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Environmental Contamination and Toxicology

Contamination of Priority Polycyclic Aromatic Hydrocarbons in Water from Guanting Reservoir and the Yongding River, China

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In the world of today the environmental pollution has increasingly become a major problem for public health. Many pollutants are ubiquitous in nature, every person is inevitably exposed to them. Among them, polycyclic aromatic hydrocarbons (PAHs) represent an important class of such compounds. More than one hundred PAHs were found in nature. The US Environmental Protection Agency (EPA) has promulgated 16 unsubstituted PAHs (16 EPA-PAHs) in its list of 129 priority pollutants. Among them, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene are typically considered to be possible or probable carcinogens (8 car-PAHs). Their occurrence in environment poses a potential threat to human health.

PAHs are introduced into the environment by natural and anthropogenic sources. Anthropogenic sources, which include emission from automobiles, industrial process, and domestic heating systems, waste incinerators and tobacco smoking, are responsible for the majority of the PAHs input to the environment (Nikolaou et al., 1984; Baek et al., 1991). Once entering the atmosphere, PAHs are redistributed between the gas and particulate phase (Bildleman, 1988; Masclet et al., 1988; Aceves et al., 1993) and can therefore be transported through atmosphere over long distances and enter water bodies by wet and dry deposition and/or gas-water interchange (Baker et al., 1990; Leister et al., 1994). Once entering the aquatic systems, most PAHs are adhered to the suspended particles due to their hydrophobic properties, and therefore sink to the bottom and accumulate in the sediments (Laflamme et al., 1978; Gschwend et al., 1981) and form a long term source of potential pollution. Atmospheric deposition has been regarded as a main pathway for the loading of PAHs to many water bodies (McVeety et al., 1988, Dickhut et al., 1995, Golomb et al., 1997).

On the basis of their molecular masses and properties, two classes of PAHs can be distinguished. 2-3 ring PAHs are defined as low molecular weight PAHs (LMW-PAHs), whereas 4-6 ring PAHs are defined as high molecular weight PAHs (HMW-PAHs). The LMW-PAHs have a significant acute toxicity, while some of the HMW-PAHs show high carcinogenic and mutagenic potentials (Doong et al 2000). Coastal and inland waters usually act as receptors for domestic

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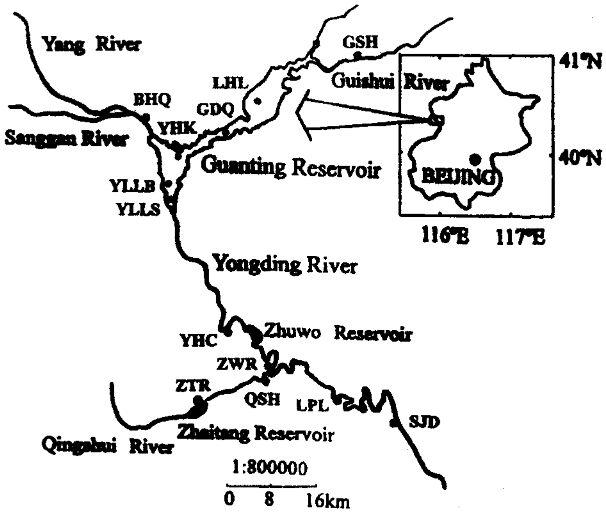

Figure 1. Geographical location of sampling sites.

sewage, industrial effluent and urban and rural runoff. As streams and rivers, lakes. and ponds are frequently used for potable water sources, contamination of which is particularly undesirable.

Guanting Reservoir is situated in the northwest of Beijing and was mainly used for irrigation, generation of electricity, raising of fish, and potable water source. The total capacity of the reservoir is about 2270 million m^3 and the catchment basin is about 47000 Km^2. Because of industrial and human activities in the process of urbanization and industrialization, it was contaminated seriously by the discharge of industrial and domestic sewage in the 1980s, so that it could not be used as potable water source. However, compared to other contamination, such as heavy metals, there is limited information regarding level of PAHs in this reservoir. With economic development and continuous drought, Beijing is now facing a water shortage. The purposes of the study were to investigate the occurrence of PAHs in Guanting Reservoir and Yongding River and their main pollution sources. The information will be useful for the management and remediation for some water system.

