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The Distribution of Polycyclic Aromatic Hydrocarbons in the Wetland Soil Irrigated by Pulp Waste Water

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Abstract: The distribution characteristics of eleven polycyclic aromatic hydrocarbons (PAHs) in the pulp waste water and in seashore wetland soil irrigated by the waste water were detected by GC-ECD. The result shows that the concentrations of PAHs in the gray water, bleached water, black liquid and integrated waste water ranged from 12.826 to 16.83 μ g^{-1}. The total amount of PAHs in the seashore wetland soil irrigated with the papermaking waste water containing PAHs increased significantly and the quantity is still increasing over time. The concentration of PAHs in the unirrigated soil and in soil after irrigated for one year and two years was 7.83, 22.04 and 29.96 mg kg^{-1}, respectively.

Key words: Pulp waste water, wetland, soil, PAHs

INTRODUCTION

PAHs refer to a group of semi-volatile organic substances that are composed of two or more fused benzene rings. They are mainly produced during human activities and energy utilization processes, such as the combustion process of oil, coal and lumber and production process of oil and chemical products (Jocobs *et al.*, 1987). In our country, due to the lack of forest resource, large quantity of straw is used for papermaking. The centralized discharge of PAHs, which is brought in by straw absorption or assimilation and is discharged along with pulping waste water, will inevitably pose adverse impact on local environment. At present, the engineering technology of using constructed wetland to treat waste water is developing rapidly (Whitney *et al.*, 2003; Julie, 1996) and the study on the distribution condition and the environmental cumulative effect of persistent organic pollutants in the wetland ecological system becomes very important. However, until now there is no document report about the analysis on the composition, distribution and precipitation condition of PAHs in the soil, which was irrigated by PAHs-containing waste water.

For the ecological project of waste water treatment by irrigating the reed wetland with waste water generated in a pulping and papermaking factory, this study, by analyzing the composition and content of PAHs in the waste water and in the seashore wetland soil which was irrigated by the waste water, to aims to understand clearly the distribution condition of PAHs in the papermaking waste water and in the soil irrigated by the waste water and provide the reference for the risk assessment pulping and papermaking waste water treatment and the ecological project of irrigating reed wetland with the waste water.

MATERIALS AND METHODS

Sample collection: Collection of water samples: The waste water samples come form one straw alkaline pulping and papermaking factory, which use straw as the raw material. The yearly pulping capacity is 2×10 t. And the waste water generated is treated according to the auxiliary plan that the waste water should be pretreated inside the factory and ecologically treated outside the factory. The waste water was first treated in the factory by aciding out lignin, producing alkali lignin and cycling fiber and then transported to the stabilization pond by steel tube. After treatment in anaerobic pond and facultative pond, the waste water was used for irrigating reed wetland. The waste water sampling time is 20th, 21st and 22nd of October 2003 and the samples were collected in the morning, at noon and in the evening, one sample for each time. The samples were classified into papermaking gray water, pulp waste water, black liquid and integrated waste water. For every sampling point, the total amount of

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Corresponding Author: Cheng Ding, Department of Environment Engineering, Southeast University, Nanjing 210096, Peoples's Republic of China samples is 9. After collecting the waste water samples, the pH value of these samples was adjusted to below 2. The samples were stored in the refrigerator under low temperature for analysis within 7 days.

Collection of soil samples: The soil samples were collected from within the seashore wetland ecological treatment project area, which was irrigated, by the papermaking waste water from this factory. Sample 1 is the wetland soil unirrigated. Sample 2 and 3 are soil irrigated with the waste water for one and two years respectively. The sample collection time is November 2003 when the reed was being collected and the collection of soil samples was easier. Fifteen soil samples were collected respectively according to the forked sample collection method. After freeze drying, removing impurities, mixing all the samples and screening, 200 g of the mixed sample was stored at the temperature of -18°C for further analysis.

Experimental facilities and methods

Apparatus and reagents: Agilent 6890GC/FID, GC/ECD (HP); Fused quartz capillary column (30 m×0.33 mm× 0.25 μm);Vacuum pump and filter holder; Centrifuge; Micro sampler (10 μL); Rotary evaporator; C18 solid phase extraction column; methanol, methylene chloride, normal hexane (HPLC grade, from Fisher America); anhydrous Na_2SO_4 (Analytical grade, from Nanjing Chemical Reagent Factory No. 1).

