# Decoupling Natural and Anthropogenic Mercury and Lead Transport from South Asia to the Himalayas

Jie Huang,* Shichang Kang, Runsheng Yin, Mang Lin, Junming Guo, Kirpa Ram, Chaoliu Li, Chhatra Sharma, Lekhendra Tripathee, Shiwei Sun, and Feiyue Wang

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**ABSTRACT:** Mercury (Hg) and lead (Pb) accumulation since the Industrial Revolution has been generally observed to increase concurrently in lake sedimentary records around the world. Located downwind during the monsoon season from the rapidly developing South Asia, the Himalayas and the Tibetan Plateau are expected to receive direct anthropogenic Hg and Pb loadings, yet the source, pathway, and effects of such transport remain poorly known due to logistic challenges in accessing this region. When studying the sediment record from Lake Gokyo (4750 m above sea level (a.s.l.)) in the Himalayas, we find remarkably different Hg and Pb accumulation trends over the past 260 years. Although Hg accumulation has continued to increase since the Industrial Revolution, Pb accumulation peaked during that time and has been decreasing since then. Stable isotope analysis reveals that the decoupling trends between these two elements are due to different sources and pathways of Hg and Pb in the region. Both $\delta^{202}$Hg and $\Delta^{199}$Hg have been increasing since the Industrial Revolution, suggesting that anthropogenic Hg emissions from South Asia have been continuously increasing and that the Indian monsoon-driven wet deposition of atmospheric Hg is the dominant pathway for Hg accumulation in the sediments. In contrast, analysis of $^{206}$Pb/$^{207}$Pb and $^{208}$Pb/$^{207}$Pb ratios suggests that Pb accumulation in the sediments originates primarily from natural sources and that the decreasing trend of Pb accumulation is most likely due to a weakening input of atmospheric mineral dust by the westerlies. These decoupling trends highlight the ongoing issue of transboundary Hg transport to the Himalayas and the Tibetan Plateau that are source waters for major freshwater systems in Asia and calls for regional and international collaborations on Hg emission controls in South Asia.
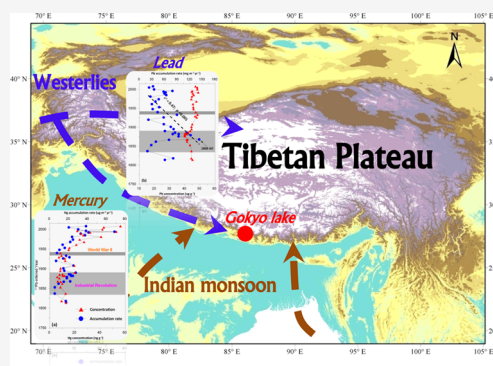
## 1. INTRODUCTION

Since the Industrial Revolution, increasing anthropogenic activities have released a wide variety of contaminants into the atmosphere regionally and globally and subsequently into the surface environment.[1] One such "hot-spot" region is South Asia that has undergone rapid economic growth and industrialization over the past several decades[2] and has become one of the world's largest anthropogenic emission sources of contaminants.[3] Located north/northeast to the region are the Himalayas and the Tibetan Plateau ("the Third Pole"), which are one of the most imposing topographic features on Earth, with an average altitude of more than 4000 m above sea level (a.s.l.). The Himalayas and the Tibetan Plateau not only are home to some of the most isolated and fragile ecosystems on our planet but also sustain water supply for major rivers in Asia.[4] Despite its perceived remoteness, the Himalayas and the Tibetan Plateau may receive contaminants from South Asia via atmospheric transport during the Indian monsoon season,[5,6] which may affect the alpine ecosystems as well as downstream ecosystems in many Asian countries.

Among various atmospheric contaminants, mercury (Hg) and lead (Pb) are of particular concern, due to their

bioaccumulation in the food chain and adverse effects on human health.[7−10] Concurrent increasing trends of Hg and Pb accumulation since the Industrial Revolution have been observed in lake sedimentary records worldwide (e.g., North America,[11] Europe,[12] the Mediterranean[13]). However, we noted that previously reported 200-yr sedimentary reconstruction of Hg[14] and Pb[15] from a Himalayan lake (Gokyo) displayed decoupling trends of historical Hg and Pb accumulation. These different trends may indicate that sources and transport pathways of Hg and Pb are different from other parts of the world. The mixed influences of anthropogenic (e.g., industrial production) and natural (e.g., mineral dust) emissions complicate the source apportionment in the Himalayas and thus require further investigation.

