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Elemental Carbon and Polycyclic Aromatic Compounds in a 150-Year Sediment Core from Lake Qinghai, Tibetan Plateau, China: Influence of Regional and Local Sources and Transport Pathways

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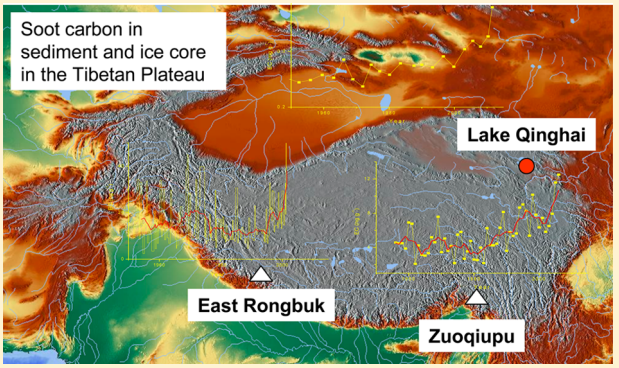
Supporting Information

ABSTRACT: Elemental carbon (EC) and polycyclic aromatic compounds (PACs) are potential proxies for the reconstruction of change in human activities and the origin of air masses in historic times. In this study, the historic deposition of char and soot (the two subtypes of EC) and PACs in a 150-year sediment core from different topographic subbasins of Lake Qinghai on the Qinghai Tibetan Plateau (QTP) were reconstructed. The objective was to explore how the variations in the concentrations of EC and PACs, in the ratios of char to soot and of oxygenated polycyclic aromatic hydrocarbons (OPAHs) to parent PAHs, and in the composition of the PAC mixtures reflect historical changes in climate and human activity and the origin of air masses arriving at the QTP. The deposition fluxes of soot in the different subbasins were similar, averaging 0.18 (range of 0.15−0.25) and 0.16 (0.13−0.23) g m^{-2} $year^{-1}$, respectively, but they varied for char (averaging 0.11 and 0.22 g m^{-2} $year^{-1}$, respectively), suggesting ubiquitous atmospheric deposition of soot and local river inputs of char. The different vertical distributions of the char/soot ratios in the different subbasins can be interpreted in terms of the different transport mechanisms of char and soot. An abrupt increase in soot concentrations since 1980 coincides with results from the QTP ice cores that were interpreted to be indicative of soot transport from South Asia. Similar concentration patterns of PAHs with soot and 9,10-anthraquinone/anthracene (9,10-AQ/ANT) ratios all >2.0 suggest regional PAC sources. Increasing PAH/soot ratios and decreasing 9,10-AQ/ANT ratios since the beginning of the 1970s indicate increasing local emissions. The historical trends of these diagnostic ratios indicate an increase in the fossil-fuel contribution since the beginning of the 1970s. The increase of perylene concentrations with increasing core depth and the ratio of perylene to its penta-aromatic isomers indicate that perylene originates mainly from in situ biogenic diagenesis. We demonstrate that the concentrations of EC, char, soot, and PACs in sediments can be used to reconstruct local, regional, and remote sources and transport pathways of pollutants to the QTP.



1. INTRODUCTION

Elemental carbon (EC) and polycyclic aromatic compounds (PACs) are produced by the incomplete combustion of fossil fuels and biomass.[1,2] EC and PACs are markers for biomass burning in preindustrial times[1,3] and useful indicators of human activities in the modern and industrial times.[4,5] EC is composed of char and soot corresponding to combusted solid residues and clusters of carbon particles formed by gas-phase processes, respectively.[1,6] Because of the differences in their particle sizes and chemophysical and optical properties,[7] char and soot have different environmental implications. Char, usually consisting of

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larger particles, generally deposits on surfaces within a short distance from the emission source and thus reflects local combustion processes, whereas the submicrometer-sized soot particles can be transported great distances and render the atmosphere an important reservoir.[6] EC records are especially sparse in China.[3−5] In addition, most of these existing records do not differentiate between char and soot (except for a study in eastern China,[5] which showed that the soot history reflects the industrialization of China well), thereby missing important information regarding the sources, transport, and climatic effects of char and soot.

