Status of Phthalate Ester Pollution in Danjiangkou Reservoir and Ecological Risk Assessment

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Abstract. Phthalate esters (PAEs) are one of the new pollutants widely used by human beings, which are widely present and not easy to be degraded, and have received much attention. In order to understand the concentration and pollution characteristics of PAEs in the water body of Danjiangkou Reservoir during the normal period, this paper analyzes the pollution characteristics, pollution level and risk of PAEs by 30 sampling points relying on the platform of Danjiangkou Reservoir water quality monitoring station network. The results showed that the concentration of PAEs in Danjiangkou Reservoir water body ΣPAEs ranged from 0 to 284.7 ng/L (mean value 96 ng/L), the overall concentration was low, which was dominated by DEHP and DBP, and its pollution level was extremely low, and there was no ecotoxicity risk to human health.

Keywords: Danjiangkou reservoir; PAEs; pollution characteristics; Ecological risk assessment

1 Introduction

Phthalates (PAEs) are a typical class of toxic organic pollutants, which are widely used as plasticizers (Simoneit et al., 2005[1]; Zhang et al., 2015[2]; Koniecki et al., 2011[3]; Benjamin et al., 2017[4]) and belong to the endocrine disruptors (VanWezel et al., 2000[5]; Xu et al., 2010[6]; Li et al., 2016[7]; Zhang et al., 2020[8]). Since PAEs molecules can be linked to polyolefin-based plastic molecules, they can easily migrate from the plastic to the external environment (Keizer-Schrama et al., 2006[9]). PAEs are ubiquitous and difficult to degrade, and they can accumulate in the water body (Bauer et al., 1997[10]). In recent years, the occurrence of PAEs in the water body, distribution and ecological risks have attracted widespread attention in recent years (Chen et al., 2019[11]; Liu et al., 2020[12]; Wang et al., 2021[13]).

Danjiangkou Reservoir, as the water source of the South-to-North Water Diversion Central Route Project, undertakes the water demand of four provinces and cities, namely Beijing, Tianjin, Hebei, and Henan, and is an important part of China's water

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resources strategic pattern. China's State Council issued the "Han River Ecological and Economic Belt Development Plan" pointed out that "accelerate the construction of ecological civilization, to create a beautiful Han River". However, there are few reports on the study of PAEs in the water body of Danjiangkou Reservoir, which is not conducive to the evaluation and protection of the water ecological environment of Danjiangkou Reservoir.

This paper systematically analyzes the concentration of PAEs in the water phase of Danjiangkou Reservoir during the normal period (June), reveals the pollution characteristics of PAEs in Danjiangkou Reservoir during the normal period at the present stage, and carries out the analysis of the pollution level and the assessment of the risk of pollution with a view to providing basic data and technical support for the effective control of PAEs in the Han River economic zone.

2 Materials and Methods

2.1 Layout of sampling points

According to the hydrological and water environment characteristics of Danjiangkou Reservoir and its inlet tributaries, relying on the platform of Danjiangkou Reservoir Area Water Quality Monitoring Station Network, 30 sampling points are deployed, among which 6 reservoir sampling points and 12 tributary sampling points are set up in Han Reservoir; and 8 reservoir sampling points and 4 tributary sampling points are set up in Dankou Reservoir, and the specific setup is as shown in Figure 1.

