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Relationship between historical changes of PBDEs, PAHs, and algal organic matter in sediments of Poyang Lake under climate warming

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ABSTRACT
Polybrominated diphenyl ethers (PBDEs) and polycyclic aromatic hydrocarbons (PAHs) were detected by gas chromatography–mass spectrometry in the sediment core form Poyang Lake. The concentrations of Σ17 PBDEs and Σ15 PAHs ranged from 1.13 to 4.64 ng/g, and from 341 to 744 ng/g, respectively. The Rock-Eval test was conducted to obtain organic matter parameters such as total organic carbon (TOC), S2, and hydrogen index (HI). The value of TOC, S2, and HI showed an increasing trend from the bottom to the surface. Source analysis results showed that the source of PAHs was combustion. Moreover, the correlation analysis of PBDEs, PAHs, and annual average temperature with S2 and HI showed that BDE-202, BDE-201, BDE-183, and BDE-154 were negatively correlated with S2 and HI, while BDE-85 and BDE-47 were positively correlated. There was no significant correlations of PAHs with S2 and HI, which is related to the disturbance of sediments. It is interesting that significantly positive correlation of HI with five-year moving averages of the air temperature was demonstrated, demonstrating that the climate warming enhanced the increase of algae in the Poyang Lake.

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Sediment core; algae organic matter; climate warming; Poyang Lake

Introduction

With the fast development of industry and other human activities, water pollution has become a worldwide environmental problem (He et al. 2019; He and Wu 2019a, 2019b; Li, He, and Guo 2019; Li, He, Li et al. 2019; Wu et al. 2019), and many new toxic contaminants have emerged in the environment (Li, Li et al. 2016; Li, Wu et al., 2016; Wang et al. 2019; Zhang et al. 2018), among which persistent organic pollutants (POPs) have received considerable attention from researchers and general public because of their potential adverse effects on human life. POPs such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs) are ubiquitous in water, soil, and sediments, posing great risks to organisms

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and humans due to their toxicity, persistence, and bioaccumulation potential. PAHs are widespread contaminants throughout the environment, originated mainly from anthropogenic sources such as the combustion of fossil fuels and the direct release of oil and oil products (Simpson and Ellwood 1996). It is known that many of the PAHs with four or more benzene rings are carcinogenic and mutagenic due to their metabolic transformation capacity (Moermond et al. 2007). It has been reported that the ratios of PAH isomers with similar molecular weights can be used as indices for source apportionment (Mai et al. 2002).

Due to the long-term impact of the Yangtze River water inflow and the water coming from the basin, a unique ecological hydrological process has been formed in Poyang Lake. The ecosystem of Poyang Lake is an important guarantee for biodiversity conservation and ecological security in the middle and lower reaches of the Yangtze River. However, changes in hydrological situation, decline in water quality, drop in water level, and intensification of eutrophication are among the main ecological and environmental problems of Poyang Lake (Guo et al. 2012; Liu et al. 2012; Liu, Liu, et al. 2016; Min and Zhan 2012; Ouyang and Liu 2014). As sediment is an important sink for non-polar organic contaminants, it is also a long-term source of these contaminants for water and biota.

Under the background of climate warming, it has been observed that greater precipitation changes have taken place in the worldwide, and more frequent droughts have a significant impact on water resources, and this situation is expected to continue over the next few decades (Milly et al. 2005; Van Loon et al. 2016). The reduction of water level may also increase the mixing depth, turbidity, and temperature of water (Braga et al. 2015; Brasil et al. 2016). Due to climate change, global heat events are more frequent (Karl and Trenberth 2003). The short-term response of these events may provide specific insights into long-term effect of climate warming in the lacustrine ecosystem (Havens et al. 2016). Therefore, under the influence of global warming, its impact on the deposition process of typical organic pollutants and algae organic matter in lake sediments is very important to the ecological environment of water bodies.

This study was carried out to estimate the historical inputs and source analysis of PBDEs and PAHs in the Poyang Lake, and investigate the effects of climate warming on algal population change and organic pollutant deposition in the lake. With these aims, one sediment core was collected, and PBDEs and PAHs were investigated. The correlations between POPs and algal organic matter (AOM) will help to illustrate the effect of AOM to the transport and fate of typical POPs under climate warming.

Materials and methods

Study area

Poyang Lake is located on the south bank of the Yangtze River and the northern part of Jiangxi Province (Figure 1). It is connected with the five major rivers of Ganjiang, Fushui, Xinjiang, Raohe, and Xiushui and forms a natural basin, which is restricted by the water level of the Yangtze River and "the five rivers." According to the hydrological station monitoring data of water level, high water level is kept from June to September,

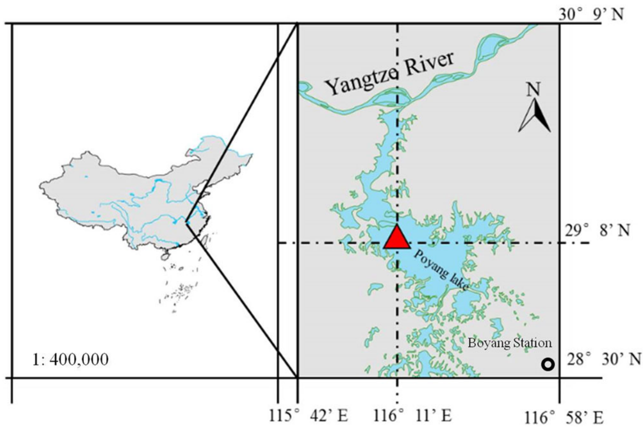

Figure 1. Location of sampling site and Boyang station.

low water level is reached from December to March each year, the flat level is kept in April, May, October, and November (Liu, Zeng et al. 2016).

