



Sedimentary record of polycyclic aromatic hydrocarbons in a reservoir in Northeast China

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ABSTRACT

A sediment core from the Dahuofang Reservoir in Northeast China was ²¹⁰Pb and ¹³⁷Cs dated and analyzed for polycyclic aromatic hydrocarbons (PAHs) to track the regional PAH pollution in the past 50 years. The 2–4 ring PAHs peaked in the early 1990s, reflecting the historical role of coal usage in the energy structure in this area. More recently, vehicle emissions caused the continuous increase of the 5 + 6 ring PAHs. However, the sixteen US EPA priority PAHs showed a significant decline since the early 1990s. This PAH temporal trend is different from the U.S., the European countries and Japan, and is also different from the other areas of China, which could be attributed to the switch from coal to oil or natural gas as the main energy, and the large-scale elimination of outdated combustion facilities and techniques in Northeast China.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), compounds containing two to eight aromatic rings, have been of concern for several decades due to their carcinogenic properties, and the US EPA has designated sixteen priority PAHs (16 PAHs) that are characteristic of environmental pollution. In China, the major anthropogenic sources of these 16 PAHs include biomass burning, coal and petroleum combustion, coking as well as metal production (Xu et al., 2006). The increase in the consumption of energy in recent years in China suggests PAH emissions will also keep on increasing (Liu et al., 2005; Guo et al., 2006; Yan et al., 2009; Hu et al., 2011).

Because of the persistent nature of some PAHs, sediment cores can provide historical records of PAHs, and perhaps even other pollutants, on a regional basis for 50–100 years (Pereira et al., 1999; Hartmann et al., 2005; Itoh et al., 2010). These records, in turn, can be used to understand the energy structure and consumption, and thus building a picture of the economic development of a region (Lima et al., 2003; Liu et al., 2005; Guo et al., 2006).

Northeast China, including Liaoning, Jilin and Heilongjiang provinces is one of the most important heavy-industry bases in China because it has bountiful of natural resources including coal, wood, shale and minerals, and in the 1960s, petroleum was discovered. In 2009, the GDP of Liaoning ranked seventh in the nation.

The industries include heavy machinery, electronics, metal refining, automobile, petroleum, chemicals, construction materials, etc. Due to the long and harsh winter there, space heating will also add to the pollution problem.

The Dahuofang Reservoir (DHF) is in the central part of Liaoning (Fig. 1) and is the largest man-made lake in Northeast China. Its sediments contain atmospheric deposition that can reveal regional pollution, in particular, PAHs and thus the energy structure in the past 50 years.

2. Materials and methods

2.1. Sampling

The DHF is located in the Northeast China among 41°41'N–41°57'N° and 124°05'E–124°20'E° as shown in Fig. 1. The DHF started to be built in 1952 and was completed in December 1958. The DHF is the biggest lake of Liaoning Province with the area of 114 km², the water volume of 21.87 × 10⁸ m³, and the watershed of 5437 km².

A sediment core, Z6, was collected using a gravity corer in January, 2010 (Fig. 1). The core Z6 was located at the center of the DHF and the water depth was 36 m. The length of core Z6 was 41 cm. There was no significant loss of surface sediments or distortion of top sediment layer during the coring. The core was cut into 1 cm samples along the length using a stainless steel cutter in the laboratory. The samples were stored at –20 °C until analysis.

2.2. PAH analysis

The PAH analysis procedure and QA/QC followed that described by Mai et al. (2003) and Guo et al. (2006). Briefly, homogenized samples were freeze-dried and ground. About 10 g of the sample was spiked with a mixture of recovery standards of five deuterated PAHs (naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀,

