Sediment records related to global and regional atmospheric Hg emissions in North China over the last three centuries

Atmospheric Hg in the region has increased since the 1900s.

The increase in Hg in the 20th century was mainly affected by regional Hg emissions.

Sediment records showed different increasing patterns related to various Hg sources.

Hg emissions from small cities in North China dominated the 21st century increase.

Abstract

Reconstructing the long-term Hg emission history in major polluting countries is important for understanding the global Hg cycle and controlling Hg pollution. In this study, the atmospheric Hg emission history was reconstructed over the last three centuries based on three lake-sediment Hg records from southeastern Inner Mongolia in North China, and its relationship with global and regional Hg emissions was revealed. These records show little Hg pollution in the 18th and 19th centuries. This implies a limited influence of Hg emitted from Europe and North America in this region, which is confirmed by the different Hg fluxes during the two World Wars and the post-1970s. Atmospheric Hg in the region has increased gradually since the 1900s and is primarily contributed by emissions from Beijing-Tianjin-Hebei in Lake Kulunnao (KLN) and from the former Soviet Union in Lake Dalihu (DLH) and Lake Zhagesitai (ZGST). In the last century, two decreases in Hg fluxes occurred in the KLN core due to the economic recession in the 1960s-1970s and reduced energy consumption and industrial production in the 1990s. However, only one decrease in the DLH and ZGST cores

corresponded with the dissolution of the Soviet Union in the 1990s. Although atmospheric Hg emissions in China have stabilized or even decreased in the last decade, atmospheric Hg continues to increase, particularly in KLN, because of emissions from small cities in the region. This study can help understand Hg emission sources and control Hg pollution in North China and supplement the understanding of the global Hg cycle.

Keywords: sediment core; mercury; pollution history; heavy metal; emission sources; North China

1. Introduction

Mercury (Hg) is one of the most significant environmental pollutants and has attracted particular attention from scientists and the public worldwide for many years (Eyrikh et al., 2017). Background Hg levels in the global environment have increased by approximately three-fold during the industrial era, and presently they may be 5-10 times higher than the natural levels (Horowitz et al., 2014). Therefore, understanding long-term Hg variations during the industrial era is important for evaluating the global Hg budget and Hg emission reduction potential (Wu et al., 2016). In recent decades, much research has been conducted to reconstruct historical Hg trends over the past centuries or even millennia using various geological records, including lacustrine sediment cores (Korosi et al., 2019; Lepak et al., 2020; Li et al., 2021; Roberts et al., 2020; Zhan et al., 2020), ice cores (Beal et al., 2015; Eyrikh et al., 2017; Kang et al., 2016), and peat cores (Bao et al., 2016; Enrico et al., 2017). However, the previous studies have primarily focused on Europe and North America.

Since the 1970s, anthropogenic Hg emissions in Europe and North America have declined significantly, with stringent environmental pollution regulations implemented by developed countries (Streets et al., 2019). In contrast, Hg emissions in China have increased sharply since the late 1970s owing to rapid economic and industrial development after the reform and opening-up. Currently, China is one of the countries with the largest Hg emissions worldwide (Fu et al., 2016; Pacyna et al., 2016; Wang et

al., 2014). Anthropogenic Hg emissions to the atmosphere in China account for 25-40% of the total global Hg emissions (UNEP, 2013). Therefore, special attention should be paid to the long-term variations in Hg emissions in China.

Few studies have been recently conducted to reconstruct the historical variations in Hg using sedimentary records from the Qinghai-Tibet Plateau and the northeastern, southeastern, and western regions of China (Table S1). These studies have provided valuable data for understanding long-term changes in Hg emissions in China. Zeng et al. (2014) analyzed Hg for a lake sediment core collected from Lake Saraym in West China and found sharp increases in Hg during 1900-1935, 1972-1985, and the 1990s. However, an ice core in Altai showed a rapid increase in Hg after the 1940s, culminating during the 1970s, associated with Hg emissions from Europe and North America (Eyrikh et al., 2017). Yang et al. (2010) investigated sediment Hg records from nine lakes across the Qinghai-Tibet Plateau and found that the most significant increase in Hg occurred after the 1970s, followed by a further considerable increase after the 1990s, primarily attributed to recent economic development in Asia. Kang et al. (2016) reported that Hg has increased in eight lacustrine and one ice core from the central and southern Plateau since the onset of the Industrial Revolution, followed by a dramatic increase after World War II. Tang et al. (2012) found a major increase in Hg in 1880-present in a peat core from the Lesser Khingan Mountain in Northeast China, primarily attributed to local anthropogenic emissions. Moreover, Hg in the peat cores from

Aershan in the Greater Khingan Mountains (Bao et al., 2016) and in the sediment core of Tianchi Crater Lake (Zhan et al., 2020) showed a major increase in the 1980s.

