An Integrated Assessment of Phthalic Acid Esters and Phenolic Compounds as Priority Concern Pollutants in Raw and Conventionally Treated Water in Plateau State, Nigeria

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ABSTRACT

Phthalate acid esters (PAEs) and phenolic compounds (PCs) exist in water bodies due to the discharge of polluted wastewater from industrial, agricultural and domestic activities into water bodies. They also occur as a result of natural phenomena. These compounds are known to be toxic and inflict both severe and long-lasting effects on both humans and animals. They act as carcinogens and cause damage to the red blood cells and the liver, even at low concentrations. For this cause, this research was carried out to assess these compounds as priority concern pollutants in raw and conventionally treated water (CTW) in Plateau State, Nigeria. Raw and treated water samples were collected from Pankshin, Shendam and Jos dams. A combination of High Performance Liquid Chromatography tandem mass spectrometry was used to analyze the two categories of pollutants. The results obtained showed that almost all the PAEs were above the given permissible limit (PL) as given by the United States Environmental Protection Agency. The PCs were however below the given PL. it was discovered that out of the 12 PAEs and PCs detected, only 3 (1 PCs and 2 PAEs) were still detected in the CTW samples, proving that the method of treatment considerably reduced the concentrations of the pollutants. However, the reoccurrence of some of the contaminants proved the method of treatment was not completely effective. It was then recommended that other sophisticated method be utilized.

Keywords: *phthalate acids, pollutants, phenols, wastewater*

INTRODUCTION

Environmental pollution is an undesirable by-product of the increased demand for natural resources in the modern civilization. The pollutants that damage the ecosystem are the pollutants from industry and mining that release toxic substances such as metals and organic pollutants. Some of these pollutants are non-degradable and therefore accumulate in nature, where they continue to affect ecosystem's function over the course of decades or even centuries.

Phthalic acid esters (PAEs) are micro-contaminants of great public concern due to their huge usage in manufacturing industries as well as their negative impacts on the human health and the ecosystem at large. PAEs are the dialkyl or alkyl arkyl esters of 1,2-benzenedicarboxylic acid (phthalic acid) produced by reacting phthalic anhydride with an appropriate alcohol (Bartsch *et al.*, 2021). They are used to increase a material's flexibility, transparency, plasticity, endurance and longevity (Kolarik *et al.*, 2008). They are important plasticizers and additives widely used in industrial production in numerous plastic applications due to their high performance and low cost (Li *et al.*, 2020). PAEs are not chemically bound to the host polymer and exposed to a higher temperature can easily migrate in the contact matrix, which may lead to the release from the life cycle of commercial and domestic products into the environment (Kiralan *et al.*, 2020). They can eventually enter the environment through multiple pathways among which are industrial and municipal waste waters after the disposal of industrial and municipal solid waste (Paluselli *et al.*, 2020).

Phenolic compounds (PCs) are among chemicals of major concern because of their tendency of being persistent in the environment for a long period of time. The phenolic micro-pollutants generally include chloro, bromo, nitro and alkyl phenol (Sun *et al.*, 2014). It is because of its toxicity and persistence in the environment, these compounds are considered as priority pollutants and appear in a list of dangerous substances of the United States Environmental Protection Agency (EPA).

It is in the light of these realities that this study is structured to assess the levels of PAEs and PCs in raw water as well as conventionally treated water consumed in three local government areas of Plateau State, Nigeria.

EXPERIMENTAL

Sampling area

Three sampling areas were considered for this research which includes Pankshin in the central Plateau, Shendam in Southern and Jos in Northern Plateau all in Plateua State, Nigeria. The dams provide raw water for various uses by the inhabitants of these communities which include drinking, domestic activities, civil construction works and irrigation.

Sample Collection

The water samples used for this study is a three-way composite (equal parts) of the water collected from three site observation dams in dry season and the conventional treated water from the three dams within the same period. The water samples were collected in clean plastic containers and stored in an ice bag at a low temperature of about $4^{o}C$. During the sampling, the plastic containers were rinsed with the sample water three times before collection.

Chromatographic analysis

A combination of High performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS) was used to permit quantification of the analytes at very low detection limits. HPLC analyses was carried out using an Alliance-2695 system (Waters, Milford, MA, USA).

Chromatographic separation was performed using a 3.5µm XTerra MS C18 column (100mm x 3mm i.d.) from Waters at a flow rate of 0.3mL min^{-1}. The column was kept at 25 ± 2^0C and the sample injection volume was 7mL. The mobile phase was (A) H_2O (acidified with 0.1% formic acid) and (B) MeOH:H_2O (90:10 v/v). A Waters Micromass Quattro Micro^{TM} API triple quadrupole mass spectrometer, equipped with a Z-spray ESI interface operating in both positive and negative mode (Manchester, UK), was used. For instrument control, data acquisition and processing, MassLynx and QuanLynx software version 4.1 (Waters) was used. The mass spectrometer was operated in MS/MS mode using multiple reactions monitoring (MRM).