Pretreatment of water samples: (1) Activation of C_{18} column: Soak the C_{18} column in about 5 mL of methanol for 1 h and then in distilled water for some time (2) Extraction of sample: Centrifuge 500 mL of water sample and collect the filtrate after the sample is vacuum-filtered. The filtrate should pass the C_{18} column at certain flow rate (about 2 mL min^{-1}). Then use N_2 to blow away the remnant water in the column. (3) Elution and drying: First, use 5 mL of methylene chloride to elute C_{18} column and then use 5 mL of the mixture of methylene chloride and normal hexane (V:V=1:1) to elute C_{18} column. Mix the eluant of these two times. Add enough anhydrous Na_2SO_4 into the eluant and vibrate it fully. Then leave it stand for some time and transfer the eluant into a dry and clean concentration tube (4) Condensation: Condense the eluant to about 1 mL by using the rotary evaporator and then blow the solution slowly with N_2 to 0.1-0.2 mL (5) Add 10 μL of internal standard (prepared before use, 20×10^6) into the condensed sample.

Pretreatment of soil samples: (1) Pretreatment of the sample: Let the soil sample air dry naturally and remove the impurities. Then use screen of 60 meshes to screen the sample and grind the sample with the mortar. Weigh 7.5 g of the soil sample and place it in the centrifuge tube with plug, then add 20 mL of normal hexane, 5 mL of methano and 5 mL of distilled water. After ultrasonic vibration for 1 h, centrifuge the mixture and get the supernatant. Then, add 20 mL of normal hexane. After ultrasonic vibration for 1 h, mix the supernatant with that got last time. Add enough anhydrous Na_2SO_4 into the extracting solution for drying. And then, condense the sample to about l mL with the rotary evaporator. Weigh 1 g of silica gel and add it into 0.07 g of distilled water for activation, then fill the mixture into the silica gel column to purify the concentrated solution. (2) Elution: Use 8 mL of normal hexane for elution. Condense the eluant to about 1 mL by using the rotary evaporator and then blow the solution slowly with N_2 to 0.1 mL.

Qualitative and quantitative analysis of PAHs: Add 10 μL of 9-Phenylanthracene (20 ppm) as internal standard into every sample and have the samples analyzed by GC/FID. The operating condition of GC/FID is described as follows: The initial temperature is 80°C and maintain this temperature for 1 min. Controlled by the program, the temperature will be raised to 160°C at the rate of 25°C min^{-1} and then raise to 300°C at the rate of 3°C min^{-1} and maintain this temperature for 2min. Carrier gas: High-purity nitrogen (Purity: 99.99%). Perfrom qualitative analysis on pollutants by comparison with the standard and perform quantitative analysis according to the internal standard.

RESULTS

The concentration of PAHs in the waste water generated from each workshop section during the papermaking process is shown in Table 1. From this table, we can see that the concentration of PAHs in the waste water from every workshop section ranges from 12.83 to 16.83 μg L^{-1} and the sequence of the concentration value is: Integrated waste water>black liquid>gray water>bleached water. But the distribution characteristics of PAHs in the waste water vary from section to section. Among the eleven PAHs, only naphthaline, acenaphthylene and acenaphthene were detected in the waste water discharged from all workshop sections, while benzophenanthrene (k) was not detected at all. Benzophenanthrene (b) was detected in the bleached water and integrated waste water. Pyrene was only detected in gray water and integrated waste water. And furthermore, PAHs with 2-3 rings were the main constituent of PAHs in the waste water discharged from every workshop section.

Table 1: PAHs in the papermaking waste water ($\mu g\ L^{-1}$)

	PAHs						
Samples	Naphthaline	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene	Anthracene	Pyrene
Gray water	2.03	1.00	1.05	3.45	1.61	0.32	1.37
Bleached water	0.44	0.016	5.34	ND	4.15	ND	ND
Black liquid	7.35	0.31	0.43	8.14	ND	0.51	ND
Integrated waste water	4.97	0.35	0.61	7.23	0.51	0.21	0.41

Table 1: Continued

	PAHs						
Samples	Benzanthracene (a)	Chrysene	Benzophenanthrene (b)	Benzophenanthrene (k)	Total	2-3 rings (%)	4-6 rings (%)
Gray water	4.12	1.16	ND	ND	16.11	58.7	41.3
Bleached water	1.29	ND	1.59	ND	12.83	77.5	22.5
Black liquid	ND	ND	ND	ND	16.74	100.0	00.0
Integrated waste water	2.10	0.12	0.32	ND	16.83	82.2	17.8

Table 2: PAHs in wetland soil ($mg\ kg^{-1}$)

	PAHs						
Samples	Naphthaline	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene	Anthracene	Pyrene
1	2.12	0.03	ND	1.21	0.54	2.12	1.46
2	7.90	0.12	ND	6.20	0.27	4.60	1.41
3	9.00	0.34	6.50	4.90	ND	5.90	2.60