Combustion is the major source of polycyclic aromatic hydrocarbons (PAHs), although some diagenetic and biological processes might also contribute.[8] PAH derivatives such as oxygenated PAHs (OPAHs) and azaarenes (AZAs, nitrogen heterocyclic polycyclic aromatic compounds) are emitted together with PAHs from combustion activities (primary sources). However, OPAHs are also formed in the environment by reactions between parent PAHs and oxidants (e.g., O_3, $OH^•$, and $NO^•$), as well as photolysis and microbial degradation of parent PAHs.[9] PAHs have been the subject of many studies because of their mutagenic and/or carcinogenic properties.[10,11] PAHs have been used as proxies for past variations in human activity because they are fire markers.[12−14] The historical deposition of PAHs in lake sediments and other environmental archives has also been studied extensively worldwide and in China,[15−17] even in our study area of Lake Qinghai.[18] However, OPAHs and AZAs have seldom been studied in China, even though the simultaneous determination of OPAHs together with their parent PAHs in dated sediment cores offers the opportunity to use the ratio of OPAHs to their parent PAHs as an indicator of the origin of the air mass during historical deposition times. The ratios of OPAHs to their parent PAHs can help to further refine our understanding of whether the human and climatic impacts, as recorded in remote environmental archives, such as the Qinghai−Tibetan Plateau (QTP) region, originate from local, regional, or long-range sources.

The QTP is the highest plateau in the world (average elevation of 4000−5000 m above sea level) and is a relatively pristine area. Because of the high elevation of this plateau, air masses on the QTP can easily enter into the top of the atmosphere and be transported worldwide,[19] so the state of atmospheric pollution above the plateau is globally important. The plateau also harbors the world's largest glaciers after the Arctic and Antarctic, and the deposition of light-absorbing pollutants, such as soot,[20,21] onto ice surfaces can promote the melting and cause the shrinkage of glaciers. Lake Qinghai is located at the edge of the northeastern QTP, where both the Asian (southwestern and eastern) summer monsoon (ASM, with a humid air atmosphere) and the westerly winds (passing through an arid atmosphere)[22] influence the wind regime [Figure S1, Supporting Information (SI)]. The ASM circulation reaches this region in summer, whereas the westerly winds dominate in winter, resulting in a clear seasonality of precipitation.

The objectives of this study are to (1) reconstruct the deposition histories of EC, char, soot, PAHs, OPAHs, and AZAs as indicators of the historical variations of human activities and climate; (2) infer sources and transport paths for these combustion-derived materials; and (3) assess the relationships between EC, char, soot, and PACs to identify the drivers of PAH, OPAH, and AZA patterns in the sediments of Lake Qinghai.

2. EXPERIMENTAL PROCEDURE

A piggyback horst separates Lake Qinghai into two subbasins (Figure S1, SI). Gangcha County, with a population of 42000 located in the northern part of the Qinghai catchment, hosts the largest number of residents around the lake. Seven large rivers flow into the lake, of which four main rivers (Buha, Ha'ergai, Quanji, and Shaliu) in the northern and northwestern parts (Figure S1B, SI) contribute over 80% of the total annual fluvial sediment inputs.[23] We could not use the samples of two previous cores (QH03-02 and QH03-14, collected in the two sub-basins in July 2003, chronologies reported[24]) for PAC analysis because they were dried at 35 °C. Therefore, a new sediment core (QH11-1), from the same site as QH03-02 in the southern part, was collected in September 2011 to compare the transport differences of carbon fractions, especially for char and soot in the two subbasins. Core QH11-1 was dated using ^{137}Cs, ^{210}Pb, and ^{226}Ra analyses (see the SI, including Figure S2), and its average sedimentation rate was similar to that of QH03-02.[24] EC, char, and soot concentrations of sediments from QH11-1 and QH03-14 were quantified using the IMPROVE (Interagency Monitoring of Protected Visual Environments) method following Han et al.[5] The concentrations of 29 parent and alkyl PAHs (including perylene here), 15 OPAHs, and 4 AZAs from QH11-1 were determined following the approach of Bandowe and co-workers.[25,26] Details of the sampling, dating, analytical procedures, and quality assurance/control for the carbon fractions and PAC analyses are further explained in the Supporting Information.

