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Polycyclic aromatic hydrocarbons and organochlorine pesticides in surface water from the Yongding River basin, China: Seasonal distribution, source apportionment, and potential risk assessment

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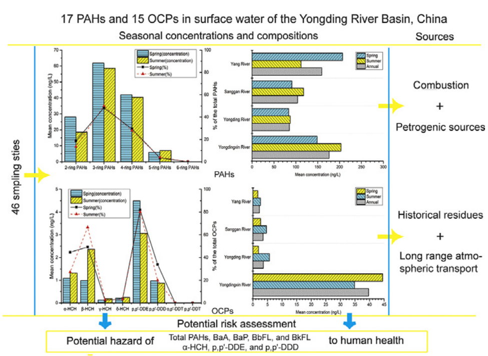
HIGHLIGHTS

- Seasonal surface water pollution characteristics for17 PAHs and 15 OCPs were investigated.
- Slightly lower levels of PAHs were detected in the spring than in the summer.
- Both combustion and petrogenic sources contributed to the main input of surface water PAHs.
- Environmental historical residues and long range atmospheric transport were the major sources for OCPs.
- PAH and OCP contamination could threaten human health at several sampling sites.

GRAPHICAL ABSTRACT



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ABSTRACT

The presence of 17 polycyclic aromatic hydrocarbons (PAHs) and 15 persistent organochlorine pesticides (OCPs) in surface water of the Yongding River Basin was analyzed through GC/MS/MS during the spring and summer at 46 sampling sites. The goal was to investigate their seasonal distribution, possible sources, and potential risk. Our results showed that the total PAH concentration in surface water of Yongding River Basin ranged from 41.60 to 1482.60 ng/L with a mean value of 137.85 ng/L in the spring, and from 53.53 to 506.53 ng/L with a mean value of 124.43 ng/L in the summer. The total OCP concentration ranged from <0.08 to 197.71 ng/L with a mean value of 7.69 ng/L in the spring, and from <0.08 to 93.58 ng/L with a mean value of 7.92 ng/L in the summer. Moreover, the total PAH concentration was slightly lower in the spring than in the summer, whereas the total OCP concentration was similar between seasons. Source analysis indicated that combustion sources and petroleum sources both contributed to the presence of PAHs. Historical environmental residues and long range atmospheric transport were the major sources of HCH and DDT contamination. The concentrations of total PAHs and single PAHs including benz(a)anthracene, benzo(a)pyrene, benz(b)fluoranthene, and benz(k)fluoranthene in surface water at some sampling sites exceeded the water environmental quality standards of China and several other countries or organizations. This indicated a potential threat to human health from the consumption of aquatic organisms due to PAH bioaccumulation. The concentrations of α-HCH, *p,p'*-DDE, and *p,p'*-DDD at several sampling sites exceeded the limit for human health specified in the ambient water quality criteria developed by

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the US Environmental Protection Agency, which indicated that these pollutants provide potential hazards to the residents around the sampling sites.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs) are two common persistent organic pollutants. PAHs are a ubiquitous group containing >10,000 complex compounds formed by two or more fused aromatic rings of carbon and hydrogen atoms (Dennis, 2007; Zhuo et al., 2017). PAHs are widely distributed in the environment and are mainly introduced into rivers and lakes through oil spillage and leakage, atmospheric deposition, surface runoff, and wastewater discharge (Eganhouse et al., 1981; Dickut and Gustafson, 1995; Heemken et al., 2000; Zhang et al., 2008; Dudhagara et al., 2016). Due to their high hydrophobicity and low solubility, PAHs that enter an aquatic ecosystem tend to be first associated with fine grained sediments and suspended particles; then remobilized in the water, becoming bioavailable to aquatic organisms (Wetzel and Van Vleet, 2004); and finally accumulated in organisms at higher trophic levels (Arias et al., 2009). The presence of PAHs in the aquatic environment can be hazardous to aquatic life, affecting the reproductive systems of invertebrates, fishes, and amphibians and causing carcinogenicity, teratogenicity, and mutagenicity (Skarphédinsdóttir et al., 2007; Engraff et al., 2011), and ultimately threatens human health. Due to strong toxicity, carcinogenicity, teratogenicity, and mutagenicity, 16 types of PAHs have been listed as prioritypollutants by the United Sates Environmental Protection Agency (USEPA) and the European Union (Manoli et al., 2000).