Stable isotope geochemistry provides a powerful tool for differentiating the sources and biogeochemical processes of Hg and Pb in the environment. Hg isotopes can undergo both mass-dependent fractionation (MDF, reported herein as $\delta^{202}Hg$) as well as mass-independent fractionation (MIF, reported herein as $\Delta^{199}Hg$).[16] Variations in Hg isotopic compositions reflect changes in Hg sources with distinct isotopic signatures and/or biogeochemical processes that fractionate Hg isotopes differently.[17] Unlike Hg, the isotopic composition of Pb is not significantly affected by physicochemical fractionation processes.[18] As a result, each source of Pb has its own specific isotopic composition and Pb isotopes can be used as "fingerprints" of Pb pollution sources.[18] Although there is a growing literature on Hg isotopic compositions in various environmental matrices of the Tibetan Plateau,[19−22] few have studied Hg isotopes in the Himalayas, which prevents us from fully understanding the potential influences of South Asian Hg pollution to the Tibetan Plateau. Lin et al.[15] were the first to report Pb isotopes in Lake Gokyo sediments and found that they were nearly identical to natural sources. However, potential implications for historical changes in Pb sources were not thoroughly investigated.

To further understand the decoupling trends of Hg and Pb deposition in the Himalayas, in this study, we simultaneously examined the profiles of Hg and Pb isotopes in Lake Gokyo sediments. The main purpose is to discriminate sources and transport pathways to sedimentary Hg and Pb accumulation. Such information could provide important insights for better assessment and mitigation of transboundary anthropogenic pollution from South Asia to the Tibetan Plateau.

## 2. MATERIALS AND METHODS

**2.1. Study Area and Sediment Coring.** Lake Gokyo (27°57.063′N; 86°41.414′E, 4750 m a.s.l.) is located in the Gokyo Valley, Sagarmatha (Everest) National Park, Nepal, in the central Himalayas on the southern edge of the Tibetan Plateau (Figure 1). The catchment of Lake Gokyo is mainly
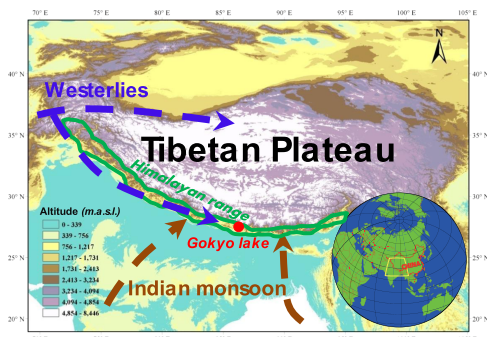


**Figure 1.** Location of Lake Gokyo in the Himalayas, and the general patterns for atmospheric circulation systems on the Tibetan Plateau.

covered by lichen or short grasses underlain by alpine permafrost (Figures S1 and S2). The climate in the Lake Gokyo region is influenced by the Indian summer monsoon with dry winters under the influence of the westerlies. Annual rainfall is ∼1000 mm, and most of the precipitation occurs in the summer season. More details about the study area are provided in Text S1 of the supporting information.

In May 2009, a sediment core (18.5 cm in length) was taken from the deepest part of Lake Gokyo (water depth: 43 m) using an HTH gravity corer (HTH-Teknik, SE-976 31 Luleå,

Sweden) fitted with a 60 mm inner diameter polycarbonate tube. The sediment core was sectioned using a stainless steel slicer at 0.5 cm intervals from the surface to the bottom of the core. All sediment samples were freeze-dried (−50 °C) and homogenized before dating and chemical analysis. The sediment chronology of the core was constructed by measuring radionuclide ($^{210}Pb$) on an ORTEC HPGe GWL series well-type coaxial low background intrinsic germanium detector. Further details about the dating of this core can be found elsewhere.[14]

