Cite this: *RSC Adv.*, 2016, 6, 96853

Aeolian input of phosphorus to a remote lake induced increase of primary production at the Tibetan Plateau

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A complete record derived from a core dated by both ^{210}Pb and ^{137}Cs chronologies from Lake Ngoring at the key headwater areas of the Yellow River provides new insight into the increase of primary production induced by aeolian input of phosphorus. This study showed that there was an inflection in the early 1960s, before which total phosphorus (TP), calcium-bound P (Ca-P), and exchangeable P (Ex-P) remained relatively steady or slowly increased (averages 403, 90, and 38 mg kg^{-1} , respectively). However, continued increases of TP, Ca-P, and Ex-P were found thereafter, reaching 460, 110, and 45 mg kg^{-1} , respectively. This distribution pattern was attributed to the increasing anthropogenic input of aeolian phosphorus, probably due to land cover changes, and to sustained urbanization/industrialization and agricultural intensification in neighboring areas. Accordingly, with the increase of limiting nutrient (P), sedimentary organic carbon increased from 7.1 g kg^{-1} (1960) to 12.0 g kg^{-1} (2000), nearly a factor of 2, which revealed explicitly that the primary production of Lake Ngoring was enhanced greatly by aeolian P input increase and resulted in the accelerated evolution process of this remote alpine lake.

Received 2nd August 2016
Accepted 4th October 2016

DOI: 10.1039/c6ra19516d

www.rsc.org/advances

1. Introduction

Phosphorus (P) is one of the major limiting nutrients in many freshwater ecosystems.¹ With the exception of trace emissions of phosphine from volcanoes, P compounds on the surface of Earth are not volatile and transport to the atmosphere through primary dust or aerosols.² Aeolian flux rates are thought to be minute and negligible compared with those in surface waters.³ However, from the oldest site of the soil chronosequence, Chadwick *et al.* found that phosphorus provided by Asian dust is substantially larger than that provided by the parent rock.⁴ This finding clearly revealed that P could be capable of undergoing long range transport (LRT) in the atmosphere and undergoes dry and/or wet deposition⁵ upon encountering relatively cold environments such as those at high latitude or elevations, including the Tibetan Plateau.⁶ There are more than 1000 lakes (surface area > 1 km^2) located in the plateau areas, most of which are oligotrophic or mesotrophic. Although aeolian phosphorus inputs are generally too low to maintain high levels of available phosphorus at the global scale,⁷ they would be an important nutrient source to those oligotrophic or mesotrophic freshwater lakes.⁸

As the Earth's third pole, the Tibetan Plateau is a modern "weathering engine"⁹ and lies above the atmospheric boundary layer,⁵ thus these alpine lakes offer 'natural experiments' of exposure to atmospheric LRT contaminants.¹⁰ Previous studies had pointed out that land cover changes in this area, such as deforestation was accelerated under the regional background of rapid economic growth,^{11,12} and increasing evidence elucidated that those changes, in turn, would increase the labile (unstable) forms of P sorbed onto soil particle surfaces, and further alter transmission of P to the atmosphere, changing the local and/or regional P cycle,⁹ which would accelerate the primary production of these alpine lakes, since these lakes are thought to be very sensitive to varying P inputs.¹ However, there have been no studies about aeolian phosphorus inputs to these remote alpine lakes, nor of long-term observed limnological data, mainly because of the harsh physical environment. Lacustrine sediments, by contrast, are thought to be natural archives that provide an historical record of environmental change both in a lake and its catchment, as well as trends of aeolian input nutrients to the lake surface.¹³ Dated lacustrine sediment cores thus allow past natural and anthropogenic environmental conditions and changes through time to be identified, whereas ^{210}Pb and ^{137}Cs chronologies are the main kinds of dating methods for recent sediment chronology.¹⁴ Using sediment records to construct limnological changes, is in many ways the most robust, and for regionally unique and highly vulnerable systems (such as these alpine lakes), the only reliable way to understand predisturbance conditions.¹⁵

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Lake Ngoring, one of the two freshwater lakes located in the key source area of Yellow River, was selected to gain a better understanding of the historical aeolian P input and its effect on the evolvement of lake eutrophication. It is in a scarcely populated zone (0.5–2 people per km², dominated by Tibetan herdsmen)¹¹ due to the harsh physical environment with absolutely no industry within the watershed, thus atmospheric deposition is the main anthropogenic source of phosphorus accumulation in the lake. Except for a few scattered water quality measurements in the 1980s, there have been no long-term limnological observations of the lake. Our former research had revealed that aeolian inputs of trace metals in this lake have been enhanced since the early 1960s.¹⁶ In this study, the same dated sediment core was deployed to reconstruct the aeolian input history of P, to examine the distribution and fractionation of sedimentary phosphorus, and further to discuss the probable origin of P and its induced effects on the increase of primary production in this remote alpine lake.

