca. 1980 AD as a result of government policy to restore the reclaimed land to forested regions (Li et al., In review). Despite regional evidence, we argue that forest clearance and agriculture, in the LGVF, has infact had minimal impact upon the small catchment of Lake Xiaolongwan, over the past ca.130 years (Panizzo, unpublished data).

However, to further look at the degree of catchment disturbance at Lake Xiaolongwan and to investigate in more detail natural versus anthropogenic contamination signals in the catchment (via in wash or atmospheric deposition), trace element analyses were conducted. Enrichment factors in trace elements after ca. 1980 AD (e.g. Zn/Ti, Cu/Ti and Ni/Ti; Figure 4) are very close to 1 and do not exceed pre-industrial values (Panizzo, unpublished data). However, Pb concentrations do show a marked increase on entering Zone 3 and Pb/Ti increases after 1970 AD. These exceed pre-industrial values and indicate atmospheric contamination at Lake Xiaolongwan. Evidence of atmospheric deposition is corroborated by increasing SCP concentrations at Lake Xiaolongwan, although the timing of highest values for both proxies differs (SCP concentrations decrease after ca. 1980 AD, when Pb/Ti increase; Figure 4). These data demonstrate anthropogenic contamination from a fossil-fuel source, most likely high temperature coal combustion (e.g. Farmer et al., 1999), has occurred at Lake Xiaolongwan, since the mid-20th century.

Very little literature documents the increase in industrialisation in this region of China to independently corroborate these data. However, one source does state that after 1945 AD and with the advent of the People's Republic of China, Jilin Province became the "industrial heartland of China", with coal-fired power stations rapidly increasing in number (Hays, 2009). Another study by Kang et al. (2009) investigating contemporary pollution aerosol transport over northeast China, South Korea and Japan, have found that dust and pollution aerosols (including Cu, Zn, P and Ni) are transported east, by westerly winds. In drawing comparisons

with the Lake Xiaolongwan pollution record, Pb aerosols were largely transported to the Japan East Sea from the Asian continent during the autumn, winter and early spring months (ibid.). Although the dominant source of Pb (leaded petrol) has been reduced over the past decade on the Asian continent (Kang et al., 2009), their findings imply that other sources must be contributing to regional atmospheric Pb. Such sources may include metallurgic dust, coal combustion and cement manufacturing (Chen et al., 2005; Kim, 2007).

The shift to higher Pb/Ti after ca. 1970 AD is coincident with a further increase in planktonic communities in the lake (Figure 5). However, it is clear that the most notable increase in planktonic species (*D. woltereckii*) is seen much earlier in the record and predates this evidence of atmospheric contamination (after ca. 1940 AD). Furthermore this is concomitant with increased mean annual temperature and reconstructed NH temperature trends (Crowley, 2000: Figure 5), regarded to be ecologically consistent changes with predicted limnological responses to climatic warming (Smol et al., 2005). This suggests that evidence of atmospheric deposition (Pb/Ti) post dates main floristic assemblage changes at Lake Xiaolongwan.

However, the boundary between Zones 3 and 2 shows the increase in P:B occurs at the same time as an initial increase in SCP concentrations (Figure 4). SCP flux rates (Figure 5) further demonstrate the increase in SCP deposition after ca. 1950 AD. To our knowledge there are no other SCP data for this region with which to compare our Lake Xiaolongwan fluxes. However, some comparisons can be made with records from other regions of Asia and southern China. For example, SCP fluxes from the more contaminated southern basin of Lake Baikal (Rose et al., 1998), reach ca. 50 cm^{-2} yr^{-1} (Rose, unpublished data) whereas at Lake Xiaolongwan, SCP fluxes reach a peak of ca. 300 $cm^{-2}yr^{-1}$, suggesting considerably higher levels of contamination. However, these values are still an order of magnitude less than records from Lake Taihu, close to Shanghai, east China, where fluxes exceed 4000 cm^{-2} yr^{-1} after 1990 AD (Rose et al., 2004). Furthermore, flux values at Lake Xiaolongwan remain close to Lake Baikal background levels until after ca. 1955 AD (when they reach ca. 75 cm^{-2} yr-1).