3. RESULTS AND DISCUSSION

3.1. Core Chronology. The chronology of sediment core QH03-14 in the northern basin was published by Jin et al.[24] and was directly used in our study. For core QH11-1 in the southern basin, the chronology obtained from the constant-rate-of-supply (CRS) ^{210}Pb model[27,28] indicated that the ^{137}Cs peak occurs at AD 1977 ± 3.4 (Figure S2C, SI). However, the 3.75-cm sediment depth corresponds to AD 1966 ± 4.4. Calculating the ^{137}Cs flux using the CRS-derived mass accumulation rate (MAR) data demonstrates that the shape of the ^{137}Cs peak becomes very broad and it is difficult to determine where the maximum flux is. In addition, the constrained model[28] forcing the chronology through the ^{137}Cs fix-point (3.75 cm = AD 1963; Figure S2D, SI) yielded a very similar chronology to the unconstrained model.[27] Therefore, the chronology obtained from the unconstrained CRS model[27] was used in this study.

3.2. Concentrations of EC, Char, and Soot. Figure 1 reveals different historical variations for EC and char but similar variations for soot in the two subbasins of Lake Qinghai. The EC and char concentrations before 1950 show relatively small variations, averaging 0.50 (range: 0.40−0.68 mg g^{-1}) and 0.25 mg g^{-1} (range: 0.18−0.45 mg g^{-1}), respectively, in the northern sub-basin, and 0.45 mg g^{-1} (range: 0.39−0.57 mg g^{-1}) and 0.20 mg g^{-1} (range: 0.14−0.30 mg g^{-1}), respectively, in the southern sub-basin. However, after 1990, the northern core shows a sharp increase (approximately 3 times higher than those before 1990) in EC and char concentrations, with a maximum of 1.45 mg g^{-1} in the top 0−0.5-cm increment of the sediment core. This is consistent with more human activities and lacustrine inputs in the northern part, whereas in the southern core, the EC and char concentrations decreased slightly during this period.

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Environ. Sci. Technol. XXXX, XXX, XXX−XXX

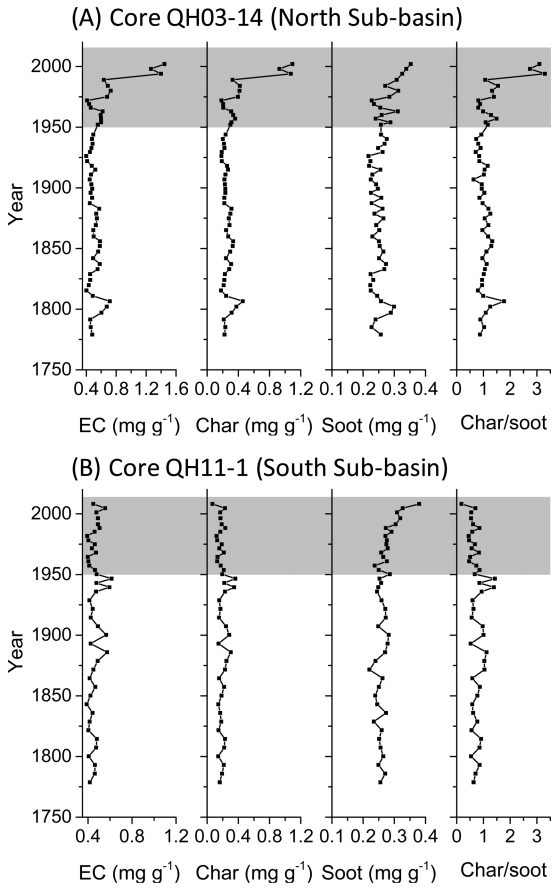

Figure 1. Comparison of the vertical distributions of EC, char, soot, and the char/soot ratio in (A) sediment core QH03-14 (northern subbasin with more anthropogenic inputs) and (B) sediment core QH11-1 (southern subbasin). The shaded portion highlights the period since 1950. Temporal variations of the char and soot fluxes in the two sediment cores are shown in Figure S4 (SI).

For soot, relatively constant concentrations between 0.2 and 0.3 mg g^{-1} were observed in the two subbasins before 1950, with a small increase between 1950 and 1980, which is similar to the anthropogenic Pb profile.[24] Since 1980, a sharp increase in both the soot concentrations and the deposition fluxes occurred (maximum in the top 0−0.5 cm) in the two subbasins, although there were fluctuations in the northern part. The average soot concentrations in the two subbasins were similar, at 0.26 and 0.27 mg g^{-1} in the northern and southern parts, respectively.