**2.2. Analytical Procedures and QA/QC.** Total Hg ($Hg_T$) concentrations in the sediments were analyzed on a Direct Mercury Analyzer (DMA, Hydra-C type) following the US EPA Method 7473. For the analysis of Hg isotopic composition, about 0.2−0.5 g of each sediment sample was digested (95 °C, 6 h) with 5 mL ultrapure aqua regia (HCl/HNO$_3$ = 3/1, v/v). Certified reference materials (MESS-1, marine sediment, from the National Research Council of Canada) were digested in the same way and analyzed for quality assurance. Digested samples were diluted to 0.3−0.5 ng mL$^{-1}$ Hg in 10−20% aqua regia before isotope analysis on a Neptune-Plus Multicollector (MC) inductively coupled plasma-mass spectrometer (ICP-MS) following the method of Yin et al.[23] $Hg_T$ in acid digests was also monitored using $^{202}Hg$ signals, and the $Hg_T$ concentration measured by MC-ICP-MS was within ±15% deviation of the $Hg_T$ measured by the DMA as mentioned above. $\delta^{202}Hg$, $\Delta^{199}Hg$, and $\Delta^{201}Hg$ were calculated relative to the NIST SRM 3133 Hg standard solution, following the method of Bergquist and Blum.[16] UM-Almadén secondary standard solutions containing 0.3 ng mL$^{-1}$ ($n = 3$) and 0.5 ng mL$^{-1}$ ($n = 3$) of $Hg_T$ were measured in the same way as the samples. The results for MESS-1 ($\delta^{202}Hg$: −1.86 ± 0.08‰; $\Delta^{199}Hg$: 0.01 ± 0.04‰; $\Delta^{200}Hg$: 0.01 ± 0.02‰; $\Delta^{201}Hg$: −0.02 ± 0.04%; 2SD, $n = 3$) and UM-Almadén ($\delta^{202}Hg$: −0.52 ± 0.08‰; $\Delta^{199}Hg$: −0.01 ± 0.03‰; $\Delta^{200}Hg$: 0.00 ± 0.02‰; $\Delta^{201}Hg$: −0.02 ± 0.03‰, 2SD, $n = 3$) were consistent with previous results.[23]

The concentrations and isotope ratios of Pb ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$) in the sediments were determined on a PerkinElmer Elan 6100 ICP-MS. An isotopic standard reference material (NIST SRM 981) was simultaneously analyzed to monitor any instrument drift and mass bias. In this study, the relative standard deviations of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ for NIST SRM 981 measurements were less than 0.45 and 0.40%, respectively ($n = 7$). Details of the ICP-MS analysis and QA/QC for Pb can be found elsewhere.[15,24]

The measurements of total organic carbon content (TOC, in %) were conducted on a PerkinElmer 2400 Series II CHNSO elemental analyzer (limit of detection ≤10 ppm) by a combustion method. Duplicated measurements for TOC were performed, and the accepted variation of the replicated measurements was below 3%. Standard reference materials (GBW07401 from the Institute of Geophysical and Geochemical Exploration, China) were measured for every 10 samples and recoveries were in the range of 96−106%.