2. Materials and methods

2.1 Study area and background

Lake Ngoring (34°46′–35°05′N, 97°32′–97°54′E), which is also called “E’ling Sea”, is situated in the hollow land of western Madoi county at the north part of Qinghai-Tibetan Plateau. It is one of the sister structural faulted lakes (the other one is Lake Gyaring) located in the watercourse, comprising the largest bodies of freshwater of the upstream Yellow River. The water surface altitude of Lake Ngoring is 4269 m above sea level.¹⁷ The length of this lake is 74 km, maximum width is 23 km, and average width is 17.4 km, covering an area of 611 km². The lake is recharged mainly by surface runoff both from snowmelt and precipitation, and the main stream of the Yellow River flows into the lake from the southwestern corner and out from the northeastern corner, bringing 12.6×10^8 m³ water and draining a watershed area of 18 188 km². The average water depth of Lake Ngoring is about 17.6 m (maximum 30.7 m), with a surface area of 610 km², resulting in a capacity of 10.7×10^9 m³, and an average water residence time of approximately 8.5 years. The average annual outflow to the downstream Yellow River is 6.4×10^8 m³. A cold and semi-arid continental climate, sensitive to the East Asian winter monsoon, Indian summer monsoon and the Westerly jet, prevails in the entire Lake Ngoring basin (Fig. 1). The air temperature varies between 7.6 °C in July and –16.5 °C in January, averaging –3.8 °C (1953–2005). The mean annual precipitation (1953–2005) is 314 mm, but evapotranspiration is three times higher than precipitation. Aquatic plants only grow on the riparian areas, and fish in the lake, are rare, thus the bioturbation in the lake sediments is considered to be negligible. Lacustrine sediment in this lake was well preserved and thought to represent ideal conditions for paleolimnological studies of P input history.

2.2 Sample collection and analysis

A sediment core (NG0607) was sampled from the southeast part of Lake Ngoring in July 2007 (Fig. 1) using a self-made core

sampler core-sampling device, with an inner diameter of 70 mm and a length of 1200 mm. There were lots of turbidites in the spare sediment core (NG0608) taken from the north pate of the lake, probably due to sediment focusing. Thus one sediment core (NG0607) was used for the present study. All of the locations where the sample was taken were publically owned, and no permits were required for the field studies described. There were no endangered or protected species in the study area. The sediment core was extruded and sectioned in 1 cm slices. Water contents were determined from a subsample of each slice, and the remaining material was freeze-dried and then ground in an agate mortar and sieved (100 µm) prior to analysis.

Sedimentation rates were calculated from the ²¹⁰Pb and ¹³⁷Cs activity and used to determine the year of deposition of each sediment layer. The procedure and results of sediment dating was described in detail elsewhere.¹⁶ The mean linear sedimentation rate generated by the constant rate of supply (CRS) dating model was 0.41 cm per year, which was sufficient to provide good temporal resolution for studying modern nutrient input trends. The average mass accumulation rates (MAR) inferred from the ²¹⁰Pb and ¹³⁷Cs dates are 391 and 383 mg per cm² per year, respectively.

The determination of total organic carbon (TOC) was carried out following the method of residual titration of K₂Cr₂O₇ and total nitrogen (TN) was analyzed by the micro-Kjeldahl method. TP of sediment samples was analyzed by the HClO₄–H₂SO₄ digestion method,¹⁸ and the P fractionation procedure was similar to the method in our previous work.¹⁹ Briefly, the P fractions extracted were exchangeable P (Ex-P, extracted by 1 M MgCl₂), aluminum bound P (Al-P, extracted by 0.5 M NH₄F), iron-bound P (Fe-P, extracted by 0.1 M NaOH buffered with 0.5 M Na₂CO₃), occluded P (Oc-P, extracted by 0.3 M C₆H₅Na₃O₇·2H₂O, 1 M NaHCO₃ and 0.675 g Na₂S₂O₄ first, then 0.1 M NaOH was added), calcium-bound P (Ca-P, extracted by 1 M HCl), and the residue left was organic P (Org-P). All of the above extracted solutions were stored at 4 °C prior to analysis by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

The long-term climate data including the precipitation and temperature were obtained from Madoi meteorological station in the watershed with monthly resolution from 1953 to 2006. The regional socio-economic data for Qinghai Province, as well as the neighboring areas (Tibet, Sinkiang, and Gansu Province) were obtained from the National Bureau of Statistics of China, including population data (both urban and rural, 1949–2006), gross domestic production (GDP, 1949–2006) data, fumes and dust exhausted from industries, and phosphorus fertilizer usage (1970–2006).

