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Environmental Risk Assessment of Exposure to Selected Emerging Contaminants in Dams and Wastewater Effluent Around the City of Bloemfontein, South Africa

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Abstract

The number of emerging contaminants in the aquatic environment is growing continuously every year. Their occurrence in water sources could be a troubling problem to aquatic ecosystem and human health. The aim of this study was to assess the environmental risks of selected emerging contaminants in dams/reservoirs and wastewater effluent samples around the city of Bloemfontein, South Africa. The high-performance liquid chromatography connected to a QTRAP hybrid triple quadrupole ion trap mass spectrometer was used to analyse emerging contaminants such as acetaminophen, carbamazepine, ibuprofen, triclosan, 17-alpha-ethynyl-estradiol, estradiol, progesterone and testosterone in dams/reservoirs and wastewater effluents. The single and mixture substance ecological risks were evaluated using the risk quotient (RQ) and risk mixture (RQmix) methods respectively. For acute toxicity in dams, results showed that emerging contaminants such as carbamazepine, and 17-alpha-ethynyl-estradiol posed high ecological risks on all aquatic organisms. In effluent, carbamazepine, ibuprofen, triclosan, 17-alpha-ethynyl-estradiol, estradiol, and progesterone posed high risks to all selected species. For chronic toxicity, ibuprofen posed high ecological risks on algae, daphnids, and fish in dams and effluents. The RQmix values in all water sources exceeded the acceptable limit for both acute and chronic toxicity on algae, daphnids, and fish. Their acute mixture risks on aquatic species were as algae>daphnids>fish in targeted water sources while chronic mixture risks were as fish>algae>daphnids in the targeted water sources. Therefore, the level of emerging contaminants in dams/reservoirs and wastewater effluent in this study is likely to negatively pose serious adverse implications on aquatic life and human beings. The outcomes of this study constitute the initial contribution for a better understanding of emerging contaminants risks on aquatic ecosystems and human health and may help in pollution control, protection of aquatic ecosystem and water consumers.

Keywords: emerging contaminants, environmental risk assessment, individual risk assessment, mixture risk assessment, water sources.

1. Introduction

As a results of population growth and widespread use of medications for human and veterinary purposes, there are more emerging contaminants in the water environment every year [1]. Emerging contaminants can enter water sources in a number of ways, including surface runoff from agriculture and animal husbandry, hospital and industrial effluents, and wastewater effluents. Among these, the wastewater effluents are a key pathway for emerging contaminants to enter the water environment [2]. These emerging contaminants (steroid hormones, pesticides, antibiotics, pharmaceuticals and personal care products) find their way to the water bodies either alone or in mixtures posing a world-wide risk to the aquatic organisms and deleteriously to human health [1]. The occurrence of emerging contaminants in water sources such as surface water, groundwater and wastewater effluents has been notably explored in many parts of the world [2, 3, 4] including South Africa [5, 6, 7]. However, the individual and mixture risks evaluation of these chemical compounds in water sources is hardly ever reported particularly in South Africa. In the light of the above, there is an urgent need to continuously monitor these compounds in water sources and assess their potential environmental risks to aquatic ecosystems. This will guarantee a good water quality in the country

particularly in the city of Bloemfontein where there is dearth of data on emerging contaminants in water sources. The objective of this research was to assess individual and mixture risks of emerging contaminants in dams/reservoirs and wastewater effluents. The results presented in this paper are the first data reported in the city of Bloemfontein, and constitute the initial contribution for a better understanding of emerging contaminants risks on aquatic ecosystems and human health. Expectantly, this works will help in pollution control, water sustainability, and ecological protection.

2. Materials and Methods

A. Study area and sample collection

Bloemfontein is the capital and the largest city of the Free State province in South Africa. The city is situated at 29°7'15.9" S 26°12.84' E at an elevation of 1 400 metres above sea level. The climate varies from warm and temperate with an annual rainfall of 1 020 mm in the east to semiarid with rainfall of only 380 mm in the far west. The city water resources include dams/reservoirs, rivers, wetlands, and groundwater resources. These dams supply water for domestic, agricultural, and industrial use in the city. Furthermore, households in the city have access to sanitation facilities and the municipality has several wastewater treatment works [8, 9]. A total of 8 samples were collected using 750 millilitre (mL) hygienic glass bottles. Eight (8) grab water samples were collected from five (5) dams and three (3) wastewater treatment works effluents. The sampling bottles were washed several times with clean water prior to sampling. All the collected samples were labelled and kept in a cooler box filled with ice cubes during field work until laboratory analysis [9].