## 3. RESULTS AND DISCUSSION

**3.1. Historical Hg and Pb Variations in the Sediment Core.** $Hg_T$ concentrations and its accumulation rates in the sediment profile of Lake Gokyo remain relatively stable since the onset of the Industrial Revolution, followed by a significant increase since World War II (Figure 2a). Due to its remote
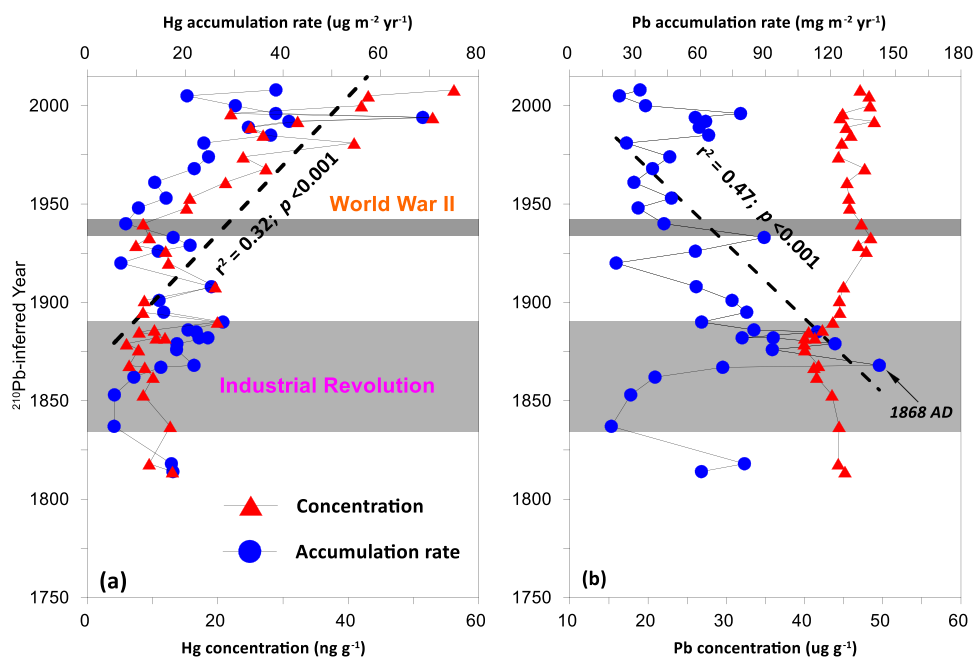
**Figure 2.** Historical profiles of concentrations and accumulation rates of Hg (a; reproduced from 14) and Pb (b; plotted based on data from 15) in Lake Gokyo sediments. The dashed lines in (a, b) represent fitting curves for the variations of Hg and Pb (since 1868 AD) accumulation rates; The gray bars represent the period of World War II and the Industrial Revolution, respectively.
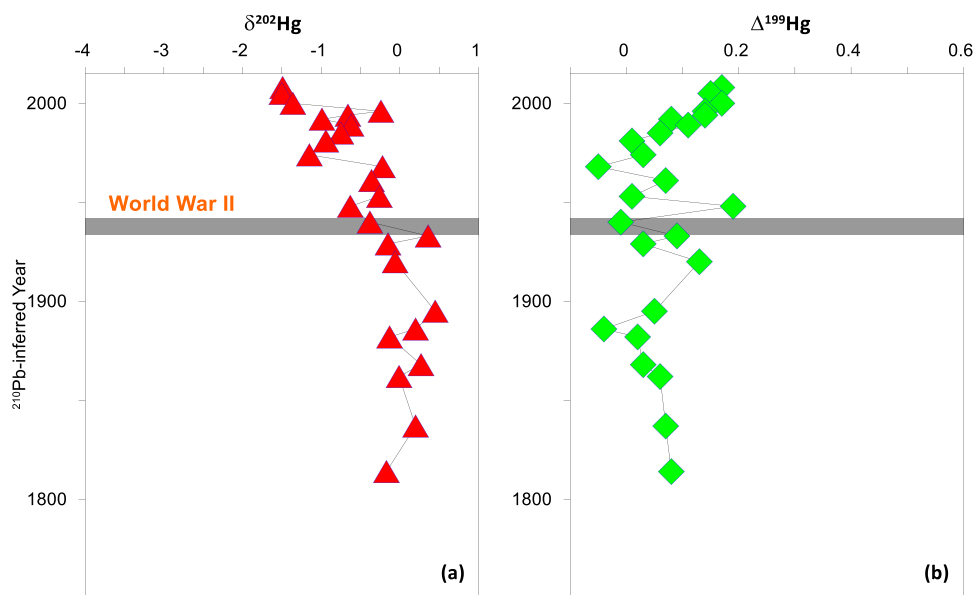


**Figure 3.** Historical profiles of $\delta^{202}Hg$ and $\Delta^{199}Hg$ values (‰) in Lake Gokyo sediments. The gray bar represents the World War II period.

location and absence of direct point anthropogenic sources in the vicinity, this increase in Hg accumulation in Tibetan sediment cores has been attributed to the enhanced transboundary pollution from South Asia,[14] particularly from India.[3]

In contrast to Hg, Pb concentrations of the Lake Gokyo sediments varied only slightly before (averaging 47.6 $\mu$g g$^{-1}$) and after World War II (averaging 44.4 $\mu$g g$^{-1}$) (Figure 2b). The Pb accumulation rates peaked in 1868 AD during the Industrial Revolution and decreased steadily significantly since then (Figure 2b). Moreover, no significant variations of TOC were observed in our sediment profile ($r^2 = 0.07$; $p = 0.111$) (Figure S3), indicating that changes in the organic carbon content of the lake sediment are not the major driver for the variations in Hg and Pb accumulation. This decoupling pattern

of historical accumulation of Pb and Hg indicates that their sources and transport pathways were different in the Himalayas.

