Determination and Analysis of Different Environmental Media and Supervision and Phthalate Content in Management Countermeasures

Linlin Du, Xingsan Li[*], Yanbo Qi, Mingxia Wang
School of Public Health, Qiqihar Medical University, Qiqihar, Heilongjiang, China
*Corresponding Author.

Abstract: By measuring the content of phthalate esters in different environmental media, this study analyzes the pollution situation in the region and provides scientific basis for putting forward targeted supervision and management countermeasures. 39 water samples and 36 soil samples from Jianhua district, Longsha and Tiefeng districts of Qiqihar City were taken as the research objects. The contents of six PAEs metabolites DEP, DBP, DEHP, DNOP, DMP and BBP were determined by gas chromatography. The results were expressed in median and quartile, and were statistically analyzed by Wilcoxon rank sum test. The test level was $\alpha=0.05$. The results showed that three compounds DEP, DEHP and DBP were detected in clean area and four compounds DEP, DEHP, DBP and DMP were detected in polluted area. The detection content of PAEs in polluted area is different from that in clean area, and the pollution area is higher than that in clean area, with statistical significance ($P < 0.05$). Among the six PAEs to be detected in soil, five compounds DEP, DEHP, DBP, DMP and BBP were detected in polluted area and clean area. The detection content of PAEs in soil in polluted area is different from that in clean area, and the pollution area is higher than that in clean area, with statistical significance ($P<0.05$). The difference of phthalate esters in different environmental media shows that it is urgent to further strengthen the supervision and management of environmental pollutants and effectively reduce the emission and use of phthalate esters to maintain environmental quality and public health.

Keywords: Environmental Media; Phthalates; Difference Analysis; Supervision and Management;

Countermeasures.

1. Introduction

The wide application of Phthalic Acid Esters (PAEs) as synthetic plasticizers in plastic products has become an important part of modern industry, and its global annual demand exceeds 8.2 million tons [1]. However, the widespread use of PAEs also comes with potential environmental and health risks. Due to its endocrine disrupting and carcinogenic effects, PAEs has attracted widespread attention, which is not only the focus of the scientific community, but also involves the global environmental protection and public health concerns [2]. The risk of PAEs is due to their relatively weak interaction with plastic products, which makes them easy to release from plastic products, and then enter the ecosystem and ultimately affect human health [3]. Air, water and food may be the transmission media of PAEs, so we need to pay attention to the pollution of PAEs in different environmental media. In recent years, remarkable progress has been made in the study of PAEs in the environment, including in-depth understanding of their distribution, migration and biotransformation in nature [4,5]. These studies not only deepen our understanding of the PAEs pollution problem, but also provide strong support for us to develop more effective environmental monitoring and control measures. However, the monitoring and control of PAEs pollution still face challenges, therefore, the development and enforcement of relevant regulations and standards need to be further strengthened to ensure comprehensive and effective monitoring and control.

In order to explore the residue level and pollution characteristics of environmental phthalates, this study determined and analyzed the content of PAEs in different environmental

media, thus providing a scientific basis for environmental ecological risk assessment and targeted supervision and management countermeasures, and providing a solid scientific basis for environmental ecological risk assessment. By measuring and analyzing the content of PAEs in different environmental media, the potential environmental and health risks can be more accurately understood, which will help to better understand and respond to the PAEs pollution problem, provide key information for future environmental protection and sustainable development, better protect the environment and promote public health.

2. Materials and Methods

2.1 Experimental Materials
2.1.1 Experimental reagents
6 kinds of phthalate mixed standard solution (DEHP, BBP, DEP, DMP, DBP, DNOP) standard. Decca Experimental Technology (Product No. : CDGG-110031-04-1ml), n-hexane; Ethyl acetate (chromatographically pure); High purity nitrogen, purity 99.999%.
2.1.2 Instruments and equipment
Gas Chromatograph (Model 7890), Agilent Technology Co., LTD. BYDCY-12SL Water bath nitrogen blowing Instrument, Shanghai Bingyue Electronic Instrument Co., LTD. LDZ5-2 Low speed automatic centrifuge, Beijing Medical Centrifuge Factory; Empty box barometer, Changchun meteorological instrument table; FC-3A double-head dust sampler, Wuhan Analytical Instrument Factory; 40mm glass fiber microporous filter membrane, Haining Yanguanfit Filter equipment Factory; Pipette; Rotary evaporator; Electronic balance; Centrifugal tube; Muffle furnace; Sample concentrator.
2.1.3 Sample selection
According to the administrative division, three areas of Jianhua, Longsha and Tiefeng in Qiqihar City are taken as the research objects. The area within 1Km around the plastic processing plant was selected as the pollution area, and the residential area or park area away from the plastic processing plant was selected as the cleaning control area. Three different environmental samples of water and soil in polluted area and control area were taken respectively. A total of 39 water samples were collected, the sampling depth of surface water

was 15cm, and the sampling volume was not less than 500ml. A total of 36 soil samples were collected, the sampling depth was 15cm, and the sampling volume was not less than 200g.