2.3 Ex-P and Ca-P flux calculations and use the sum as a proxy for aeolian P input

Aeolian P primary occurs in minerals of the apatite family and as sorbed species onto soil particle surfaces.¹ Apatite P (Ca-P) was thought to be natural sources originated from lithosphere, with relatively stable contents, and it can't be utilized by organisms until being transformed to Ex-P.¹ Whereas most of P

Fig. 1 Map of Lake Ngoring (located in Qinghai Province) with sampling sites in the bathymetric map, and map of the climatic system of China, including the East Asian Winter Monsoon (EAWM), the Indian Summer Monsoon (ISM) and the Westerly Jet (WJ) prevailing in the study area, as well as the locations of neighboring areas such as Tibet Autonomous Region, Sinkiang Province, and Gansu Province.

species that sorbed onto soil particle surfaces was labile and exchangeable,²⁰ these P were thought to be very sensitive to varying atmospheric P inputs resulted from land cover changes, such as deforestation, overgrazing, grassland degradation, and desertification.²¹

For a mechanic perspective, aeolian P transported to the lake includes the Ca-P in the dust, and Ex-P sorbed onto the dust, thus the sum of Ca-P and Ex-P could be used as a proxy for ascending aeolian P input. In sediment profile, the fluctuation of mass accumulation rates of lacustrine sediment may cause dilution or accumulation of P in sediments,¹³ thus fluxes were calculated by multiplying the content of (Ex-P + Ca-P) in a specific slice by the corresponding sedimentation rate for a certain year (layer). In this research, the sum amount of Ex-P and Ca-P fluxes was used as an indicator of aeolian P input.

2.4 Quality assurance and quality control

Quality assurance and quality control of the analytical procedure for sedimentary N, P, and TOC determinations was carried out using method blanks and certified reference material (GBW 07309) purchased from the National Research Center for Certified Reference Materials of China. 5 blanks were treated identically to the samples in each batch, and the mean concentrations over all batches were 3.28 ± 0.21 (mean $\pm$ SD) mg P kg⁻¹, 6.9 ± 0.38 mg N kg⁻¹, and 0.3 ± 0.01 g TOC kg⁻¹, assuming 0.1 g weight, respectively, which had been subtracted correspondingly from sediment samples. Recoveries for TP and TN, and TOC were 97.3%, 99.1%, and 97.2% averaged over all batches, respectively. 5 replicates of the certified reference standards showed relative standard deviations for TP, TN, and

TOC of 7.6%, 8.2%, and 4.4%, respectively. For P fractionation analysis the variations within triplicates were <10%. The difference between measured TP and calculated TP (summing all fractions together) varied but all fell within 10%.

3. Results and discussion

3.1 Spatial characteristics of PAHs in surface sediments

Plots in Fig. 2 show the sedimentary profiles of TP, TN, and TOC during the past approximately 250 years, spanning *ca.* 1750 to 2006. TP ranged from 391 to 552 mg kg⁻¹, with 424–2274 mg kg⁻¹, and 2.9–18.2 g kg⁻¹ for TN and TOC, respectively. In the temporal scale, they all displayed a similar increasing trend, *i.e.*, they remained relatively stable or slightly increased since *ca.* 1750, however, an inflection could be observed in the 1960s, and thereafter, which was followed thereafter by a rapid ascending pattern until the 1990s, then sharply increasing values could be found in recent years (surface layers of the sediment core). Taking TP for instance, the values ranged from 385 mg kg⁻¹ to 446 mg kg⁻¹ (403 mg kg⁻¹ on average), staying relatively constant before *ca.* 1960; while during the 40 years from *ca.* 1960 to 2000, TP contents displayed a steadily increasing trend although they fluctuated, and rising to 460 mg kg⁻¹ averagely. Similar trends could also be observed in the profiles of both TN and TOC (Fig. 2). N : P ratio was around 2 but steadily increased to 7 from *ca.* 1750 to 2000, and a slightly increase of N : C ratio was also observed in Fig. 2.