These studies showed discrepancies in the reconstructed Hg trends between different studies, even those in the same region. The discrepancies are caused partly by the fact that most of these reconstructions were conducted based on only a single sedimentary record, so that Hg variations are difficult to distinguish between natural causes and regional or local anthropogenic sources. Although Beijing-Tianjin-Hebei is one of the most important industrial centers in China, no such long-term Hg reconstruction exists in or around the region. To date, little is known about the changes in the regional environmental Hg over the past centuries, and the extent to which Hg emissions have affected the background environment in the region. Therefore, long-term Hg reconstructions based on multiple sedimentary records around the Beijing-Tianjin-Hebei region in North China are necessary to reveal the evolution and mechanisms of past Hg pollution more accurately and comprehensively.

Sediment cores retrieved from remote lakes can be used to reconstruct past atmospheric Hg trends, as they are rarely affected directly by human activities, and their Hg pollution is derived primarily from atmospheric deposition (Kang et al., 2016; Korosi et al., 2019; Yang et al., 2010). In this study, sediment cores were collected from three lakes in relatively remote areas situated north of the Beijing-Tianjin-Hebei region in North China (Fig. 1) and used to reconstruct the long-term regional Hg pollution history. Based on the comparison of Hg profiles between these records, atmospheric Hg

pollution history in the past three centuries was reconstructed, and major sources and pollution mechanisms of Hg were discussed by analyzing data on temporal variations in the concentrations of other heavy metals and lead (Pb) isotopes, economic/industrial development, and backward trajectories. Additionally, the similarities and differences in atmospheric Hg evolution between different regions in China are discussed. This study is significant for understanding the long-term evolution and sources of atmospheric Hg in North China and for identifying the global and regional Hg contributions to the region.

2. Materials and methods

2.1. Sampling and analysis

Details of the three lakes considered as the study area are provided in Section S1 of the Supporting Information (SI). In 2016, sediment cores were retrieved from the lake center areas (deep water areas) of Lake Zhagesitai (ZGST) and Lake Kulunnao (KLN) with water depths of 1.8 m and 4 m, respectively, and from the deep water area of Lake Dalihu (DLH) (approximately 10 m) using a self-developed gravity corer. Sediment cores with lengths of 73 cm (ZGST), 45 cm (KLN), and 97 cm (DLH) were sectioned at intervals of 1.0 cm. The lithological characteristics of the sediment cores were observed during the slicing. Finally, sediment samples were dried in a vacuum-freezing dryer at -25 °C, homogenized, and sub-samples were ground to smaller than 63 μm. All the samples were sealed in plastic bags and stored at approximately 4 °C in

a refrigerator. Surface soil samples were also collected from the DLH catchment, and the sampling details are provided in the SI.

The activities of ^{210}Pb, ^{137}Cs, and ^{226}Ra in the sediment cores of DLH and KLN were analyzed using a low-background germanium detector (EG&G ORTEC gamma spectrometer) at the State Key Laboratory of Lake Science and Environment at Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, and those in the ZGST core were analyzed by direct gamma assay at the Environmental Radiometric Facility at the Department of Geography, University College London, using a well-type coaxial low-background intrinsic germanium detector (ORTEC HPGe GWL series) (Wan et al., 2016b; Yang et al., 2010). ^{137}Cs was detected at 662 keV and ^{210}Pb activities at 46.5 keV. The activities of ^{226}Ra were determined at 295 keV and 352 keV, and γ-rays were emitted by its daughter isotope ^{214}Pb. The unsupported ^{210}Pb activities ($^{210}Pb_{ex}$) were calculated by subtracting ^{226}Ra activities from total ^{210}Pb activities. Detector efficiencies were determined using sediment samples of known activity and calibrated sources (Yang et al., 2010).

