

Analysis of PAEs contaminants in water sources for agriculture, industrial and residential areas from local city district

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Abstract. The technology of DEHP and DBP detection by high performance liquid chromatography coupled with ultraviolet detection (HPLC-UV) was developed and applied in analysis of local water sources from agriculture, industrial and residential areas. Under the optimized sample pretreatment and detection conditions, DEHP and DBP were well separated and detected in 4 mins. The detection limit of DBP was 0.002 mg/L and DEHP was 0.006 mg/L, and it meets the Chinese National Standard limitations for drinking water quality. The linear correlation coefficient of DBP and DEHP standard calibration curves was 0.9998 and 0.9995. The linear range of DBP was 0.020 mg/L ~20.0 mg/L, with the standard deviation of 0.560% ~5.07%, and the linear range of DEHP was 0.060 mg/L ~15.0 mg/L, with the standard deviation of 0.546% ~5.74%. Ten water samples from Jinwan district of Zhuhai in Guangdong province of China were analyzed. However, the PAEs amounts found in the water sources from industrial areas were higher than the agriculture and residential areas, industries grow incredibly fast in the district in recently years and more attention should be paid to the increasing risks of water sources pollution.

1. Introduction

Nowadays, the water pollution is a worldwide problem, and nearly 2 billion people drink contaminated water that could be harmful to their health on the earth. The role of water as a potential source of hazards should not be overlooked. There will be many polluted problems caused from industrial discharging, agriculture waste and house building etc., such as volatile organic compounds (VOCs), heavy metals, pesticides residues, phthalic acid esters (PAEs) and other contaminants. However, the production of PAEs is estimated at six million tons per year, phthalates may cause a potential threat to human health [1, 2]. Plenty of epidemiological and toxicological studies have proved that are endocrine disrupting compounds [3, 4], which will effect on metabolism [5-7], reproductive system [8-11] and even intelligence and behavior of children [12-14]. PAEs are released to the environment from multiple sources including industrial releases, the disposal of manufacturing, municipal solid waste, land application of sewage sludge, and release from products containing PAEs. Eight PAEs compounds, including the dibutyl phthalate (DBP), diisobutyl phthalate (DIBP), butyl benzyl phthalate (BBP), di-n-pentyl phthalate (DnPP), di(2-ethylhexyl) phthalate (DEHP), di-n-octyl phthalate (DnOP),



diisononyl phthalate (DINP), and diisodecyl phthalate (DIDP), are classified as priority contaminants by the U.S. Environmental Protection Agency (EPA). Two of the 8 phthalates (DBP and DEHP) are listed on EPA's Toxics Release Inventory (TRI) list of toxic chemicals [15]. DEHP and DBP are also on the list of the dominant restricted phthalates contaminants in water sources in China and most of the other countries. Major industrial polluters include chemical factories, drug manufactures, electronics manufactures etc., and a study reported that eighty percent of Chinese coastal cities discharge excessive amounts of sewage and contaminants into the sea, usually near sea farming and coastal resorts areas [16].

Zhuhai is in the southwest of the Pearl River estuary in Guangdong Province of China, with Hong Kong in the east and Macao in the south. It's the second largest port city (after Shenzhen) in China and Jinwan district located in the southwest part of the city which has formed three characteristic industries including general aviation, biomedicine and new energy. However, industries grow incredibly fast in the district in recently years and more attention should be paid to the increasing risks of water sources pollution.

In our study, DEHP and DBP values in the collected water samples from industrial, agriculture and residential areas in Jinwan district of Zhuhai were analyzed.

2. Materials and methods

2.1. Sample collection

Ten water samples were collected from different areas in Jinwan district of Zhuhai as Table 1 shown. There should be no rain at the collecting day and the before two days. Some notes in the sample collecting steps are as following: Firstly, let the stale water and possible impurities in the pipes flow away for 3 to 5 mins at the beginning. Secondly, the collecting bottles should be rinsed by the water samples 3 to 5 times. Thirdly, the collecting bottles should be filled with water samples, and no air space should be left. Finally, the water samples should be stored in refrigerator at 4 °C within two days for analysis.

Table 1. Sample collection information.