**3.2. Hg-MDF Records in the Sediment Core.** $\delta^{202}Hg$ values of the Lake Gokyo sediment core vary from −1.50 to 0.45‰ (Figure 3a and Table S1). They are much more positive than those in sediments from two other remote lakes Namco (−5.04 to −2.16‰, mean = −3.58 ± 0.05‰, 2SD, $n = 25$) and Qinghai (−4.55 to −3.15‰, mean = −3.84 ± 0.04‰, 2SD, $n = 11$) in the inland Tibetan Plateau[20] but are similar to those of major anthropogenic Hg emissions from India, such as those from industrial and traffic emissions and waste incineration in Kolkata, India (−1.64 ± 1.02‰, 2SD, $n = 52$),[25] and Indian feed coal (−1.87 ± 0.54‰, 2SD, $n = 12$)[26]

(Figure 4). Our study site is located at the forefront of the atmospheric pollution export from South Asia (Figure 1),
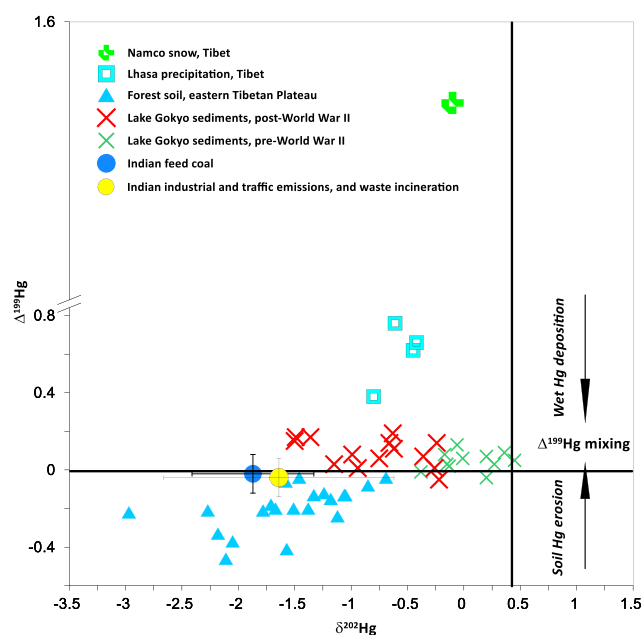


**Figure 4.** Hg-MIF (expressed as $\Delta^{199}$Hg) vs Hg-MDF (expressed as $\delta^{202}$Hg) in Lake Gokyo sediments. Also shown are Hg isotopic signatures in snow,[30] precipitation,[19] and surface soils[21] from the Tibetan Plateau and those in anthropogenic emissions from South Asia.[25,26]

which has the highest population density and the third-largest source for global anthropogenic Hg emissions.[27] Due to its close proximity to South Asia (Figure 1), therefore, the fractionation of anthropogenic Hg isotopes should be less affected during transport from the source region (e.g., Kolkata) to Lake Gokyo when compared with westerlies-sourced anthropogenic $\delta^{202}$Hg signatures, which traveled far away from the upwind sources (e.g., Central Asia). Therefore, a strong $\delta^{202}$Hg signature overprinting between sediment and anthropogenic sources (Figure 4) supports that Lake Gokyo mainly received anthropogenic Hg emissions from South Asia under the influence of the monsoon. This is further supported by the fact that the post-World War II sediments have more negative $\delta^{202}$Hg values (mean = −0.80 ± 0.06‰, 2SD, $n$ = 15) that are closer to the anthropogenic end-member than the pre-World War II sediments (mean = −0.05 ± 0.07‰, 2SD, $n$ = 10) (Figure 3a). The negative shift of $\delta^{202}$Hg values after World War II, especially around 1990 AD (Figure 3a), also suggests the contribution of enhanced anthropogenic emissions from South Asia with the emission intensity of different anthropogenic sources varying during different economic development periods.

**3.3. Hg-MIF Records in the Sediment Core.** Hg enters remote lakes mainly through atmospheric deposition and watershed input of terrestrial soils.[20] Since local anthropogenic Hg sources from the vicinity could be neglected in the Gokyo Valley, atmospheric deposition of long-range transported Hg is the major source of Hg entering Lake Gokyo. Hg is removed from the atmosphere via dry or wet deposition, which mainly contains oxidized atmospheric Hg(II), or via vegetation uptake of atmospheric Hg(0) followed by litterfall deposition into soils.[20,28] Hg-MIF signatures can be used to distinguish these