Sample collection

In May 2017, a plexiglass column with a diameter of 6 cm was used to collect the sediment cores from an undisturbed sedimentary column in the middle of Poyang Lake (116°11′E, 29°8′N), with a sampling depth at about 15 m. The deposition columns were sliced at 2 cm intervals, and these subsamples were immediately placed in plastic bags, sealed and stored, and transported at low temperatures (0–10 °C). Samples were shipped back to the laboratory and stored in a (–20 °C) refrigerator. After lyophilization, grinding, and passing through a screen (80 mesh), further chemical treatment and instrumental analysis are required.

Temperature data and ^{210}Pb dating

The temperature data used in this study is from National Meteorological Information Center, and the selected station is Boyang station. The sample dating was sent to the Institute of Geochemistry, Chinese Academy of Sciences, Guiyang for the determination of nuclide activity. The results of ^{210}Pb dating were calculated by using a constant rate supply (CRS) model (Duan et al. 2016

Elemental analyses

Total organic carbon (TOC) and nitrogen (TN) were analyzed with a Vario EL III Elementar analyzer (Germany). Prior to analysis, the samples (300–500 mg) were treated with 1 M HCl vapor to remove carbonates and analyzed in silver boats. All samples were analyzed in duplicate. The mean deviations of the duplicate samples for C and N were <0.05%. EDTA was used as an external standard.

Rock-Eval pyrolysis analysis

All the samples were analyzed by Rock-Eval 6 (Vinci Technologies, France). This method can determine the quality of the organic matter in a sample based on the rate of thermal pyrolysis and evolution of various organic compounds. Bulk sediment is first heated in an inert, O_2-free oven (100–650 °C), followed by combustion in an oxidation oven (400–850 °C). The pyrolysis step releases two specific classes of hydrocarbons (HC), defined as S1 and S2, which can be detected with a flame ionization detector (FID). S1 is mainly composed of small molecules, which is formed during pyrolysis at 300 °C and is extremely sensitive to degradation. S2 is released by thermal cracking of organic matter at 650 °C, representing higher molecular weight, kerogen-derived aliphatic hydrocarbons; CO and CO_2 are also continuously released, representing oxygenates in organic matter, measured by an in-line infrared (IR) detector and defined as S3. Then the oxidation part, the sample is transferred to the oxidation furnace and heated under aerobic conditions. The temperature is from 400 °C to 850 °C. The CO and CO_2 released during the whole process are the combustion products of residual organic matter, which is represented by S4. After the end of the two parts, the instrument can also quantitatively analyze residual carbon (RC). TOC is the sum of the organic matter produced by the above pyrolysis process and oxidation process. Other pyrolysis parameters can be calculated and derived from the peak areas of S1, S2, S3, and RC. The ratio of hydrocarbons produced by pyrolysis to TOC is HI, and the ratio of CO_2 produced by pyrolysis to TOC is oxygen index (OI).

Analysis of PBDEs

Analysis of PBDE congeners was performed through multi-step procedure including microwave synergistic extraction, chromatographic column purification, and gas chromatography-negative chemical ionization mass spetrometer (GC-NCI-MS) analysis. First, about 10 g freeze-dried and grinded samples were spiked with two surrogate standards (PCB-209 and ^{13}C-PCB-141), extracted with acetone and hexane mixture (1:1, vol:vol) by using microwave synergistic extractors, and activated copper was added for desulfurization during the extraction. Then, the extracts were concentrated, purified, and consequently fractionated on a 1-cm i.d. silica/alumina column. The purified column was packed with neutral alumina (5 cm, 3% deactivated), neutral silica gel (5 cm, 3% deactivated), sulfuric acid silica (10 cm), and anhydrous sodium sulfate (1 cm). Prior to instrumental analysis, ^{13}C-PCB-208 was added to each of the extracts as the internal standard, and finally the extracts were analyzed by GC-NCI-MS using a DB-5MS capillary column (15 m $\times$ 0.25 mm i.d. with 0.25 μm film thickness) to separate PBDE congeners.

The quality assurance and quality control (QA/QC) samples included procedural blanks and spiked blanks. The recovery efficiency of PBDE congeners in spiked blanks was 86.5%–147%. The relative standard deviations for individual PBDE congeners measured in duplicate samples were $<$12%. The average recoveries of ^{13}C-PCB-141 and PCB-209 were 92.4% and 92.3%, respectively, with the relative standard deviations $<$10%. The reported data were not corrected by surrogate recoveries. The experiments were performed in dark to minimize photodegradation.

Analysis of PAHs

The analytical procedure used for extraction, separation, and measurement of PAHs in the sediments was detailed elsewhere (Mai et al. 2002), and only a brief description is given here. A mixture of deuterated PAH compounds (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}) as recovery surrogate standards was added to all the samples prior to extraction. About 10 g freeze-dried sediment samples were Soxhlet-extracted with methylene chloride. The extracts were concentrated, solvent-exchanged to hexane, and purified using a 1:2 alumina:silica column chromatography. A known amount of internal standard (hexamethylbenzene) was added to the extract prior to instrumental analysis.

Mean percentage of analyte recoveries calculated from surrogate data were 44%, 74%, 83%, 105%, and 135% for naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}, respectively. Final PAHs' concentrations in this study were not corrected by the recoveries of the surrogate standards.

Results and discussion

^{210}Pb dating data

The ^{210}Pb activity in the sediment core of Poyang Lake was measured. The depth of the sediment column was 40 cm. The $^{210}Pb_{ex}$ activity was calculated using 39 cm as the underlying ^{210}Pb activity. The calculation results of 0–29 cm were finally used to estimate the sedimentary age in this study. The highest lead activity occurred at 19 cm (280 Bq/kg), followed by 29 cm (244 Bq/kg). The corresponding sedimentary age ranged from 1980 to 2017, and average sedimentation rate was 0.181 g/cm^2/yr.

