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Chemical monitoring and temporal variation in levels of endocrine disrupting chemicals (priority phenols and phthalate esters) from selected wastewater treatment plant and freshwater systems in Republic of South Africa

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ABSTRACT

This study presents a quantitative estimation of the simultaneous analysis of 11 priority phenols and six phthalate esters in surface water from five rivers collected from the upstream and downstream of wastewater treatment plants (WWTPs) that emptied their final effluents into the rivers. In addition, influents and effluents from the WWTPs were collected on a quarterly basis between April 2010 and March 2011. Kirstenbosch Botanical Garden stream was used as a control site. Gas chromatography–mass spectrometry (GC–MS) was used for identification and quantification using N-methyl-N-(tert-butyldimethylsilyl)trifluoroacetamide (MTBSTFA). Chemical analysis by GC–MS revealed the presence of DEP, POH, PCP, DEHP, DBP, BBP, 2,4-DMP and 2-NP as the most abundant congeners. Zandvliet WWTP showed to be the most polluted as it receives wastewater from the largest informal settlement in the city. Generally, concentration ranged from below detection limit (LOD) for most of the congeners to 34.520 mg l^{-1} for DBP at Zandvliet WWTP. Also, statistical analysis showed correlation between levels of analytes in effluent and downstream water samples, an indication of pollution from the WWTP. From the monitoring exercise, data obtained for most compounds analyzed showed that the congeners are effectively removed (approximately 80 to 100%) with the exception of 2-nitro phenol that was poorly removed. The production of 2,4-DMP is also noteworthy in the final effluent of all the investigated treatment plants.

1. Introduction

Increased living standards, rise in population, and agricultural and industrial development have put pressure on the existing scarce water resources in many countries. Consequent upon this upsurge, there is an urgent need to further treat, recycle and reuse available water resources. To complement scarce water resources, there has been an increase in the number of wastewater facilities in many countries. This is to forestall the outbreak of environmental pollution and spread of diseases, to remove conventional pollutants (such as ammonia and phosphate), and to maintain and restore the biologic integrity of surface waters [1,2]. A wide variety of pollutants have received significant attention due to their potential estrogenic effect and are classified as endocrine disrupting compounds (EDCs) [3].

This is due to their ability to disrupt the endocrine systems of higher life forms such as fish, wildlife and even human. These endocrine disrupting compounds are widespread in the environment and are more persistent than first anticipated [4]. Although, the ecotoxicological and human risks remain unclear, many of the endocrine disrupting chemicals are known to mimic, antagonize or bind to hormone receptor [5–7].

EDCs comprise many classes of organic compounds such as alkylphenols, alkylphenol ethoxylates, polychlorinated biphenyls, selected pesticides, bisphenol A, pharmaceutical products, polybrominated compounds, steroid sex hormones and phthalates; most of which are widely reported in wastewater facilities [8–10]. Domestic and industrial wastewaters are significant sources of EDCs to the receiving surface, coastal waters and regional environments [4,11,12].

A number of investigations suggested that final effluents of wastewater treatment plants (WWTPs) were mainly responsible for the increasing estrogenic activity in many aquatic environments [13]. Removing microconstituents in a wastewater treatment plant can be important in many ways. The effluents from WWTPs are usually discharged into surface waters, such as rivers. Contaminants from the treated wastewater have been shown to adversely affect surrounding wildlife and the aquatic environment. Processes such as transformation and biodegradation may remove a large fraction of EDCs in WWTPs, and physical processes like coagulation, sedimentation, filtration and membrane separation might result in EDC accumulation in sludge that might require further treatment [14].

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Removal rate of EDCs from the effluent of WWTPs varies greatly due to plant location and physico-chemical parameters of the contaminants [15,16]. Generally, fate of organic compounds in a water cycle is greatly dependent on its ability to interact with particulates. These can include clay, sediments, colloid coated with organic material and microorganisms. The fate is often not well understood, however, it is dependent on particulate contaminant interactions [14].

Presently, there is no information about the temporal and spatial variation in occurrence and removal of EDCs (phthalate and priority phenols) in wastewater treatment plants in South Africa. Though recently, Olujimi et al. [16] reported in their method development for simultaneous method for the determination of phthalates and phenols some temporal occurrence concentration and removal efficiency of two treatment plants in Cape Town. This result could not however be taken as better representation of the selected EDCs in wastewater treatment plants in Cape Town. The aims of this study were (i) to investigate the seasonal variation in level of phenols and phthalate esters in wastewater treatment plants, (ii) to assess the efficiency of the treatment at removing analytes of interest and (iii) to assess the impact of waste effluent on the level of analytes downstream.