For elemental analyses, each sediment sample was weighed accurately for approximately 0.12 g with a one ten-thousandth balance and digested with mixture of nitric acid, perchloric acid, hydrochloric acid, and hydrofluoric acid at 145-165 °C. Concentrations of major and minor elements (Al, Ti and Zn) in the sediment samples were measured using a Profile inductively coupled plasma atomic emission spectrometer (ICP-AES; Leeman Labs Inc., USA). Moreover, trace metals including

Cd and Pb, as well as Pb isotopes, were detected using a inductively coupled plasma mass spectrometer (ICP-MS; Agilent 7700x) at the State Key Laboratory of Lake Science and Environment. The detection limits for these metal measurements were 20 (Al), 1 (Ti), 0.2 (Zn), 0.01 (Cd), and 0.01 (Pb) mg kg^{-1}, respectively. Data quality was ensured by analyzing duplicates for every ten samples and the Chinese standard reference material (GBW07358, stream sediment) manufactured by the Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geological Sciences (www.bzwz.com/p_64/p_5209.html). The accuracy, expressed by the recoveries to the certified values, was within 93-106%. The results of duplicates and standard materials suggest that the errors in these measurements were less than 5% for their relative standard deviations (RSDs) (Wan et al., 2019b; 2020). Mercury concentrations in the sediment and soil samples were measured using a direct mercury analyzer (Hydra-C, Leeman Labs Inc.) following the USEPA method. Standard geological reference material (GSD-23) and duplicate measurements were used to control the quality of the analysis. The measurement errors were less than 5% with a detection limit of 0.6 ng g^{-1}. The grain sizes and contents of total organic carbon (TOC) and total nitrogen (TN) of the sediment samples were also measured, and their pretreatment and analysis details are provided in the SI.

2.2. Backward trajectory

Based on gridded meteorological data from the U.S. National Oceanic and Atmospheric Administration (NOAA), air mass backward trajectories arriving at lakes at a height of 500 m above ground level were calculated using Geographical Information System (GIS)-based software (Wang et al., 2009). The meteorological data covered the entire calendar year of 2014 from 01.01.2014 to 12.31.2014. Backward trajectories were calculated using data covering the past 72 h. To show the major directions of air masses in these lakes, clustering analyses of the trajectories were conducted using a angle distance algorithm provided by TrajStat (Wang et al., 2009). Finally, six major air mass directions were obtained for each lake, and the contribution of each direction was calculated.

3. Results and discussion

3.1. Lithology and chronology

The lithologies of the sediment cores of DLH and KLN are similar and relatively uniform, primarily consisting of gray silt, with 2-3 cm pale-yellow silt at the core tops. The ZGST core consists primarily of dark-gray silt with a few gastropod shells at a depth of 28-39 cm. Compared with the KLN core, DLH and ZGST cores are coarser at their mean grain sizes (KLN, 19.1 um; DLH, 24.9 um; ZGST, 39.1 um), and contain higher amounts of sand and coarse silt (Fig. 2), corresponding well with their locations close to Hunshandake Sandy Land.

Chronologies of the three sediment cores were established using ^{210}Pb (constant rate of supply (CRS) model) and ^{137}Cs dating method. The details are provided in the SI (Section 2 and Fig. S1). The dating results suggest that these sediment cores cover periods of approximately 310 y (ZGST), 230 y (DLH), and 150 y (KLN).

3.2. Concentration, flux, and EF of Hg in the three lake sediment cores

Ranges (averages) of Hg concentrations in the sediment cores of DLH, ZGST, and KLN were found to be 11.0-43.7 (25.8) ng g^{-1}, 20.0-52.4 (35.1) ng g^{-1}, and 12.1-87.3 (41.1) ng g^{-1}, respectively (Table 1). The total Hg fluxes in the cores of DLH, ZGST and KLN had ranges (averages) of 8.5-35.5 (20.2) μg m^{-2} y^{-1}, 13.3-49.1 (25.5) μg m^{-2} y^{-1}, and 21.3-155.8 (74.3) μg m^{-2} y^{-1}, respectively. In all the cores, both the concentrations and total fluxes of Hg were the lowest and relatively stable in their pre-1900 sections (Fig. 2), which can be considered as backgrounds. Hg concentrations in the background core sections of DLH, ZGST, and KLN were 11.0-15.5 (13.2) ng g^{-1}, 20.0-25.3 (23.0) ng g^{-1}, and 12.1-12.9 (12.6) ng g^{-1}, respectively (Table 1), whereas the total Hg fluxes were 8.5-11.2 (9.9) μg m^{-2} y^{-1}, 13.3-16.8 (15.3) μg m^{-2} y^{-1}, and 21.3-22.7 (22.2) μg m^{-2} y^{-1}, respectively. In the upper sections of the three cores, both the concentrations and total Hg fluxes showed an increase trend toward the sediment surface (Fig. 2). Compared to their backgrounds, Hg concentrations in the surface sediments increased by 196% (DLH), 115% (ZGST), and 593% (KLN), whereas the total Hg fluxes increased by 206% (DLH), 221% (ZGST), and 602% (KLN).