Levels and distribution of PBDEs in the sediment core

The concentrations and relative abundance of PBDEs in the sediment core are presented in Table 1 and Figure 2, respectively. Obviously, BDE-209 was the highest BDE congener indicating that large quantities of deca-BDE were used in this region. In the past 30 years, the contents of PBDEs increased nearly three times from the bottom to the top of the sediment core, except for the content at 29 cm where the content is higher than in upper layers. This phenomenon may be due to a sudden increase in PBDEs input or a disturbance in the deposition process. Combined with the measured ^{210}Pb activity, it was found that its value at 29 cm was relatively high. The concentrations of $\sum$17 PBDEs and BDE-209 in the Poyang Lake ranged from 1.13 to 4.64 ng/g and from 0.750 to 4.06 ng/g, respectively (Table 1). High levels of PBDEs were also detected in the Pearl River Delta (PRD) region of China, ranging from 12.2 to 488 ng/g (Huang et al. 2018).

As shown in Figure 3, the concentrations of BDE-28, BDE-47, and BDE-99 were lower than 0.02 ng/g, the concentration of BDE-100 was lower than 0.065 ng/g, and the concentration of BDE-209 was higher than 0.6 ng/g. Because commercial brominated flame retardants (BFRs) consist of BDE-47, BDE-99, BDE-100, and BED-209, their concentrations could indicate the use of BFRs. Penta-BDE was calculated from the percentage of the sum of the major congeners BDE-47, BDE-99, and BDE-100 in the technical

Table 1. Concentrations of PBDEs in sediment core from Poyang Lake (ng/g).

Depth (cm)	BDE-17	BDE-28	BDE-47	BDE-66	BDE-71	BDE-85	BDE-99	BDE-100	BDE-138	BDE-154 (ng/g)	BDE-153	BDE-183	BDE-190	BDE-202	BDE-201	BDE-207	BDE-209	∑16BDEs	∑17 BDEs
1	0.0107	0.00760	0.0179	0.00946	0.00706	0.0215	0.0187	0.00840	0.0113	0.00893	0.0161	0.0185	0.0291	0.0665	0.0251	0.112	2.01	0.388	2.40
3	0.0100	0.00655	0.0179	0.00949	0.00708	0.0215	0.0187	0.00842	0.0114	0.00895	0.0162	0.0186	0.0291	0.0667	0.0251	0.112	2.02	0.388	2.40
5	0.0101	0.00627	0.00587	0.00787	0.00934	0.0113	0.0103	0.00761	0.00681	0.00774	0.0159	0.0160	0.0286	0.0615	0.0206	0.0803	1.21	0.306	1.51
7	0.00988	0.00654	0.0168	0.00934	0.00694	0.0219	0.0162	0.0586	0.00707	0.00881	0.0160	0.0178	0.0276	0.0646	0.0240	0.101	1.87	0.413	2.28
9	0.0105	0.00640	0.0108	0.00853	0.00759	0.0113	0.0120	0.0481	0.00733	0.00853	0.0159	0.0176	0.0263	0.0641	0.0232	0.107	2.09	0.385	2.48
11	0.0101	0.00678	0.00692	0.00692	0.0104	0.0104	0.00998	0.0422	0.00625	0.00812	0.0157	0.0157	0.0259	0.0636	0.0200	0.0821	1.62	0.341	1.96
13	0.0148	0.0103	0.00769	0.00809	0.0116	0.0140	0.0138	0.0107	0.00907	0.0114	0.0233	0.0211	0.0389	0.0882	0.0276	0.0862	1.32	0.397	1.71
15	0.0150	0.0128	0.00758	0.00639	0.00719	0.0121	0.0124	0.0105	0.00838	0.0122	0.0238	0.0214	0.0393	0.0842	0.0252	0.0786	1.19	0.377	1.56
17	0.0148	0.00960	0.00940	0.00680	0.00880	0.0100	0.0132	0.0454	0.00860	0.0116	0.0238	0.0210	0.0390	0.0854	0.0228	0.0530	0.750	0.383	1.13
19	0.0152	0.0103	0.00809	0.00730	0.00730	0.0142	0.0142	0.0113	0.0144	0.0113	0.0235	0.0247	0.0408	0.0931	0.0361	0.164	3.14	0.496	3.64
23	0.0152	0.00920	0.00680	0.00680	0.00880	0.0124	0.0130	0.0402	0.00860	0.0116	0.0234	0.0204	0.0390	0.0940	0.0270	0.100	1.74	0.436	2.17
27	0.0154	0.00978	0.00699	0.00639	0.00799	0.0132	0.0128	0.0108	0.00898	0.0120	0.0240	0.0218	0.0389	0.0855	0.0252	0.0727	1.08	0.372	1.45
29	0.0156	0.0108	0.00859	0.00899	0.00939	0.0106	0.0140	0.0559	0.0104	0.0140	0.0240	0.0246	0.0396	0.106	0.0372	0.189	4.06	0.579	4.64

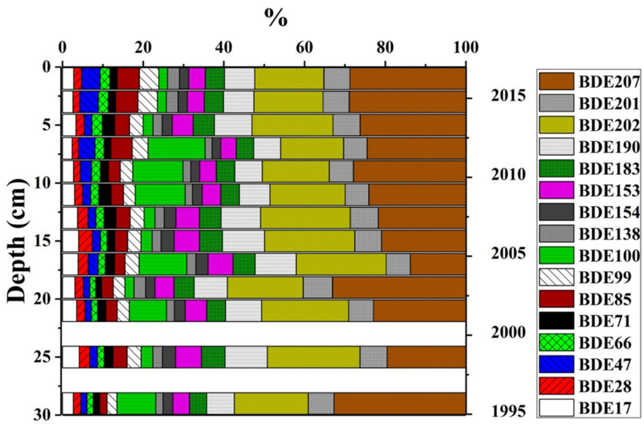

Figure 2. The relative abundance of BDE congeners of sediment core from Poyang Lake.