two pathways. As shown in Figure S4, Lake Gokyo sediments yield a slope of 0.98 for the $\Delta^{199}$Hg/$\Delta^{201}$Hg ratio, which is consistent with the value reported during aqueous Hg(II) photoreduction.[16] Aqueous Hg(II) photoreduction in raindrops and water columns results in negative $\Delta^{199}$Hg in the product Hg(0) and positive $\Delta^{199}$Hg in the residual Hg(II).[17] Precipitation can strongly scavenge oxidized Hg(II) species from the atmosphere and is thus characterized by positive $\Delta^{199}$Hg values.[19,29,30] Terrestrial soils, which primarily accumulate Hg(0) through litterfall and/or direct deposition of Hg(0), are characterized by negative $\Delta^{199}$Hg values.[21,28] As seen in Figure 4, $\Delta^{199}$Hg values of Lake Gokyo sediments (−0.06 to 0.19‰) fall in between reported values for Tibetan precipitation (0.80 ± 0.45‰; 2SD, $n$ = 5)[19,30] and soils (−0.19 ± 0.12‰; 2SD, $n$ = 21),[21] confirming that sedimentary Hg accumulation can be from both atmospheric deposition via precipitation and soil erosion. However, as most sediment samples are characterized by positive $\Delta^{199}$Hg values (Figure 4 and Table S1), atmospheric Hg deposition through precipitation appears to play a more important pathway for sedimentary Hg accumulation.

Moreover, the post-World War II sediments are significantly characterized by more positive $\Delta^{199}$Hg values (0.09 ± 0.03‰, 2SD, $n$ = 15) than the pre-World War II sediments (0.05 ± 0.02‰, 2SD, $n$ = 10) ($p$ <0.01, analysis of variance (ANOVA) test) (Figure 3b and Table S1). This trend of $\Delta^{199}$Hg values agrees with previous results obtained from remote alpine lake sedimentary records in the Tibetan Plateau[20] and in the USA.[31] The exact cause for this increase remains unknown. One possibility is that the Tibetan Plateau has experienced a significant increase in precipitation during the past few decades,[32] which could have enhanced the wet scavenging of Hg(II) species. A declining trend in sedimentation was observed in Lake Gokyo since about 1870,[14] suggesting a decrease of soil erosion in this lake, which dominates the sedimentation in Lake Gokyo. Therefore, the recent positive shift of $\Delta^{199}$Hg could also be due to a decrease in soil Hg input with negative $\Delta^{199}$Hg values.

**3.4. Pb Isotope Records in the Sediment Core.** Similar to Hg, Pb accumulation in Lake Gokyo sediments could be from either direct atmospheric input and/or watershed input of terrestrial soils. To discriminate between these potential Pb sources, we compiled and plotted Pb isotope ratios ($^{206}$Pb/$^{207}$Pb and $^{208}$Pb/$^{207}$Pb) of Lake Gokyo sediments and anthropogenic/background end-members from its neighboring regions. As shown in Figure 5, anthropogenic Pb emissions from South Asia,[33−36] East Asia,[34] and European air[37] are not isotopically overprinted in Lake Gokyo. In contrast, Pb isotopes in Lake Gokyo sediments overlap and/or are closer to those determined from natural background sources including the mineral dust from Asian drylands/deserts (e.g., Thar, Takilimakan, Tengger, and Badian Jaran deserts),[38] Tibetan river sediments[39] and surface soils.[40,41] It has been shown that glacier snow/ice can serve as natural archives for documenting modern and past changes in the atmospheric Pb input. Similarly, the observed Pb isotope ratios in snowpits[42] and ice cores[43] of Mt. Everest, collected ∼15 km from Lake Gokyo, are also identical to natural sources (Figure 5). Altogether, this Pb isotope distribution pattern in Figure 5 suggests that historical Pb accumulation in the Himalayas was less influenced by anthropogenic emissions from South Asia than natural sources.
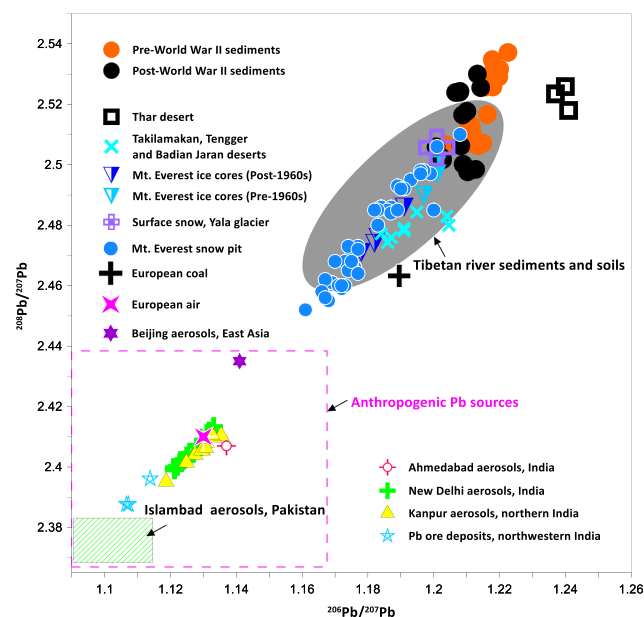
**Figure 5.** Lead isotope ratios in Lake Gokyo sediments (this study), Thar, Takilimakan, Tengger, and Badian Jaran deserts,[38] Tibetan river sediments[39] and surface soils,[40,41] surface snow of Yala glacier,[46] Mt. Everest snowpits,[42] Mt. Everest ice cores,[43] northwestern Indian Pb ore deposits,[33] aerosols of Islamabad (Pakistan), Indian cities (Ahmedabad,[34] New Delhi,[35] and Kanpur[36]), Beijing in East Asia,[34] European air,[37] and European coal.[57]