The Enrichment Factors (EFs) of Hg in the DLH, ZGST, and KLN cores had ranges (averages) of 0.9-3.6 (2.1), 0.9-2.3 (1.5), and 1.0-5.9 (2.8), respectively. The corrected anthropogenic Hg fluxes in the cores of DLH, ZGST, and KLN have ranges (averages) of 0-33.5 (14.1) μg m^{-2} y^{-1}, 0-30.9 (10.7) μg m^{-2} y^{-1}, and 0-91.0 (33.9) μg m^{-2} y^{-1}, respectively. The Hg EFs and anthropogenic flux profiles of the cores showed an upward increase in the upper core sections. In the surface sediments, the corrected anthropogenic Hg fluxes in the DLH, ZGST, and KLN cores increased to 27.9 μg m^{-2} y^{-1}, 30.9 μg m^{-2} y^{-1}, and 91.0 μg m^{-2} y^{-1}, respectively (Table 1).

Among the lakes, KLN exhibited the highest anthropogenic Hg fluxes in the 21st century, which are approximately three times higher than those from DLH and ZGST. This is primarily because the location of KLN is closer to the Beijing-Tianjin-Hebei industrial area and a few small cities than the other two lakes (Section 3.7.). The Hg fluxes are similar for the relatively remote DLH and ZGST in the 21st century and may represent regional atmospheric Hg deposition in the southeastern Mongolian Plateau. The fluxes in DLH and ZGST are only approximately 1/3 of those from Huguangyan Maar Lake (Li et al. 2021; Zeng et al. 2017), a lake in one of the most economically developed regions in Southeast China, but are at a similar level to those from more remote areas such as the Qinghai-Tibet Plateau (Kang et al., 2016; Yang et al., 2010) and West China (Zeng et al., 2014) (Table S1 and Fig. 4). However, the Hg fluxes in the KLN are close to those from Southeast China (Li et al., 2021; Zeng et al., 2017).

3.3. Causes of increases in Hg in these lakes

Increases in Hg in lake sediments are normally related to human activities and/or volcanic emissions. In North China, no extreme volcanic eruption has occurred in the last three centuries, therefore, the influence of volcanic emissions can be excluded. Human-induced Hg in lake sediments is primarily derived from three pathways: the direct dumping of Hg into lakes, atmospheric wet and dry deposition, and catchment erosion (Chen et al., 2016; Wan et al., 2020; Yang, 2015).

The lakes of DLH and ZGST are situated remotely in the Hunshandake Sandy Land, with no industry around them and no direct dumping of Hg into them. Although Lake KLN is 5 km from Guyuan City, a small city with a fading economy in North China (Yang et al., 2021), no direct dumping of Hg into the lake was found in the 2016 field survey. In 2010, the urban population (permanent residents) in Guyuan City was only 38,585, with a gross national product of 4.82 billion Yuan in 2016 (GYLCCC, 2003), which was less than 0.2% of Beijing. Additionally, catchment erosion can incorporate Hg into thelakes, including a certain amount of anthropogenic Hg previously deposited and stored in thecatchments (Wan et al., 2019b). However, such input of Hg into these lakes might be only a minor source, as this region has an arid and semi-arid climate with relatively low (approximately 300-500 mm y^{-1}) precipitation and no large rivers connected to the lakes. Another reason is that the surface soils in this region are dominated by sand and have a low Hg concentration compared to the sediment background (SI, Section 4). An estimation by Yang et al. (2010) in a similar arid and semi-arid region (rainfall 250-500 mm y^{-1}) of the Tibetan Plateau showed that the

contribution of Hg caused by catchment input accounted for no more than 11% of the Hg in the sediments. These results revealed that anthropogenic Hg in these lakes was predominantly derived from atmospheric deposition.

