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Occurrence, behavior and removal of typical substituted and parent polycyclic aromatic hydrocarbons in a biological wastewater treatment plant

Meng Qiao [a,b], Weixiao Qi [a], Huijuan Liu [a], Jiuhui Qu [a,*]

[a] State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

[b] University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

Wastewater treatment plant (WWTP) effluent is the major source for substituted polycyclic aromatic hydrocarbons (SPAHs) to the receiving rivers, as well as the parent PAHs. Some of the SPAHs showed higher toxicities and levels than their parent PAHs. The occurrence and behavior of typical SPAHs were investigated in a representative biological WWTP in Beijing, China. Methyl PAHs (MPAHs) (149–221 ng/L in the influent; 29.6–56.3 ng/L in the effluent; 202–375 ng/g in the activated sludge), oxygenated PAHs (OPAHs) (139–155 ng/L; 69.9–109 ng/L; 695–1533 ng/g) and PAHs (372–749 ng/L; 182–241 ng/L; 2402–3321 ng/g) existed, but nitrated PAHs (NPAHs) were not detected. 2-Methylnaphthalene, anthraquinone, 9-fluorenone and 2-methylanthraquinone were the predominant SPAHs. OPAHs were deduced to be formed from PAHs especially during summer, based on the ratios variation and removal efficiencies of the two seasons, and the surplus mass in the outflows. Low molecular weight compounds (2–3 rings) might be mainly removed by mineralization/transformation and adsorption in the anaerobic unit, and by volatilization in the aerobic unit. High molecular weight compounds (4–6 rings) might be mainly removed by adsorption in the anaerobic unit. The total outflows of SPAHs and PAHs were 66 g/d in summer and 148 g/d in winter from the WWTP to the receiving river. The percentage of OPAHs was higher in summer than in winter.

1. Introduction

Effluent from wastewater treatment plants (WWTPs) in urban cities has been identified as the major direct source for organic pollutants entering the receiving rivers (Tian et al., 2012). A previous study has figured out that the WWTPs effluent was the main contributor for dissolved polycyclic aromatic hydrocarbons (PAHs) to the rivers in Beijing and Tianjin (Qi et al., 2013). Though PAHs originated from incomplete combustion and vehicle emission (Manoli and Samara, 1999), the contribution of direct atmospheric deposition to the rivers was only 7% (Qi et al., 2013). In recent years, some typical substituted

* *Corresponding author*. Tel.: +86 10 62849151; fax: +86 10 62923558.
E-mail address: jhqu@rcees.ac.cn (J. Qu).

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PAHs (SPAHs), including methyl PAHs (MPAHs), oxygenated PAHs (OPAHs) and nitrated PAHs (NPAHs) have been paid much attention due to their higher toxicities than PAHs, such as carcinogenicity, mutagenicity and allergic diseases (Tokiwa et al., 1986; Durant et al., 1996). Besides the similar sources to PAHs, NPAHs and OPAHs can also be formed from PAHs by photo-chemical oxidation in atmosphere with NO_x, O_3 and OH (Bamford and Baker, 2003; Wang et al., 2007; Kojima et al., 2010), and OPAHs from biological transformation in soil with white rot fungi (Lundstedt et al., 2007; Haritash and Kaushik, 2009), respectively. Previous studies mainly focused on the pollution levels of SPAHs in the atmospheric and soil environment (Vincenti et al., 1996; Niederer, 1998; Lundstedt et al., 2007; Di Filippo et al., 2010). Our recent study demonstrated that WWTP effluent contributed 62–93% PAHs and SPAHs (dissolved and absorbed phase) of the total input to the receiving rivers (Qiao et al.). Consequently, it is imperative to investigate this type of pollutant in the main direct source, WWTPs for a better understanding of their behaviors.

As is known that PAH is a type of ubiquitous pollutant in WWTPs (Pham and Proulx, 1997; Manoli and Samara, 1999; Busetti et al., 2006; Vogelsang et al., 2006). Previous studies have well documented the removal efficiencies and potential mechanisms of PAHs during biological treatment processes. The reduction of the low molecular weight (LMW) PAHs (33–100%) was higher than the high molecular weight (HMW) PAHs (18–60%) (Bergqvist et al., 2006). LMW PAHs were lost possibly due to biodegradation and volatilization and HMW PAHs due to adsorption (Manoli and Samara, 1999). Though PAHs may undergo photolysis and chemical degradation, microbiological degradation is the major degradation pathway (Haritash and Kaushik, 2009). PAHs do not only mineralize to CO_2, H_2O and CH_4, but also can transform to OPAHs in the presence of laccase (Cañas et al., 2007). Anthraquinone is the main oxidation product of anthracene and can be accumulated (Haritash and Kaushik, 2009). However, until now, no literature has been reported the possible transformation from PAHs to OPAHs during a biological treatment process in WWTP.