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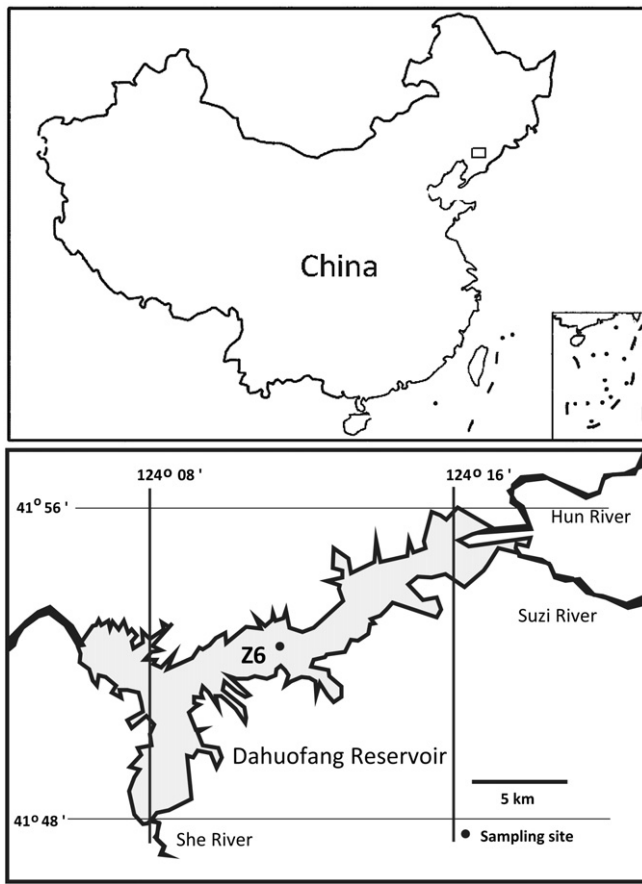


Fig. 1. Map of the sampling site.

chrysene- d_{12} , and perylene- d_{12}). The samples were extracted with dichloromethane in a Soxhlet extractor for 72 h, with activated copper added to remove the sulfur in the samples. The extract was concentrated and fractionated using a silica–alumina (1:1) column. PAHs were eluted using 35 ml of hexane/dichloromethane (1:1). The PAHs fraction was concentrated to 0.5 ml, and hexamethylbenzene was added as internal standard. The mixture was further reduced to 0.2 ml and subjected to GC–MS analysis. A Agilent 5975C mass spectrometer interfaced to a Agilent 7890 gas chromatography was used to analyze the samples. The GC was equipped with a DB-5MS capillary column (30 m long \times 0.25 mm inside diameter \times 0.25 μ m film thickness), with He as carrier gas. The chromatographic conditions were as follows: injector temperature, 290 °C; detector temperature, 300 °C; temperature program: 60 °C (3 min), 60–290 °C at 3 °C/min, held at 290 °C for 20 min. The MS was operated in the electron impact (EI) mode at 70 eV and the total-ion-monitoring (TIM) mode. The PAHs quantified were as follows: naphthalene (Nap), acenaphthylene (Ac), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), methylphenanthrene (MP), anthracene (Ant), acephenanthrylene (Acp), fluoranthene (Flu), pyrene (Pyr), retene (1-methyl-7-isopropylphenanthrene) (Ret), benz[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IP), dibenz[a,h]anthracene (DBA), perylene (Pery), and benzo[ghi]perylene (BghiP).

A National Institute of Standards and Technology (NIST, Gaithersburg, MD) 1941 standard reference material (SRM), standard-spiked matrix, duplicate samples and procedural blank were analyzed for quality assurance and control. Recoveries of the PAHs in the SRM were between 80% and 120% of the certified values. PAH recoveries of standard-spiked matrix ranged from 85–95%, the relative precision of paired duplicated samples was below 15% ($n=6$), and the targeted compounds were not detected in procedural blank ($n=6$). All results for QA/QC met the experimental quality requirements. The average recovery of the standards spiked into each sample prior to analysis was $81 \pm 9\%$ for naphthalene- d_8 , $89 \pm 12\%$ for acenaphthene- d_{10} , $96 \pm 7\%$ for phenanthrene- d_{10} , $96 \pm 7\%$ for chrysene- d_{12} , and $97 \pm 11\%$ for perylene- d_{12} . PAH concentrations were recovery corrected.

2.3. ^{210}Pb and ^{137}Cs dating

The sediment core was dated at the Nanjing Institute of Geography and Limnology based on the method described by Guo et al. (2007). Briefly, ^{210}Pb and

^{226}Ra activities were measured using an Ortec HPGc GWL series well-type coaxial low background intrinsic germanium detector. ^{210}Pb was determined by gamma emissions at 46.5 keV, and ^{226}Ra by 295 keV and 352 keV gamma rays emitted by the daughter isotope ^{214}Pb following 3 weeks of storage in sealed containers to allow radioactive equilibration. $^{210}\text{Pb}_{\text{ex}}$ was calculated by subtracting ^{226}Ra activities from the total ^{210}Pb activities. The relative error for this method was $<10\%$.