B. Sample preparation and analysis

In this study, the laboratory procedure was performed based on our previous studies [9]. Briefly, the samples were filtered through glass fibre filters to remove particulate matter before being concentrated at a flow rate of 5 mL/minutes (min) onto methanol conditioned C18-6 mL solid phase extraction cartridges. The bound samples were slowly eluted from the dried cartridges with 2 mL methanol and 2 mL ethyl acetate. The eluants were vacuum dried until almost dry and reconstituted in 1 mL purified water. High-performance liquid chromatography (HPLC) was used to analyse the water samples. The HPLC was linked to a QTRAP hybrid triple quadrupole ion trap mass spectrometer. Analyst 1.5 (AB SCIEX) software was used for all data acquisition and processing. Positive and negative ionisation modes were used to analyse the samples. During analysis, 20 microliter of each extracted sample was separated on a C18 (150 mm × 4.6 mm, Gemini NX, Phenomenex) column at a flow rate of 300 µL/min using a 5 min gradient from 5% solvent A (H2O/0.1% formic acid) to 95% solvent B (MeOH/0.1% formic acid) with a total run time of 9 min and 10 min in positive and negative ionisation modes, respectively, to allow for column re-equilibration. Eluting analytes were electrospray ionised in the TurboV ion source with a heater temperature of 500 ^{o}C to evaporate the excess solvent, 40 psi nebuliser gas, 40 psi heater gas, and a curtain gas of 15 psi. In positive ionisation mode, the ion spray voltage was set at 5500 V, while in the negative ionisation mode, it was set at -4500 V. Analysis of target analytes was carried out using multiple reaction monitoring transitions per analyte. The quantifier was the peak area on the chromatogram generated by the first and most sensitive transition, while the qualifier was the peak area generated by the second transition. The qualifier served as an additional level of confirmation for the analytes presence and the retention time for these two transitions must be the same. For quality assurance and control, selectivity, linearity and limit of quantification were taken into account. Solvent blank and standards were prepared for quality assurance and quality control. For each analyte, a four-point calibration curve with a linear fit through the origin was generated, ranging in concentration from 0.001 ppm to 1 ppm. The linear fit yielded a correlation coefficient (r) value above 0.98 while the quantification limits ranged from 0.0001 mg/L to 0.1 mg/L.

C. Single and mixture ecological risk assessment

The single ecological risk was calculated using the risk quotient (RQ) method, where RQ is defined as the ratio of the measured environmental concentration (MEC) to the predicted no effect concentration (PNEC). The toxicity data were obtained from the published literature and ECOTOX database. The risks (RQ) were categorised as (i) low (RQ ≤ 0.1); (ii) medium (0.1 < RQ < 1); or (iii) high (RQ ≥ 1) [2, 9].

The mixture risk assessment was approximated based on the traditional approach of concentration addition.

In this study only the sums of risk quotient values (RQmix) approach was adopted. In this approach, when the RQmix was below 1 (RQmix<1), it connoted a sufficient safety for the ecosystem. When the RQmix was above 1 (RQmix>1), the environmental quality standard was exceeded [10, 11, 12].

