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Spatial correlation analysis of polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs) in sediments between Taihu Lake and its tributary rivers

Zhonghua Zhao[a,*], Yu Jiang[b], Qianyu Li[a], Yongjiu Cai[a], Hongbin Yin[a], Lu Zhang[a], Jin Zhang[c]

[a] *State Key Laboratory of Lake Science and Environment, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, 210008 Nanjing, China*
[b] *Nanjing Forestry University, 210037 Nanjing, China*
[c] *Institute of Urban Water Management, Technische Universität Dresden, 01062 Dresden, Germany*

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ABSTRACT

The residues of polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs) in surface sediments from Taihu Lake basin (THB) and Taihu Lake body (THL) were investigated. Higher concentrations of both PAHs and OCPs were observed for THB than THL. The concentrations of PAHs ranged from 12.1 to 2281.1 ng g^{-1} dw for THB and from 11.4 to 209.9 ng g^{-1} dw for THL, while OCPs ranged from 16.3 to 96.9 ng g^{-1} dw and from 16.8 to 61.9 ng g^{-1} dw for THB and THL, respectively. Spatial distribution of PAHs and OCPs showed a high correspondence with the land use of THB and surrounding anthropogenic activity. Additionally, the Kriging interpolation plots demonstrated that the major upper reaches were more polluted than the lower reaches, indicating the transport of pollutants with the water flow direction. The organic matter contents were responsible for OCP distribution other than PAHs due to the biodegradation capacity difference of chemicals. Similar compositions of pollutants were observed with 3- and 4-ringed PAHs accounting for a total of 78.3% for THB and 85.8% for THL, respectively. HCHs and DDTs were predominant OCPs, which contributed to 31.8% and 21.7% for THB, and 33.6% and 21.9% for THL, respectively. The isomeric and parent substance/metabolite ratios implied fresh inputs of DDTs and chlordanes, while HCHs and endosulfans were mainly from old usage. PAH source identification performed by diagnostic ratios demonstrated the mixed sources of petrogenic and pyrogenic ones dominated by grass, wood and coal combustion. Furthermore, the hazard quotient (HQ) based on the consensus-based sediment quality guidelines (SQGs) was used to evaluate the ecological risks of sediments. Although no frequently adverse effects were observed, potential ecological risks induced by Ant, BaA, γ-HCH, dieldrin, p,p′-DDT and chlordanes should also be paid attention to considering the continuous inputs of such pollutants.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are highly toxic organic pollutants containing typically two to eight benzene-member rings (Zhao et al., 2016; Heywood et al., 2006). They are ubiquitous derived primarily during the pyrolysis of organic materials typical of some processes used in the iron and steel industry, heating and power generation, petroleum refining and the release of petroleum products, among which 16 congeners were defined as the priority pollutants by USEPA due to their highly mutagenic and carcinogenic toxicity and have been widely used to evaluate the pollution of PAHs in environment (Feng et al., 2012; Wang et al., 2015). Organochlorine pesticides (OCPs) containing at least one covalently bonded atom of chlorine were once widely produced and used globally with a long history (Zhao et al., 2009). Although the production and use of OCPs have been banned after the mid-1970s, they are still found in almost all the environmental matrices such as air, water, snow, soil and biota due to their long half-life. Both PAHs and OCPs are of great concern around the world for their persistence, impact on non-target organisms, and bioaccumulation in the tissues of animals as well as humans via the food chain (Nakata et al., 2002; Tang et al., 2007; Ogbeide et al., 2016). More explicit, four or more rings PAHs, hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethanes (DDTs) may induce a number of adverse effects, such as immunotoxicity, genotoxicity, carcinogenicity, and reproductive toxicity. Consequently, they are considered as endocrine-disrupting chemicals with great potential risk to human health (Sverdrup et al.,

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[*] Correspondence to: State Key Laboratory of Lake Science and Environment Research, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, China.
E-mail address: zhzhao@niglas.ac.cn (Z. Zhao).

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2002; Qiao et al., 2006).

Due to the low water solubility and high *n*-octanol/water partition coefficient (Kow) values, PAHs and OCPs have strong affinities for suspended particulate matter and are subsequently accumulated into stream, river, ocean and marine sediments. PAHs and OCPs can be absorbed by suspended materials from water and then deposited to become a part of the bottom sediments (Yang et al., 2005; Barhoumi et al., 2014). Thus, sediments can serve as sinks of PAHs and OCPs. Moreover, PAHs and OCPs that were historically deposited can be remobilized upward in sediments and re-suspended into the aquatic environment and, resulting in a long term contamination of aquatic environments. The transfer of PAHs and OCPs from sediments to benthic organisms, through interaction between water and sediment, is now considered as a major route of exposure for many species (Zoumis et al., 2001). Therefore, as a sink of pollutants in aquatic environments, the residues of PAHs and OCPs in sediments can provide valuable records of pollution and denote environmental risks. An investigation into the occurrence, sources and ecological risks of PAHs and OCPs in aquatic sediments can contribute to a better understating of the status of these pollutants in sediments and can facilitate the maintenance of the aquatic ecosystem health and ecological safety.