The EC concentrations are at the lower end of the range of values reported for lake sediments of China,[3−5] as well as of those reported worldwide using different methods[17,29−31] (Table 1). Interestingly, the soot concentrations in sediments from different locations in China are all similar; the average concentrations vary from 0.20 to 0.27 mg g^{-1}, with the exception of Lake Taihu (0.42 mg g^{-1}), which is located in the strongly industrialized region of eastern China. The char concentrations in Lake Qinghai sediments are generally lower than those in other published studies from China, in good agreement with the fact that emissions from local human activities are small in this pristine area. Deposition fluxes of EC, char, and soot show regional differences among the different locations, with low fluxes in remote areas, such as Lake Qinghai and Lake Nam Co,[4] and high fluxes in more populated locations, such as Taihu.[5] This distribution pattern is

Table 1. Comparison of Concentrations and Deposition Fluxes of EC, Char, and Soot and Char/Soot Ratios in Lake Qinghai with Other Records Worldwide

area	description	concentration (mg g^{-1})			deposition flux (g m^{-2} $year^{-1}$)			char/soot	method
		EC	char	soot	EC	char	soot		
Lake Qinghai (north)	north Tibetan Plateau, past 150 years	0.40−1.45 (0.57)	0.18−1.09 (0.31)	0.22−0.35 (0.26)	0.27−0.98 (0.39)	0.12−0.74 (0.21)	0.15−0.24 (0.18)	0.63−3.30 (1.16)	IMPROVE
Lake Qinghai (south)		0.39−0.61 (0.46)	0.07−0.36 (0.19)	0.22−0.38 (0.27)	0.22−0.36 (0.27)	0.04−0.21 (0.11)	0.13−0.20 (0.16)	0.18−1.43 (0.73)	
Lake Nam Co[4]	central Tibetan Plateau, past 150 years	0.49−1.09 (0.74)			0.12−0.44 (0.26)				
Lake Daihai[3]	rural mountains, North China, past 150 years	0.52−4.90 (2.26)	0.37−4.69 (2.05)	0.12−0.35 (0.21)	0.6−7.0 (3.1)	0.45−6.7 (2.7)	0.14−0.43 (0.3)	2.09−21.64 (9.76)	
Lake Chaohu[5]	suburban, eastern China, past 150 years	0.61−2.03 (1.13)	0.48−1.58 (0.93)	0.08−0.47 (0.20)	1.70−5.67 (3.16)	1.35−4.43 (2.59)	0.23−1.31 (0.57)	2.82−8.02 (5.14)	
Lake Taihu[5]	well-industrialized urban, eastern China, past 150 years	0.41−1.95 (1.01)	0.01−1.43 (0.60)	0.31−1.09 (0.42)	1.15−6.89 (3.3)	0.03−5.55 (2.0)	0.86−3.12 (1.30)	0.03−4.21 (1.51)	
Aspvreten, Sweden[17]	background area, past 700 years				0.071−0.4				CTO-375
pan-Arctic[29]	Arctic, surface sediments	0.17−1.5			0.0013−0.056				
lakes in Slovenia[31]	Alps, past 100−200 years	0.09−1.93			0.3−11				
West Pine Pond[30]	rural, New York state, past 150 years	0.6−8			0.026−0.77				STN

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Environ. Sci. Technol. XXXX, XXX, XXX−XXX

particularly pronounced for soot, with its concentrations in sediments decreasing consistently in the order urban > suburban > rural mountain > remote areas (Table 1).

3.3. Sources and Transport Paths of Char and Soot in Lake Qinghai. Although char and soot are both produced from combustion activities, different sources contribute different proportions of char and soot to total EC. In general, biomass burning generates a much higher percentage of char than soot, with a char/soot ratio of >5−10.[7] The contribution in Lake Qinghai from biomass burning mainly originates from the combustion of yak dung and grass. However, the char/soot ratios in both subbasins before 1980 were between 0.4 and 1.8, which is even lower than those from sediments of Lake Taihu[5] but close to those from motor vehicle emissions.[7] Obviously, motor vehicle emissions could not have been the main source in this region at that time because motor vehicles were not present in the study region. This indicates the influence of long-range transport and deposition of the soot fraction of EC on the char/soot ratio in Lake Qinghai.