MATERIALS AND METHODS

A composite stock standard solutions of 16 PAHs including naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (F), phenanthrene (Phe), anthracene (An), fluoranthene (Flu), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF) , benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-cd)pyrene (INP), dibenzo(a,h)anthracene (DBA) and benzo(g,h,i)perylene (BP) at a concentration of 100 mg/L each and 2-florobiphenyl were purchased from ChemService Inc. XAD-2 resin (20-60 mesh) was purchased from Rohm and Haas (Philadelphia, Pa., USA). All solvents including acetone, methylene chloride, hexane, iso-octane, methanol and diethyl ether used in the sample processes were of analytical grade and redistilled in all-glass system prior to use. Glass fiber filter (type A/E) was purchased from Gelman Sciences Inc.

Water samples were collected in October 2000 in Guanting Reservoir and in November 2000 in Yongding River. Thirteen sampling sites were selected in the areas investigated, seven (BHQ, GSH, LHL, GDQ, YHK, YLLB and YLLS, among them BHQ and GSH are two inlets situated in Yang River and Guishui River, respectively) at Guanting Reservoir and six (YHC, ZTR, QSH, ZWR, LPL and SJD) at Yongding River, respectively, were selected in the areas for investigation. The geographical location of Guanting Reservoir, the Yongding River and the sampling sites are shown in Figure1. 20 L of water from each site was collected and filtered by glass fiber filter. The filtered water was passed through the XAD-2 resin column (200 mm×10 mm id) by siphonage at a flow rate of less than 15 mL/min. After adsorption, the pollutants trapped on XAD-2 resin were eluted with 90 mL of diethyl ether. The eluate was divided into two parts, one was used for organochlorine compound analyses (Wang et al., 2003), and the other for PAHs analyses. The latter was dried with anhydrous sodium sulfate (purified previously at 400°C for 4 hr in a shallow tray) and concentrated to 2 mL, which was cleaned up by silica gel column (300mm×10mm id) chromatography according to USEPA method 3630C. The sample was concentrated and reduced finally to 0.2 mL by a gentle nitrogen steam for GC analysis.

The analyses of PAHs were carried out on a HP 5890 GC equipped with a split-splitless injection port and a flame ionization detector (FID) system. The analytical column used was DB-5 (30 m×0.25 mm id, and 0.25μm film thickness). The GC oven temperature was programmed as follows: initial temperature of 50°C was held for 3 min, increased at a rate of 4°C /min to 300°C, then held for 35min.The injector and detector temperature were 280°C and 300°C, respectively. The carrier gas was pure nitrogen. The gas chromatograph was operated in the splitless mode. The splitless time was 1.0 min.

Identification of individual PAHs was carried out by comparison of GC retention times with those of standard PAHs, and confirmed on an Agilent 6890 GC equipped with a model 5973 mass selective detector(MSD). A HP-5ms column with dimensions of 30 m ×0.25 mm id (0.25 μm film thickness) was used. Helium was used as carrier gas. The GC operating conditions were as above and MS condition as follows: The ionizition was carried out in the electron impact (EI) mode (70 eV). The transfer line and ion-trap manifold were set at 280°C and 300°C. The mass range scanned was from 50 to 550 amu under full-scan acquisition mode. Target analytes were quantified using the external standard technique.