2.2 Research Methods
2.2.1 Sample treatment
Pretreatment of water samples: HCl or NaOH is used to adjust the pH of the collected samples to about 7.0, shake well, filter to remove impurities, and then conduct the following pretreatment. Add 200ml water sample into 500ml liquid separator funnel, add 5gNaCl into it successively, and oscillate evenly, add $CH_2Cl_2$10ml, and oscillate for 5min, pay attention to releasing all the gas inside during oscillation. After a period of time when clear limits appear, dry with anhydrous Na_2SO_4 before placing in the nitrogen blowpipe, and extract again according to the above steps. The organic phase is retained, the separation funnel and anhydrous Na_2SO_4 are cleaned with a small amount of CH_2Cl_2. The dried extract was concentrated to less than 1ml with a sample concentrator and diluted to 1ml with CH_2Cl_2, to be measured.
Pre-treatment of soil samples: remove impurities such as stones and roots in the soil, air dry for 24h, grind fully, and pass 80 screens. Accurately weigh 50g sample, add 100ml n-hexane, stir the sample evenly, put it in a constant temperature water bath, adjust the temperature to 20℃, ultrasonic extraction for 1h, and soak for half a day. When refining, it was filtered by anhydrous sodium sulfate and concentrated to 1ml by sample concentrator, to be measured.
2.2.2 Conditions of gas chromatography
Column: DB-23, manufactured by Agilent Technology Co., LTD., column length 60m, inner diameter 0.25mm, inner membrane thickness 0.25m; Gasification chamber temperature 250℃, FID detector temperature 280℃; The carrier gas was nitrogen, and the nitrogen flow rate was 1.2ml/min. Hydrogen flow rate: 30ml/min; Air flow rate: 350ml/min; Tail blow 20ml/min; The temperature of the column box was initially 50℃, kept for 1min, then increased to 175℃ at 25℃/min, immediately increased to 250℃ at 5℃/min, and kept for 8min. Gasification temperature 260℃; The injection volume is 1.00l, no shunt injection is set.

2.2.3 Measuring indicators
The measuring indicators as shown in Table 1.

Table 1. Measuring indicators

Name	Abbreviation
Di(2-ethylhexyl) phthalate	DEHP
Dimethyl phthalate	DMP
Diethyl phthalate	DEP
Dibutyl phthalate	DBP
Benzyl butyl phthalate	BBP
Di-n-octyl phthalate	DNOP

2.2.4 Statistical method
Median and quartile were used for statistical description of the analysis variables, and Wilcoxon rank sum test was used for statistical analysis, the test level $\alpha=0.05$.

3. Results

3.1 Results of PAEs Determination in Water
Among the six PAEs to be measured in water, three compounds DEP, DEHP and DBP were detected in the clean area, and four compounds DEP, DEHP, DBP and DMP were detected in the polluted area. The detected content of PAEs in the polluted area was different from that in the clean area, and the detected content in the polluted area was higher than that in the clean area, with statistical significance ($P < 0.05$). The results are shown in Table 2.

Table 2. Comparison of water bodies in clean and polluted areas (g/L)

PAEs	Clean areas N=33		Contaminated areas N=6		Z	P
	M	$Q_L \sim Q_U$	M	$Q_L \sim Q_U$		
DEP	0.54	0.37~0.57	1.36	1.26~1.51	8.53	0.004*
DEHP	0.98	0.82~1.51	4.78	3.96~5.04	9.46	0.002*
DBP	0.61	0.36~0.89	8.96	7.68~9.83	9.94	0.002*
DMP	—	—	1.82	1.06~2.57	—	—
DNOP	—	—	—	—	—	—
BBP	—	—	—	—	—	—

Note: - Indicates that it is not detected. * indicates $P < 0.05$, and the difference is statistically significant.

3.2 Results of PAEs Determination in Soil
Of the six PAEs to be measured in soil, five compounds DEP, DEHP, DBP, DMP and BBP were detected in contaminated and clean areas. The detected content of PAEs in soil in the polluted area was different from that in the clean area, and the detected content in the polluted area was higher than that in the clean area, with statistical significance ($P < 0.05$). The results are shown in Table 3.