3.4. Limited influence of atmospheric Hg emissions from Europe and North America

In the 18th and 19th centuries, anthropogenic Hg fluxes in the sediment cores were close to zero, and EFs were approximately 1 (Fig. 3), implying that no or limited anthropogenic Hg pollution occurred. This suggests that atmospheric Hg in southeastern Inner Mongolia (North China) was scarcely affected by anthropogenic Hg emissions. This fact contradicts global Hg variations revealed by both estimations (Hylander and Meili, 2003; Streets et al., 2019) and sediment archives (Beal et al., 2015; Enrico et al., 2017; Lepak et al., 2020; Li et al., 2020) which suggests considerable increases since the latter half of the 19th century (Fig. 3). This difference suggests a limited influence of the increased global anthropogenic Hg emissions in the region, as most of them (approximately 80% in the 1880s and 1890s) were derived from developed countries in Europe and North America (Streets et al. 2019). This finding corresponds with the backward trajectory analyses, which may provide insight into the historically important sources of Hg and the relative unimportance of contributions of Hg emissions from North America and Europe to these lakes. However, the analyses only covered a recent time period and may not represent the time scale covered by the entire cores (Fig. 5).

Most other sedimentary records from relatively remote areas of China (Fig. 4) also show insignificant human-related Hg increases in the latter 19th century, such as the Badain Jaran Desert (Liu et al., 2015), Lake Sayram in West China (Zeng et al., 2014), Lake Tianchi in Northeast China (Zhan et al., 2020), and Lake Qinghai and Lake Keluke on the Qinghai-Tibet Plateau (Yang et al., 2010). This further suggests a relatively limited influence of Hg emitted from Europe and North America in many regions of China.

In addition, the estimation of long-term historical global Hg emissions (Fig. 3) (Streets et al., 2019) suggests that (1) the global atmospheric Hg emissions decreased by nearly one-half in the 1910-20s and 1940s owing to the influence of the two World Wars, and (2) since the 1970s, atmospheric Hg decreased rapidly in Europe and North America. However, Hg fluxes determined from the three sediments records in this study did not decrease but increased during all the above periods, further indicating that Hg emitted from Europe and North America had a relatively limited influence on Hg pollution in this region.

3.5. Major sources of Hg in the three lakes during the 1900s-1980s

During the 1900s-1980s, anthropogenic Hg fluxes exhibited rapid increases in the three cores, but their increases varied among the different records (Fig. 3): (1) the anthropogenic Hg fluxes in DLH and ZGST were similar and notably lower than those in KLN, and (2) in the 1950s-1960s, Hg fluxes in KLN showed a notable decline,

whereas those in DLH and ZGST increased during the entire time. These differences imply that the three lakes were affected by different Hg sources.

As mentioned in *Section 3.3.*, DLH and ZGST lakes are located in relatively remote non-industrial areas. Although Lake KLN is close to Guyuan City, it might be subjected to a minor influence of Hg emissions from the county as (1) electricity was not officially connected until 1985, and the city was very small with a population of 177,143 in 2000, and (2) no large polluting factories and enterprises existed before the 1980s (GYLCCC, 2003). Additionally, the anthropogenic fluxes of heavy metals (Zn, Cd, and Pb) and Pb isotopes in all three lakes did not significantly increase before the 1980s (Yang et al., 2021) (Fig. 5). These results suggest that the three records were affected by different regional Hg sources rather than local sources in the 1900s-1980s.

The anthropogenic Hg fluxes in the KLN core experienced a notable decrease during the 1950s-1960s. Compared to the historical trends of Hg emissions and economic/industrial developments in surrounding regions (Fig. 3 and S2), the decrease may have corresponded with China's economic recession caused by the 1960s-1970s Cultural Revolution (Tian et al. 2015), despite a slight time discrepancy, which was probably caused by uncertainties in sediment dating. Backward trajectories (Fig. 5) suggest that the potential Hg sources in KLN were Beijing-Tianjin-Hebei and Inner Mongolia. Considering the opposite Hg trends in the DLH and ZGST cores in the 1950s-1960s (Fig. 3), which implies a relatively limited influence of Hg emissions from Inner Mongolia, we can further infer that Hg variations in KLN during this period were

controlled by emissions from Beijing-Tianjin-Hebei. This corresponded well with the fact that (1) KLN is closer to and more influenced by the south and southwest airflow from the Beijing-Tianjin-Hebei region (Fig. 5), and (2) anthropogenic Hg fluxes in KLN were notably higher than those in DLH and ZGST.