Method blank, spiked blank and matrix spikes were analyzed. Blank procedures showed no detectable interference. The method detection limits (MDLs) of PAHs are from 1.5 to 8.9 ng/L. The spike recoveries of PAHs at a level of 10 mg/L from distilled water ranged from 79.86 ± 6.17 % to 103.57 ± 8.57 % (n= 5). Surrogate standard was added to all the samples. The recoveries of surrogate

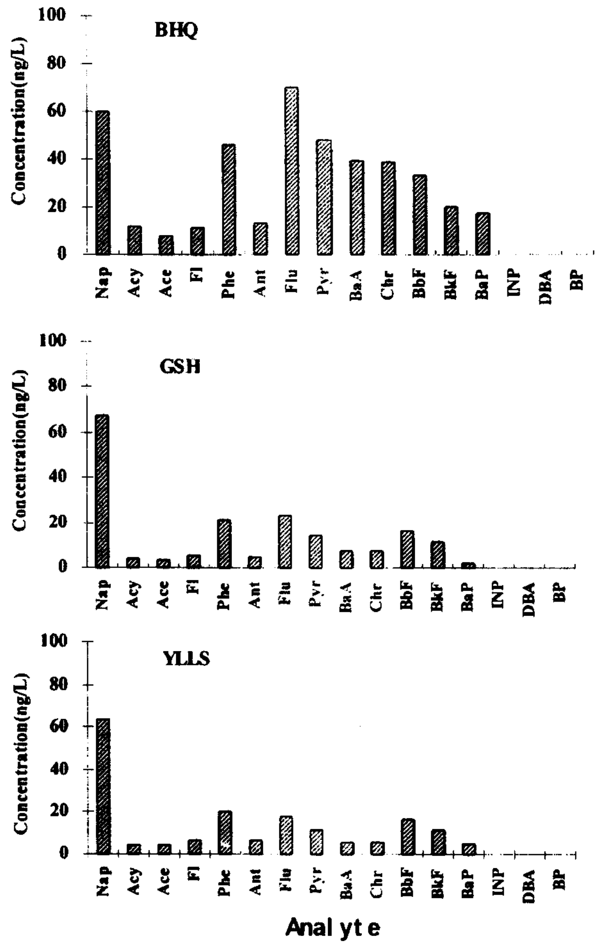

Figure 2. Distribution patterns of individual PAHs in water from different sampling sites selected from Guanting Reservoir.

standard (2-florobiphenyl) spiked in all the samples were in the range of 82.45 to120.74 %. All results were corrected for recoveries.

RESULTS AND DISCUSSION

The distribution patterns of each PAH at some selected sampling sites from Guanting Reservoir and Yongding River were shown in Figure 2 and 3, respectively. From which we may find that there were two different types in distribution pattern. One included BHQ and SJD, which had basically similar distribution features. Naphthalene and phenanthrtene were dominant among the LMW-PAHs, while the HMW-PAHs at the two sites were in the same order: fluoranthene > pyrene > chrysene > benzo(a)anthracene > benzo(b)fluoranthene > benzo(k)fluoranthene > benzo(a)pyrene, ranged from 17.07 to 69.68 ng/L at BHQ and from 10.05