There is a notable decrease in SCP concentrations and flux rates after ca. 1980 AD (Figure 4), while abundances of *D. woltereckii* continue to dominate the Lake Xiaolongwan record. This suggests that, although evidence of anthropogenic contamination form fossil fuel combustion has been recorded at the once perceived pristine lake, it may not be the dominant driving force for high compositional (beta diversity) change at the site in the 20^{th} century. As highlighted earlier, the shift from benthic to planktonic assemblages has been identified in Arctic, alpine and increasingly in non-acidified, non-enriched temperate lakes due to longer ice free periods and warming-induced changes in water column properties induced by warming climate trends (Smol et al., 2005; Rühland et al., 2008). On the basis of the data

presented in this study, we argue that positive temperature anomalies/trends are trigger factors for significant species turnover during the late 20th century at Lake Xiaolongwan, particularly prior to ca. 1950 AD. After which, anthropogenic contamination (SCPs) may also be acting in tandem, although concentrations of these pollutants are considerably lower than highly impacted sites in southern China (Rose et al., 2004) and are close to background levels in northern Europe (e.g. Rose, 1995). However, it is increasingly recognised that the interplay between atmospheric aerosols and changing climate are complex, and their dual impact on freshwater ecosystems is poorly understood. Use of palaeoecological records can further our understanding, at least of the timing of potential impacts from different drivers.

5.2. Species turnover at Lake Xiaolongwan

Lake Xiaolongwan is located in the remote region of the LGVF National Park. As discussed, palaeoecological changes from the record are concomitant with changes in temperature trends across this region, with clearest changes (e.g. increase in P:B and appearance and increase in *D. woltereckii*) seen over the past ca. 70 years (entering Zone 2; Figure 5). The DCCA results of estimated compositional turnover (SD units) are summarised in Table 1. When compared to DCCA results from an unpublished, longer (ca. 2000 years) diatom record from the same site, it is clear to see that species turnover for the 20th century is greater (SD unit of 1.17 vs 1.78 presented here; Table 1) (Panizzo, unpublished data). This is similarly highlighted at other regions in central Asia, e.g. the East Sayan Mountains, where Holocene beta diversity changes (SD = 1.194) are lower than those presented here for Lake Xiaologwan (Mackay et al., In press). However, such trends are not so clear-cut in the southeastern Tibetan Plateau (Wischnewski et al., 2011), which had very stable species (diatom and pollen) compositional change over the past 200 years (Table 1). Wischnewski et al. (2011) argued that both lakes and catchments in this region were resilient to current rates and magnitude of climate change and that as a result, ecological species thresholds have not yet been crossed. This is interesting as it could suggest the use of these lakes as reference sites for the Lake Xiaolongwan (sensu Smol et al, 2005). Furthermore, they highlight that only muted regime shifts (< 1 SD) are seen in this region, despite evidence of long-range atmospheric deposition and contamination in the Tibetan Plateau (e.g. Wang et al., 2010; Yang et al., 2010a; Yang et al., 2010b). Our data is also compared with Arctic lakes presented by Smol et al (2005) where, as at Lake Xiaolongwan (Figure 3), an increase in planktonic diatoms can be seen at the expense of benthic genera (e.g. *Fragilaria* and *Achnanthidium* species) (Table 1).