In contrast, anthropogenic Hg fluxes in DLH and ZGST showed continuous increases during the 1960s-1970s, implying that they were affected by different Hg sources from KLN. Compared to the historical trends of Hg emissions and economic/industrial developments in the surrounding regions (Fig. 3 and S2), the Hg increase corresponded with the rapid and continuous development trends of the economy and industry in the former Soviet Union (Fig. S2), the estimated atmospheric Hg emission trend of the former Soviet Union (Streets et al., 2019), and the Baikal Hg record (Roberts et al., 2020). This implies the potential sources of Hg in DLH and ZGST could be the former Soviet Union during this period. This inference corresponds well with the fact that the two lakes are located further away from the Beijing-Tianjin-Hebei region (Fig. 1) and receive less south airflow than KLN (Fig. 5). However, at the regional scale, KLN might have received similar levels of Hg from the former Soviet Union as DLH and ZGST in the 1960s-1970s, but the KLN record showed different Hg trends from the other two lakes. This is because KLN received notably higher levels of Hg from Beijing-Tianjin-Hebei compared to the former Soviet Union, which had obscured the signal from the former Soviet Union.

3.6. Decreases in Hg during the 1990s due to different causes among these lakes

Since the 1980s, anthropogenic fluxes of Hg in the three lakes had increased gradually, but they experienced a certain degree of decrease in the 1990s: DLH during 1989-2004, KLN during 1990-2000, and ZGST during 1998-2008 (Fig. 3).

In 1991, the Soviet Union disintegrated, resulting in a sharp decline (39 %) in GDP in the 1990s (Fig. S2). Moreover, the estimated atmospheric Hg emissions (Streets et al., 2019) as well as the Baikal Hg record (Roberts et al., 2020) show notable decreases (Fig. 3). These changes corresponded well with the remarkable decrease in Hg in DLH and ZGST. The slightly later occurrence time (1998-2008) of the decrease in the ZGST core was probably because of the uncertainties in sediment core dating.

The Hg decrease in KLN in the 1990s might be related not only to Hg emissions from the Soviet Union but also to those from the Beijing-Tianjin-Hebei region, which experienced slow growth in energy consumption and industrial production due to the Asian financial crisis and stricter pollution emission standards (Wang et al., 2019). Compared with the DLH and ZGST cores, the KLN core experienced a lower decrease in anthropogenic Hg fluxes in the 1990s (Fig. 3). This corresponds well with the fact that the Soviet Union has experienced a more significant economic recession (Fig. S2) and a higher reduction in atmospheric Hg emissions (Fig. 4) in the 1990s than in China. This suggests that the Hg in KLN was affected more by the emissions from the Beijing-Tianjin-Hebei region than from the Soviet Union.

3.7. Mercury increases in the 21st century

In the 21st century, anthropogenic Hg fluxes in these lakes have increased sharply, particularly in the KLN and ZGST (Fig. 3). In 2016, anthropogenic Hg fluxes in the KLN, DLH, and ZGST cores increased to 129.3 μg m^{-2} y^{-1}, 21.4 μg m^{-2} y^{-1}, and 27.2 μg m^{-2} y^{-1}, respectively. Among the three lakes, KLN experienced the highest Hg increase during this period, which was approximately double that of 2000.

Since the revision of the Air Pollution Prevention and Control Law in 2000, the Chinese government has been stricter in controlling emissions of Hg and other air pollutants (Wang et al., 2019), particularly in large cities such as Beijing (Schleicher et al., 2016) and Shanghai (Tang et al., 2018). Atmospheric Hg emissions in China have stabilized or even decreased since approximately 2006 (Tang et al., 2018; Wu et al., 2016). The contradictory variations between the regional Hg emissions in North China and the rapid Hg increase in these lakes in the 21st century imply changes in the Hg sources for the lakes.