Moreover, it is known that surface runoff picks up and carries natural and anthropogenic pollutants as the water flow moves, which eventually transports these pollutants into receiving waters (Chen et al., 2004). Due to their persistence, PAHs and OCPs could move long distances in surface runoff, which could be originated far away from the receiving waters. The freshwater lakes, especially those large shallow lakes which are very susceptible to wind-generated sediment resuspension, are the major water supplies for the public and suffering from a large amount of pollutant inputs due to the surrounding anthropogenic activities. It has been certified that the universe eutrophication status of such freshwater lakes are mainly induced by the nutrient inputs from point or no-point sources around (Wang et al., 2004; Qin et al., 2007). However, most previous studies focused on the fate of PAHs and OCPs in lake or river sediments were conducted separately without considering the potential interactions between the surrounding basin and the lake body. These former studies ignored the ecosystem integrity of lakes and their surrounding tributary rivers as well as the internal interaction between these two compartments, which will induce the one-sidedness of related investigation and quality assessment of lakes. It is necessary to elucidate the pollution status of PAHs and OCPs in both freshwater lakes and its surrounding tributary rivers not only from the understanding of the biogeochemical processes of such pollutants but also from the lake protection perspective.

Subsequently, the objective of this study was to elucidate the residues of PAHs and OCPs in surface sediments from both tributary rivers and lake body, and then the spatial correlations between upper reaches and lower reaches of the specific freshwater lake could be analyzed, which would provide a comprehensive view point to study on the transport of these hydrophobic pollutants. Additionally, source identifications based on typical chemical indexes were performed to demonstrate the origins of such pollutants. Moreover, potential ecological risks of sediments induced by target pollutants were also evaluated, which were helpful for establishing field monitoring and pollution control plans.

2. Materials and methods

2.1. Study area and Sampling

The Taihu Lake Basin (30°7′19″ to 32°14′56″N and 119°3′1″ to 121°54′26″E) is situated in the Yangtze River Delta in eastern China and covers an area of approximately 36,900 km^2 including a water area of approximately 6134 km^2, of which rivers and lakes comprise around 50%. The basin is covered naturally by subtropical evergreen broadleaf forest, and there are various topographical types, including hilly areas toward the west, and low-lying flood plain in the northern and eastern parts occupying 83% of the basin. There are more than 200 rivers distributed in the basin, and 172 rivers of channels are connected to Taihu Lake (Zhang et al., 2014). The dense river network comprises 7% of the total drainage area, with a total tributary length of around 120,000 km (Huang et al., 2015). The Taihu Lake Basin is one of the most industrialized areas in China. With a population of more than 37 million (2.7% of the total population of China), and as a significant industrial complex, this area contributes 11% to China's gross domestic product (GDP). The plain river network is the main wastewater discharge region of Southern Jiangsu province, and thus, the freshwater ecosystem of the basin is suffering from severe pollution induced by nutrients and kinds of toxic chemicals from point or non-point sources. Although there have been many studies performing the residues, sources and bioaccumulation of PAHs and OCPs in Taihu Lake, little information can be found referring to the fate of such pollutants in rivers surrounding Taihu Lake, not to mention the investigation about possible interactions of pollutants between lakes and rivers.

According to the spatial distribution of major rivers around Taihu Lake, the Taihu Lake Basin (THB) was divided into 7 different districts such as the West Lake Area, the Yangchengdianmao Area, the Wuchengxiyu Area, the Hangjia Lake Area, the Puxi Area, the Pudong Area, the Zhexi Area, of which the West Lake Area, the Zhexi Area and the Wuchengxiyu Area are defined as the upper reaches of Taihu Lake, while the others are belong to the lower reaches. In addition, the Taihu Lake body (THL) was divided into the Meiliang Bay, the Center Lake, the Western Coastal Lake, the Gonghu Bay, the Zhushan Bay, the East Lake and the Eastern Coastal Lake. The major river catchment areas were designed as sampling sites, and then a total of 81 river sediments from THB as well as 31 lake sediments from THL were used to investigate the residues of PAHs and OCPs. The detailed sampling sites can be found in Fig. 1. The sediments were collected with a stainless grab sampler, and the surface sediments (0–5 cm) were homogenized from triplicate samples and immediately stored in a freezer (−20 °C) before pretreatment.

2.2. Chemicals

A mixture of standard solution of OCPs containing α-, β-, γ-, δ-HCH, heptachlor, heptachlor epoxide, α-chlordane, γ-chlordane, aldrin, endrin, dieldrin, endosulfan I, endosulfan II, endrin aldehyde, endosulfan sulfate, endrin ketone, p,p′-DDE, p,p′-DDD, p,p′-DDT, and methoxychlor was defined as the target pesticides. The 16 priority PAH compounds included naphthalene (NaP), acenaphthylene (Any), acenaphthene (Ana), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]flouranthene (BkF), benzo[a]pyrene (BaP), dibenz[ah]anthracene (DahA), benzo [ghi]perylene (BghiP), and indeno[1,2,3-cd]pyrene (InP) were analyzed in the present study. Both standard solutions were purchased from Supleco (USA). The stock standard solutions were dissolved in the suggested solvents with methanol/dichloromethane (1:1, v/v) for PAHs and n-hexane for OCPs, respectively. The working solutions were stored at 4 °C and prepared daily with suitable dilutions before use.

All solvents used for pretreatment and instrumental analysis were chromatographic grade. The copper powder and anhydrous sodium sulfate were Soxhlet treated for 48 h using dichloromethane and then kept in n-hexane before use. The silica gel (80–100 mesh) and alumina (120–200 mesh) used for purification were also extracted for 48 h in a Soxhlet apparatus, activated in the oven at 180 °C and 250 °C for 12 h, respectively, and then deactivated with distilled water at a ratio of 3% (m/m).

2.3. Extraction and quantitative determination

The detailed procedures of extraction and purification were per-