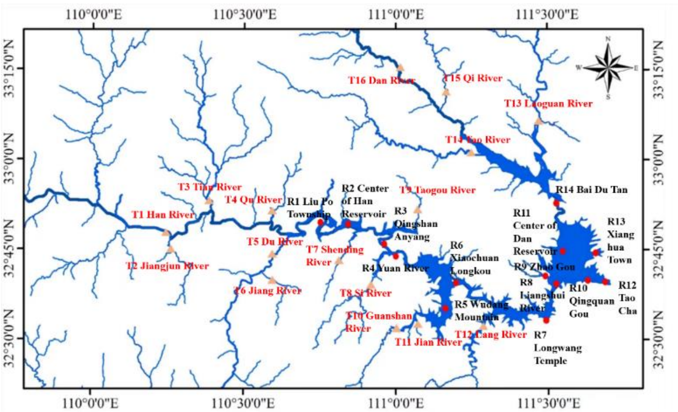

Fig. 1. Danjiangkou New Pollutant Survey Sampling Sites Layout Map

2.2 Organic pre-treatment process

After the solid-phase extraction membrane was brought back to the laboratory, 10 mL of ethyl acetate was added to the extraction membrane, and the eluent was allowed to come into contact with the extraction membrane for a period of time (about 3 min), and then the vacuum pump was turned on for a short period of time to allow the eluent to flow slowly into the receiving bottle through the solid-phase extraction device; 10 mL of ethyl acetate was added again to repeat the above steps; and then 10 mL of (1+1) methylene chloride-ethyl acetate eluent was added to the membrane to repeat the step 2 times. The eluate was dewatered with anhydrous sodium sulfate, concentrated and fixed, and analyzed on the machine.

3 Results and Discussions

3.1 Pollution Characterization

The minimum, maximum, mean, median and standard deviation of ΣPAEs concentrations in the water body during the normal period of Danjiangkou Reservoir in 2022 are shown in Table 1. Six kinds of PAEs in the water body, except BBP, DNOP was not detected, DMP, DEP, DBP, DEHP, all detected, the detection rate of 93.3%, 3.3%, 96.7% and 96.7% 0 sampling points were detected in PAEs, indicating that PAEs are widely present in the environment. The concentration of ΣPAEs in the Danjiangkou Reservoir water body during the normal period ranged from 1.0 to 284.7 ng/L (mean value 96.0 ng/L), which was significantly lower than that of the Jiangsu section of the Yangtze River in 2004-2005, which ranged from 178 to 1474 ng/L (mean value 902 ng/L) (He et al., 2011[14]). The content of ΣPAEs in the water body of Danjiangkou Reservoir during the normal period was significantly lower than significantly lower than that in the middle and lower reaches of the Yangtze River, and the pollution level was low.

Table 1. PAEs content in Danjiangkou Reservoir water body

Sampling site	sports event	concentration /ng/L
R1~R16 T1~T14	Min	0
	Max	284.7
	Mean	96
	Median	64.2
	SD	100

Figure 2 shows the concentrations of PAEs monomers in the water body during the nromal period of Danjiangkou Reservoir in 2022. The concentration ranges of DMP and DEP were 0-22.3 ng/L (mean 6.60 ng/L) and 0-10.7 ng/L (mean 0.37 ng/L), respectively, DBP and DEHP were the main pollutants in the water body, and the concentration ranges were 0~184 ng/L (mean 68.0 ng/L) and 0~161 ng/L (mean 21.0 ng/L). DBP and DEHP were the PAEs with the highest concentrations, which was consistent with the results of the 2005 study of the Wuhan section of the Yangtze River reported in the literature (Wang et al., 2008[15]).

Specifically, among the PAEs in the water bodies of Danjiangkou reservoir area, sampling points R7 (Longwangmiao on the dam) and R9 (Zhaogou) had high levels of ΣPAEs, with 284.7 ng/L and 277.7 ng/L, respectively.

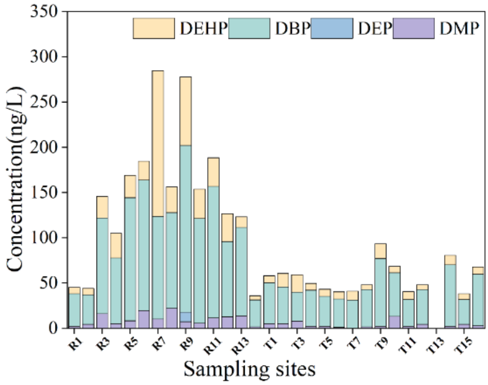

Fig. 2. Distribution of ΣPAEs in water bodies in June in sampling section of Danjiangkou reservoir