First, the sedimentation rates of the three cores were relatively stable in the 21st century, except for an increase of approximately 40% in 2015 and 2016 in the ZGST core, suggesting that the above Hg increases were not related to the catchment in-wash. Second, in the KLN core, both TOC content (1.9-2.4%) and TOC/TN ratio (7.4-8.7) did not show any increasing/decreasing trends in the 21st century, except for the surface sediment sample; in the DLH core, the TOC content increased gradually from 3.4% in 2000 to 5.3% in 2016, but the TOC/TN ratios (8.9-10.1) were relatively stable; and in the ZGST core, the TOC content (10.5-12.6%) did not show any increasing/decreasing

trend. These findings suggest no evident change in the primary productivity in these lakes, implying that Hg increases in these lakes in the 21st century have little relation with primary productivity. Third, temporal variations in typical heavy metals of Zn, Cd, and Pb in the three lakes (Yang et al., 2021; Fig. 5) show that most of them also increased rapidly in the 21st century. These facts indicate that the rapid increase in Hg during this period was primarily affected by emissions from sub-regional and/or local rather than regional pollution sources. This corresponds well with the fact that (1) the economy in the small cities of the region has developed rapidly since the early 2000s (e.g. Guyuan, Fig. S3), and (2) heavily polluting enterprises in big cities began to shift to small cities in the 2000s, and pollution emission standards were relatively low in small cities (Wang et al., 2019). Among the three lakes, the increase in Hg in the KLN core during 2000-2016 was the most significant. This corresponds well with the fact that KLN is relatively close to a few small cities compared to the other two lakes, suggesting that the small cities in the region have become important Hg sources.

To date, few atmospheric Hg monitorings have been done in small cities and remote areas in China, and data on pollution emissions and energy consumption are limited. The accurate estimation of Hg emissions in such areas is difficult and uncertain. Therefore, this historical reconstruction of atmospheric Hg is important for understanding Hg trends in the remote areas of China.

4. Conclusions

In this study, sediment cores were retrieved from three lakes in southeastern Inner Mongolia. Based on Hg and other metals in these cores, the atmospheric Hg emission history was reconstructed in the last three centuries by calculating the anthropogenic Hg fluxes and analyzing sediment focusing effects as well as potential catchment contributions. In the 18th and 19th centuries, anthropogenic Hg fluxes in these records were small and relatively stable, implying negligible atmospheric Hg pollution in the region. By comparing the Hg emissions from Europe and North America during the two World Wars and the post-1970s, the Hg emissions from Europe and North America had a limited influence on the atmosphere in this region. The increases in the relatively remote lakes of DLH and ZGST in the 1900s-1990s were primarily related to Hg emissions from the former Soviet Union, whereas the increase in KLN was contributed primarily by emissions from the Beijing-Tianjin-Hebei region. The decrease in Hg in the 1990s in DLH and ZGST corresponded with the collapse and economic recession of the Soviet Union, whereas decreases in KLN in the 1960s-1970s and 1990s were related to the Cultural Revolution and slowed growth in energy consumption and industrial production in North China, respectively. In the 21st century, atmospheric Hg increases were primarily linked to emissions from nearby small cities in the region, which should be the focus of future environmental pollution control.

Study areas

Lake Dalihu (DLH), Lake Zhagesitai (ZGST), and Lake Kulunnao (KLN) lie on the southeastern Mongolian Plateau in North China (Fig. 1), with a temperate continental climate. They are all inland and are approximately closed basin lakes. Lake DLH (116°29′–116°45′E, 43°13′–43°23′N, approximately 1230 m above sea level), the second-largest lake in Inner Mongolia, has a water surface area of approximately 238 km^2 and a maximum water depth of approximately 11 m (Xiao et al., 2009). Two permanent rivers from the east and two intermittent streams from the southwest enter the lake, but without outflows (Wan et al., 2019).

In the Lake DLH area, the average annual precipitation is 350-400 mm and approximately 70% of the annual precipitation occurs between June and August. The average annual evaporation is 1287 mm. The average annual temperature is 1-2 ℃ with an average of -17 to -24 ℃ and a July average of 16-18 ℃ (Xiao et al., 2009). During November-April, the lake is covered with 0.5-1-m ice (Xiao et al., 2009).

The area of the lake catchment is 3912 km^2 (Ma et al., 2017), with a catchment area to lake area ratio of 16.4. In the Dalinur National Wetland Nature Reserve, the dominant land-use types were grassland and forests, accounting for approximately two-thirds in 2016 (Chun et al., 2018). Overall, only minor changes were observed in the land use in this area. In 1994, the area of grassland and forests accounted for 61%, whereas that in 2016 accounted for 67%, with only a slight increase in grassland area (Chun et al., 2018). A few farmhouses were dotted in the southeast catchment. In recent years, some

tourists have visited Lake DLH in the summer, from July to August, but their activities are primarily distributed in the northern and southeastern areas. As the lake area is dominated by westerly and northerly winds, these human activities may have a limited impact on sediment pollution in the central area of the lake (Wan et al., 2019).