3.2 P fractionations in sediments

In order to refine our information on P sedimentation and benthic metabolism, sequential P extraction of the sediment core was performed and the results are depicted in Fig. 3. The Ex-P, representing the labile inorganic P in sediment which is important in plant growth and in controlling the P concentration of the overlying water column,²² accounted for 9.4% of TP on average (40 mg kg⁻¹). The Al-P and Fe-P representing the P associated with Al and

Fe oxyhydroxides,²³ accounted for 13%, and 9.5% of TP on average, respectively. The Al-P fluctuated between 47 and 62 mg kg⁻¹, while the Fe-P ranged from 20 to 49 mg kg⁻¹ before 1995, and a peak in the 2000s could be observed, reaching as high as 98 mg kg⁻¹. The Oc-P is considered to be resistant to biological breakdown²³ and accounted for only 0.02% to 1.26% of TP, thus it was almost negligible in the sediments. The Ca-P, representing P bound to calcium, was the dominant P in sediments, accounting for 38% to 55%. As the major fraction of P, the Ca-P exhibited a slow increase in concentration although it fluctuated. The Org-P, consisting of immobile organic phosphorus and resistant apatite, was the second most dominant fraction of P in sediments (accounting for 11% to 31% of TP), ranging from 42 to 173 mg kg⁻¹.

4. Discussion

4.1 Sedimentation rates in Lake Ngoring

The average mass accumulation rate (MAR) inferred from this study was relatively higher than that in Lake Qinghai by a factor of 5,²⁴ although both are remote lakes in the Tibetan Plateau. The MAR in Lake Ngoring was also higher compared with shallow lakes in southeast of China, such as Lake Chaohu and Lake Taihu.^{22,25} This was attributed to the high suspended solids concentration of the inflowing river from the upper lake (Lake Gyaring). The Yellow River is known around the world as a silt-carrying river, especially in headwater areas, and Gyaring means the white long lake in the Tibetan language because of high load of silt and sand inputs of the Yellow River. Although a majority of the silt and sand is deposited in the Lake Gyaring, the particle content in the inflowing water to Lake Ngoring is still relatively high, resulting in a higher MAR for this lake.

4.2 Sedimentation rates of P and its fractionations in Lake Ngoring

The inflections of ascending TP, and the rising TN fluxes, as well as TOC contents occur in the same time period (the 1960s), and

Fig. 2 Contents profiles of total phosphorus (TP), total nitrogen (TN), and organic carbon (TOC) in the sediment core from Lake Ngoring.

Fig. 3 Phosphorus fractions including exchangeable (Ex-P, (a)), bound to aluminum (Al-P, (b)), bound to iron (Fe-P, (c)), occluded (Oc-P, (d)), bound to calcium (Ca-P, (e)), and organic phosphorus (Org-P, f) extracted from the sediment core of Lake Ngoring showing P concentration versus time.

a further calculation showed C : N ratios (on a mole basis) remained relatively constant (15.3 ± 1.5) since the 1750s, which indicated that there was no change in the sediment regime for this lake. At first glance, sedimentary TP remained relatively stable before *ca.* 1960, and then fluctuated with somewhat increase during *ca.* 1960 to 2000. A closer look on Ex-P fractions (Fig. 2) revealed that the shape of Ex-P, which showed a steady increase since the 1960s, was similar to that of TP, it tended much more to mirror TP increase in the sediment core. Ca-P displayed a slight increasing trend as well (Fig. 3). Generally, Ex-P is under 5% of TP in both stream sediments and wetland soils, and it readily responds to external P loadings, as was measured in natural wetlands.¹ Furthermore, Ex-P in the sediment core showed a strong dependence on sediment depth (time), and displayed a slow, steady increase in concentration before the 1960s and followed by a rapid increase in recent decades. Thus, high values of Ex-P in sediments from Lake Ngoring were attributed to ascending external P inputs to this lake.