Table 3. Comparison of soil in clean and contaminated areas (mg/kg)

PAEs	Clean areas N=30		Contaminated areas N=6		Z	P
	M	$Q_L \sim Q_U$	M	$Q_L \sim Q_U$		
DEP	0.27	0.19~0.36	0.51	0.42~0.61	6.94	0.008*
DEHP	0.79	0.58~1.17	1.29	1.10~1.40	4.60	0.032*
DBP	0.39	0.30~0.46	0.57	0.48~0.66	4.08	0.043*
DMP	0.09	0.06~0.13	0.83	0.51~0.87	12.18	<0.001*
DNOP	—	—	—	—	—	—
BBP	0.23	0.16~0.31	0.71	0.65~0.85	7.89	0.005*

Note: - Indicates that it is not detected. * indicates $P < 0.05$, and the difference is statistically significant.

4. Discussion

4.1 Quality Control
In order to ensure the accuracy and reliability of the measurement results, sample collection, storage and quality assurance measures refer to the Practical Manual of Environmental Monitoring Method Standards [6]. Phthalate contamination of instruments and reagents was strictly avoided during the test process. All glass instruments should be immersed in K_2CrO_4/H_2SO_4 solution and washed with NaOH, acetone and ultra-pure water before use. After cleaning, use the Muffle oven to bake for half a day, adjust the temperature to 400℃, remove the temperature, and the indoor temperature, sealed with tin foil for use. Ensure samples are tested in a timely manner, within seven days. Using ultra-pure water as blank control, the random error was controlled by parallel bidirectional measurement, and the recovery rate was calculated to ensure the accuracy and reliability of the measurement results. The recovery rate of standard addition in this study is controlled at 90%-110%, which meets the requirements.

4.2 Analysis of the Results of PAEs Determination in Water
Referring to China's Surface Water Environmental Quality Standard (GB3838-2002), the limit values of DEHP and DBP are 8g/L and 3g/L, respectively [7]. The test

results show that DEHP and DBP in the clean area are not exceeding the standard. The result of DEHP in the contaminated area did not exceed the standard, but the result of DBP exceeded the limit standard. Although the reference limit standard of PAEs is still not perfect, a statistically significant difference has been reached based on the determination results of the current clean area and polluted area, which suggests that environmental health workers should pay attention to the problem of PAEs pollution in order to obtain more scientific data and provide scientific basis for further supplementing and improving environmental quality standards. Yasser V et al. conducted a global meta-analysis of phthalates and associated health risks in drinking water sources from January 1, 1976 to April 30, 2021, which included 109 articles, 4,061 samples, 4 water types, and 27 countries. Among all types of water sources, river water and lake water are the most seriously polluted by PAEs. The most seriously polluted water source is Nigeria, while the least polluted water source is China [8]. Wang Manli et al. evaluated the level and risk of phthalate content in the surface water of Bosten Lake in China, and the research results showed that the content of ∑PAEs in the water body during dry season and flood season was ND-26.226g/L and ND-7.179g/L, respectively, and the PAEs in the water mainly came from domestic pollution and chemical production [9]. Zhu Qingqing et al. analyzed 9 kinds of phthalates (PAEs) in 96 water, soil and sediment samples collected from 32 sampling sites in the Yangtze River Delta region. Among the 9 PAEs, DBP is the most important homologous of PAE in water, accounting for 50.6% of ∑9PAE, which is consistent with the results of this study [10].