The ranges of char/soot ratios from 0.18 to 1.43 for the southern subbasin and from 0.63 to 3.30 for the northern subbasin (Figure 1) can be explained by a decoupling of the soot and char sources. The north subbasin, with higher char/soot ratios, is located close to local anthropogenic sources, such as the city of Gangcha (with a population of ∼42000). In addition, because all large rivers, including the Buha, which contributes more than 70% of the detrital inputs to Lake Qinghai,[24] are located in the northwestern part (Figure S1, SI), fluvial inputs could also be the reason for the high char/soot ratios. The abrupt increase in char/soot ratios in the 1980s for the northern subbasin coincides with the rapid increase in population, the development of the local tourist industry, and the accompanying rapid rise in human activities in this region (Figure S3, SI). However, the char/soot ratios decreased at the same time for the southern subbasin (Figure 1), which might be associated with the weakening of the summer monsoon shown by the decrease in the lake water level (Figure S4, SI). The similar patterns of concentrations and deposition fluxes for soot in the two sediment cores and the different profiles for char in the two subbasins also support our assumption of local river inputs of char and regional atmospheric deposition of soot into the lake [Figure 1, Figure S5 (SI), and Table 1].

Comparison of soot concentrations with the published EC history from ice core records in the QTP (which cover only the past 50 years and for which Indian EC sources are assumed[21])[32,33] reveals similar EC patterns in the ice and Lake Qinghai sediment cores. This is particularly true since 1980, the year in which a sharp increase in EC concentrations in ice cores of the Tibetan Plateau[21] and the sediment core of Lake Qinghai was observed. Rapid industrialization in China began in the late 1970s,[5] only a little earlier than the increase in soot concentrations in Lake Qinghai. We suggest that both the Indian emissions and the inland EC emissions from eastern China contribute to soot deposition in this region, as the study area is located at the boundary of both the eastern Asian monsoon and the Indian monsoon.[22] Previous modeling[34] suggested that southern and eastern Asia contribute 67% and 17%, respectively, to the total EC transported to the Tibetan Plateau.

3.4. Historic Variation of PAHs, OPAHs, and AZAs. The temporal variations in the concentrations of ∑28PAHs (total concentration of all analyzed PAHs without perylene; Figure 2), low-molecular-weight (LMW) PAHs (two- to three-ring parent PAHs), and high-molecular-weight (HMW) PAHs (four- to seven-ring parent PAHs; Figure S6, SI) are similar to that of soot, with relatively stable concentrations before 1980 and a sharp increase thereafter. However, the temporal variation of ∑28PAHs in the Lake Qinghai sediment core is different from that of char (Figures 1 and 2). This suggests that the parent PAHs might also originate from long-range atmospheric transport associated with soot. Soot has sources similar to those of PAHs and a high sorption capacity for PAHs. The long-range transport of PAHs to Lake Qinghai is further supported by the 9,10-anthraquinone/anthracene (9,10-AQ/ANT) ratio (see section 3.5). The increase in the ∑28PAHs/soot ratio since the 1990s marks a partial decoupling of the joint deposition of PAHs and soot from distant sources. Since the 1980s, local contributions of PAHs likely have increased, because of the increase in population, tourists, and electricity generation in Qinghai Province (Figure S3, SI). Char concentrations show a negative correlation with those of ∑28PAHs (Table S2, SI), indicating different controlling factors on char and PAH deposition, which might involve different transport distances, different local sources, and different formation pathways (see section 3.4).

The ∑15OPAHs concentration also increased in recent times, but in a different manner from that of of ∑28PAHs (Figure 2). The first increase in the ∑15OPAHs and ∑4AZAs