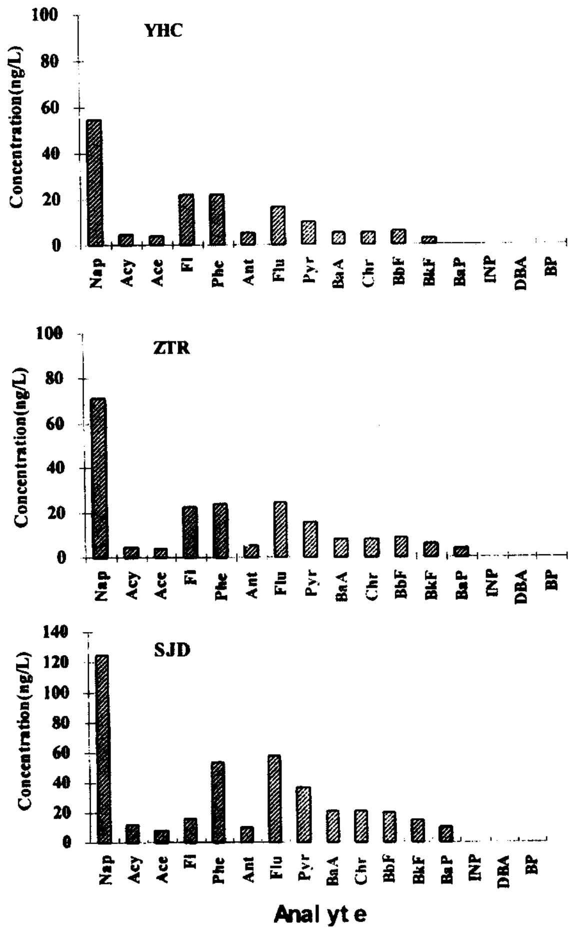

Figure 3. Distribution patterns of individual PAHs in water from different sampling sites selected from the Yongding River.

to 58.04 ng/L at SJD, respectively. The other included all sampling sites except BHQ and SJD. Naphthalene and phenanthrtene were also predominate among the LMW-PAHs, at a range of 42.84—151.53 ng/L and 21.44—53.89 ng/L, respectively. Fluoranthene, pyrene and benzo(b)fluo- ranthene were predominant at the higher molecular range, ranged from 15.12 to 69.68 ng/L, 8.65 to 48.33 ng/L, and 5.12 to 38.52 ng/L, respectively. Indeno(1,2,3-cd)pyrene, dibenzo(a,h)-anthracene and benzo(g,h,i)perylene were below their MDLs at all sampling sites. Benzo(a)pyrene was detectable at most of sites except site YHC in the Yongding Rive, ranged from 2.28 to 17.07 ng/L. From the distribution patterns of each PAH in water from Guanting Reservoir and Yongding River, it can be seen that the pollutants in water at all sampling sites may originate from non-point pollution source. In addition, the water at BHQ and SJD was more seriously polluted. It suggested that other pollution source may still exist at the two sites.

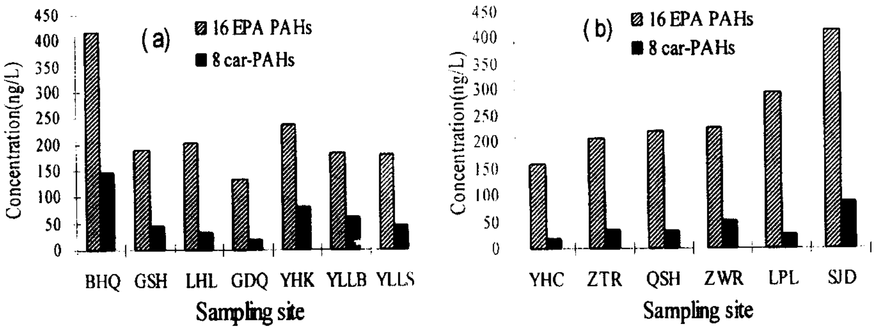

Figure 4. Spacial distribution of PAHs in water.

The spacial distribution patterns of 16 EPA-PAHs and 8 car-PAHs in water samples from Guanting reservoir (a) and Yongding River (b) are shown in figure 4. The concentrations of 16 EPA PAHs varied from 132.4 ng/L at GDQ to 416.9 ng/L at BHQ with a mean value of 219.7 ng/L in Guanting reservoir and from 158.3 ng/L at YHC to 407.5 ng/L at SJD with a mean value of 251.8 ng/L, respectively. The concentrations of 8 car-PAHs ranged from 20.8 to 148.1 ng/L with an average of 62.5 ng/L in Guanting Reservoir and 19.1 to 87.9 ng/L with an average of 42.5 ng/L in the Yongding River. It is reported that the concentration of 8 car-PAHs from surface water were frequently found to be in the range of 2 to 50 ng/L (Menzie et al., 1992). This suggests that the levels of 8 car-PAHs were higher both in Guanting Reservoir and Yongding River.