Beta diversity values are on a par with those from sites in northern Labrador, at Saglek Lake-2 and -15 (1.10 SD units and 0.79 SD units respectively: Table 1), where the absence of recent warming (despite evidence of PCB deposition at Saglek-2) and minimal diatom assemblage change are seen (Paterson et al., 2003). In particular, it may highlight the

negligible effects of pollution in driving such compositional changes (compared to clear temperature trends: Figure 5). Indeed, Smol et al (2005) conclude that diatom changes (e.g. beta diversity) in Arctic lakes (notably those cited in Table 1, which document increased *D woltereckii*:*Fragilariaceae* benthic ratios comparable with Lake Xiaolongwan: Figure 5) show dramatic, unidirectional regime shifts within the past ca. 130 years (e.g. SD >1). Furthermore, these ecological shifts are consistent with the predicted limnological responses that would be expected due to climatic warming (e.g. increased competitiveness of planktonic, *Discostella,* species due to reduced ice cover duration and/or enhanced thermal stratification) (Sorvari et al., 2002; Rühland et al., 2003a; Winder and Hunter, 2008; Winder et al., 2009) and in the absence of anthropogenic impacts (e.g. increased nutrients, heavy metal deposition) which are often found to postdate the observed initiation of algal changes (Smol et al., 2005).

5.3 Palaeoecological changes and natural variability

The beginning of the diatom record at Xiaolongwan is dominated by *S. construens* var *venter* and *P. discoidea* (Figure 3). These species, based on sediment trap data from Lake Xiaolongwan (Rioual et al., unpublished data) are more abundant at the end of summer thermal stratification and during autumn lake turnover. After ca. 1920 AD *A. minutissimum* and *T. flocculosa* increase in relative abundance, which at the site today are also most abundant during periods of lake stratification and autumn turnover. After ca. 1935 AD (Zone 2) *D. woltereckii* appears for the first time. Contemporary sediment trap data shows that this species is most abundant during spring and autumn turnover and is also present during summer stratification (Rioual et al., unpublished). Regional timeseries data has demonstrated a clear increase in spring and summer growing seasons over the past 50 years (Dong et al., 2010; Liu et al., 2010). We argue that the increase in *D. woltereckii* since ca. 1950 AD is reflecting this increased growing season trend (resulting from earlier/later ice off/on dates). These small-sized species (*D. woltereckii* ranges between 5-8υm in diameter) have been found to have high growth rates, low nutrient requirements and a low sinking velocity (a high surface area/volume (SA/V)), a competitive advantage with prolonged periods of stratification and nutrient deplete conditions (Winder et al., 2009). However, as at Lake Xiaolongwan, the species is today also found to dominate during spring an autumn turnover, we argue that this relationship is more complex at the site and the increase in the species also reflects an increase in the duration of the growing season as a whole.

However, trap data from neighbouring Lake Sihailongwan (Rioual, unpublished data) shows that the closely related *Discostella pseudostelligera* species is more abundant during summer stratification. When looking at the main floristic changes driving species turnover in the Lake Xiaolongwan record, it is clear to see a shift from a benthic to planktonic assemblage. This is clearly summarised by P:B ratios and PCA Axis 1 scores (Figure 5). P:B ratios and *D. woltereckii* abundances increase on entering Zone 2, after ca. 1935 AD. Instrumental records

from Changchun and Jingyu meteorological stations (Figure 1) have shown that after ca. 1900 AD there have been increasing trends in mean annual temperatures (Figure 5). These trends are concomitant with increased reconstructed temperature anomalies for northern China (> 0^{o}C) and the NH (> 0^{o}C) (Figure 5; Crowley, 2000, respectively; Gong et al., 2011). Furthermore, the greatest increase seen in mean annual temperatures, at Changchun, after ca. 1980 AD is concomitant with the increase in *D .woltereckii: Fragilariaceae* benthic ratios.