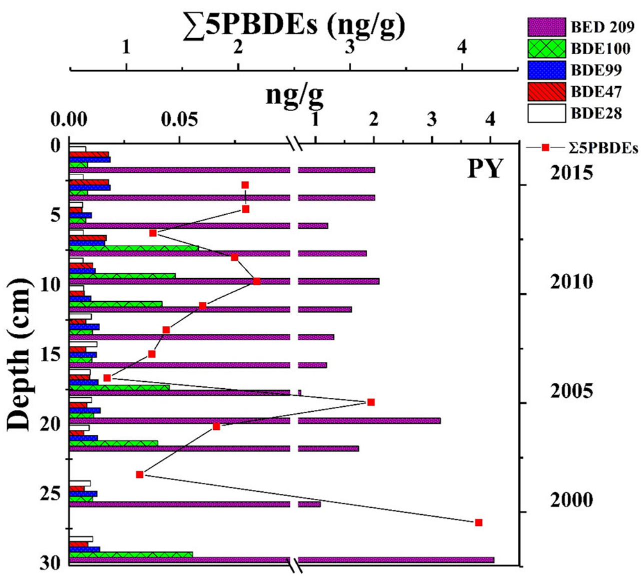

Figure 3. Levels of BDE congeners (including BDE28, -47, -99, -100, -209) of sediment core from Poyang Lake.

mixture. It was assumed that deca-BDE mainly consists of BDE-209. It is known from Table 1 that deca-BDE was the dominant congener in all of the samples, illustrating the extensive use of technical formulations containing deca-BDE in the regions (Mai et al. 2005). Figure 3 illustrates that the usage of penta-BDE was smaller than deca-BDE in Poyang Lake and the degradation of BDE-209 was more difficult than other BDE congeners. BDE-28 is a low brominated BDE, which is produced during the degradation of highly brominated BDE, and its concentration is relatively low, which indicates that the degradation rate of PBDEs in the natural environment is slow, which is consistent with others (Niu et al. 2015).

The contents of PBDEs in Poyang Lake were relatively low, but the overall trend is increasing, and it will be transferred through the food chain to affect human health.

With the increasing input and degradation of high-brominated BDEs, the impact of low-brominated BDEs on the ecological environment also needs further research.

Levels and distribution of PAHs in the sediment core

The concentrations of PAHs in the sediment core are presented in Table 2 and Figure 4. The concentrations of $\sum$15 PAHs in the Poyang Lake ranged from 341 to 744 ng/g (Table 2), and they increased about twice from the bottom to the top of the sediment core in past 30 years, and except for the content at 29 cm showed the same trend as PBDEs. Figure 4 shows that autochthonous source was the main source of PAHs, but the concentrations of phenanthrene (Phe) were high, ranging from 48.5 to 98.4 ng/g from the bottom to the top. It implied the Phe adsorbed on organic matter tightly. This phenomenon is likely related to the fact that the lower-molecular PAHs in the sediments were derived from the long-range atmospheric transport and were the main source of contamination; while the higher-molecular PAHs in the sediments were derived from the local source of contamination, as they were not easily vaporized into the atmosphere.

Three PAH isomer ratios, including benzo(*a*)anthracene/(benzo(*a*)anthracene + chrysene) (BaA/(BaA + Chry)), fluoranthene/(fluoranthene + pyrene) (Fla/(Fla + Pyr)), and indene(1,2,3-c,d) pyrene/(indene(1,2,3-c,d) pyrene + benzo(g,h,i)perylene) (InP/(InP + BgP)) were used to identify the different sources of PAHs in the sediment core from the Poyang Lake. The criteria for the source identification are as follows: (a) Fla/(Fla + Pry) ratio <0.40 indicates dominance of petroleum, 0.40–0.50 indicates petroleum combustion, and >0.50 combustion of coal, grasses, and wood; (b) BaA/(BaA + Chry) ratio <0.20 indicates petroleum, 0.20–0.35 petroleum and combustion, and >0.35 combustion; (c) InP/(InP + BgP) <0.20 indicates petroleum, 0.20–0.50 petroleum combustion, and >0.50 combustion of coal, grasses, and wood (Yunker et al. 2002). PAH ratios and their temporal variations are shown in Figure 5.

The profiles of Fla/(Fla + Pyr) ratios were much higher than 0.5 (Figure 5). These values suggested that PAHs in the Poyang Lake were derived mostly from biomass and coal combustion, rather than from unburned petroleum, but only one sample showed petroleum combustion source. In addition, the vertical changes of BaA/(BaA + Chry) ratios also confirmed that the above results in the Poyang Lake showed the predominance of biomass and coal combustion sources. InP/(InP + BgP) ratios were similar to Fla/(Fla + Pyr) ratios and BaA/(BaA + Chry) ratios. PAHs were derived from combustion as suggested by the values of InP/(InP + BgP) ratios, which were slightly higher than 0.5 (Figure 5). Thus, PAHs in the Poyang Lake were originated from biomass and coal combustion sources. Other studies indicated that the straw burning was the dominated combustion source in Jiangxi Province, where rice and cotton are the main crops, and the open straw burning was only banned in 2017.

In recent years, PAHs in the Poyang Lake sediments showed an increasing trend, and these mainly originated from the combustion source. This observation indicated that human activities also intensified the emission of PAHs to the environment and had a direct impact not only on the atmospheric environment, but also on the lake water environment.

Table 2. Concentrations of PAHs in sediment core from Poyang Lake (ng/g).

