Removal efficiency of polycyclic aromatic hydrocarbons and phthalate esters by surface flow wetland in Shunyi district, Beijing

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Abstract. The surface flow wetland (SFW) system was located on Shunyi district, Beijing. It was built to treat industrial wastewater and domestic sewage, which were looked as its influent. Here sixteen polycyclic aromatic hydrocarbons (PAHs) and six phthalate esters (PAEs) were detected by gas chromatography-mass spectrometry (GC-MS). To determine treatment effect of SFW system, concentrations of targeted compounds in the influent were compared with those in the effluent. Results showed typical compounds of industrial wastewater were naphthalene (NAP), phenanthrene (PHE), dibutyl phthalate (DBP), di-(2-ethylhexyl) phthalate (DEHP), and their concentrations were ranged from 122.6 ng.L⁻¹ to 760.6 ng.L⁻¹. However typical compounds of domestic sewage were NAP, anthracene (ANT), PHE, DBP, diethyl phthalate (DEP), DEHP, and their concentrations were ranged from 280 ng.L⁻¹ to 7998.1 ng.L⁻¹. Typical compounds of effluent were NAP, PHE, DBP, DEHP, and their concentrations changed between 4.2 ng.L⁻¹ and 1430.74 ng.L⁻¹. The removal rate of those compounds were 10% ~ 99%, and nineteen compounds removal rate reached above 70%. Therefore, it can be concluded that SFW system had a strong effect on the removal of these compounds.

1. Introduction

Surface flow wetland (SFW) is an ecological treatment technique for slightly polluted wastewater. It utilizes the synergetic reaction of soil, plant and microorganisms for purification wastewater; especially the interaction of microorganisms with other organisms and plants plays an important role for the absorption and degradation of pollutants [1, 2]. This technique is widely used because of high efficiency, low operation cost and convenient maintenance.

Here the SFW system was located in Shunyi district, Beijing, China. Its area was about 17.3 hm², and consisted of two stabilization ponds, eight grade series SFWs and one water storage pond. It was built to treat industrial wastewater and domestic sewage nearby with total 7500m³ per day. Effluent of this SFW system was mainly used for forest irrigation, and some was discharged into Chaobai River.

Polycyclic aromatic hydrocarbons (PAHs) and phthalate esters (PAEs) are two kinds of trace organic compounds with mutagenic effect. They belong to typical persistent organic compounds (POPs), and are ubiquitous in aquatic environment. Moreover, they can be bioaccumulation and threaten the ecological safety and human health [3, 4]. Thus they should be paid more attention.

This study aimed to determine the removal efficiency of SFW system in Shunyi district, Beijing by comparing concentrations of compounds in the influent and effluent of that SWF system.
2. Methods
Water samples were filtered by 0.45 µm thickness glass fiber film. Then the filtered water were added with substitute and evenly passed through the activated solid phase extraction (SPE) for elution. Finally, the elution liquid was dewatered and stored in refrigerator. Quantitative of PAHs and PAEs was performed by GC-MS. All samples were added indicators to control the recovery rate of the whole analysis process, thus ensure accuracy of this detection. Detection limit and recovery rate of the method was ranged from 0.10 ng.L\(^{-1}\) to 0.40 ng.L\(^{-1}\), and 85.2% to 96.3%, respectively.

3. Results and discussions
3.1. Detection of PAHs and PAEs in influent water and effluent water
3.1.1. Detection of PAHs. The detection of PAHs in industrial wastewater, domestic sewage and wetland water were shown in Table 1.