Among these three natural sources (mineral dust, river sediments, and surface soils), mineral dust is of particular significance (Figure 5). Numerous studies have suggested that the westerlies could transport significant amounts of natural dust emissions to the atmosphere compared to the monsoon system.[44] A recent estimate suggests that up to 800 Tg of mineral dust can be injected annually into the atmosphere when high surface westerly winds blow over the Asian drylands/deserts,[44] and the dust can be transported and deposited around the globe in about 13 days.[45] An earlier study has demonstrated that the contribution from mineral dust accounts for more than 80% Pb in the Himalayan snow.[46] Therefore, we believe that Pb in Lake Gokyo sediments originates primarily from the Asian mineral dust delivered by the westerlies.

Mineral dust as the main source of sedimentary Pb in Lake Gokyo also explains the change in Pb concentrations and accumulation rates with time (Figure 2b). Long-term variations of dust events over the Tibetan Plateau have shown a decreasing trend during the past 200 years due to reduced westerly wind speeds in winter.[47] The frequency of the dust storm in the Himalayas has also decreased over the same period.[48] This would have limited atmospheric loadings of mineral dust and Pb from Asian deserts to our study site. In addition, changes in $^{206}Pb/^{207}Pb$ ratios showed a decreasing trend in lake sediments (Figure S5). These less-radiogenic Pb isotopes after World War II could be partly due to anthropogenic emissions such as the use of leaded gasoline in South Asia. Therefore, although precipitation-induced soil erosion[15] and anthropogenic emissions from South Asia[49] could have contributed Pb loadings to Lake Gokyo sediments, the significantly weakened input of natural-sourced Pb from Asian mineral dust is mainly responsible for the observed

decreasing trend of Pb accumulation since the Industrial Revolution (Figure 2b).

A recent study examined atmospheric deposition of metals in an ice-core record from the Central Himalayas and found that the atmospheric deposition of (nonvolatile) metals peaked in the mid-1800s.[50] The authors attributed that to early metal pollution by coal burning in Western Europe, which was transported by the westerlies. We compared our Pb isotope data to Pb isotope ratios of coal in Europe. As shown in Figure 5, Pb isotope ratios of European coal are closer to those determined from the natural sources in our study. This supports the hypothesis of Gabrielli et al.[50] and suggests that coal burning in Europe may have caused the high Pb accumulation at Lake Gokyo in the mid-1800s (e.g., 1868 AD) (Figure 2b).

**3.5. Environmental Implications and Outlook.** The decoupling trends of Hg and Pb in the sediment core from Lake Gokyo reflect their different origins and transport pathways over the Himalayas, as well as their different geochemical behaviors. First, anthropogenic Hg is emitted to and transported in the atmosphere primarily in the form of gaseous Hg(0) with a long residence time of 6 months to 2 years,[51] whereas Pb from anthropogenic origins is emitted predominantly in the form of particulate Pb (i.e., adsorbed on particles) with a shorter residence time of only a few days.[18] The differences in the atmospheric residence time of Hg and Pb affect their long-range transport and atmospheric deposition. Therefore, anthropogenic emissions of Hg from South Asia could be transported over a longer distance to the Himalayas, compared to that of anthropogenic Pb aerosols that tend to deposit before reaching the Himalayas. Second, anthropogenic Hg emissions from South Asia increased continuously since the Industrial Revolution,[52] while anthropogenic Pb emissions decreased during the past few decades due to the reduction of Pb in gasoline and subsequent phase-out of leaded gasoline in South Asia.[49] This further reduces the contribution of anthropogenic Pb to the Himalayas. As a result, high winds of the westerlies carrying a significant amount of mineral dust from natural emission sources (e.g., Asian drylands/deserts) become a more important source of Pb deposition in Lake Gokyo.