Table 2: Continued

	PAHs						
Samples	Benzanthracene (a)	Chrysene	Benzophenanthrene (b)	Benzophenanthrene (k)	Total PAHs	2-3 rings (%)	4-6 rings (%)
1	0.12	ND	0.11	0.12	7.83	76.8	23.2
2	0.15	ND	0.29	0.11	22.04	86.6	13.4
3	0.43	0.09	0.13	0.07	29.96	88.9	11.1

Table 2 shows the distribution condition of PAHs in the soil of unirrigated wetland and wetland irrigated for one year and two years respectively. The total amount of PAHs in these three kinds of soil is 7.83, 22.04 and 29.96 mg kg^{-1} respectively. The total amount of PAHs in soil sample 2 and 3 is 2.81 and 3.82 times of that in sample 1 respectively. and the total amount of PAHs in soil sample 3 is increased by 35.9% compared with that in sample 2, which shows relatively large difference. In terms of individual PAHs, the content of six PAHs out of eleven PAHs in soil sample 2 is higher than that in sample 1 and these PAHs includes naphthaline, acenaphthylene, fluorine, anthracene, Benzanthracene (a), anthracene, benzanthracene (b). Furthermore, the content of the other three PAHs is decreased and two PAHs were not detected in soil sample 1 and 2. Among the seven PAHs which concentrations are increased, the contribution of acenaphthene is the largest. Acenaphthene was not detected in sample 1 and 2, while its concentration in sample 3 was detected at 6.5 mg kg^{-1}.

DISCUSSION

PAHs in the papermaking waste water: Low molecular weight PAHs are easily to be decomposed and desorbed during their transport, diffusion and deposition process, the number of the PAHs with 2-3 rings detected (Naphthaline, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene) in the black liquid, which is generated during the first working procedure of pulping (namely the boiling of straw), is relatively large and the number of PAHs detected in the gray water and bleached water is smaller in turn. As for PAHs with 4-6 rings, since they are not decomposed and desorbed easily, they couldn't be detected in the black liquid and only a small number of PAHs could be detected in gray water and bleached water. The integrated waste water is the mixture of black liquid, gray water and bleached water; so ten out of eleven PAHs were detected in the black liquid. Since the integrated waste water was used for irrigating the reed in the wetland, the concentration of PAHs in the integrated waste water would directly affect the wetland ecological system.

PAHs in the wetland soil: Except for the natural formation of PAHs, PAHs mainly come from the emission of the incomplete combustion products during the burning process of fossil fuel, lumber, etc. Generally, during the pulping process, there won't be any PAHs produced. The PAHs in the waste water mainly come from the atmospheric precipitation during the growing process of plants, while PAHs in the atmosphere mainly come from products released during the incomplete combustion of oil and lumber. PAHs carried by plants might also come from the precipitation of atmospheric pollutants. Most of the PAHs carried by plants are those with low number of rings, which is easy to be adsorbed or assimilated by the surface of plants. Also, there are still some PAHs with high number of rings, which is absorbed by the plants through particles. Notably, in the bleached water, benzophenanthrene (k) has been detected, while in gray water and black liquid, it has not been found. So whether benzophenanthrene (k) is brought in from straw or generated from the bleaching process by using chlorine gas is still a question requiring further study.

After PAHs deposits in the soil, the pollutants at the surface soil might be transported to undersoil and groundwater, thus cause undersoil and groundwater pollution. It is much easier for wetland ecological waste water treatment system, which has long been under water saturation condition, to be polluted. Since the soil is a kind of granular material consisting of mineral substances and organic compound, it can adsorb organic substances effectively. PAHs might also react with other materials in the soil and will be transformed at the presence of mineral substances.

Located in the east coast, the seashore wetland of Yancheng is featured by its unique ecological environment. Due to the rapid industrialization of the peripheral cities, pollutants of PAHs brought by the air pollution have caused certain adverse impact on the local ecological environment. The analysis on the soil unirrigated by the waste water shows that the background level of PAHs, most of which are PAHs with 2-3 rings (accounts for 76.8% of the total amount of PAHs), is already relatively high and the total amount is 7.83 mg kg^{-1}. This is mainly because the seashore wetland of Yancheng is far away from the city, gas phase PAHs with 2-3 rings can be transported far away; while PAHs with higher number of rings, which are easy to precipitate, is relatively low in the wetland soil.