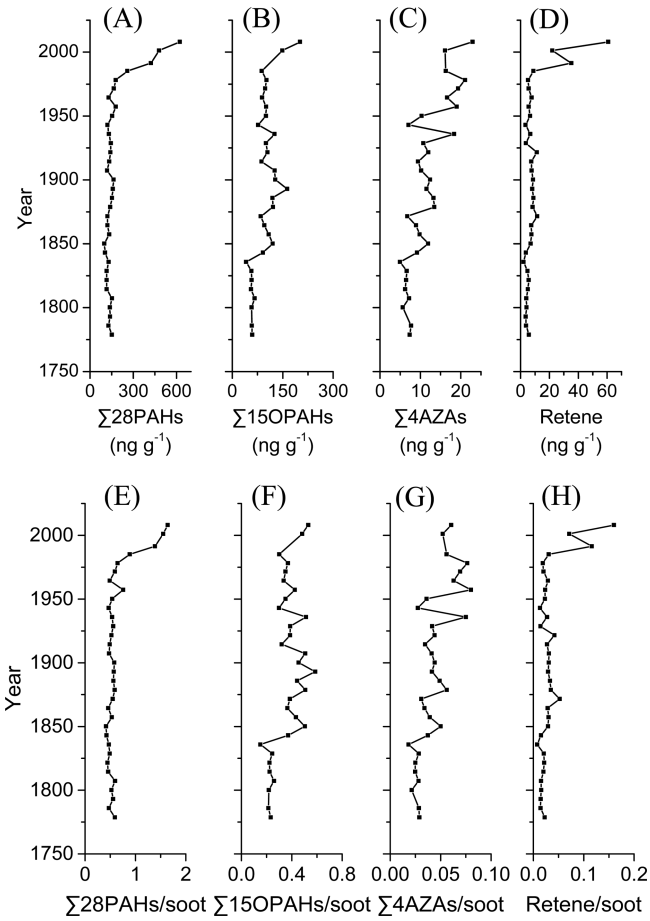

Figure 2. (A−D) Vertical distributions and (E−H) concentration ratios to soot (which are indicative of variations in atmospheric deposition and local inputs) of (A,E) ∑28PAHs (all analyzed PAHs without perylene), (B,F) ∑15oxygenated PAHs, (C,G) ∑4azaarenes (AZAs), and (D,H) retene.

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Environ. Sci. Technol. XXXX, XXX, XXX−XXX

concentrations occurred around ~1850 (Figure 2), at the beginning of the Industrial Revolution in western Europe. The long-range transport of pollutants by the westerly winds (the northern branch surrounding the QTP; see Xu et al.[21]) to the QTP was shown in previous studies.[21,35] The strong correlation between the ∑15OPAHs concentration and retene, an indicator of biomass burning[36] (Table S2, SI), suggests that primary combustion, especially from biomass burning, might be one of the main sources for OPAHs in the old part of the sediment core. The peak of ∑15OPAHs in the 1910s occurred together with high concentrations of ∑4AZAs and ∑Comb-PAHs[37] [combustion-derived PAHs; see footnote of Table S1 (SI) for definition] and Pb.[24] The increase in Pb concentrations at that time has been attributed to enhanced agricultural activities[24] that used fires for land reclamation.

Similarly to the concentrations of ∑28PAHs, those of ∑4AZAs also increased in the upper part of the sediment core, reaching the highest values in the 21th century (Figure 2). The ∑4AZAs concentrations ranged from 5.0 to 23.0 ng g^{-1} and averaged 11.6 ng g^{-1}, which is lower than the concentration range reported for Danshuei River, Taiwan, of 3.7−154 ng g^{-1}.[38] It is widely believed that PAHs and AZAs have similar anthropogenic sources, but their fates in the environment are different.[39] In this study, the PAH concentrations were closely correlated with those of three-ring AZAs (r = 0.51, p = 0.002) but poorly correlated with those of two-ring AZAs (r = 0.16, p = 0.385). This suggests that three-ring AZAs have sources and fates similar to those of PAHs, whereas two-ring AZAs have different sources and/or fates in the sediment because of the higher solubility of two-ring AZAs in water.[39] Before the 1960s, when long-range-transported PAHs dominated, there were relatively more two-ring than three-ring AZAs, whereas after the end of the 1960s, with the increase in local inputs, three-ring AZAs became more prominent (see the change in slopes in Figure S7, SI).

3.5. Covariation of PACs with TOC, EC, Char, and Soot. The closest correlation coefficient (Table S2 and Figure S8, SI) exists between the concentrations of soot and ∑28PAHs (r = 0.84, p < 0.001), followed by TOC with ∑28PAHs and ∑15OPAHs (r = 0.61, p < 0.01). Although close correlations between the concentrations of PAHs and EC have been reported by others and attributed to coemission, cotransport, and sorption of these materials,[40] the EC and char concentrations in Lake Qinghai sediments correlate only weakly with those of ∑28PAHs and ∑15OPAHs. Nam et al.[40] suggested that the associations between EC and PAHs are more important in closer proximity to combustion sources, whereas PAH partitioning to soil organic matter (measured as TOC) is more important in remote sites. However, because both soot and PAHs can originate from long-range atmospheric transport, the PAH−soot partitioning is likely to be more important in remote areas. The mixing of char and soot in EC might obscure the correlation between the concentrations of EC and ∑28PAHs, emphasizing the importance to differentiate between char and soot.