Hg behaves differently from Pb (and other nonvolatile metals), not only because Hg has a gaseous phase but also because gaseous elemental Hg is also the dominant Hg species in the global atmosphere.[51] A global treaty, the Minamata Convention, is thus needed as local and regional efforts alone cannot control Hg pollution.[9] Different from many other regions in the world where sedimentary Hg records have shown a decreasing trend in the past few decades,[53] the continuously increasing trend in sedimentary Hg records in the Himalayas and the Tibetan Plateau is worrisome.[14,54] Based on the anthropogenic Hg emission inventory for the period 1970−2012,[55,56] India is the largest Hg emission source country in South Asia, and its emissions have increased considerably over the past few decades (Figure S6). More importantly, as Hg emissions from South Asia are projected to increase despite the Minamata Convention,[3] more Hg will be transported to the roof of the world. Its impingement on the fragile alpine and cryospheric ecosystem, downstream major rivers, and human populations needs to be better characterized and assessed. International efforts, such as those prescribed in the Minamata Convention, are thus needed to curb Hg

emissions from South Asia and to mitigate Hg pollution in the Himalayas and the Tibetan Plateau.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.0c00429.

> Landscapes of Lake Gokyo and the Gokyo valley; lichen vegetation cover on the shore of Lake; historical profiles of TOC (%) in Lake Gokyo sediments; $\Delta^{199}$Hg vs $\Delta$201Hg (‰) in Lake Gokyo sediments; records of the 207Pb/206Pb-isotopic ratios in the Lake Gokyo sediment core; variations of anthropogenic Hg emissions from India for the period 1970−2012; Hg$_T$ concentrations and isotope compositions in Lake Gokyo sediments (PDF)

## AUTHOR INFORMATION

### Corresponding Author

**Jie Huang** − *Key Laboratory of Tibetan Environment Changes and Land Surface Processes, Institute of Tibetan Plateau Research and CAS Center for Excellence in Tibetan Plateau Earth Sciences, Chinese Academy of Sciences, Beijing 100101, China;* orcid.org/0000-0002-3060-0862; Phone: +86-10-80497034; Email: huangjie@itpcas.ac.cn

### Authors

**Shichang Kang** − *State Key Laboratory of Cryospheric Science, Northwest Institute of Eco-Environment and Resources and CAS Center for Excellence in Tibetan Plateau Earth Sciences, Chinese Academy of Sciences, Lanzhou 730000, China; University of the Chinese Academy of Sciences, Beijing 100049, China;* orcid.org/0000-0003-2115-9005

**Runsheng Yin** − *State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China;* orcid.org/0000-0001-9631-5303

**Mang Lin** − *State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China;* orcid.org/0000-0001-8904-7697

**Junming Guo** − *State Key Laboratory of Cryospheric Science, Northwest Institute of Eco-Environment and Resources, Chinese Academy of Sciences, Lanzhou 730000, China*

**Kirpa Ram** − *Institute of Environment and Sustainable Development, Banaras Hindu University, Varanasi 221005, India*

**Chaoliu Li** − *Key Laboratory of Tibetan Environment Changes and Land Surface Processes, Institute of Tibetan Plateau Research and CAS Center for Excellence in Tibetan Plateau Earth Sciences, Chinese Academy of Sciences, Beijing 100101, China*

**Chhatra Sharma** − *State Key Laboratory of Cryospheric Science, Northwest Institute of Eco-Environment and Resources, Chinese Academy of Sciences, Lanzhou 730000, China; Central Department of Environmental Science, Tribhuvan University, Kathmandu 6133, Nepal*

**Lekhendra Tripathee** − *State Key Laboratory of Cryospheric Science, Northwest Institute of Eco-Environment and Resources, Chinese Academy of Sciences, Lanzhou 730000, China*

**Shiwei Sun** − *State Key Laboratory of Cryospheric Science, Northwest Institute of Eco-Environment and Resources, Chinese Academy of Sciences, Lanzhou 730000, China; University of the Chinese Academy of Sciences, Beijing 100049, China;* orcid.org/0000-0001-7273-4087

**Feiyue Wang** − *Centre for Earth Observation Science and Department of Environment and Geography, University of Manitoba, Winnipeg, MB R3T 2N2, Canada;* orcid.org/0000-0001-5297-0859

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.est.0c00429

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

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