OCPs are a type of chlorinated hydrocarbon compound with properties of biodegradability, bioaccumulation, semivolatilization, and high toxicity. They can be transported on a global level in various manners (Akshayya et al., 2009). Some studies have identified OCPs as endocrine disruptors that affect the function of the reproductive systems of humans and wildlife (Briz et al., 2011; Gao et al., 2013; Wu et al., 2014). OCPs have been extensively used in agriculture worldwide for several decades. Several types of OCPs, including hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethanes (DDTs) are still widely present in water, sediments, the atmosphere, fish, and even food because of their persistence, even though the production and use of these pesticides were banned in developed countries in the 1970s and 1980s (Montuori et al., 2016; Montory et al., 2017). Most OCPs, such as DDTs, HCHs, lindane, and dicofol, have still been used in agricultural production in some developing countries for the last 10 years (Li et al., 2006a; Yuan et al., 2015). OCPs can spread into rivers and lakes through different pathways, including surface runoff, industrial wastewater discharge, wet and dry atmospheric deposition, and long distance transmission (Feng et al., 2011; Ali et al., 2014). Because of their high refractiveness and hydrophobicity, OCPs can be easily adsorbed on to suspended solids and sediments when entering the water environment. They can be subsequently released into the water column under certain conditions such as water turbulence, posing a serious threat to aquatic organisms and human health. Therefore, OCPs are listed as priority control pollutants by environmental protection departments in many countries, and they are frequently detected in water environments. The presence and distribution of PAHs and OCPs in different environmental mediums of rivers and lakes have attracted wide attention and are the subject of serious consideration (Konstantinou et al., 2006; Guan et al., 2009; Vryzas et al., 2009; Zhang et al., 2012a; Kafilzadeh, 2015; Zheng et al., 2016; Eremina et al., 2016).

As an important river system of the Haihe River Basin, the Yongding River Basin is crucial for providing safe drinking water and ecological services to large urban cities such as Beijing and Tianjin. Because of rapid economic growth and population expansion, marked increases in water resource development and utilization have aggravated the shortage of water resources in the Yongding River Basin, resulting in increasingly severe ecological and environmental problems. Some studies have investigated PAH and OCP pollution in the Yongding River Basin, but they mainly focused on the water environment in specific river sections or several reservoirs (Qi et al., 2010; Wang et al., 2015). This provides inadequate information to assess the overall pollutant status and determine the level of risk to aquatic ecosystems and humans. The present study investigated the distribution, composition, and concentration of 17 PAHs and 15 OCPs in surface water of the entire Yongding River Basin and identified their seasonal pollution characteristics, possible sources and potential risk, thus providing scientific information for formulating effective control practices.

2. Materials and methods

2.1. Study area and sample collection

The Yongding River Basin is one of the seven water systems and the longest tributary of the Haihe River. It is located in northern China and passes through five provinces and municipalities, namely Shanxi, Inner Mongolia, Hebei, Beijing, and Tianjin. The Yongding River flows into the Haihe River and then into the Bohai Sea from Tanggu district. The Yongding River is 747 km long and covers an area of 47,000 km^2. The four main tributaries composing the river network of the Yongding River Basin are the Sanggan River and the Yang River upstream, and the Yongding River and the Yongdingxin River downstream. Annual precipitation in the basin is about 450 mm (Fu et al., 2012), and 70%–80% of the annual precipitation and rainfall is concentrated in flood season (from July to September) (Wang et al., 2010). The Sanggan River and the Yang River are major water source for agriculture and industiral activities located in upstream area, where Zhangjiakou City in Hebei Province, as well as Datong, Shuozhou and Xinzhou City in Shanxi province are the main cities (Guo et al., 2014), and human population in this area exceed 10 million. Two large cities including Beijing and Tianjin are located in the downstream, an area with developed agriculture and industries, as well as enormous population beyond 37 million. The most water consumption industries in the Yongding River Basin were steel, automobile, pharmaceutical, textile, chemical and thermal power industry, etc. The Yongding River Basin has the main field crops including maize (corn) and wheat, and agricultural production of this area is more developed with large amount of chmeical fertilizer application (Guo et al., 2014). The ecosystem of the Yongding River Basin showed sevre stress to support human society development demangs. Due to the growing population, agriculture and industiral activities, water quality of the entier basin is degraded to class IV and V based on China's Environmental Quality Standards for Surface Water (GB3838-2002) (Fu et al., 2012).

Surface water samples were collected at 46 sampling sites of the Yongding River Basin in two seasons, spring (April 13 to May 23, 2016) and summer (August 10 to September 2, 2016) (Fig. 1). Sampling sites were chosen to cover the entire river basin, ranging from the upstream tributary source to the estuary. Specifically, six sites were located in the Yongdingxin River (sampling sites S1 to S6), seven were located in the Yongding River (sampling sites S7 to S13), eighteen were located in the Sanggan River (sampling sites S14 to S31), and fifteen were located in the Yang River (sampling sites S32 to S46). Two sampling sites including Luogupan Village (S7) and Yongding River Bridge (S8) were dried up and no samples were collected. Collected water samples were stored in 1 L brown glass bottles and transported to the laboratory for analysis.