Depth (cm)	NaP	Acy	Ace	Flu	Phe	Ant	Fla	Pyr	BaA	Chry	BbF	BkF	BaP	InP	DbA	BgP	Σ15 PAHs
	ng/g																
3	8.71	3.38	3.41	27.1	97.6	10.7	56.0	43.5	48.9	42.9	102	33.6	73.4	97.4	23.8	80.3	744
7	4.19	2.45	2.09	16.7	64.6	7.07	37.6	27.7	31.6	27.7	67.9	23.1	46.5	62.6	16.6	53.6	488
9	3.63	2.11	1.23	10.3	49.3	5.43	29.4	21.6	27.3	23.7	59.0	21.4	41.4	54.4	14.9	46.0	407
11	11.5	2.35	2.28	17.5	76.0	6.28	33.0	22.8	25.0	22.3	54.9	21.9	38.3	51.8	14.2	43.4	432
13	9.75	2.63	2.80	19.7	66.5	6.84	35.4	25.1	29.1	26.0	65.8	23.9	45.1	62.3	16.4	51.7	479
15	2.22	2.46	1.88	21.3	67.1	6.39	27.4	19.0	21.0	19.8	47.4	19.0	33.2	43.0	12.7	36.7	378
17	5.61	2.40	1.87	15.9	48.5	5.68	31.4	21.9	26.2	24.4	59.4	21.2	40.3	54.2	14.9	45.9	414
19	7.30	2.70	2.34	18.2	61.2	7.37	43.4	31.5	38.4	34.5	88.7	31.7	62.3	85.5	21.1	70.8	600
23	8.23	2.32	2.51	18.9	73.0	6.41	29.0	18.7	17.4	15.8	39.3	15.9	26.6	34.5	10.7	30.2	341
25	8.80	2.44	1.83	14.6	55.3	5.75	30.4	21.0	24.1	21.9	53.6	20.5	36.4	47.7	13.3	40.3	389
27	11.7	2.58	2.59	25.0	92.6	7.85	34.7	23.0	24.0	22.3	54.1	21.0	36.4	49.7	13.7	41.4	451
29	13.3	3.01	3. 30	22.9	98.4	9.76	45.8	32.0	35.0	31.5	79.0	28.9	55.3	76.5	19.2	62.7	603

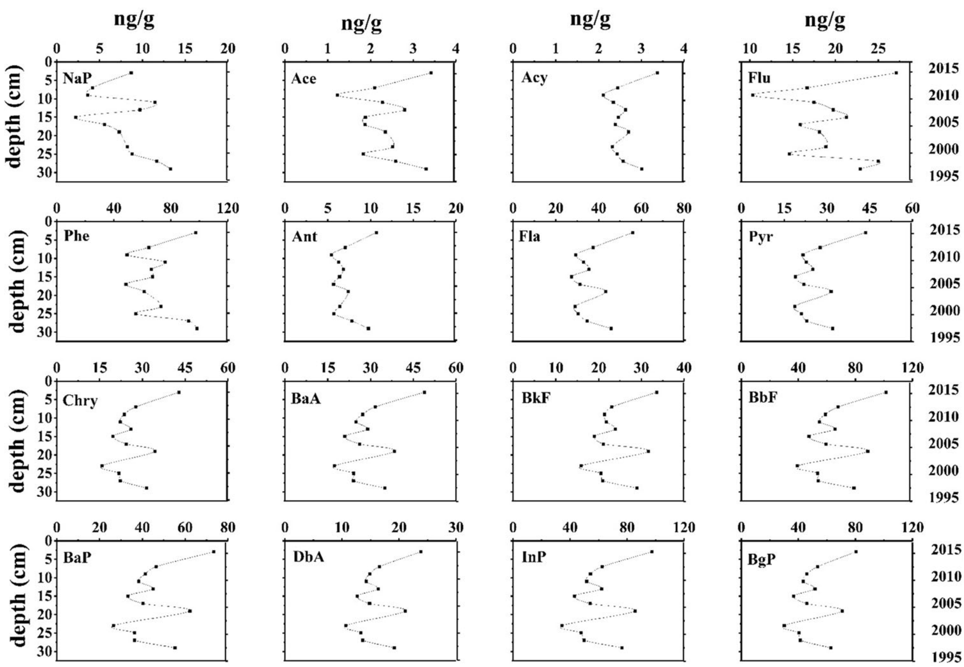

Figure 4. Concentrations of 16 PAHs in sediment core from Poyang Lake.

OM input and variation in the sediment core

Rock-Eval pyrolysis is a simple and rapid method for determination of free and volatile hydrocarbons (S1), kerogen-derived hydrocarbons (S2), and residual carbon or dead carbon (RC), depending on pyrolysis temperature, peak position, and organic carbon origin. This technique has been demonstrated to be suitable for organic matter characterization (Duan et al. 2016). TOC, S1, S2, S3, HI, and OI were determined by Rock-Eval pyrolysis. Their values were in the ranges of 0.573%–0.893%, 0.060–0.100 mg/g, 0.590–0.840 mg/g, 1.71–2.52 mg/g, 82.3–95.8, and 201–305 (Table 3), respectively. As shown in Figure 6, TOC, S2, and HI showed increasing trends from the bottom layers to the top sections, while the OI illustrated a decreasing trend to the top layer. The

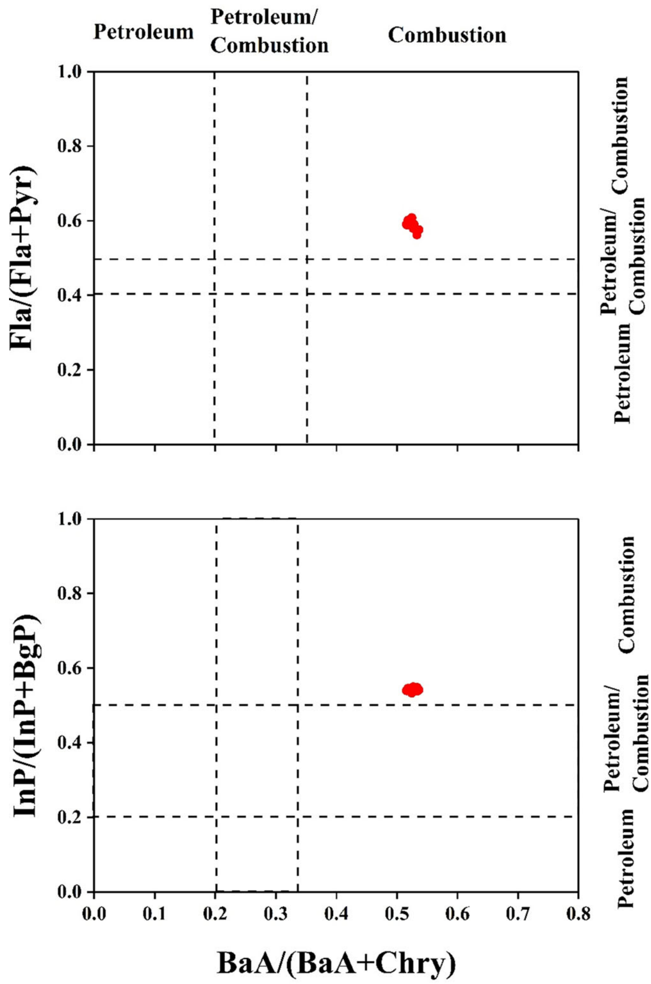

Figure 5. Sources of PAHs of sediment core from Poyang Lake.