In addition, the ^{137}Cs profile (Fig. 2) was employed to verify the dating suggested by ^{210}Pb activity. ^{137}Cs was measured by its emissions at 662 keV. The highest ^{137}Cs activity was found at a depth of 36 cm, which can be regarded as 1963, most likely originating from nuclear explosion test in the atmosphere in 1963.

The sediments of the core were mainly clayey silt with gray color. The down-core grain size variation of Z6 was small, indicating a stable sedimentary dynamic environment at sampling site. Based on this, the average constant sedimentation rates of 0.75 cm/a at site Z6 could be calculated using a constant flux–constant sedimentation rate (cf:cs) model (Fig. 2). Fig. 2 showed that the ^{137}Cs dating was consistent with the ^{210}Pb dating.

3. Results and discussion

3.1. Occurrence level of PAHs

The 16 PAH concentration range is 590–638 ng/g in the surface and subsurface sediments (0–3 cm). Comparing to the other lakes in China, it is lower than Nansi Lake, North China (160–32,600 ng/g) (Li et al., 2009), Taihu Lake, East China (1207–4754 ng/g) (Qiao et al., 2006), and it is also lower than the Pearl River, South China (Luo et al., 2008), Haihe River, North China (Jiang et al., 2007), but comparable to Qiantang River, East China (Chen et al., 2007), Yangtze River (East China) and Yellow River (North China) (Hui et al., 2009).

3.2. Temporal trends of 16 PAHs

The 16 PAHs concentrations in the sediment core Z6 are in Table S1, and the vertical concentration profiles of the 2–3 rings, 4 rings, 5–6 rings and 16 PAHs are in Fig. 3. The concentrations of 16 PAHs ranged from 243 to 1004 ng/g dry wt and there was a marked increase from 1960 to the early 1990s followed by an obvious decreasing trend with some rebounds in recent years. The recent concentrations were, however, much lower than the peak levels. The vertical profile of the 5–6 ring PAHs showed an increase from the bottom layer to the top layer, which was quite different from those of 2–3 or 4 ring PAHs observed in the DHF. Changes in the PAH pattern could reflect changes in the source of PAHs, such as grass, coal, oil, gas and petroleum combustion, as well as combustion conditions.

The ratios of PAH congeners has been used for source apportionment (Yunker et al., 2002). They summarized that petrogenic sources have Flu/Flu + Pyr < 0.4 , while a ratio > 0.5 suggests wood and coal combustion, and between 0.4 and 0.5 is characteristic of

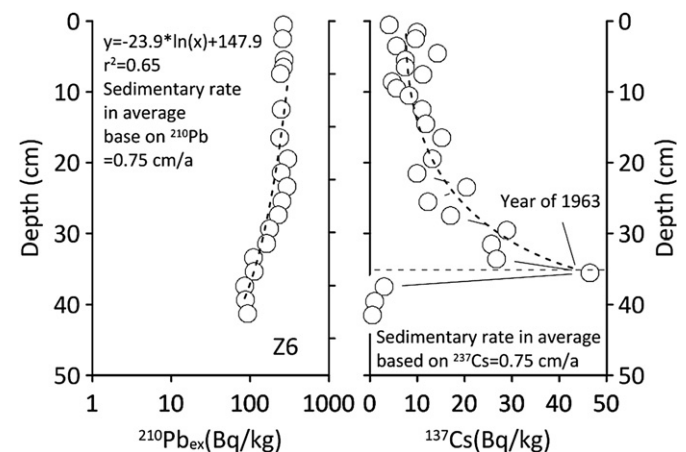


Fig. 2. ^{210}Pb and ^{137}Cs dating of sediment core Z6.