3.6. Temporal Trends of PAC Composition Patterns and Concentration Ratios. Numerous markers have been used to infer different sources of PAHs. For example, retene was suggested as an indicator of biomass burning,[36] and indeno[1,2,3-*cd*]pyrene, benzo[*g*,*h*,*i*]perylene, and coronene were proposed as indicators for oil combustion emissions.[41] The concentrations of indeno[1,2,3-*cd*]pyrene, benzo[*g*,*h*,*i*]-perylene, and coronene began to increase in ~1980 (Figure S6, SI), coinciding with increasing oil production (or use) in Qinghai Province (Figure S3, SI). The retene concentrations increased only beginning in the late-1990s (Figure 2), when the "Scenic district of Lake Qinghai" was established as a tourist attraction. Since then, the number of tourists has increased sharply (Figure S3, SI), resulting in increased use of yak dung for residential heating in this area.

A previous study suggested that the 9,10-AQ/ANT concentration ratio remains constant in sediments, in contrast to that in the atmosphere, because sediments are not exposed to UV radiation[42] and that a 9,10-AQ/ANT ratio greater than 1 indicates primary input from atmospheric deposition whereas a 9,10-AQ/ANT ratio less than 1 means lacustrine input.[42] In this study, the 9,10-AQ/ANT ratios (Figure 3) ranged from 2.4 to 10.3 with an average of 5.2, indicating the dominance of atmospheric deposition. Since the beginning of the 1970s, the ratios have decreased, consistent with the time of increase in ∑28PAHs concentrations originating from local inputs (see section 3.3), suggesting increasing inputs of pollutants from local emissions. Other ratios of individual OPAHs to their parent PAHs show temporal trends similar to that of the 9,10-AQ/ANT ratio, whereas this is not the case for the ∑15OPAHs/∑28PAHs ratio (Figure 3). Before the 1840s, the ∑15OPAHs/∑28PAHs ratios were low (i.e., 0.44), and

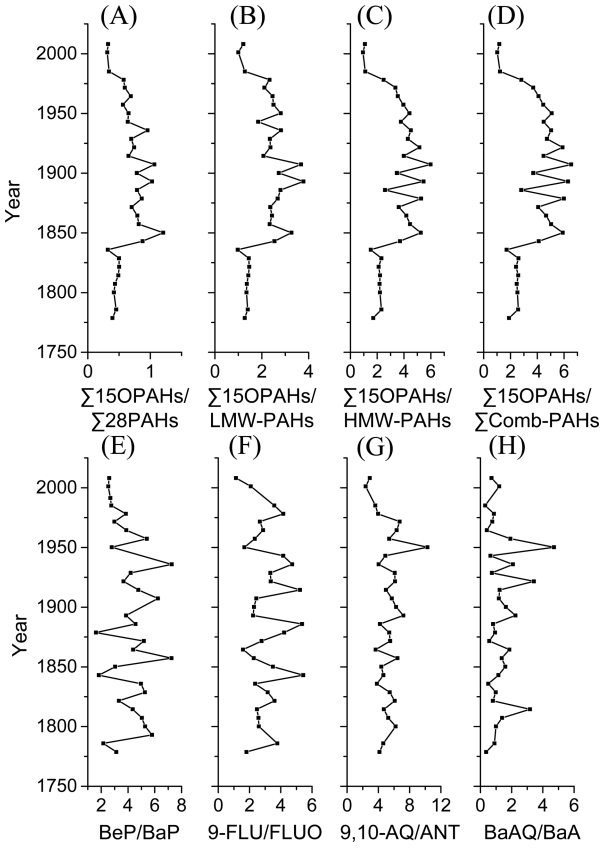

Figure 3. Vertical distributions of the concentration ratios of (A) total OPAHs to total PAHs, (B) total OPAHs to LMW PAHs, (C) total OPAHs to HMW PAHs, (D) total OPAHs to combustion-derived PAHs (∑Comb-PAH), and (E−H) individual OPAHs to their parent PAHs. BeP/BaP, 9-FLU/FLUO, 9,10-AQ/ANT, and BaAQ/BaA refer to benzo[*e*]pyrene/benzo[*a*]pyrene, 9-fluorenone/fluorene, 9,10-anthraquinone/anthracene, and benzo[*a*]anthracene-7,12-dione/benzo-[*a*]anthracene, respectively.