A sharp increase or decrease could be observed in surface layers in the TP profile, as well as in profiles for the fractions of Ex-P, Fe-P, Ca-P, and Org-P, which was thought to have resulted from the early diagenesis of sedimentary P. These fractions are subject to a number of biogeochemical process that affect the extent to which they are retained in the sediment, and the form in which they are ultimately buried and become part of the sedimentary record.²⁶ Thus the relatively high Org-P would be broken down to dissolved inorganic and organic phosphorus and the ascending contents of Ex-P, Fe-P, and Ca-P might have resulted from benthic efflux of dissolved phosphorus from surface sediments to bottom lake waters.²

4.3 The probable origin and increasing P since the 1960s

Lake Ngoring is situated at the head areas of the Yellow River, and it is a scarcely populated zone (less than 4 people per km^2) with absolutely no industry within the watershed. The origin of phosphorus was thought to be from lithospheric weathering, *i.e.*, in-washed eroded soil within the watershed, and snow/ice melting from snow mountains at the west and south parts of the watershed, as well as aeolian inputs from neighbouring areas. For the lithogenic P input mainly from soil erosion, little change was found in annual precipitation although it fluctuated (Fig. 5a) in this region, and human activities within the watershed were relatively scarce, thus lithogenic phosphorus was thought to be remaining relatively stable in this area.

Temperature data from Madoi station showed that the linear rate of temperature increase in the watershed during the period of 1953–2005 was about $0.23\text{ }^{\circ}\text{C}$ per decade for the annual mean and $0.42\text{ }^{\circ}\text{C}$ per decade for the winter mean (Fig. 5b), exceeding the rates for the Northern Hemisphere and the same latitudinal zone in the same period,²⁷ but still comparable with the overall values in the Tibetan Plateau.^{28,29} The increase in warming is always accompanied by early snowmelt, and retreat of high mountain glaciers in the Tibetan Plateau region,^{28,29} and some further studies revealed that the human activities and feedback processes could play an important role in causing the faster warming rate, such as aerosols.³⁰ In our study scarcely populated area, those anthropogenic processes seem to be very weak, and there were no changes of the water areas of Lake Ngoring during 40 years of observation by remote sensing images.¹⁷ Further evidence showed that sediment accumulation rates remained relatively steady (Fig. 4), thus to some extent, we could draw the conclusion that changes in snowmelt, and

Fig. 4 Mass accumulation rate (MAR) in Lake Ngoring, indicating relative steady sedimentation rate during 1930 to 2000.

consequently runoff and erosion in within the watershed, were not the main causes for P increase in recent decades.

Aeolian input of phosphorus seems to be the most probable P source as Lake Ngoring lies above the atmospheric boundary layer, and the East Asian winter monsoons, the Indian summer monsoon and the Westerly jet prevail in this area (Fig. 1), carrying dusts from Gansu Province, Tibet Autonomous Region, and Sinkiang Province, respectively, as well as local dust in Qinghai Province. The increase of sedimentary P indicated that atmospheric P in those regions had been enhanced by anthropogenic activities. This may be explained by the following reasons.

(i) Many previous studies on the Tibetan Plateau had pointed out that anthropogenic activity inducing land cover changes, such as deforestation, overgrazing, grassland degradation, and

desertification, was accelerated under the regional background of rapid economic growth.¹² Deforestation on the Tibetan Plateau started in the 1950s and accelerated in the 1960s,³¹ due to unsustainable logging practices, agriculture intensification, and urbanization.¹¹ The Tibetan Plateau was very vulnerable, and these changes in land cover would alter not only the hydrological process and nutrient availabilities in the local scale,^{32,33} but also the nutrient cycling at the regional scale, especially aeolian transport of the increasing levels of particulate phosphorus, resulting in an enhanced deposition level of P to surface waters, such as lakes and rivers.

The increase of P in Lake Ngoring synchronized with the land cover changes since the 1960s in the neighbouring regions indicated that aeolian P induced by land cover change was an important potential input to this lake. Although a new forest policy called the Natural Forest Conservation Program (NFCP) was implemented in 1998³⁴ when the Chinese central government recognized the disastrous consequences of forest degradation resulting in the loss of biodiversity, unacceptable levels of soil erosion and catastrophic flooding, nevertheless, the induced soil erosion and subsequently aeolian input will continue for a long time in the Tibetan Plateau.