No.	Date	Temperature (°C)	Humidity (%)
1 ^a	2016/4/2	23	89
2 ^a	2016/4/3	23	87
3 ^b	2016/4/5	22	95
4 ^b	2016/4/6	22	98
5 ^c	2016/4/6	21	98
6 ^c	2016/4/6	21	98
7 ^c	2016/4/6	21	98
8 ^d	2016/4/6	21	98
9 ^d	2016/4/6	21	98
10 ^e	2016/4/7	21	98

^a No.1,2-tap water from electronics manufacturing related industries area.

^b No.3,4-tap water from residential communities.

^c No.5,6,7-tap water from chemical related industries area.

^d No.8,9-tap water from farming village.

^e No.10-water from local mountain fountain.

2.2. Sample pretreatment

Sample pretreatment process was optimized as our previous work [17]. Under the best conditions, 10 mL water sample was added in 0.160 g NaCl and mixed with 5.28 mL n-hexane solvent. The mixture was then eddied for 90 s by Vortex (Scientific Industries, Vortex-Genie 2) and then stood for 30 mins.

The supernatant was extracted and the left was extracted twice with n-hexane, the supernatants were collected and dehydrated by nitrogen (TianJing Heng'ao Limited Co., HSC-12A) and resolved by 2 mL methanol. Finally, the samples were filtered by 0.45 μm filter membrane and prepared for HPLC-UV analysis.

2.3. HPLC-UV detection

The best conditions of HPLC-UV by Agilent-HPLC1200 are as following, column: Agilent C18 (250 mm \times 4.6 mm, 5 μm), 25 $^{\circ}\text{C}$; mobile phase, 98% methanol: 2% deionized water; flow rate, 1 mL/min; detection wavelength of 225 nm; sample injection volume of 20 μL .

The scheme of the experimental process of water sample analysis is shown in Figure 1.

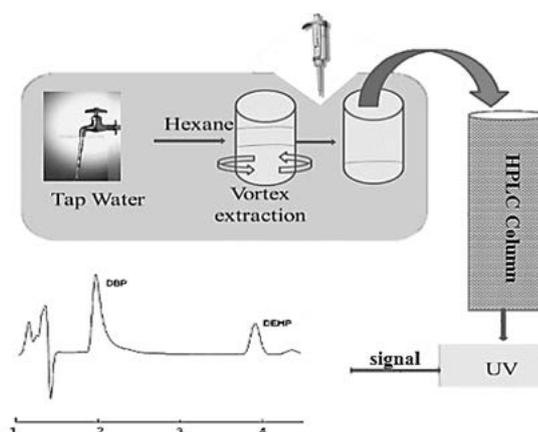


Figure 1. Experimental flow chart of water sample analysis.

3. Results and discussions

DBP and DEHP standards in methanol solution were from Sigma-Aldrich. The calibration curves of the standard solutions are shown in Figure 2. As the results shown, both of the PAEs are in a good linear relation. The linear correlation coefficient of DBP and DEHP was 0.9998 and 0.9995. The linear range of DBP was 0.020 mg/L \sim 20.0 mg/L, with the standard deviation of 0.56% \sim 5.07%. And the linear range of DEHP was 0.060 mg/L \sim 15.0 mg/L, with the standard deviation of 0.546% \sim 5.74%.

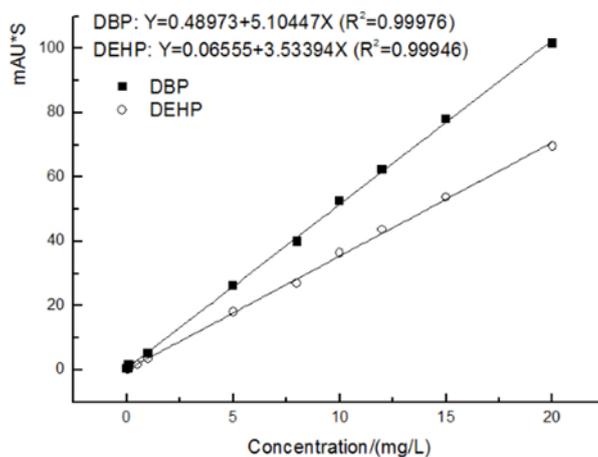


Figure 2. Calibration curves of DBP and DEHP standard solutions.