Comparative analysis of the content of PAHs in the straw pulp and in the soil irrigated by waste water: The waste water used to irrigate the reed wetland is the integrated waste water, the mixed waste water of gray water, bleached water and black liquid after aciding out the lignin. After treated by oxidation pond, this integrated waste water was used to irrigate reed wetland. It can be observed from Table 1 and 2, the increase of content of PAHs in soil sample 2 and 3 mainly comes from the irrigation waste water. Among the eleven PAHs, only benzophenanthrene (k) was not detected in the integrated waste water, while the content of benzophenanthrene (k) in the soil decreased gradually. Another compound which is detected in the integrated waste water and whose content in the soil decreased gradually is phenanthrene. According to the author, the decrease in the concentration of these pollutants was mainly resulted in by the absorption by reed or the seepage along with waste water into the underlayer of the soil and the absence of new pollutants. The analysis shows that, after one year's irrigation, the content of PAHs in the soil increased by 2.81 times, while the total amount of PAHs in the soil irrigated for two years increased only by 35.9% compared with that in the soil irrigated for one year. This means, although some PAHs might enter the wetland system continuously along with waste water, they won't cause a rapid accumulation of PAHs in the soil. The observational study on the growing condition of reed shows that, the output of reed increased continuously after the irrigation with the papermaking waste water. The reed's prosperous growth leads to its increasing ability of absorption and degradation of various pollutants. That's why the content of some PAHs decreased in the soil, for example, the content of fluorene and benzophenanthrene (b) in soil sample 2 is higher than that in sample 1, while the content of these two PAHs in sample 3 is lower than that in sample 2.

Researchers from home and abroad have studied the content and distribution of PAHs in the soil. The content of PAHs in the soil, which was under long-term fertilization with sludge ranges from 1.031 to 2.978 mg kg^{-1}. The content of PAHs in the urban soil of the city of Estonia ranges from 2.200 to 12.390 mg kg^{-1}, while PAHs content in the soil in rural area in Estonia ranges from 0.223-0.770 mg kg^{-1} (Trapido, 1999). Holland and Canada provided that the controlled value of total amount of PAHs in the unpolluted soil should be 1 mg kg^{-1} (CCME, 1991). From the Table 1 and 2, we can see that, the content of PAHs in the soil, whether irrigated with papermaking waste water or not, has far exceeded the total controlled value of PAHs in Holland and Canada. This shows the deterioration condition of the wetland environment and the potential environment risk caused by irrigating papermaking waste water.

CONCLUSIONS

- Different amount of PAHs was detected in the waste water discharged from all workshop sections from the straw alkaline pulping process. The concentration ranges from 12.83 to 16.83 μg L^{-1} and PAHs detected are mostly those with 2-3 rings.

- The irrigation of the seashore reed wetland with papermaking integrated waste water leads to a significant increase in PAHs content in the soil. PAHs content in unirrigated soil and in soil after 1 year's and 2 year's irrigation is 7.83, 22.04 and 29.96 mg kg^{-1} respectively. However, after the irrigation with the waste water, the output of reed increased dramatically, which made the amount of PAHs carried out of the ecological system increase accordingly due to the adsorption and assimilation effect.
- The content of PAHs in the seashore wetland soil of Yancheng exceeded the controlled value of total amount provided by our country, which shows the deterioration of environmental condition in the wetland soil of this area. So, the supervision on the waste water irrigation project should be strengthened, to prevent the harmful effect on local ecological environment caused by centralized discharge of toxic organic pollutants, such as PAHs, etc. and to the potential environment risk in this area.

REFERENCES

CCME., 1991. Canadian Council of Ministers of Environmental: Interim Canadian Environmental Qual[S]. Criteria for Contaminated Site. Report CCEM EPC-C Winnipeg, Manitobe, Canada, September.

Jocobs, L.W., G.A. O'Connor and M.R. Overcash, 1987. Effects of Trace Organics in Sewage Sludge on Soil-plant Systems and Assessing Their Risk to Humans [M]. In: Land Application of Sludge. Page, A.L., T.G. Logan and J.A. Ryan (Eds.). Lwewis Publisher, Chelsea, MI, pp: 101-143.

Julie, K. and Cronk, 1996. Constructed wetlands to treat waste water from dairy and swine operations: A review. Agric. Ecosys. Environ., 58: 97-114.

Trapido, 1999. Polycyclic aromatic hydrocarbons in estonian soil: Contamination and profiles. Environ. Pollut., 105: 67-74.

Whitney, D., A. Rossman and N. Hayden, 2003. Evaluating an existing subsurface flow constructed wetland in Akumal, Mexico. Ecol. Engo., 20: 105-111.