interpretation of this could be that the bottom organic matter was buried by young organic matter, degraded by chemicals or microorganisms and protected by mineral.

The HI and OI are presented in Table 3, which are calculated by normalizing the contents of S2 and S3 to TOC. They can provide more evidences for the source of organic matter. The HI was particularly observed to be a good proxy for the lacustrine productivity in an investigation on AOM in different trophic lakes (Duan et al. 2014). In recent sediments, an HI value lower than 100 mg/g indicates a dominantly terrigenous (higher plant) source of the organic matter, whereas an HI value higher than 100 mg/g indicates a dominant contribution of aquatic algae and/or microbial biomass. All the samples in this study are recent sediments and their HI values are lower than 100 mg/g, suggesting a dominant terrigenous source to the sediments in the Poyang Lake.

Liu, Li et al. (2016) have shown that the blooms occurred in Poyang Lake since 2000 were mainly derived cyanobacteria. Although no large-scale blooms occurred so far,

Table 3. Rock-Eval parameters in sediment core from Poyang Lake.

Depth (cm)	TOC (%)	S1 (mg/g)	S2 (mg/g)	S3 (mg/g)	HI (%)	OI	RC
3	0.850	0.100	0.810	1.71	95.3	201	0.0200
5	0.835	0.0900	0.800	1.94	95.9	232	0.0100
7	0.893	0.0900	0.820	2.03	91.9	227	0.0100
9	0.881	0.0900	0.840	2.12	95.3	241	–
11	0.823	0.0900	0.780	2.16	94.7	262	–
13	0.875	0.0900	0.820	2.31	93.7	264	0.0100
15	0.827	0.0800	0.750	2.52	90.7	305	0.0100
17	0.774	0.0800	0.690	2.07	89.1	267	–
19	0.773	0.0800	0.680	2.23	87.9	288	–
21	0.835	0.0800	0.690	1.81	82.6	217	0.0100
25	0.697	0.0600	0.590	1.87	84.7	268	0.0100
27	0.790	0.0700	0.650	2.18	82.3	276	0.0100
29	0.741	0.0700	0.630	2.19	85.0	295	0.0100

AOM was still showing an increasing trend in this investigation. Hence, more attentions should be paid to the amount and species of algae communities in Poyang Lake and the investigation on other water quality parameters.

The TOC, S2, and HI showed the same pattern that their value decreased with the depth. This pattern indicated that: (a) the input of organic matter was increasing in Poyang Lake; (b) the terrigenous organic matter was decreasing from bottom layer to the top layer. In other words, the content of the AOM was increasing which is consistent with the record of algal blooms in past 30 years. At present, although there is no large-scale bloom in Poyang Lake, and the increase of AOM will lead to algal blooms to a certain extent. So, more attentions should be paid to the investigations on algae populations and aquatic quality parameters in Poyang Lake.

Relationships between PBDEs, PAHs, and OM

In the past 30 years, the content of PBDEs and PAHs has increased by three times and twice from the bottom to the top of the sediment core. Factors affecting this phenomenon may be related to the biological pump effect, atmospheric deposition, and global warming. PBDEs and PAHs are highly hydrophobic; they are expected to be associated mainly with organic carbon-rich particles. S2 is a good proxy of AOM source and helps to illustrate how biological pump affects the process of the deposition and transformation of hydrophobic organic contaminants. In addition, the contents of TN showed the same trend as the OM parameters in past 30 years (Figure 6), but the TN contents were very low, which indicated that the impact of human activities was not the major factor. The trend is consistent with the investigation from Duan et al. (2016). But the correlations of PAHs with S2 and HI were not significant, which may be related to the disturbance.

Figure 7 shows the relationships between BDE congeners (BDE-47, BDE-85, BDE-154, BDE-183, BDE-201, BDE-202) and S2. The negative correlations were found for higher brominated BDE congeners (BDE-154, BDE-183, BDE-201, BDE-202), while the positive correlations were found for lower brominated BDE congeners (BDE-47, BDE-85). It suggested that there are different mechanisms for higher brominated BDE congeners and lower brominated BDE congeners in association with AOM.