2. Material and methods

2.1. Chemicals and reagents

The following phenols were of analytical grade and were purchased from Supelco (Bellefonte, PA, USA): phenol (PH) 99.9%, 2-nitrophenol (2-NP) 99%, 4-nitrophenol (4-NP) 99%, 2,4-dinitrophenol (2,4-DNP) 99.7%, 4,6-dinitro-2-methylphenol (DNMP) 98%, 2,4-dimethylphenol (2,4-DMP) 98%, 2-chlorophenol (2-CP) 99.8%, 4-chlorophenol (4-CP) 99%, 2,4-dichlorophenol (2,4-DCP) 100%, 4-chloro-3-methylphenol (4-C-3-MP) 99%, pentachlorophenol (PCP) 99.6%, dimethyl phthalate (DMP), diethyl phthalate (DEP), benzylbutyl phthalate (BBP), dioctyl phthalate (DOP), diethylhexyl phthalate (DEHP), and dibutyl phthalate (DBP). The solvents (methanol, n-hexane, acetone and acetonitrile) were of analytical grade from Sigma Aldrich and were further purified by distillation. Separate stock solutions of individual analytes were prepared in methanol (1000 mg l^{-1}). A working mixture containing each compound at 10 mg l^{-1} was also prepared and stored at 4 °C in the dark. Milli-Q water used was from apparatus Millipore (Bedford, MA, USA). C18-E cartridges (strata) containing 500 mg/6 ml of adsorbent (Separations, South Africa) were used.

2.2. Cleaning of glassware

All glassware is cleaned by soaking in 10% nitric acid followed by soaking in acetone for at least 30 min, then rinsed with hexane, and dried at 200 °C for at least 4 h consecutive rinsing using pesticide-grade acetone just before use to remove phthalate contamination. The caps or lids of all sample bottles, jars and vials were lined with PTFE.

2.3. Sample collection

Six wastewater treatment plants were namely: Athlone, Bellville (which consists of the Old and New plants), Kraaifontein, Potsdam, Stellenbosch and Zandvliet. Five of these WWTPs were located in the City of Cape Town, while one is located in Stellenbosch. Rivers associated with each treatment plant are: Athlone — Vygekraal River; Bellville — Kuils River; Kraaifontein — Mosselbank River; Potsdam — Diep River; Zandvliet — Kuils River and Stellenbosch — Veldwachters River. The WWTPs investigated in this study were monitored for influent and final effluent samples. To assess the possible impact of the WWTP on the freshwater systems, water samples were collected about 1 to 2 km upstream and downstream of discharge point of each of the WWTP. The geographical location, treatment processes, and people equivalence of each WWTP are presented in Table 1. Samples were collected in a 1 liter pre-cleaned amber glass bottles with methanol to prevent analytes from adhering onto the glass wall [3]. Sample bottles were kept cold on ice while transported back to the laboratory. Once received in the laboratory, samples were extracted and analyzed within 12 h after collection.

2.4. SPE extraction procedure

C18-E cartridges (strata) containing 500 mg/6 ml from separations were used for the extraction of phenols and phthalates from aqueous samples based on recoveries for phenols as reported by Olujimi et al. [16]. Prior to sample processing, the cartridges were fitted onto a vacuum manifold (Supelco) connected to a pump and the cartridges were conditioned with 5 ml of n-hexane:acetone (50:50, v/v), followed sequentially by 5 ml of methanol and 10 ml of Milli-Q purified water (purified by Milli-Q Synthesis A 10 System, Millipore, Bedford, MA, USA). Prior to extraction of each 500 ml, water samples were filtered on vacuum using a 0.22 μm filter to remove suspended particulate matter that might block the SPE cartridges. Hydrochloric acid was used to adjust the pH of the water sample to pH of between 2 and 3 before passing it through the conditioned cartridge. After the sample was passed through the cartridge, 5 ml of Milli-Q was passed through and left on the vacuum manifold for 30 min to dry (−70 kPa). The retained analytes of interest were eluted with 3.5 ml of methanol followed by 3.5 ml of n-hexane:acetone (50:50, v/v) into 10 ml glass vial. This was blown to dryness on hot plate at 70 °C under gentle flow of nitrogen followed by derivatization. The

Table 1
Description of the six wastewater treatment plants investigated.

WWTP ID	Geographical location of plant	People equivalent	Source	Treatment process	River
A	S33.5709° E18.3048°	900,000	Domestic Industrial	S + G + Sed + AS (BNR) + Sed + Chl + AD + Dew	Vyeekraal River
B	S33.5923° E18.4332°	591,000	Domestic Industrial	S + G + EAAS (N) + Sed + UVdis + Dew	Kuils River
C	S33.82539° E18.70442°	133,000	Domestic	S + G + Sed + AS (N) + Sed + Chl + AD + Dew	Mosselbank River
D	S33.5070° E18.3108°	385,000	Domestic Industrial	S + G + Sed + AS (BNR) + Sed + Chl + AD + Dew	Diep River
E	S33.94345° E18.82492°	N/K	Domestic Industrial	S + G + Sed + FB + AS (BNR) + Sed + Chl + AD + Dew	Veldwatcher River
F	S34.0312° E18.4259°	400,000	Domestic Industrial	S + G + EAAS (N) + Sed + UVdis + Dew	Kuils River

Abbreviations: S = screening; G = grit removal; Sed = sedimentation; AS = activated sludge; EAAS = extended aeration activated sludge; N = nitrogen; BNR = biological nutrient removal; Chl = chlorination; UVdis = UV disinfection; AD = anaerobic digestion; FB = filter bed; N/K = not known; WWTP ID = wastewater treatment plant identification.