4.3 Analysis of PAEs Determination Results in Soil

In our country, the relevant standard and reference literature about PAEs are limited. For example, the soil Environmental quality construction land soil pollution risk control standards: The screening value and control value of soil pollutants in the secondary land use of GB 36600-2018 are as follows: the screening value of DEHP is 121 mg/kg and the control value is 1 210 mg/kg, and the screening value of DNOP is 2 812 mg/kg and the control value is 5 700mg/kg[11]. The Technical Guidelines for Risk Assessment of Soil Pollution for Construction Land: HJ 25.3-2019, launched in 2019, currently only includes DEHP, DEP, DBP, BBP and DNOP pollutants and lacks some toxicity parameter data for risk assessment, which cannot complete the calculation of risk assessment [12]. This study also referred to the U.S. Environmental Protection Agency (EPA)'s control and management standards for PAEs compounds in soil. The control standards for DEP, DEHP, DBP, DMP, BBP and DNOP were 0.071, 4.350, 0.081, 0.020, 1.215 and 1.200mg/kg, respectively. The recommended soil management indexes are 7.100, 50.000, 8.100, 2.000, 50.000 and 50.0mg/kg, respectively [13]. Comprehensive analysis showed that the contents of 6 kinds of phthalates in the soil of pollutants and clean areas in this study were all within the recommended soil treatment standards. Although this study did not find significant soil pollution, the situation is not optimistic compared with other cities. For example, in the analysis of the content and composition of phthalates (PAEs) in the surface soil of Xi'an city, Zhang Wenjuan et al. showed that The concentrations of DMP, DEP, DBP, BBP, DNOP and DEHP in Xi 'an urban soil were 0.188, 0.187, 4.174, 0.091, 0.188 and 6.122mg/kg, respectively [14]. According to the characteristics and risk assessment of phthalate pollution in the soil of northeastern Shenyang, the concentrations of DMP, DEP, DBP, BBP, DNOP and DEHP in Shenyang urban soil were 0.105, 0.177, 0.157, 0.035, 0.003 and 0.175mg/kg, respectively. PAEs mainly comes from industrial pollution, transportation and human activities. As time goes by, pollution will accumulate continuously, and the soil pollution degree of PAEs will gradually deepen, and active control measures should be taken to avoid the potential harm caused by PAES [15].

4.4 Limitations of the Study

Limited by the experimental conditions, the national standard method was not selected for sample determination in the study design process, but in the process of this experiment, the researchers ensured the accuracy and reliability of the results through laboratory quality control. In sample collection, although it is a small sample study, the sampling points are evenly distributed in the clean area and the

polluted area, which is representative. In terms of data analysis, this study adopts non-parametric statistical analysis method to deal with the uncertainty of data distribution. In short, the results of this study can represent the PAEs levels in polluted areas and clean areas to a certain extent, and can provide references for regional environmental governance.

4.5 Monitoring and Management Countermeasures

Environmental health is an important issue related to people's healthy life, and environmental health monitoring plays an important role in maintaining public health security [16]. In the context of China's continuous promotion of ecological undertakings and building a beautiful China, it has become the consensus of all walks of life to combine economic and social development with environmental protection [17]. Taking into account the problem of phthalate (PAEs) pollution in water and soil environments, as well as the potential environmental hazards and health risks, the following recommendations are made. First, establish a comprehensive regulatory framework to cover PAEs pollution in the water environment and soil environment. This includes the development and implementation of regulations, standards and policies to ensure effective regulation of emissions and use of PAEs. The regulatory framework should cover multiple aspects such as monitoring, risk assessment, emission control, soil remediation and public engagement to achieve comprehensive governance. Second, surveillance and data collection should be further strengthened. A comprehensive monitoring network covering water bodies and soils, as well as potential sources of PAEs, is recommended. Monitoring data should be collected and reported in a timely and accurate manner to better understand the spatial and temporal distribution of pollution. These data will provide a basis for developing effective countermeasures. Third, do a good job in risk assessment and management. Conduct risk assessments to identify potential threats to the environment and human health from PAEs. Based on the assessment results, a risk management plan is developed, including limiting PAEs use, reducing emissions, soil remediation and health risk reduction strategies.

Fourth, promote the development of environmental protection technologies and innovative research and development of green alternatives. Encourage enterprises to adopt environmentally friendly production technologies to reduce PAEs emissions. Governments can provide incentives to encourage innovation and the development of green alternatives to reduce reliance on PAEs. Fifth, promote public education and social participation. Conduct extensive public education campaigns to raise awareness of the PAEs pollution problem and motivate the public to take environmental action. At the same time, the public is encouraged to participate in monitoring and reporting potential pollution sources to strengthen social supervision. Sixth, we need to strengthen environmental restoration and protection. To repair the environment polluted by PAEs, and establish appropriate quality standards to ensure that the content of PAEs in environmental media is within an acceptable range, and promote environmental sustainable development. Seventh, cross-departmental cooperation. Departments work closely together to share information and resources to ensure coordinated implementation of regulatory and management measures. Intersectoral cooperation is the key to solving the PAEs pollution problem. Eighth, policy update and implementation. Regularly assess and update regulatory policies and measures to adapt to the changing environmental pollution situation. Strengthen policy implementation and supervision to ensure the effectiveness of measures. Ninth, scientific research and technological innovation. Support research institutions and industries to carry out PAEs pollution-related research and promote the innovation and development of environmental protection technologies. Scientific research will support the development of more precise countermeasures. Tenth, strengthen international cooperation. Share experiences and best practices to tackle PAEs pollution around the world. These comprehensive guidelines and recommendations are designed to assist governments at all levels, enterprises and all sectors of society to jointly address PAEs pollution in water and soil environments to safeguard environmental quality and public health.