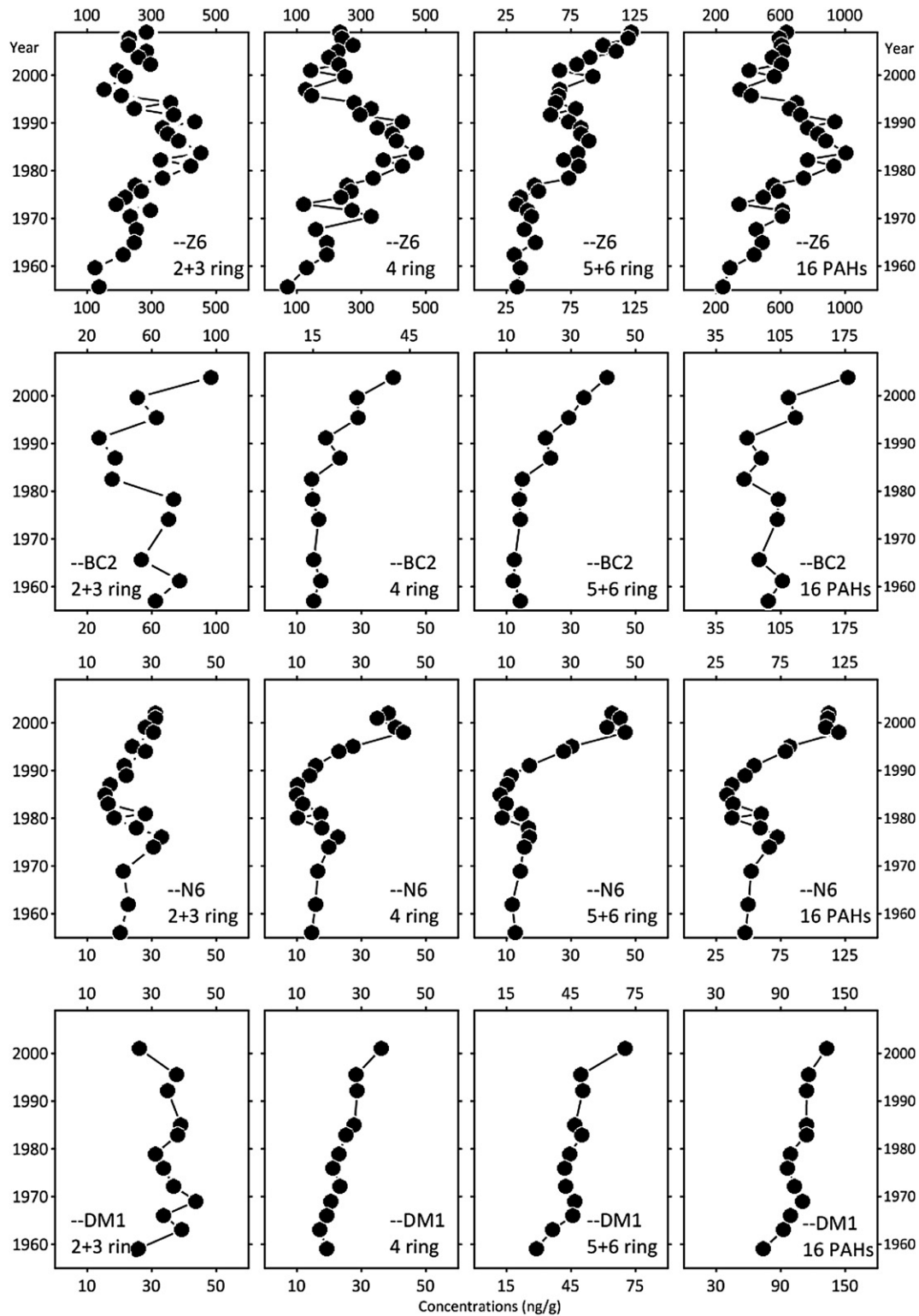


Fig. 3. Time trends of 16 PAHs, 2 + 3 ring, 4 ring and 5 + 6 ring PAH concentrations in sediment core Z6, and comparison with other cores of regional settings around China. Core BC2 is from the Bohai Sea (Hu et al., 2011), core N6 is from the Yangtze River Estuary (Guo et al., 2007), and core DM1 is from the central shelf of the East China Sea (Guo et al., 2006).

petroleum combustion; IP/IP + BghiP of 0.2–0.5 is possibly petroleum combustion, while coal, grass and wood combustion would yield a ratio >0.5. The ratios of Flu/Flu + Pyr and IP/IP + BghiP are in Fig. 4. Flu/Flu + Pyr ratios were all >0.5, suggesting that the 4 ring PAH sources are mainly grass, wood and coal combustion; while,

IP/IP + BghiP ratios were <0.5, implying petroleum combustion source for the 5–6 ring PAHs.