| Compounds | Industrial wastewater | Domestic sewage | effluent | Standard\(^\circ\) |
|-----------|------------------------|-----------------|----------|-----------------|
| NAP       | 182.3                  | 1 168.7         | 76.5     |                 |
| ANY       | 5.0                    | 21.1            | 19.0     |                 |
| ANA       | 26.7                   | 31.4            | 14.0     |                 |
| FLU       | 73.2                   | 125.2           | 33.4     |                 |
| PHE       | 122.6                  | 280.2           | 42.00    |                 |
| ANT       | 11.7                   | 395.8           | 5.5      |                 |
| FLT       | 36.8                   | 88.9            | 9.2      |                 |
| PYR       | 27.7                   | 81.4            | 7.6      |                 |
| BaA       | 13.0                   | 22.6            | 2.5      |                 |
| CHR       | 14.4                   | 17.5            | 10.0     |                 |
| BbF       | 11.8                   | 22.2            | 3.0      |                 |
| BKF       | 1.7                    | 2.8             | 0.7      |                 |
| BaP       | 2.9 ND\(^\circ\)       |                 | 0.5      | 2.8             |
| IPY       | 9.1                    | 2.4             | 3.5      |                 |
| DBA       | 3.4                    | 3.8             | 1.4      |                 |
| BPR       | 5.2                    | 6.5             | 2.5      |                 |
| ∑PAHs     | 547.5                  | 2 270.6         | 231.3    | 2 000           |

\(^\circ\) Chinese standard of surface water environment quality (GB3838-2002), "ND" means not detected.

As can be seen all sixteen PAHs were detected in industrial wastewater, and concentrations of PHE, NAP were relatively higher, which were 182.3 ng.L\(^{-1}\) and 122.6 ng.L\(^{-1}\). The other compounds concentration was between 1.7 ng.L\(^{-1}\) and 73.2 ng.L\(^{-1}\). Total PAHs was 547.5 ng.L\(^{-1}\), which did not exceed Chinese standard of surface water environment quality (GB3838-2002). However, it should be noted that the concentration of BaP in industrial wastewater slightly exceeded that standard limit. Except for BaP, the other fifteen PAHs were detected in domestic sewage, and concentrations of NAP, ANT, PHE were relatively larger, which were 1168.7 ng.L\(^{-1}\), 395.8 ng.L\(^{-1}\), 280.2 ng.L\(^{-1}\), respectively. The other PAHs concentration was changed between 2.4 ng.L\(^{-1}\) and 125.2 ng.L\(^{-1}\). Total PAHs was 2270.6 ng.L\(^{-1}\). All sixteen PAHs in wetland effluent were detected. The concentrations of PHE and NAP were 76.5 ng.L\(^{-1}\), 42.0 ng.L\(^{-1}\), and the others were ranged from 0.5 ng.L\(^{-1}\) to 33.4 ng.L\(^{-1}\). Total PAHs was 231.3 ng.L\(^{-1}\), and did not exceed Chinese standard of surface water environment quality.

3.1.2. Detection of PAEs. The detection of PAEs in industrial wastewater, domestic sewage and wetland water were shown in Table 2. As can be seen all six PAEs were detected in industrial
wastewater. Concentration of DEHP was the highest, which reached to 760.6 ng.L\(^{-1}\), and concentration of DnOP was the lowest, which was only 4.7 ng.L\(^{-1}\). Those six PAEs were also detected in domestic sewage. The concentrations of DBP, DEHP and DEP were relatively higher, which were 7998.0 ng.L\(^{-1}\), 2889.0 ng.L\(^{-1}\), 1584.4 ng.L\(^{-1}\), respectively. Moreover, the concentration of DBP was 2.7 times of that Chinese standard of surface water environment quality. The concentration of BBP was the lowest, which was only 29.85 ng.L\(^{-1}\). Compared with the concentrations of PAEs in industrial wastewater, those in domestic sewage were one order higher. Six PAEs were all detected in the wetland effluent. The concentration of DBP and DEHP were 1430.7 ng.L\(^{-1}\), 410.9 ng.L\(^{-1}\), and the concentration of BBP was the lowest, which was only 0.7ng.L\(^{-1}\).