3.2 Analysis of pollution levels

The range of ΣPAEs in Danjiangkou Reservoir water was 0~284.7 ng/L, in which DMP, DEP, DBP, and DEHP were detected, with concentrations ranging from 0~22.3 ng/L, 0~10.7 ng/L, 0~184.0 ng/L, and 0~161.0 ng/L, respectively. As shown in Table 2, the ΣPAEs in the water body of Danjiangkou Reservoir during the normal period of 2022 were all lower than the relevant standards (China Surface Water Quality Standards (GB 3838-2002[16]), U.S. EPA National Water Quality Standards (USEPA2009[17]), and the National Water Quality Standards of the United States Environmental Protection Agency). water body ΣPAEs are lower than the limits specified in the relevant standards (China Surface Water Environmental Quality Standards (GB 3838-2002 Surface Water Environmental Quality Standards), U.S. Environmental Protection Agency National Water Quality Criteria (USEPA2009[17]), and the Canadian Code of Environmental Quality (CCME)[18].

Table 2. Water quality standards for PAEs in different countries 1)/ng/L

country	DMP	DEP	DBP	BBP	DEHP	renferences
China	—	—	3×10^3	—	8×10^3	GB 3838-2002 EQSSWR
America	2.7×10^8	1.7×10^7	2×10^6	1.5×10^6	1.2×10^3	USENPA (2009). NRWQC
Canada	—	—	1.9×10^4	—	1.6×10^4	CCME

"—" Indicates no data

Table 3 shows the comparison of the pollution status of PAEs in Danjiangkou Reservoir and other river water bodies at home and abroad. It can be concluded that the pollution level of PAEs in the water body of Danjiangkou Reservoir is lower than that in the Jiangsu section of the Yangtze River, the Yangtze River Delta, the middle and lower reaches of the Yellow River, and the Trent River of the United Kingdom, etc., in which the mean value of ΣPAEs in the Yangtze River Delta is about 283.5 times of that of the Danjiangkou Reservoir water body, and the mean value of ΣPAEs in the water body of Jiangsu section of the Yangtze River is about 56.4 times of that of the Danjiangkou Reservoir water body. Overall, the pollution level of ΣPAEs in the water body of Danjiangkou Reservoir during the normal period is also extremely low compared with other rivers at home and abroad.

Table 3. Pollution status of PAEs in water bodies and sediments of other rivers in China and abroad

position	Year	sample size	Number of PAEs	DBP	DEHP	Range of PAEs concentrations	Mean values of PAEs
River Trent, UK (Turner and Rawling, 2000[19])	1995-1996	6	—	—	740~18 000	—	—
Jiangsu section of the Yangtze River (He et al., 2011[14])	2004-2005	15	6	105~2 86	ND~83 6	178~1474	902
Yangtze River Delta (Zhang et al., 2012[20])	2010	13	6	ND~7 188	ND~28 403	61~28550	4536
the middle and lower reaches of the Yellow River (Sha et al., 2006[21])	2004	12	5	ND~2 6000	347~31 800	—	—
Taiwan River (Yuan et al., 2002[22])	2000	14	8	1000~ 13500	ND~18 500	—	—
Danjiangkou reservoir (this study)	2022	30	16	0~184	0~161	0~184	16

1) "—" means no data; ND means not detected

3.3 Pollution risk assessments

Environmental water quality benchmarks are the basis for setting limits for environmental quality standards for water bodies, and are important for predicting, evaluating, controlling and treating pollutants entering the water environment, and maintaining a good ecological environment. PAEs are enriched in aquatic organisms, such as fish and shellfish, through the food chain, and enter the human body through drinking water, skin contact, and consumption of fish or shellfish, which can have a potentially harmful effect on human health. The potential harmful effects on human health.