Lake ZGST is situated approximately 40 km northeast of Lake DLH (Fig. 1). The lake has a surface area of approximately 2 km^2 and maximum water depth of approximately 2 m. Only small, intermittent streams enter the lake and the area of the lake catchment is approximately 140 km^2, with a catchment area to lake area ratio of approximately 70. In the catchment, land use is dominated by fine sandy and silty grassland as well as fixed and semi-fixed dunes covered by a few grasses and laigh frutex. Some forest land occurs in the sub-mountain/mountain areas and the area is in a natural reserve area in Hunshandake Sandy Land. Compared to Lake DLH, it is remote and less affected by human activities in its catchment (Wan et al., 2019). We did not obtain any data on the climate of Lake ZGST area, but it may be similar to that of Lake DLH because of the short distance (approximately 40 km) between them and their similar natural environment (Wan et al., 2019).

Lake KLN (114°50′-116°04′E, 41°14′-41°56′N, approximately 1536 m above sea level) is approximately 200 km southwest of DLH (Fig. 1). The lake has a water surface area of approximately 9.5 km^2, with a maximum water depth of approximately 6 m, and it receives precipitation and riverine inputs. Two major rivers input into the lake, but they have only small flows and occur primarily during the summer season. The area of

the lake catchment is approximately 1100 km^2, with a catchment area to lake area ratio of 116. In the catchment, the land-use/cover types were dominated by grasslands around the lake, and cultivated land was distributed in the ulterior areas of the lake (Zhang, 2009). Compared to 1998, land use/cover in the region was relatively stable until 2008 (Zhang, 2009). There are villages around the lake, but almost no industrial activities. In recent years, tourist activities have occurred in and near the lake, primarily during the summer season. To the south (approximately 5 km) of the lake, it is a small county of Guyuan, in a relatively remote area in North China with a backward economy. In 2010, the urban population (permanent residents) of Guyuan was 38,575. In 2016, the gross national product of the entire county was 4.82 billion Yuan, primarily focusing on agriculture, forestry, animal husbandry and fishery (GYLCCC, 2003; Yang et al., 2021). In Lake DLN, the average annual precipitation is 426 mm, annual average evaporation is approximately 1612 mm, and average annual temperature is 1.6 ℃.

Section S2

Analysis

The grain sizes of the sediment samples were measured using a laser diffraction analyzer (Mastersizer 2000, Malvern Panalytical). Before analysis, the samples were pretreated with 10% hydrogen peroxide and 30% hydrochloric acid to remove organic matter and carbonate components, respectively, and then dispersed by ultrasonication with 10 ml 10% $(NaPO_3)_6$ solution. The grain-size measurement range of the analyzer was between 0.02 and 2000 μm. Replicate analyses indicated that the mean grain-size measurement error was less than 2%.

To obtain the contents of TOC and TN in the sediment samples, total carbon and nitrogen contents were determined using an elemental analyzer (Elemental Analyzer vario EL III). The inorganic carbon content of the sediment samples was measured using the volumetric method. The inorganic carbon content was converted to carbonate content by multiplying by a coefficient of 8.33 (Wan et al., 2016). Finally, the TOC content of each sediment sample was calculated by subtracting the inorganic carbon content from the total carbon content. The errors in these measurements were less than 3%.

Section S3

Sediment core dating

Logarithmic fitting analyses of unsupported ^{210}Pb activities versus depth showed results of $y = -74.52\ln(x) + 276.79$ ($R^2 = 0.9306$) for the DLH core, $y = -64.51\ln(x) + 282.09$ ($R^2 = 0.6216$) for the ZGST core, and $y = -47.55\ln(x) + 228.26$ ($R^2 = 0.8239$) for the DLN core. These results suggested that the unsupported ^{210}Pb activities in these cores declined following approximately exponential trends with depth (Fig. S1). The three cores were dated using the constant rate of ^{210}Pb supply (CRS) model (Appleby, 2001). The CRS dating results suggest that the ages of 1963 are found at a depth of 18 cm in the DLH core, 24.5 cm in the ZGST core, and 24 cm in the KLN core. These findings agree with their ^{137}Cs records, showing that the 1963 ^{137}Cs peaks might be at 15-20 cm depth in the DLH core, 18-25 cm in the ZGST core, and 20-26 cm in the KLN core (Fig. S1).