(ii) There is steady evidence that the most recent 3 decades, especially since the 1990s, was the fastest industrialization or urbanization, as well as agricultural intensification period that West China has ever experienced, and the socio-economic development; and related anthropogenic activities have already induced increasing aeolian input of sedimentary trace metals in Lake Ngoring. Fig. 6a shows that the industrial gross domestic production (GDP per capita) increased exponentially since the 1980s, accompanied by rapid increasing levels of industrial fume and dust production (Fig. 6b). However, treatment measures in these areas remained at a very low level

Fig. 5 Variations of annual mean precipitation (upper black dots, (a)), annual winter mean temperature (red dots, (b)), and annual mean temperature (black dots, (b)) at Madoi meteorological station in the watershed, showing no changes of the annual precipitation, while changes of 0.23 °C per decade for the annual mean and 0.42 °C per decade for the winter mean air temperature were observed from 1953 to 2004.

Fig. 6 Regional development of gross domestic production (GDP per capita, industrial and agricultural, (a) and (c), respectively), fumes and dust from industry (b), and phosphorus fertilizer usage (d) of Qinghai Province, as well as neighboring areas including Gansu Province, Sinkiang Province, and Tibet Autonomous Region, China. Data were obtained from the National Bureau of Statistics of China.

during this period. This contradiction between fast socio-economic development and neglected industrial dust treatment resulted in the steep increase of effluents to the atmosphere and subsequent deposition in surface waters, which we observe in Lake Ngoring. Furthermore, since the agricultural reform in the 1980s, agricultural cultivation in the neighbouring areas was intensified (Fig. 6c) under the pressure of the steady increase of the population and the relative scarcity of arable land. This resulted in a dramatic increase in fertilizer application (Fig. 6d) mainly due to the poor soil fertility in West China. It has been pointed out that over-fertilized soils become increasingly important as a P source to atmospheric dusts. This synchronized anthropogenic activity explains how under the pressure of both rapid industrialization and agricultural intensification of neighbouring areas, the input of aeolian P increased greatly since the 1960s, especially during the last three decades.

(iii) As mentioned before, most of the deforestation was in the southeastern and northern regions of the Tibetan Plateau (Tibet Autonomous and Gansu Province, respectively), while the desertification was in the western part (Qinghai and Sinkiang Province), and those land cover changes since the 1960s were then coupled with rapid social-economic development in those regions. The Indian summer monsoon from the southern to northern direction, East Asian winter monsoons from north to south, and the Westerly jet from west to east of the plateau, would bring the atmospheric P the Ngoring watershed at high elevation (about 4300 m above sea level), where the P was believed to be deposited along with a precipitation, often in the form of snow, to the watershed not detected in an increased sedimentation rate, since the sedimentation rate is already very high (0.41 cm per year) for a remote alpine lake due to the large silt fraction.

The increasing Ca-P in Fig. 2 also lent evidence to the enhanced aeolian P input because it was thought to be soil particles of neighbouring areas, otherwise Ca-P would be relatively stable because it is natural sources originated from lithosphere. The aeolian P data was rarely linked with P budget for lakes in this area. A study by Jin *et al.*,³⁵ however, showed that, atmospheric deposition is an important way for mass transportation in Lake Qinghai, 300 km at the northeast of Lake Ngoring. Giving consideration of the same prevailing monsoons in this area, the aeolian input of P is probable for Lake Ngoring. Of course, a measurement or quantification of aeolian input of P is necessary to investigate this point further.

4.4 Changes of the primary production in Lake Ngoring induced by increasing P input

According to an investigation of the water quality of Lake Ngoring in 1989, the average total nitrogen (TN) was 0.45 mg L⁻¹, and 0.01 mg L⁻¹ or less for total phosphorus (TP), thus it is an oligotrophic lake and P is the limiting element.³⁶ During the past 200 years, sedimentary P and N increased synchronized, the increasing N : P ratio lent evidence that the intensity of N is stronger than P, which is the case in North China.³⁷ Thus it was indicated that the lake became more P

limiting recently, which agree with the findings from Anderson *et al.*³⁸ that lakes fed by atmospheric nutrients would tend towards P limitation because of high N : P ratio in aeolian input. Increases in sediment P together with TN and TOC contents are well-established indicators of increasing primary production in lakes,³⁹ so long as sediment accumulation rates remains relatively steady,⁴⁰ which they do in the Ngoring core post-1960.¹⁶ The ascending TP, especially the rapid increase of the sum flux of Ex-P and Ca-P since the 1960s, and the rising TN fluxes as well as TOC contents in the same time period points to increasing primary production in this oligotrophic lake, causing TOC accumulation subsequently,³⁸ which had already been reported in other 6 Tibetan Plateau lakes.⁴¹ The slightly increase of sedimentary C : N ratio (Fig. 2) revealed that the accumulation of TOC was even faster than N. As depicted in Fig. 6, sedimentary TOC contents decreased steadily downcore before 1960 due to TOC mineralization (with slope of 0.034 g per kg per year), and average mass accumulation rate is 0.391 mg per m² per year during this period, thus yielded a mean mineralization rate of 133 mg per cm² per year. Since the 1960s, with the steep increases of Ex-P and Ca-P fluxes, TOC contents increased from 7.2 g kg⁻¹ (1960) to 12.0 g kg⁻¹ (2000), nearly by a factor of 2 (Fig. 7).