Results and Discussion

Table 1. Result of the analysis of PAEs and PCs from Jos sampling site

S/No.	Organic Pollutants	Conc. In raw water (µg/l)	Conc. in C.T.W (µg/l)	Permissible Limit (µg/l)
	Phenolic Compounds			
1.	1,2-dihydro-acetate-2-naphthaneol	2.75	N.D	
2.	2,4-bis(1,1-dimethylethyl)-phenol	1.61	0.89	1.6-10
	PAEs			
3.	Dibutyl phthalate	13.26	N.D	
4.	Chloromethyl-3-chlorododecanoate	1.95	N.D	1.3

Key: N.D – Not detected

Table 2. Result of the analysis of PAEs and PCs from Pankshin sampling site

S/No.	Organic Pollutants	Conc. In raw water (µg/l)	Conc. in C.T.W (µg/l)	Permissible Limit (µg/l)
	Phenolic Compounds			
1.	2,4-bis(1,1-dimethylethyl)-phenol	6.26	N.D	1.6-10
	PAEs			
2.	Dibutyl phthalate	13.31	N.D	
3.	Dihydrosteviobiside	0.38	N.D	1.3
4.	Methyl stearate	2.94	2.47	

Key: N.D – Not detected

Table 3. Result of the analysis of PAEs and PCs from Shendam sampling site

S/No.	Organic Pollutants	Conc. In raw water (µg/l)	Conc. in C.T.W (µg/l)	Permissible Limit (µg/l)
	Phenolic Compounds			
1.	2,6-dimethoxy-phenol	0.27	N.D	1.6-10
	PAEs			
2.	Isobutyl undecylphthalic acid	17.41	N.D	
3.	9,19-cycloanost-23-ene-3,25-diol,3-acetate	3.08	N.D	1.3
4.	Methyl stearate	2.40	4.40	

Key: N.D – Not detected

Discussion

PAEs were more predominant in the tested water samples especially in their raw forms. The raw water from Jos showed the presence of two forms PAEs and two forms of PCs. The concentrations of phenols were 1.6µg/l and 2.75µg/l which were within the 1.6-10 µg/l Permissible Limit (PL) given by EPA. However, the PAEs detected were within the concentration range of 1.95-13.26µg/l far exceeding the 1.3µg/l permissible limit.

Three PAEs were detected in the raw water samples from Pankshin with concentration range between 0.38-13.31µg/l above the PL. Only a single form of phenolic compounds was detected in raw water obtained from Pankshin with a concentration of 6.26µg/l within the acceptable limits. Raw water obtained from Shendam had the presence of 2,6-dimethoxy-phenol with a concentration of 0.27µg/l as well as three forms of PAEs all above the permissible limit.

Humans are continually exposed to PAEs daily as these compounds are found in little quantities in literally thousands of industrial and household products ranging from cosmetics, toys, curtains, electrical appliances, food, packaging materials, beverages and drinking water (Baloyi, 2012; Gong et al., 2018; Luo et al., 2018; Abtahi et al., 2019; He et al., 2020). Upon exposure or uptake, effects exerted range from mutagenicity, teratogenicity, and carcinogenicity. In fact, global concern about PEs arise due to their hazardous, toxicity, mutagenic, teratogenic and carcinogenic characteristics to humans on exposure (Gao and Wen, 2016; Zarean et al., 2016; Zacharia, 2019; Li et al., 2020; USEPA, 2021). From the results obtained for the detection of PAEs almost all of them detected were above the permissible limit given, hence raising the concern of their health effect of people consuming these waters.

In the case of phenolic compounds, it has been discovered to be able to easily penetrate the skin through absorption and can readily be absorbed from the gastrointestinal tract of humans. Once in the system, they undergo metabolism and transform to various reactive intermediate forms particularly quinone moieties, which can easily form covalent bonds with proteins, resulting in their ability to exert toxic effects on humans (Schweigert *et al.*, 2001). However, since the phenolic compounds detected in the water samples were not above the permissible limit, the water could be said to be free from the side effects of exposure to phenolic contaminants.

It can also be seen from the tables that out of 12 PAEs and PCs detected, only 3 (1 PCs and 2 PAEs) were still detected after the water samples were treated before being tested. It is worthy to note that the concentration of the contaminants reduced quite considerable with some not even detected after treating the water.

Conclusion and Recommendation

The rapid increase in industrial and domestic activities as a result of the desire to meet the demands of the ever-increasing human population creates the possibility of phthalate acid esters and phenolic compounds introduction into water bodies. Extensive research has been performed on these compounds resulting in the elucidation of their structure or classification, their sources of entry into the aquatic environment and their reactivity or interaction with other components of

the aquatic environment. Research has also unveiled the significant toxic effects that these compounds exert on humans and wildlife upon exposure. The need to protect water resources and the aquatic ecosystem is well demonstrated through the multitude monitoring and toxicity data availed from various researches. Different sources of exposure to PAEs and PCs are well documented but several questions about cumulative exposures, contributions of various sources in toxicity and mixed exposures remain partially answered. In this regard, an assessment of these compounds was conducted on raw and treated water collected from the sampling areas. It was discovered that PAEs detected were above the standard permissible limits while the PCs were below the permissible limits. It is then concluded that the conventional treatment methods utilized to treat the water samples proved efficient in considerably reducing the concentration of the pollutants while also eliminating some. It is however recommended that other sophisticated methods of treatment be utilized to ensure complete removal of these contaminants.

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