Table 2. Concentrations of PAEs in influent and effluent of SWF system (unit: ng.L\(^{-1}\))

| Compounds | Industrial wastewater | Domestic sewage | effluent | Standard* |
|-----------|-----------------------|----------------|----------|-----------|
| DMP       | 73.3                  | 671.4          | 53.5     |
| DEP       | 256.4                 | 1584.4         | 56.8     |
| DBP       | 392.0                 | 7998.1         | 1430.7   | 3000      |
| BBP       | 6.9                   | 29.8           | 0.7      |
| DEHP      | 760.6                 | 2889.0         | 410.9    | 8000      |
| DnOP      | 4.7                   | 31.6           | 2.2      |
| ΣPAEs     | 1493.8                | 13204.2        | 1954.8   |

*: Chinese standard of surface water environment quality (GB3838-2002)

3.2. Difference of PAHs and PAEs in influent water and effluent water
Concentrations of ten PAHs including NAP, ANY, FLU, PHE and ANT in domestic sewage was higher than those in industrial wastewater, and especially the concentration of ANT in domestic sewage was 34 times of that in industrial waste. However, the other six PAHs concentrations were roughly similar. In addition, concentration of individual PAH and total PAHs in effluent water was significantly lower than that of industrial wastewater and domestic sewage.

As for six PAEs, concentrations in domestic sewage were all higher than those in industrial wastewater and effluent, especially that of DBP, which was 20 times of that in industrial wastewater. One reason of this difference was that their origin was different. The other reason maybe that domestic sewage was directly discharged without any treatment, but industrial wastewater was sedimentation, filtration and other processes before flowing into the SWF system.

3.3. Removal rate of PAHs and PAEs by the SWF system
The removal rates of targeted compounds by the SWF system were shown in Table 3. It revealed that the wetland system had a strong effect on the removal of PAHs and PAEs. Removal rate of nineteen compounds including NAP, ANT, DMP and BBP were over 70%, especially those of ANT and BBP, which reached 98%. The main mechanism for the removal of trace organic compounds in wetland system was the degradation of organic compounds by heterotrophic microorganisms, which transformed those compounds to CO\(_2\) and H\(_2\)O. Insoluble trace organic compounds after precipitation, filtration and assimilation can be used by microorganisms, and those soluble organic compounds were easily metabolism. One reason for higher removal of ANT was its strong volatilization, the other maybe that it was small molecular weight and apt to be degradation\(^{[3]}\). As for BBP, its higher removal rate maybe closely relate to degradation under suitable environment. There were reports that BBP were reduced to 10% by activated sludge after one day.
Table 3. Removal rate of PAHs and PAEs by the SWF system

| Compound | Removal rate (%) | Compound | Removal rate (%) |
|----------|------------------|----------|------------------|
| NAP      | 93               | BaP      | 74               |
| ANY      | 12               | IPY      | 60               |
| ANA      | 70               | DBA      | 76               |
| FLU      | 79               | BPR      | 74               |
| PHE      | 87               | Σ PAHs   | 90               |
| ANT      | 98               | DMP      | 92               |
| FLT      | 91               | DEP      | 96               |
| PYR      | 92               | DBP      | 80               |
| BaA      | 91               | BBP      | 98               |
| CHR      | 61               | DEHP     | 86               |
| BbF      | 89               | DNOP     | 93               |
| BkF      | 81               | Σ PAEs   | 84               |

4. Conclusions
(1) Most of target PAHs and PAEs were detected in influent and effluent of the SWF system. Typical organic compounds of SWF system were NAP, PHE, DBP and DEHP, which were 76.5 ng.L$^{-1}$, 42.0 ng.L$^{-1}$, 1430.7 ng.L$^{-1}$, 410.9 ng.L$^{-1}$, respectively.
(2) Generally concentrations of PAHs in industrial wastewater were the highest, and concentrations of PAEs in domestic sewage were higher than those in industrial wastewater and effluent of SWF system. (3) The SWF system had good removal effect on PAHs and PAEs, most removal rate of target compounds was over 70%.

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