%TOC showed only small increases between ca. 1885 – 1985 AD, but increased to highest values during the past 20 years, perhaps related to increased lake productivity. Because $\delta^{13}C$ values fluctuate between –27‰ to –30‰, we can rule out any significant contribution of routinely higher $\delta^{13}C$ values (ca. –8‰ to –15‰) from C_4 land vegetation. Moreover, there is no pollen evidence of C_4 plants from nearby maar lake sediments deposited over the past ca. 150 years (e.g. Mingram et al., 2004; Li et al., In review). It is likely therefore that C_3 plants are the main source of terrestrial carbon to Lake Xiaolongwan. C/N ratios are used to help discriminate between autochthonous and allochthonous sources of carbon to lake sediments, especially vascular and aquatic plants (algae) (Leng et al., 2006). At Lake Xiaolongwan, the importance of autochthonous sources of carbon to the lake is highlighted due to low C/N ratios (C/N <12 indicates a phytoplanktonic source of carbon; Meyers and Teranes, 2001), although continuous delivery of allochthonous matter cannot be ruled out either (Meyers, 1994), especially at the very top of the core where values increase > 16. Interpretation of changing $\delta^{13}C$ values in lake sediments is complex. While increasing values can be used to infer primary production in lakes (e.g. Leng and Marshall, 2004), burial of ^{12}C-enriched organic matter into bottom sediments can also result in less negative $\delta^{13}C$ values (Meyers and Lallier-Vergès, 1999). Changes to catchment vegetation and associated soil respiration can also alter $\delta^{13}C$ values in lakes (Reuss et al., 2010), although being a maar lake, the catchment of Lake Xiaolongwan is small and may not be a significant factor. The ratio of planktonic to benthic species (P:B) may also influence $\delta^{13}C$ values in lake sediments because planktonic algae have on average lower $\delta^{13}C$ values (–32‰) than benthic species (–26‰) (France, 1995) due to the diffusive boundary layer effect. This is a result of the difference in the turbulence of water surrounding benthic and planktonic valves, benthic diatoms can have a diffusive layer around them of > 1mm, while phytoplankton only ca. 10υm (Smith and Walker, 1980; Jorgensen and Revsbech, 1985; Riber and Wetzel, 1987). This diffusive layer affects the potential for CO_2 or HCO_3^- to exchange with the valves (ibid.)

In Lake Xiaolongwan $\delta^{13}C$ values increased from approximately –29.5‰ at ca. 1885 AD to –27.5‰ by ca. 1955 AD, concurrent with a small increase in %TOC and decline in C/N ratios, which may suggest that $\delta^{13}C$ values were influenced by a small increase in lake productivity. The decline in $\delta^{13}C$ values from ca. 1970 AD to ca. 2000 AD however, also occur at the same time as an increase in %TOC (particularly after 1985 AD), and therefore their relationship to primary production is not straightforward. The decline in $\delta^{13}C$ values occurs at the same time

as very large increases in the proportion of planktonic taxa in the lake and therefore might be indicative of a shift in productivity from littoral to pelagic regions. These changes are also coincident with the notable increase in the planktonic *Fragilaria nanoides* and *Fragilaria delicatissima* further supporting this argument. However, increases are also seen in the epiphytic species *B. neoexilis* and *E. descripta*, which are today found on the macrophytes *Phragmites*, *Typha* and *Utricularia*. These emergent macrophytes are found in large populations, in the extensive littoral regions of the lake (Figure 1c). The increase in the epiphytic diatoms may suggest a shift to a larger macrophyte population in response to longer summer seasons, although C/N values remain for the most part < 12, apart from a brief increase at ca. 1990 AD and in surface sediments, suggesting small changes may have occurred. Nevertheless, it does demonstrate a regime shift to different species after ca. 1980 AD when temperature trends increase further.