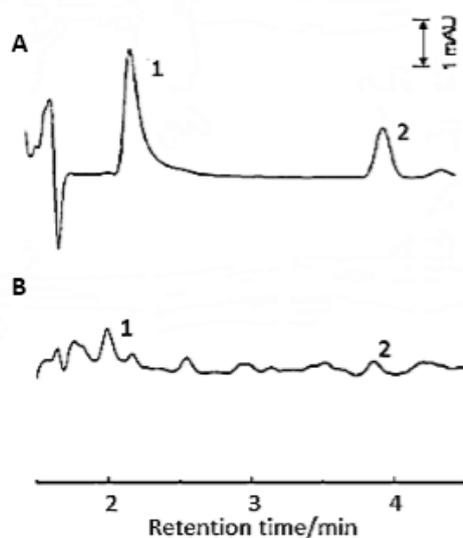


Figure 3. Chromatograms obtained from (A) a mixture of standard DBP and DEHP at 5 mg/L and (B) DBP and DEHP in No.1 water sample. HPLC-UV conditions: Column, C18 (250 mm ×4.6 mm, 5 μm), 25°C; mobile phase, 98% methanol /2% deionized water; flow rate, 1 mL/min; detection wavelength of 225 nm; sample injection volume of 20 μL. Peak: 1. DBP; 2. DEHP.

Table 2. The DEHP and DBP values in water samples.

No.	DEHP (mg/L)	RSD(n=3)	DBP (mg/L)	RSD(n=3)
1 ^a	0.0950	5.4	0.0652	1.2
2 ^a	0.0854	1.9	0.0751	3.0
3 ^b	ND	-	0.0148	0.6
4 ^b	ND	-	0.0375	0.7
5 ^c	0.0463	5.7	0.0248	1.3
6 ^c	0.0754	2.3	0.0199	5.1
7 ^c	0.0646	5.6	0.0180	2.5
8 ^d	ND	-	0.0413	0.05
9 ^d	ND	-	0.0340	0.6
10 ^e	ND	-	0.0422	0.6

^a No.1,2-tap water from electronics manufacturing related industries area.

^b No.3,4-tap water from residential communities.

^c No.5,6,7-tap water from chemical related industries area.

^d No.8,9-tap water from farming village.

^e No.10-water from local mountain fountain.

^f ND-not detected.

As shown in Figure 3, DEHP and DBP were well separated and determined in standard and real samples in 4 mins by the method. The results in Table 2 showed that the values are ranging from 0.0463 to 0.0950 mg/L of DEHP (except not detected) and 0.0148 to 0.0422 mg/L of DBP. However, DEHP values in sample 1, 2, 5, 6, 7 were above the Chinese national standard limitation of 0.008 mg/L, in addition, DBP values in all the samples were excessive the limitation of 0.003 mg/L [18]. The results indicated that the PAEs values in water supply samples of the local district were excessive the levels of the Chinese national standard limitations of drinking water and most of them are from the industrial areas.

4. Conclusions

In our work, trace level of dominant PAEs contaminants (DEHP and DBP) in local water sources from agriculture, industrial and residential areas were analyzed by HPLC-UV method. The detection limit of DBP was 0.002 mg/L and DEHP was 0.006 mg/L, which meets the Chinese National Standards for drinking water quality. As the results shown, PAEs values in ten samples of tap water from local district were ranging from 0.0463 to 0.0950 mg/L of DEHP and 0.0148 to 0.0422 mg/L of DBP. Half of the DEHP values were above the Chinese national standard limitation (0.008 mg/L), in addition, DBP values in all the samples were also excessive the limitation (0.003 mg/L). PAEs contaminants in the water supply were higher from the industrial areas than the agriculture and residential areas, however, the risks of PAEs pollution in water supply still exist. Water pollution is especially bad along the coastal manufacturing belt. In order to reduce the amount of contaminants in the water supply systems, the government has implemented more strict environmental regulations and laws and taken more action to clean up water sources over ten years, however, there is still a long way to go for water pollution prevention and treatment.

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