The average level of 16 EPA-PAHs in Guanting Reservoir was lower than that in Yongding River, while 8 car-PAHs were higher than that in the Yongding River. It suggests that the water was more seriously polluted by HMW-PAHs in Guanting Reservoir compared to Yongding River. It also can be seen from the survey that the levels of total PAHs at BHQ were higher than those at LHL, GDQ, YHK, YLLB and YLLS. It is obvious that the water coming from the Yang River is pollution source for Guanting Reservoir. The level of total PAHs at GSH was approximate to these at other 5 sites in Guanting Reservoir. It showed that water coming from Guishui River was not pollution source for Guanting Reservoir. While in Yongding River, the concentrations of total PAHs increased gradually from YHC to SJD. It suggests that the contamination of PAHs in the Yongding River may be caused by the atmospheric deposition coming from the industrial area.

The distribution patterns of LMW-PAHs and HMW-PAHs in Guanting Reservoir (a) and Yongding River (b) are shown in figure 5. A distinct characteristic in relative proportion of LMW-PAHs and HMW-PAHs found at BHQ was that the level of HMW-PAHs exceeded that of LMW-PAHs. In addition, the level of HMW-PAHs at YHK was slightly higher than that of LMW-PAH. It meant that the water at YHK probably polluted by water coming from the upper reaches of the Yang River. At all sampling sites except BHQ and YHK in Guanting Reservoir, the concentration of LMW-PAHs was predominant. However, in Yongding River, the HMW-PAHs level at SJD was also markedly higher than those at other sites. It may be caused by

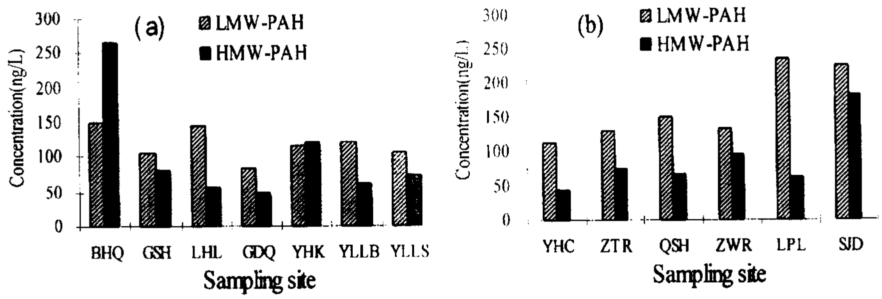

Figure 5. Concentration of LMW-PAHs and HMW-PAHs in water.

traffic nearby the site.

Water quality guidelines for aquatic life are 12 ng/L for anthracene 18 ng/L for benzo(a)anthracene and 15 ng /L for benzo(a)pyrene recommended by Canadian Council of Ministers of the Environment (1999). Compared with the guidelines, concentrations of anthracene at BHQ (13.2 ng/L) and YHK (14.2 ng/L), benzo(a)anthracene at BHQ (39.0 ng/L) and SJD (21.1 ng/L), benzo(a)pyrene at BHQ (17.1 ng/L) were above guideline values. The criteria for surface water classifications provided that the 10 PAHs (sum of acenaphthylene, phenanthrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene), dibenzo(a,h)anthracene, indeno(1,2,3-cd)pyrene, and benzo-(g,h,i)perylene) should not exceed 2.8 ng/L for class I , 31 ng/L for class II and III recommended by Florida Department of Environmental Protection (1996). The sum of 10 PAHs ranged from 46.0 to 206.1 ng/L in Guanting Reservoir and from 45.4 to 153.4 ng/L in Yongding River, respectively. This indicates that the levels of 10 PAHs at all sampling sites were above the criteria of class II and III.

We may conclude from our survey that the levels of PAHs measured in Guanting Reservoir and Yongding River exceed those stricter surface water quality guidelines mentioned above. The main pollution sources for the waters investigated may be the contaminated water coming from the Yang River and atmospheric deposition. The data obtained in the present study may be useful to local government for the remediation of the contaminated waters in the near future.

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