The reduction in benthic assemblages after ca. 1975 AD, may also be reflecting an increase in DOC (increased %TOC) and therefore increased light attenuation in these habitats. Laird et al. (2011) have detailed that changes in DOC can have significant impacts on light transparency and lake thermal structure (Fee et al., 1996; Snucins and Gunn, 2000; Keller et al., 2006) which in turn can influence algal productivity and dominant assemblage structure (Adrian et al., 2009; Heino et al., 2009; Karlsson et al., 2009). Evidence has shown the favourable increase of planktonic diatoms (predominantly *D. pseudostelligera*: a species which belongs to the same species complex) over benthic assemblages (due to their high growth rates and small cell size: Winder et al., 2009) with values of increased %TOC and DOC concentrations, from boreal North American lakes (e.g. Laird et al., 2011). Such increases in planktonic assemblages have been noted after 1990 AD at these sites. As a result, it is possible that *D. woltereckii* increases at Lake Xiaolongwan (percentage abundances and *D. woltereckii: Fragilariaceae* benthic ratios), as well as other planktonic species (P:B ratios > 1) after ca. 1985 AD, are also responding to similar increased DOC conditions (greatest increase in %TOC). Currently the presence of *D. woltereckii* at the site is associated with DOC concentration values between 7 and 12 mg l^{-1}. *D. stelligera* complex has high DOC species optima (ca. 14 mg l^{-1}) (Enache and Prairie, 2002), although other authors have identified this group as generalists in terms of DOC optima (Rühland et al., 2003b). Following detailed monitoring of contemporary diatoms from other sites in the LGVF, Rioual (unpublished) outlines that *D. woltereckii* is found at sites with higher DOC values (e.g. Lake Xiaolongwan) compared with the other *Discostella* species such as *D. pseudostelligera* and *D. stelligera*.

It is clear that further investigation into this argument is needed as variations in DOC concentrations in lakes are very complex and largely driven by climatic processes (Pace and Cole, 2002). Evidence has looked at the effects of precipitation and ice cover variations (Pace and Cole, 2002), changes in residence times (Curtis and Schindler, 1997), catchment

changes (e.g. peat formation; Dillon and Mollot, 1997) and changes in sulphur and chloride deposition (Monteith et al., 2007; Keller, 2009). Indeed, the discussion that increased DOC at Lake Xiaolongwan is in fact acting in tandem with other forcing factors could be quite important. While increased %TOC is seen after ca. 1940 AD, concomitant with the large increase in *D. woltereckii,* these changes are < 10% (Figure 4), and the greatest increase is seen much later in Zone 3. Temperature trends however, show an increasing trend concomitant with the increase of *D. woltereckii*. As such, this is likely a response to increased warming at the site, which shows increasing trends prior to the largest increase in %TOC.

6. Conclusions

Significant species turnover from Lake Xiaolongwan over the 20th century is concomitant with positive temperature anomalies over the NH and China, and positive trends in regional mean annual temperature records since ca. 1900 AD. Most notable floristic changes in diatoms are seen after ca. 1940 AD when an increase in P:B ratios and a notable increase in *D. woltereckii* occurs, coincident with increasing trends in mean annual temperature. However, this study also provides one of the first detailed reconstructions of anthropogenic contamination in northeast China. Our results show that after ca. 1940 AD there is an increase in contamination as indicated by SCP fluxes (until ca. 1980 AD) and Pb enrichment (from ca. 1970 AD). Nevertheless, following the decrease in SCP fluxes and the later increase of Pb/Ti ratios (appearing after ca. 1970 AD) the dominance of *D. woltereckii* remains and epiphytic assemblages increase, concomitant with even greater regional warming trends after ca. 1985 AD. We conclude that recent warming, over the 20th century, has led to increased beta diversity (namely a significant increase in the planktonic species *D. woltereckii*) at Lake Xiaolongwan since ca. 1950 AD. This is comparable with other studies of Arctic, alpine and non-acidified, non-enriched temperate lakes across the NH, where with evidence of recent warming, has lead to planktonic assemblages dominating lacustrine ecosystems.