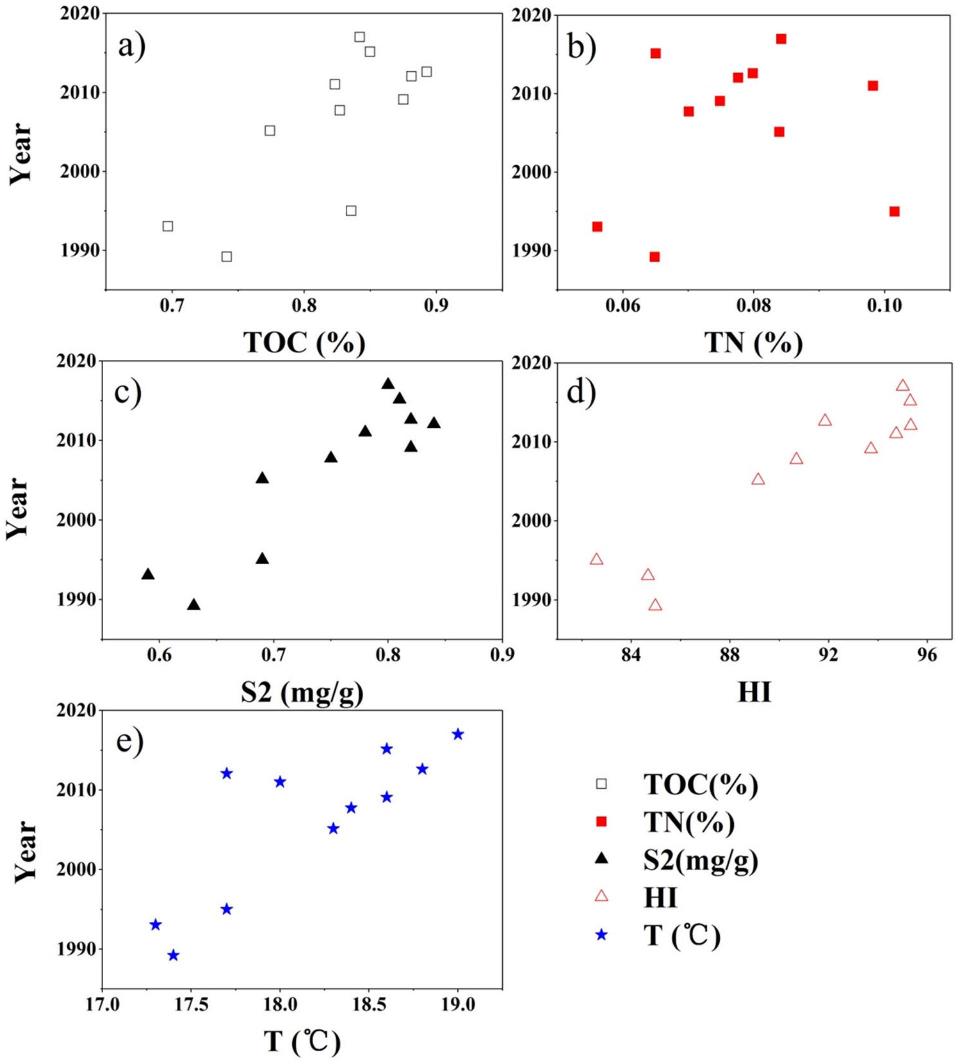

Figure 6. Organic matter parameters and temperature parameters of sediments in Poyang Lake (a): TOC; (b): TN; (c): S2; (d): HI; (e): *T*.

The BDE-154 and BDE-183 are the main components of octa-product, and the BDE-201 and BDE-202 are the degradation products of BDE-209. As shown in Figure 7, with the increase of AOM, the octa-product and its degradation products tended to be associated with AOM, but BED-47 is the main components of penta-product, and BDE-85 is degradation products of the higher brominated BDEs. The differences in Figure 7 suggested that the AOM exhibited a great influence on the distribution of octa-product and its degradation products than that of penta-product and degradation product of the higher brominated BDEs. These differences in the correlations may be related to differences in accessibility of organic matter to PBDEs and need further investigation.