The 5–6 ring PAHs increased threefold from 40 to 120 ng/g from 1960s to recent years as similar as our previous studies of samples obtained elsewhere (Guo et al., 2006, 2007; Hu et al., 2011) (Fig. 3).

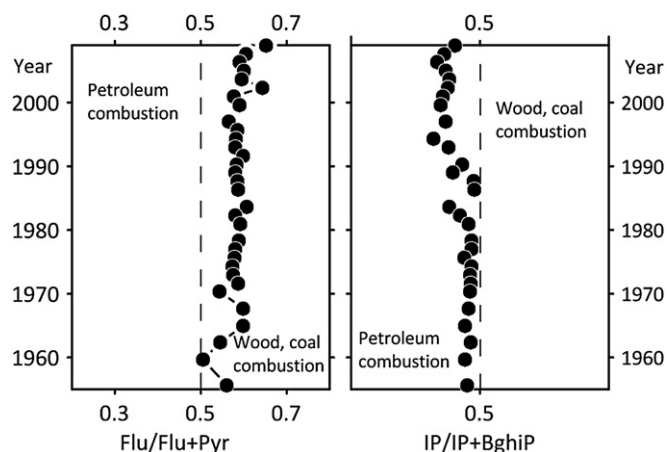


Fig. 4. Flu/(Flu + Pyr) and IP/(IP + BghiP) profiles for source identification in sediment core Z6. PAH source diagnostic ratios are from Yunker et al. (2002).

This suggests that there was increasingly more contribution from high-temperature combustion processes such as vehicular emissions (Mai et al., 2003; Guo et al., 2006). This was, also found in other studies in urban areas in Northeast China (Tian et al., 2009; Ma et al., 2010; Wang et al., 2009). Vehicle emitted PAHs increased three times in the past two decades in China, and it was estimated to be 15 Gg in 2004 accounting for 13% of the total PAH emitted in China (Shen et al., 2011). As of 2010, Liaoning had 2.4 million registered vehicles, a 20% increase over the previous year and 9 times of 2000 (LPBS, 2009).

Coal combustion, in general, is an important source of the 4-ring PAHs (Li et al., 2003). Northeast China was once the most important and largest heavy industrial base which relied heavily on coal for energy that was readily available nearby. The air pollution issue is further worsened by the use of coal for cooking and space-heating in winter. In the 1990s, Northeast China was revitalized and modernized its industrial capability. The energy consumption (per 10,000 yuan (Chinese currency, RMB) GDP energy consumption) improved from 6.75 tons of standard coal in 1990 to 1.63 tons in 2006 (LPBS, 2009). At the same time, measures were taken to clean up household pollution due to energy use by switching from coal to oil fuel or liquefied gases, and community central heating was encouraged, to upgrade or replace outdated energy facilities and technology, and the introduction of clean technology. The peaking of the 4-ring PAHs profile in the early 1990s now becomes a historical mark in the energy structure of Northeast China.

Since 1950, down-core increases of PAHs in the sediment cores of the Pearl River Delta (Liu et al., 2005), Daya Bay, South

China (Qiu et al., 2009; Yan et al., 2009), and Taihu Lake, East China (Liu et al., 2009), and Bohai Sea, North China (Hu et al., 2011) have been observed. This increase is especially prominent in the past 20 years because of the rapid economic growth and higher energy consumption (Fig. S1). In this study, the trend of the 16 PAH concentration is obviously different from those reported in other areas of China. One important factor is the switch from coal to oil as the primary fossil fuel since 1990s. Coal consumption increased 1.5 times from 1990 to 2006 while oil consumption increased 8 times, and by 2006 it was close to 50% of the total energy used in Liaoning Province (LPBS, 2009, Fig. S1). Coal-burning emits much more PAHs than the release from the combustion of petroleum product or natural gas (Ravindra et al., 2008), thus the substitution of coal by oil fuel or natural gas can effectively reduce PAH emission under the same energy consumption level. To date, the amount of oil used in Liaoning has exceeded coal. China's onshore oil resources are mostly in the Northeast. Daqing Oilfield is in Heilongjiang Province and Liaohe Oilfield in Liaoning Province, and they are the largest and third largest oilfields in the nation, respectively. This presumably benefited Liaoning's industries, allowing them to switch from coal to oil sooner and faster than the rest of the country.