As shown in Table 4, based on toxicological data and numerical calculations, the U.S. EPA has developed human health water quality benchmarks for PAEs. The human health water quality benchmarks represent the maximum acceptable concentrations of contaminants that do not adversely affect humans through drinking water and consumption of aquatic organisms or only through consumption of aquatic organisms. Referring to the water quality benchmarks, from which the range of DMP, DEP, DBP, and DEHP concentrations in the Danjiangkou Reservoir water body during the 2022 normal period are 0 to 22.3 ng/L (mean value 6.6 ng/L), 0 to 10.7 ng/L (mean value 0.4 ng/L), 0 to 184.0 ng/L (mean value 68.0 ng/L), 0 to 161 ng/L (mean value 21.0 ng/L), which are all significantly lower than the human health water quality benchmarks and pose negligible health risks to humans.

Table 4. U.S. EPA human health water quality benchmarks for PAEs /μg/L

PAEs	Human Health Water Quality Benchmark Drinking water + consumption of aquatic organisms	 Edible aquatic organisms	Mass concentration in this study (normal period) $\times 10^{-3}$
DMP	2000	2000	0~22.3（Mean 6.6）
DEP	600	600	0~10.7（Mean 0.4）
DBP	20	30	0~184（Mean 68）
BBP	0.10	0.10	ND
DEHP	0.32	0.37	0~161（Mean 21）
DNOP	—	—	ND

"—" means no data

3.4 Human Health Risk Assessment Model

Environmental risk evaluation models generally target chemical carcinogens, non-chemical carcinogens and radioactive substances, and are mostly applied to the first 2 types of substances in the health risk evaluation of drinking water sources. In this paper, the health risk evaluation model recommended by USEPA was used to evaluate the risk of PAEs in Danjiangkou Reservoir to human health through the drinking water exposure pathway by selecting four PAEs (DBP, DEHP, DMP and DEP) occurring in the study area. The carcinogenic risk of DEHP and the non-carcinogenic risk of DBP, DMP, and DEP were evaluated in this paper based on existing studies (He et al., 2013[23]) and the classification of carcinogenicity of chemical substances by the International Agency for Research on Cancer (IARC). The formula for non-carcinogenic risk (HI) is as follows:

$$HI = \frac{CDI}{RfD} \quad (1)$$

Where: CDI is the chronic daily intake dose, mg/(kg·d); RfD is the reference dose of the pollutant, mg/(kg·d).

The non-carcinogenic risk (R) is defined as the product of the chronic daily intake dose and the carcinogenicity slope factor, which indicates the lifetime cancer incidence rate above the normal level resulting from exposure to the substance, and is calculated as follows:

$$R = S_F \cdot CDI \quad (2)$$

Where: S_F is the carcinogenicity slope factor of the pollutant, (kg·d)/mg. When R > 0.01, the formula is replaced by equation (3).

$$R = 1 - exp^{(-S_F \cdot CDI)} \tag{3}$$

The long-term daily intake dose (CDI) for the drinking water route was calculated using the formula used by the U.S. EPA:

$$CDI = \frac{C \cdot U \cdot EF \cdot ED}{BW \cdot AT} \tag{4}$$

Where C is the mass concentration of chemical substances in water (mg/L); U is the daily amount of drinking water (L/d); EF is the exposure frequency (d/a); ED is the exposure delay (a); BW is the average body weight (kg); AT is the average exposure time (d), and the formula for the calculation of non-carcinogens is ED × 365 d/a, and that for carcinogens is 70 a × 365 d/a. The mass concentration C of chemical substances in water was calculated by taking the maximum value (max) of the sampling area.

According to the Manual of Exposure Parameters for the Chinese Population (Adult Volume) (MEP)[24] and related literature (Zhang et al., 2007[25]), the parameters were taken as follows: daily drinking water volume U was 1.625 L/d (Hubei Province); exposure frequency (EF) was 365 d/a; exposure delay (ED) was 30 a for non-carcinogens, and 70 a for carcinogens; the average body mass (BW) was 60.1 kg (Hubei Province); the average exposure time (AD) was 70 a × 365 d/a; and the mean body mass (BW) was 60.1 kg (Hubei Province). The average exposure time (AT) was 30 a (i.e., 10,950 d) for noncarcinogens and 70 a (i.e., 25,550 d) for carcinogens; S_F was taken as 0.014 (kg·d)/mg for DEHP, and the RfDs were 0.1, 0.8, 10 and 0.02 mg/(kg·d) for DBP, DEP, DMP and DEHP.