Sedimentary TOC contents always act as an indicator of the trophic state of a lake or a reservoir.³⁶ Ascending TOC contents from sediments in recent decades revealed explicitly that the primary production of Lake Ngoring was enhanced greatly by the aeolian P input increase. Correll⁷ promoted a conceptualization of the process of freshwater eutrophication including P input, primary production, dissolved oxygen, biodiversity, and trophic status. Although long-term data of the water quality were not available for Lake Ngoring, using the sedimentary TOC as an archive of the primary production, the increasing P input, especially the Ex-P fraction of aeolian sources from neighbouring areas, we could trace an increase in the primary production in this lake since the 1960s.

Fig. 7 The flux of Ex-P and Ca-P, TN flux, and TOC profiles in the sediment core showing the enhanced primary production (using the TOC as an archive) induced by aeolian phosphorus input, especially the Ex-P and Ca-P fractions.

5. Conclusions

As an example for many remote lakes in Tibetan Plateau, this study conducted in Lake Ngoring illustrates that concentrations and fluxes of aeolian input of phosphorus, especially for the Ex-P, which is thought to be bioavailable generally show little increase since the 1750s, followed by a rapid increase since the 1960s, in parallel to the rapid land cover changes, industrialization and agricultural intensification of the neighbouring regions. Using the sedimentary TOC as an archive, the increase of the aeolian input of phosphorus has already enhanced the primary production, accelerating the evolvement of such a remote lake.

Acknowledgements

The authors wish to thank Wei Zhang and Nan Li for analytical and technical help. We especially wish to thank Beat Müller who gave us valuable advice on this work and we are greatly indebted to him. And we also thank Dr Catherine Rice for English grammar revision. This work was supported by the National Natural Science Foundation of China (No. 21547009) and the Major Science and Technology Program for Water Pollution Control and Treatment (2012ZX07101-002).