During 1960–1970, Europe, the U.S. and Japan switched from coal to oil and natural gas as energy source and experienced a large decrease in PAH emissions (Fernández et al., 2000; Lima et al., 2003; Moriwakia et al., 2005).

The “Reform and Open” policy embarked by China in 1978, industrialized the coastal areas in East and South China, and led to a remarkable economic development in the past 30 some years. Although coal and oil consumption simultaneously increased in the past 20 years, the consumption of coal still accounted for 76% of the total energy used nationwide (NBSC, 2011, Fig. S1). Thus, the burning of coal is still an important source of PAHs in the environment in most parts of China.

3.3. Temporal trend and sources of other PAHs

Pery was abundant in the sediment core with a range of 4–191 ng/g (69 ± 41 ng/g, average). More interestingly, the trend of Pery totally differed from the 16 PAHs suggesting different origins, and the average Pery/(16 PAHs) ratio was 0.12 ± 0.06 . Hites et al. (1980) suggested when this ratio is >0.1 , the Pery is considered to be from diagenetic processes of organic matter in anoxic conditions.

Ret was in the range of 7–57 ng/g, significantly lower than those observed in the sediment samples from the Pearl River Delta (21.2–554.1 ng/g) (Mai et al., 2001). Some studies reported that the Ret and its precursors are derived from diagenetic sources (Hites et al., 1980; Wakeham et al., 1980), while others attributed wood combustion as the source. No clear trend of vertical Ret distribution

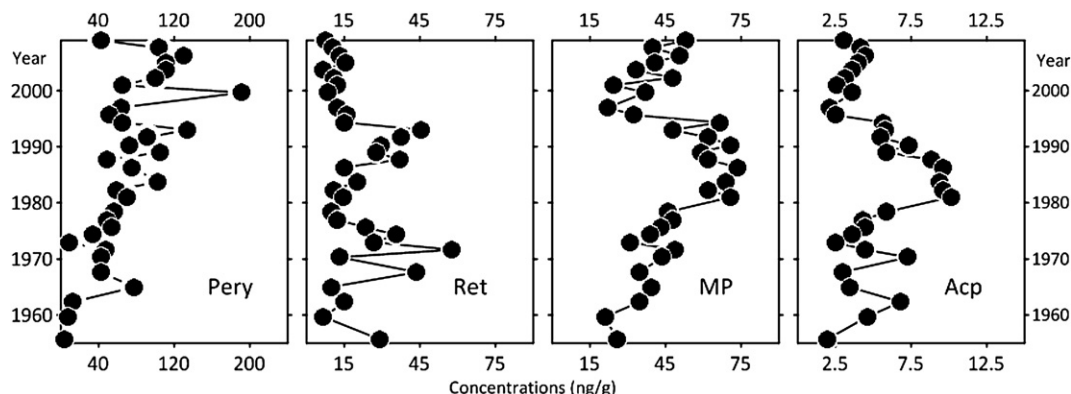


Fig. 5. Time trends of Pery, Ret, MP and Acp concentrations in sediment core Z6.

was observed, suggesting that the Ret may be of mixed sources (Fig. 5).

The down-core distribution of MP was basically consistent with that of the 16 PAHs, suggesting that it was possibly indicative of anthropogenic origin rather than diagenetic products. MP/Phe was <1, also suggesting that MP was of pyrogenic origin (Mai et al., 2001).

4. Conclusions

The sediment core extracted from the DHF reservoir in Liaoning Province in Northeast China in January 2010 showed a significant decline in the 16 PAHs concentrations after the early 1990s despite the rapid economic development that started in 1978. This decrease is quite different from the studies from the other areas in China. The reasonable explanation is because of the availability of petroleum products in Liaoning and the surrounding provinces. Liaoning was able to switch from coal to oil/natural gas as energy source earlier (1990), and the upgrading of industrial and domestic combustion technology also lowered emissions. The increase of the 5 + 6 ring PAHs in the core is an indication of the increase of transportation emissions as the economy grows.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.envpol.2012.01.005.

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