According to the USEPA definition, for non-carcinogenic risks, when the risk value is less than 1, the risk is acceptable; when the risk value is greater than 1, the risk is considered unacceptable. Studies have shown that when the carcinogenic risk is less than 10^{-6}, the risk is negligible; when the carcinogenic risk is between 10^{-6} and 10^{-4}, there is a potential risk to humans; and when the carcinogenic risk is higher than 10^{-4}, there is an unacceptable risk to humans (Chang et al., 2019[26]). Calculations showed that the carcinogenic risk of DEHP was 6.09×10^{-8}, and its carcinogenic risk to human health was negligible. The non-carcinogenic risks of DBP, DMP, and DEP were 4.98×10^{-5}, 6.30×10^{-8}, and 3.62×10^{-7}, respectively, which were all much lower than 1, suggesting that the PAEs in the water bodies of the Danjiangkou do not pose any obvious non-carcinogenic health hazards to human beings.

4 Conclusion

This paper systematically studied the concentration characteristics, main sources and pollution levels of PAEs in the water body of Danjiangkou Reservoir during the normal period in 2022, and the main conclusions are as follows:

(1) The concentration of PAEs in Danjiangkou Reservoir water body ΣPAEs ranged from 0 to 284.7 ng/L (mean value 96 ng/L), and the overall concentration was low;

(2) PAEs in Danjiangkou Reservoir water bodies were dominated by DEHP and DBP, and their pollution levels were extremely low, and there is no ecotoxicity risk to human health.

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References

1. Simoneit B R, Medeiros P M, Didyk B M. Combustion products of plastics as indicators for refuse burning in the atmosphere. Environmental Science & Technology, 39(18): 6961-6970 (2005).
2. Zhang L, Liu J, Liu H, Wan G, S Zhang. The occurrence and ecological risk assessment of phthalate esters (PAEs) in urban aquatic environments of China[J]. Ecotoxicology, 24 (5):967–984(2015).
3. Koniecki D, Rong W, Moody R P, Zhu J. Phthalates in cosmetic and personal care products: Concentrations and possible dermal exposure[J]. Environmental Research, 111 (3): 329-336(2011).
4. Benjamin S, Masai E, Kamimura N, Takahashi K, Anderson R.C, Faisal P.A. Phthalates impact human health: Epidemiological evidences and plausible mechanism of action[J]. Journal of Hazardous Materials 340, 360–383(2017).
5. VanWezel A P, Van Vlaardingen P, Posthumus R,Crommentuijn G H, Sijm D T H M. Environmental risk limits for two phthalates, with special emphasis on endocrine disruptive properties[J]. Ecotoxicology and Environmental Safety, 46(3):305-321(2000).
6. Xu Z, Zhang W, Lv L, Pan B, Lan P, Zhang Q. A new approach to catalytic degradation of dimethyl phthlate by a macroporous OH-type strongly basic anion exchange resin[J]. Environmental Science & Technology, 44 (8): 3130–3135(2010).
7. Li B, Liu R X, Gao H J, Tan R J, Zeng P, Song Y H. Spatial distribution and ecological risk assessment of phthalic acid esters and phenols in surface sediment from urban rivers in Northeast China[J]. Environmental Pollution, 219: 409-415(2016).
8. Zhang W Z, Zheng X W, Gu P, Wang N, Lai Z N, He J, Zheng Z. Distribution and risk assessment of phthalates in water and sediment of the Pearl River Delta. Environmental Science and Pollution Research. 27, 12550–12565(2020).
9. Keizer-Schrama S D, Main K M, Swan S, Foster P, Jensen A A. Possible impact of phthalates on infant reproductive health - discussion. International Journal of Andrology. 29(1):180-180(2006).
10. Bauer M J, Herrmann R. Estimation of the environmental contamination by phthalic acid esters leaching from household wastes[J]. Science of the Total Environment, 208(1-2):49-57 (1997).