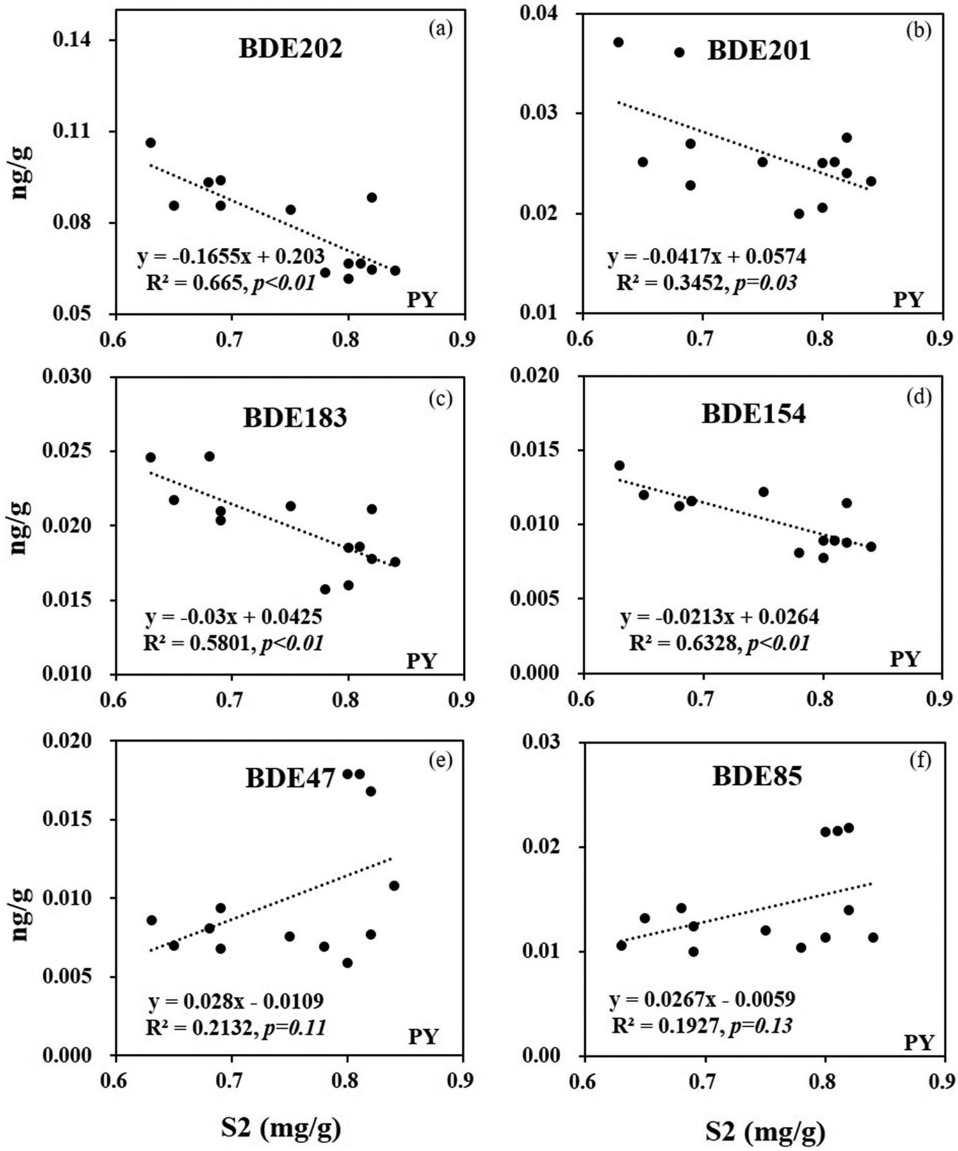

Figure 7. Correlations between BDE congeners (including BDE202, -201, -183, 154, -47, -85) and S2 of sediment core from Poyang Lake.

Effects of climate warming on AOM, PBDEs, and PAHs

Global warming is an accepted fact. Some studies showed that the increasing temperature trend was 0.2 °C/(10 a) in the middle and lower reaches of the Yangtze river of China; and was 0.2–0.8 °C/(10 a) in the Northern region of China (Qin et al. 2002). The meteorological data were obtained from Nanchang fiducial stations, which is built for monitoring climate change in a very broad area and is different from the weather stations designed for city weather report. The trends are plotted in Figure 8. The mean air temperature in the Nanchang area has increased by about 2.6 °C since 1951.

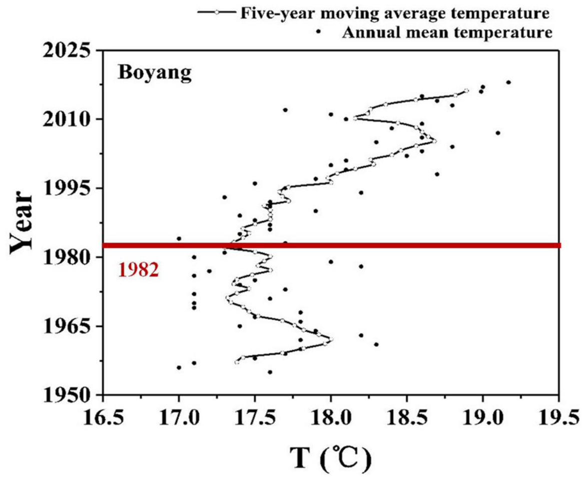

Figure 8. Annual mean temperature and five-year moving average temperature at Boyang station.

Table 4. Correlation coefficients between PBDEs, PAHs, HI, and T_5.

R^2	PBDEs	PAHs	HI	T_5
PBDEs		0.008	0.084	0.336
PAHs			0.004	0.147
HI				0.411*
T_5				

*Correlation is significant at 0.05 level.

Therefore, the above evidence supports an overall climate warming during the last six decades. We examined this effect using the annual average air temperature and five-year moving averages of the air temperature (T_5) on the time scale of 66 years for the Boyang station. A significant increase in temperature was observed since 1982 as shown in Figure 8, which showed that T_5 increased by 1.6 °C from 1982 to 2016.

Correlation coefficients between PBDEs, PAHs, HI, and T_5 are detailed in Table 4. The result suggested that there is a significant positive correlation between HI and T_5, but there is no or a slight correlation between PBDEs, PAHs, and T_5. HI is a proxy to estimate the algae primary productivity, and the trend of T_5 indicated the impact of climate warming. The impact of climate warming on algae is direct, and the impact on POPs is indirect. Some studies have shown that the impact of climate warming on the marine POPs is caused by changing the phytoplankton biomass indirectly (Galbán-Malagón et al. 2012).

Climate warming is gradually considered as one of the main factors threatening the global ecosystem, and it is a great potential threat to global biodiversity and ecosystem functions (Hoegh-Guldberg and Bruno 2010; Jeppesen et al. 2007). In the past century, the globe has been warmed at an unusual rate. The recent assessment report of the United Nations Intergovernmental Panel on Climate Change (IPCC) clearly states that human activities have been the main reason for the global warming. Lake ecosystems are considered the most sensitive indicator of climate warming (Adrian et al. 2009). The feedback mechanism of aquatic plants and phytoplankton leads to two steady states of temperate lakes. Phytoplankton is often used to indicate the response of lake ecosystems to the external environment due to its fast growth cycle and its environmental sensitivity. In addition, in recent years, the water level of Poyang Lake has been continuously lowered. Liu, Li et al. (2016) have illustrated the responses of nutrients to water level in Poyang Lake, and the results indicated that low water levels corresponded to high nutrient concentrations. Hence, the lowered water level also affected the phytoplankton productivity, and the sorption, transport, and deposition of POPs.

AOM, PBDEs, and PAHs respond differently to climate warming. During the same period, the concentrations of POPs change asynchronously, but HI shows the same trend. In other words, the climate warming of Poyang Lake has accelerated algae growth in the past 30 years.

Conclusions

This study investigated the historical change of PBDEs and PAHs, in combination with organic matter parameters and T_5 in Poyang Lake. Several conclusions could be drawn as follows:

1. In the past 30 years, the contents of PBDEs and PAHs from the bottom to the top of the sediment core increased by 2–3 times except for their contents at 29 cm, which suggested that the risk on aquatic ecosystem and human health was getting higher.
2. The source of PAHs was derived from the combustion of biomass and coal. It suggested that human activity was the major factor for the emission of PAHs.
3. Climate warming enhanced the algae growth and showed indirect impact on the accumulation of PBDEs and PAHs. More attention should be paid to the investigation on algae community in order to avoid large-scale blooms in Poyang Lake.

In general, in the case of climate warming, more attention should be paid to the accumulation and exposure risk of typical organic pollutants, and investigation on algae communities in Poyang Lake.

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