In order to reduce the pollution levels of these targets in WWTP effluent, it is essential to understand the removal mechanisms of SPAHs and PAHs. Not only the pollutants in the effluent, but also in the dewatered sludge, should be paid severe attention to. The contents of SPAHs and PAHs in the sludge may be higher than in the effluent, due to their lipophilic property. Meanwhile, the transformation from PAHs to OPAHs may also occur. The disposal of the sewage sludge for land use may be harmful to the human health (Villar et al., 2009) by the accumulation of these toxic pollutants if they enter the drinking water sources and/or food chains (Beck et al., 1996). To the best of our knowledge, the removal mechanisms of OPAHs and NPAHs have also never been reported in water and sludge from a WWTP.

This work aimed (1) to investigate the occurrence of SPAHs in a WWTP; (2) to figure out the transformation from PAHs to OPAHs, a possible degradation pathway of PAHs besides mineralization; (3) to gain an insight of the removal mechanisms of SPAHs and PAHs during a biological wastewater treatment process; and (4) to primarily discuss the impact of SPAHs and PAHs from the WWTP to the receiving river.

2. Materials and methods

2.1. Wastewater treatment process

The studied WWTP, located in the northwest of Beijing, serves a population of 814 000 and an area of 159.42 km^2. The biological treatment of this plant contains two parallel processes, the anoxic – anaerobic – aerobic (inversed A^2/O) process and the anaerobic – anoxic – aerobic (A^2/O) process (Fig. 1). The capacity of each process is 200 000 m^3 per day. The hydraulic retention times (HRTs) of the inversed A^2/O process are 1.5 h, 2.5 h and 10.0 h, and of the A^2/O process are 1.5 h, 3 h and 10.8 h, respectively. The total solid retention times (SRTs) are 6–7 d for the inversed A^2/O process and 20–25 d for the A^2/O process.

2.2. Sample collection and analytical procedure

Samples were collected from the effluent of each unit (a, b, c, d, ib, ic, id) of the secondary treatment process during summer (the non-heating season, July 2012), as signed in Fig. 1. Due to the frequent rainfall in this season, the day we chose was after several-day rainfall as a typical case (Table S1). 4 L water (W, dissolved phase) and sludge (S, absorbed phase) mixed samples were grabbed at each site at 10:00, 13:00 and 16:00. During winter (the heating season), the samples were collected on three separate days from February to March 2013, at 7 sampling sites (a, b, c, d, e, f, g) of the A^2/O process. The days we sampled on in this season were during the dry weather condition, before which there was almost no snowfall (Table S1). Physical–chemical parameters of each sample are listed in Table S2. Sodium azide was added to each sample immediately after collection, in order to prevent microbial degradation. All samples were stored in darkness. The details of the pretreatment and instrument analysis procedure, quality assurance and quality control are given in the Supporting information.

2.3. Chemicals and materials

Thirteen individual SPAH standards, including 2-methylnaphthalene (2-MN, in solid 100%), 1-methylfluoranthene (1-MF, 10 μg/mL), 2,6-dimethylnaphthalene (2,6-DMN, in solid 100%), 3,6-dimethylphenanthrene (3,6-DMP, in solid 100%), 9-fluorenone (9-FL, in solid 100%), anthraquinone (AQ, 100 μg/mL), 2-methylanthraquinone (2-MAQ, in solid 99.0%), benz[a]anthracene-7,12-dione (BA-7,12-D, 50 μg/mL), 2-nitrofluorene (2-NF, in solid 99.9%), 9-nitroanthracene (9-NA, 100 μg/mL), 3-nitrofluoranthene (3-NF, in solid 100%), 1-nitropyrene (1-NP, in solid 99.8%), 7-nitrobenz[a]anthracene (7-NBA, 100 μg/mL), and the sixteen USEPA priority PAHs, including naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fluo), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flua), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Chry), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenz[a,h]anthracene (DBA), and benzo[g,h,i]perylene (BghiP), in a mixture (200 μg/mL) were purchased from AccuStandard, Inc., New Haven, USA.