Acknowledgements

This project was funded by the National Environmental Research Council (NERC) (NER/S/A/2006/14046) and the work was conducted at University College London, UK. It was a tied CASE studentship with the NERC Isotope Geosciences Laboratory (NIGL). Thanks go to NIGL for carbon isotope analyses, Dr. Andy Cundy, University of Sussex, for radiometric measurements and Dr. Handong Yang for age model advice. Gratitude also to Prof. Wang Luo for fieldwork assistance and Prof. Chu Guoqiang for his collaboration with this project.

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Figure captions:

Figure 1a) A map of northeast China detailing the present day East Asian Summer Monsoon limit and the location of the Long Gang Volcanic Field (LGVF); b) the area of the LGVF, with the eight lakes located in the park and the main geology of the region; c) The basin of Lake Xiaolongwan, with sediment trap and XLW2 core locations detailed. Images redrawn from Mingram et al (2004) and Chu et al (2008).

Figure. 2. The ^{210}Pb downcore activity (Bq kg^{-1}) and^{137}Cs activity (Bq kg^{-1}) for the core XLW2 against depth. The derived chronology, with standard errors (age against depth) for the core and sedimentation rates (g cm^{-2} yr^{-1}) are also displayed.

Figure 3. Diatom floristic assemblages for core XLW2 displayed in years AD and sediment depth (cm). Species with most dominant abundances were selected to view in the stratigraphy. Planktonic:Benthic (P:B) species ratios, along with *D. woltereckii:Fragilariaceae* benthic and *Planktonic:Fragliariaceae* benthic ratios are shown. Summary scores of PCA analyses (Axis 1) are displayed to highlight main floristic changes. OPTIMAL zonation applied to the diatom species data, where three zones were delimited, is also displayed

Figure 4. Stable organic isotope analyses conducted on XLW2: %TOC, C/N, δ^{13}C (‰). The reference line on the C/N plot corresponds to the threshold for an aquatic source of carbon (< 12). Trace element results from XRF analyses (Fe, Ti, Pb) and their respective units, are also displayed. Pollution indices, which show largest shifts are also shown (Pb/Ti, Zn/Ti, Cu/Ti, Ni/Ti) as are SCP concentrations (g DM^{-1}). Chronology is in Years AD and the diatom zonation is applied to the stratigraphy.

Figure 5. Temperature anomalies for the NH derived by Crowley (2000) are shown along with reconstructed temperature anomalies from northern China (Yang et al, 2002). Mean annual temperature timeseries (^{o}C) from Changchun and Jingyu meteorological stations are also displayed. A composite of XLW2 data is also displayed, including percentage abundances of *D. woltereckii*, P:B ratios, *D. woltereckii:Fragliariaceae* benthic ratios and diatom PCA Axis 1 scores. δ^{13}C(‰), Pb/Ti and SCP flux rates (no. cm^{-2} yr^{-1}) are also displayed.

Table captions:

Table 1. Results of DCCA on diatom species data from the core XLW2. As SD for core XLW2 is >1, results are classified as significant. They SD from this study is presented in bold italics. Data from Wischnewski et al. (2011) are also presented, acting as reference sites (displayed in grey) for Lake Xiaolongwan. Lakes cited in Smol et al (2005), which show diatom species compositional changes similar to those presented in this paper are also shown (Lakes Saanajarvi, Finnish Lapland; Birgervatnet, Spitsbergen; CF11, Baffin Island and Slipper Lake, Northwest Territories). Reference site PC4, northern Québec, presented in Smol et al (2005) is also displayed, in grey.

Table 1.

Site name	Location	Author	Turnover (SD)
Lake Xiaolongwan	Temperate north east China	This study	***1.78***
Wuxu Lake	Montane-boreal, Tibetan Plateau	Wischnewski et al 2011	0.36
LC6 Lake	Montane-boreal, Tibetan Plateau	Wischnewski et al 2011	0.94
Saanajarvi	Finnish Lapland, Arctic	Smol et al 2005	1.19
Birgervatnet	Spitsbergen, Arctic	"	1.40
CF 11	Baffin Island, Arctic	"	1.20
Slipper Lake	Northwest Territories, Arctic	"	1.25
PC4	Northern Québec, Arctic	"	0.84

Figure 1.