References

- 1 K. R. Reddy, R. H. Kadlec, E. Flaig and P. M. Gale, *Crit. Rev. Environ. Sci. Technol.*, 1999, **29**, 83–146.
- 2 K. C. Ruttenberg, *The Global Phosphorus Cycle*, Oxford, 2003, pp. 585–643.
- 3 G. M. Filippelli, *Rev. Mineral. Geochem.*, 2002, **48**, 391–425.
- 4 O. A. Chadwick, L. A. Derry, P. M. Vitousek, B. J. Huebert and L. O. Hedin, *Nature*, 1999, **397**, 491–497.
- 5 D. Jeffries and W. Snyder, *Water, Air, Soil Pollut.*, 1981, **15**, 127–152.
- 6 R. Q. Yang, T. D. Yao, B. Q. Xu, G. B. Jiang and X. D. Xin, *Environ. Int.*, 2007, **33**, 151–156.
- 7 D. L. Correll, *J. Environ. Qual.*, 1998, **27**, 261–266.
- 8 A. D. Jassby, J. E. Reuter, R. P. Axler, C. R. Goldman and D. H. Hackley, *Water Res.*, 1994, **30**, 2207–2216.
- 9 G. M. Filippelli, *Elements*, 2008, **4**, 89–95.
- 10 X. P. Wang, H. D. Yang, P. Gong, X. Zhao, G. J. Wu, S. Turner and T. D. Yao, *Environ. Pollut.*, 2010, **158**, 3065–3070.
- 11 X. F. Cui, H. F. Graf, B. Langmann, W. Chen and R. H. Huang, *Earth Interact.*, 2007, **11**, 1–18.
- 12 X. Cui and H. F. Graf, *Clim. Change*, 2009, **94**, 47–61.
- 13 H. R. VonGunten, M. Sturm and R. N. Moser, *Environ. Sci. Technol.*, 1997, **31**, 2193–2197.
- 14 F. Wu, J. Zheng, H. Liao, M. Yamada and G. Wan, *Environ. Sci. Technol.*, 2011, **45**, 9188–9194.
- 15 D. R. Engstrom, S. P. Schottler, P. R. Leavitt and K. E. Havens, *Ecol. Appl.*, 2006, **16**, 1194–1206.
- 16 H. Zhang, B. Shan, L. Ao, W. Tang and S. Wen, *Environ. Earth Sci.*, 2014, **72**, 399–406.
- 17 Z. Shao, X. Meng, D. Zhu, D. Zheng, Z. Qiao, C. Yang, J. Han, J. Yu, Q. Meng and R. Lü, *Front. Earth Sci. China*, 2008, **2**, 364–377.
- 18 S. D. Bao, *Chemical Analysis for Agricultural Soil*, China Agriculture Press, 2000.
- 19 H. Zhang and B. Shan, *Environ. Sci. Technol.*, 2008, **42**, 2328–2333.
- 20 K. A. Hudson-Edwards, C. S. Bristow, G. Cibin, G. Mason and C. L. Peacock, *Chem. Geol.*, 2014, **384**, 16–26.
- 21 X. Song, G. X. Yang, C. Z. Yan, H. C. Duan, G. Y. Liu and Y. L. Zhu, *Environ. Earth Sci.*, 2009, **59**, 793–801.
- 22 H. J. Bing, Y. H. Wu, Z. B. Sun and S. C. Yao, *J. Environ. Sci.*, 2011, **23**, 1671–1678.
- 23 K. R. Reddy, O. A. Diaz, L. J. Scinto and M. Agami, *Ecol. Eng.*, 1995, **5**, 183–207.
- 24 Y. M. Han, Z. D. Jin, J. J. Cao, E. S. Posmentier and Z. S. An, *Water, Air, Soil Pollut.*, 2007, **179**, 167–181.
- 25 F. Y. Zan, S. L. Huo, B. D. Xi, C. W. Zhu, H. Q. Liao, J. Zhang and K. M. Yeager, *J. Environ. Monit.*, 2012, **14**, 804–816.
- 26 M. R. Penn, M. T. Auer, E. L. Van Orman and J. J. Korienek, *Mar. Freshwater Res.*, 1995, **46**, 89–99.
- 27 X. Liu and B. Chen, *Int. J. Climatol.*, 2000, **20**, 1729–1742.
- 28 S. Chen, Y. Liu and T. Alex, *Clim. Change*, 2006, **76**, 291–319.
- 29 R. A. Houghton and J. L. Hackler, *Global Biogeochem. Cycles*, 2003, **17**, 1–3.
- 30 W. K. Lau, M. K. Kim and W. S. Lee, *Environ. Res. Lett.*, 2010, **5**, 025204.
- 31 Y. He, Z. Zhang, W. H. Theakstone, T. Chen, T. Yao and H. X. Pang, *J. Geophys. Res.*, 2003, **108**, 4530.
- 32 G. X. Wang, Y. B. Wang, J. Qian and Q. B. Wu, *Mt. Res. Dev.*, 2006, **26**, 153–162.
- 33 C. Neill, L. A. Deegan, S. M. Thomas and C. C. Cerri, *Ecol. Appl.*, 2001, **11**, 1817–1828.
- 34 P. Zhang, G. Shao, G. Zhao, D. C. LeMaster, G. R. Parker, J. B. Dunning and Q. L. Li, *Science*, 2000, **288**, 2135–2136.
- 35 Z. D. Jin, Y. M. Han and L. Chen, *J. Paleolimnol.*, 2009, **43**, 551–563.
- 36 D. W. Schindler, *Science*, 1977, **195**, 260–262.
- 37 Y. Zhang, X. Liu, F. Zhang, X. Ju, G. Zou and K. Hu, *Acta Ecol. Sin.*, 2006, **26**, 1633–1639.
- 38 K. A. Anderson and J. A. Downing, *Water, Air, Soil Pollut.*, 2006, **176**, 351–374.
- 39 A. F. Lotter and H. J. B. Birks, *Aquat. Sci.*, 1997, **59**, 362–375.
- 40 J. F. Boyle, *Inorganic Geochemical Methods in Palaeolimnology*, Springer, Netherlands, 2002, vol. 2, pp. 83–141.
- 41 A. Lami, S. Turner, S. Musazzi, S. Gerli, P. Guilizzoni, N. L. Rose, H. Yang, G. Wu and R. Yang, *Hydrobiologia*, 2010, **648**, 175–187.