5. Conclusion

To sum up, dealing with PAEs pollution requires the joint efforts of the government, enterprises, scientific research institutions and the public. Call on the public to work together to reduce PAEs emissions and exposure in order to protect environmental quality and public health. The government should formulate more stringent laws, regulations and standards to restrict the production and use of PAEs. Enterprises should strengthen technological innovation and research and development, find more environmentally friendly and healthy alternatives, and gradually reduce the dependence on PAEs. At the same time, a sound environmental management system should be established to strictly control the production and use process of PAEs to prevent environmental pollution. Enterprises should assume more social responsibilities, actively participate in the cause of environmental protection, and make contributions to sustainable development and environmental protection. Scientific research institutions need to continue to deeply study the pollution mechanism and harm of PAEs, and provide support for the formulation of more scientific and effective policies and measures. In addition, publicity and education should be strengthened to improve the public's awareness of and attention to PAEs pollution, and guide the public to form healthy consumption concepts and behavior habits. In conclusion, this study provides an important scientific basis for formulating relevant policies and measures in the future, and reminds health workers that there is still much work to be done in sustainable development and environmental protection.

References
[1] WANG L X. Research on protection of in-situ phthalate pollution. Shandong Agricultural University, 2008. (in Chinese)
[2] LAN Minyi, Li Huiru, Hu Lixin et al. Environmental pollution of plastic food packaging materials. Chinese Journal of Ecotoxicology, 2019, 16(05):186-210. (in Chinese)
[3] Yang Xiaohui, Zhu Jiashu, Zhang Pengju. Detection and migration of phthalate plasticizers in food contact materials. Journal of Shaanxi University of Science and Technology, 2022, 40(06):49-54.
[4] ZHANG Yue, Yuan Qi, Jiang Mei et al. Research progress on toxicity of phthalates and detection methods. Environmental Chemistry, 2019, 38(05):1035-1046. (in Chinese)
[5] Wang M Z. Study on the detection and migration of phthalate plasticizers in beverage plastic packaging materials. Ningbo University, 2022.
[6] China Environmental Monitoring Station. Practical Manual of Environmental Monitoring method standards. Beijing: China Environmental Science Press, 2013.
[7] GB 3838-2002, Environmental Quality Standards for surface water, Ministry of Ecology and Environment of the People's Republic of China, 2002.
[8] Vasseghian Y, Alimohamadi M, Dragoi EN, et al. A global meta-analysis of phthalate esters in drinking water sources and associated health risks. Sci Total Environ. 2023 Sep 9; 903:166846.
[9] Wang M, Su Y, Lu J, et al. Content level and risk assessment of phthalate esters in surface water of Bosten Lake, China. Environ Sci Pollut Res Int. 2023 Jun; 30(30):74991-75001. doi: 10.1007/s11356-023-27627-5.Epub 2023 May 20.
[10] Zhu Q, Xu L, Wang W, et al. Occurrence, spatial distribution and ecological risk assessment of phthalate esters in water, soil and sediment from Yangtze River Delta, China. Sci Total Environ. 2022 Feb 1; 806(Pt 4):150966.
[11] GB 36600-2018, Soil Environmental quality construction land soil pollution risk control standard, Ministry of Ecology and Environment of the People's Republic of China, 2018.
[12] HJ 25.3-2019, Technical Guidelines for Soil Pollution Risk Assessment of Construction Land, Ministry of Ecology and Environment of the People's Republic of China, 2019.
[13] Dai Huaxin, Zhang Yanling, Li Liang et al. Analysis of pollution characteristics of 6 phthalates in tobacco-growing soil in

Henan Province. Chinese Journal of Tobacco, 201, 27(03):56-64. (in Chinese)

[14] Zhang Wenjuan, Wang Lijun, Su Shaolin et al. Content and composition of phthalates (PAEs) in surface soil of Xi 'an. Environmental Monitoring Management and Technology, 2019, 32(02):37-41. (in Chinese)

[15] Liu J. Pollution characteristics and risk assessment of phthalates in soil of northeastern Shenyang City. Shenyang University, 2020.

[16] CAI Changzhi. Analysis on the role of environmental health monitoring in disease prevention and control. China Health Industry, 2019, 16(13):162-163. (in Chinese)

[17] Wang Jin-Yuan, Chen Yi-Fan. Research on the construction of environmental finance index system of domestic heavy polluting enterprises. Environmental Engineering, 2022, 40(01):295.