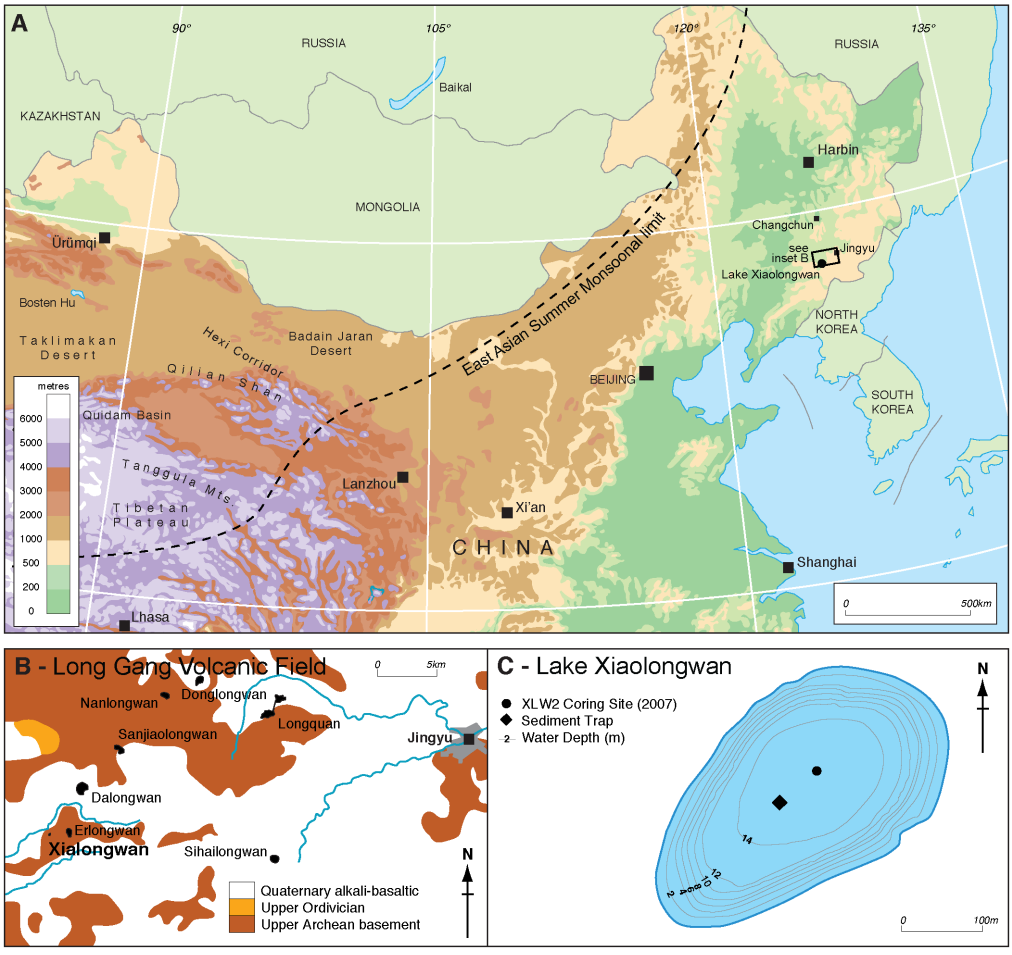
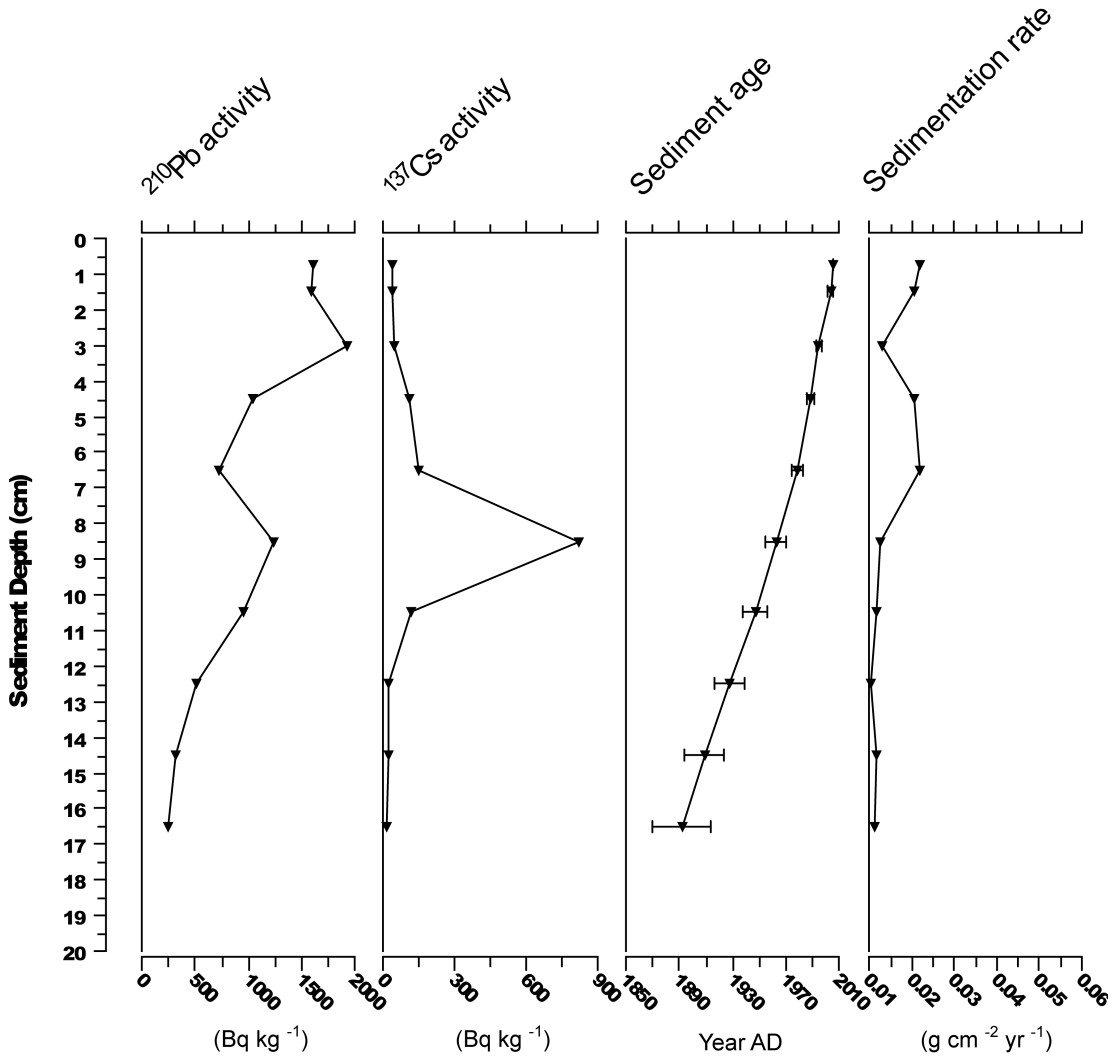


Figure 2.


^{210}Pb activity
^{137}Cs activity
Sediment age
Sedimentation rate
Sediment Depth (cm)
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
0
500
1000
1500
2000
(Bq kg $^{-1}$)
0
300
600
900
(Bq kg $^{-1}$)
1850
1890
1930
1970
2010
Year AD
0.01
0.02
0.03
0.04
0.05
0.06
(g cm $^{-2}$ yr $^{-1}$)