11. Chen H, Mao W, Shen Y, Feng W, Mao G, Zhao T, Yang L Q, Yang L Q, Meng C, Li Y, Wu X. Distribution, source, and environmental risk assessment of phthalate esters (PAEs) in water, suspended particulate matter, and sediment of a typical Yangtze River Delta City, China. Environmental Science and Pollution Research, 26, 24609–24619(2019).
12. Liu Y, He Y, Zhang J, Cai C, Breider F, Tao S, Liu W. Distribution, partitioning behavior, and ecological risk assessment of phthalate esters in sediment particle-pore water systems from the main stream of the Haihe River, Northern China[J]. Science of The Total Environment 745, 141131(2020).
13. L Y, Gu Y Y, Zhang Z M, Sun A L, Shi X Z, Chen J, Lu Y. Contaminant occurrence, mobility and ecological risk assessment of phthalate esters in the sediment-water system of the Hangzhou Bay[J]. Science of The Total Environment 770, 144705 (2021).
14. He H, Hu G J, Sun C, Chen S L, Yang M N, Li J, Zhao Y, Wang H. Trace analysis of persistent toxic substances in the main stream of Jiangsu section of the Yangtze River, China[J]. Environmental Science and Pollution Research, 18(4): 638–648(2011).
15. Wang F, Xia X, Sha Y. Distribution of Phthalic Acid Esters in Wuhan section of the Yangtze River, China[J]. Journal of Hazardous Materials, 154(1-3): 317–324.
16. GB 3838-2002 Environmental quality standards for surface water (GB 3838-2002 EQSSW) [S] (2008).
17. US Environmental Protection Agency. National recommended water quality criteria (USEPA 2009) [S].
18. Canadian Council of Ministers of the Environment (CCME). Canadian environmental quality guidelines (CCME CEQG) [S].
19. Turner A, Rawling M.C. The behaviour of di-(2-ethylhexyl) phthalate in estuaries. Marine Chemistry 68, 203–217(2000).
20. Zhang L F, Dong L, Ren L J, Shi S X, Zhou L. Concentration and source identification of polycyclic aromatic hydrocarbons and phthalic acid esters in the surface water of the Yangtze River Delta, China[J]. Journal of Environmental Sciences, 24 (2): 335-342 (2012).
21. Sha Y J, Xia X H, Xiao X Q. Distribution characters of phthalic acid ester in the waters middle and lower reaches of the Yellow River[J]. China Environmental Science, 26(1): 120-124(2006).
22. Yuan S Y, Liu C, Liao C S, Chang, B. V. Chang. Occurrence and microbial degradation of phthalate esters in Taiwan river sediments[J]. Chemosphere, 49(10): 1295-1299(2002).
23. He W, Qin N, Kong X Z, Liu W X, He Q S, Ouyang H L, Yang C, Jiang Y J, Wang Q M, Yang B, Xu F L. Spatio-temporal distributions and the ecological and health risks of phthalate esters (PAEs) in the surface water of a large shallow Chinese Lake [J]. Science of the Total Environment, 461-462:672-680 (2013).
24. Ministry of Environmental Protection of the People's Republic of China. Exposure Factors Handbook of Chinese Population (Adults)[M]. Beijing: China Environmental Science Pres (2013).
25. Zhang Y Y, Feng L, Liu Z T. Health Risk Assessment on Semivolatile Organic Compounds in Water of Yangtze Estuary Area[J]. Research of Environmental Sciences, 20 (1):18-23 (2007). (In Chinese)
26. Chang S, Fan Y T, Fu Q, Han X Y, Zhao S Y, Wang S J, Yang G. Distribution Characteristics and Risk Assessment of Phthalic Acid Esters in Surface Water and Sediment of Qingyuan Section of Beijiang River[J]. Ecology and Environmental Sciences, 28(4):822-830(2019). (In Chinese)