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Environ. Sci. Technol. XXXX, XXX, XXX−XXX

the ratios then increased and reached the highest value of 1.21 in the 1870s. Thereafter, the ∑15OPAHs/∑28PAHs ratios in the sediments decreased until recently. This change might be associated with secondary formation of OPAHs during long-range transport. Low ∑15OPAHs/∑28PAHs ratios before the 1840s might indicate the dominance of background local inputs. After the 1870s, the stepwise increases in industrialization in China, such as the Westernization Movement (1861−1895) and the Golden Decade (1927−1937),[43] might have resulted in the decrease of the ∑15OPAHs/∑28PAHs ratios because of the increase in local compared to regional emissions, especially after the political reform and economic opening of China in the later 1970s.

3.7. Evidence of Nonpyrogenic Sources of Perylene. Perylene is absent from the surficial sediments of Lake Qinghai, and its concentration generally increases with depth and reaches 39.5 ng g^{-1} at the lake bottom. The surficial perylene concentrations are lower than the sum of the concentrations of its penta-aromatic isomer PAHs (benzo[*a*]pyrene, benzo[*e*]-pyrene, and benzo[*b*,*j*,*k*]fluoranthene; Figure S9, SI), whereas the perylene concentrations were higher than the sum of these isomers in deeper sediments. These results suggest that most of the perylene in Lake Qinghai likely originates mainly from in situ biogenic diagenesis under anoxic conditions.[44] The contribution of the perylene concentrations to the total concentrations of all penta-aromatic isomers (PAIs) is ∼8% in surficial sediments and increases with depth to values of >10% (Figure S10, SI), which are considered indicative of a diagenetic source of perylene.[18] The concentration ratios of perylene to TOC, PAI, and ∑28PAHs generally increase with increasing sediment depth and therefore age, suggesting the continuous formation of perylene over time (Figure S10, SI). Furthermore, it can be concluded that the formation of perylene in Lake Qinghai is a first-order reaction (Figure 4), implying that the production of perylene depends simply on the availability of precursors and the age of the sediment.

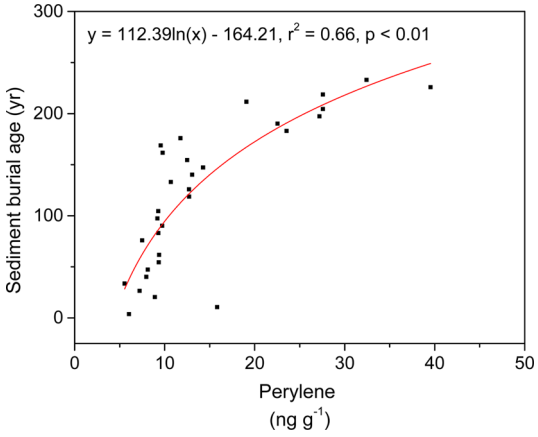

Figure 4. Relationship between perylene concentration and sediment burial age in Lake Qinghai.

Perylene has a significant negative correlation with TOC (r = −0.51, p = 0.003) and C/N ratio (r = −0.50, p = 0.004), supporting our assumption that some components of TOC are precursors of perylene formation. The organic matter in the sediment of Lake Qinghai originates mainly from terrestrial plants, such as alpine meadows and steppe grasses, shown by the C/N ratio (ranging from 9.1 to 23.4 and averaging 14.4) and *n*-alkane data.[45] Perylenequinone, one of the probable precursors of perylene in "P-type" humic acid, can occur in the podzolic grassland soils surrounding Lake Qinghai[46] and thus could have contributed to perylene formation in Lake Qinghai.

■ ASSOCIATED CONTENT

Supporting Information

Methods section. Locations of sediment cores (Figure S1) and sediment chronology (Figure S2). Temporal variations in human activities (Figure S3), lake surface size (Figure S4), char and soot fluxes (Figure S5), and concentrations of selected PACs (Figure S6). Relationships between the concentrations of two-ring and three-ring AZAs and PAHs (Figure S7) and between the concentrations of PAHs and AZAs char (soot) (Figure S8). Vertical distributions of the concentrations of perylene and its combustion-derived isomers in sediments (Figure S9). Perylene/PAI, perylene/TOC, and perylene/∑28PAHs concentration ratios, together with C/N ratios (Figure S10). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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