3. Results and Discussion

A. Single substance risk assessment

The ecological risks assessment of individual emerging contaminants in dams and wastewater effluents are presented in Table 1. The risk assessment was based on acute and chronic toxicity on algae, daphnids, and fish in all water sources. The risks of contaminants with concentration below limit of quantification (<LOQ) and with no toxicity data were not assessed. In this study, the risks of individual contaminants were ranging from low ecological risks (RQ≤0.1) to high ecological risks (RQ≥1). For acute toxicity in dams, 17-alpha-ethynly-estradiol and carbamazepine posed high ecological risks to all selected species. High ecological risks (RQ≥1) of ibuprofen were noticed in daphnids and fish while acetaminophen posed high ecological risk only on daphnids. In effluents, carbamazepine, ibuprofen, triclosan, 17-alpha-ethynly-estradiol, estradiol, and progesterone showed high ecological risks on all aquatic species. Chronic toxicity in dams showed high risks of ibuprofen in all aquatic species. There was high risk of carbamazepine on algae and daphnids while 17-alpha-ethynly-estradiol also posed high risk to fish. In effluent, ibuprofen showed high risks to all aquatic species. Carbamazepine posed high chronic risks on algae and daphnids while 17-alpha-ethynly-estradiol posed high risk on fish.

The study showed that contaminants in dams and effluents have possibility to cause high acute and chronic ecological risks to aquatic ecosystems. The high ecological risks of acetaminophen, ibuprofen, triclosan, estradiol, 17-alpha-ethynyl-estradiol, and progesterone in effluent were also reported in other studies [13]. These contaminants with high ecological risks in dams may be attributed to runoff from settlements, agricultural areas, and sewage systems. Low removal rate in wastewater treatment works [13], working faults, current electricity load shedding problems in the country may cause the composition of influent not to change much in effluent leading to high ecological risks. High acute and chronic ecological risks of these compounds may affect the survival of aquatic organisms [14] and the health of the local population through food chain. Some of the dams are used as a fishing spot which present a potential threat to human health via consumption due to the bioaccumulation of these compounds [15, 16]. The release of effluents with pollutants of high ecological risks into nearby water streams may contribute to the river contamination which may lead to detrimental effects to aquatic organisms and human beings. During field work it was noticed that wastewater effluent were being used by small scale farmers for irrigating vegetables which entail a potential threat to human health due to the bioaccumulation. Exposure to emerging contaminants may cause endocrine disorders, decreased reproductive rates, decreased life expectancy [14], disruption of red and white blood cells, and insomnia, among other things [17].

B. Substance mixture risk assessment

As shown in Table 1, the acute mixture risk of emerging contaminants on algae, daphnids, and fish exceeded the threshold of 1 by a wide margin. For acute toxicity, the RQmix values in dams, and effluents exceeded the acceptable limit (RQ ≥ 1) for algae, daphnids, and fish. Algae were most sensitive to the substance mixture risks in all water sources and their acute mixture risks were trending as algae >daphnids >fish in all water sources. For chronic toxicity, the RQmix values in all water were also above the acceptable limit. In all water sources, fish were most sensitive to the substance mixture risks. The chronic mixture risks on aquatic species were as fish >algae >daphnids in all water sources. A study conducted in European wastewater treatment plants [18] and in wastewater effluent from the Republic of Ireland [19], reported that the mixture risk assessment of emerging contaminants in effluent samples were greater than one which is comparable to the findings of these study. The majority of wastewater effluents are discharged into nearby streams. In addition, rivers that receive effluent from treatment plants discharge their water in dams within the Modder river catchment, potentially endangering the water ecosystem. The high acute and chronic mixture risks of compounds detected in these water sources are alarming because they can have serious consequences on aquatic organisms and reach the top of the food chain via bioaccumulation and biomagnification processes [20]. According to Bouzas-Monroy et al. [21], contaminated sites with intolerable mixture risks may have unacceptable effects on algal growth, daphnia

reproduction, and fish biochemistry and physiology. Furthermore, degradation products of these compounds may be more toxic in the short and long term than their parent compounds and may contribute to the development of antibiotic resistance genes [3]. They may also cause morbidity and mortality in organisms by interfering with processes like reproduction and development [22]. Continuous monitoring and improvement of the treatment methods should be implemented in this area in order to decrease the high ecological risks of these compounds for safer reuse in the future.

Table 1. Single and mixture risk assessment of emerging contaminants in dams and wastewater effluents.

Contaminants	Mean (mg/L)	RQ (Acute Risk)			RQ (Chronic risk)		
		Algae	Daphnids	Fish	Algae	Daphnids	Fish
Reservoirs/Dams							
Acetaminophen	0.06	0.5	8	0.2	0.1	0.6	0.07
Carbamazepine	0.29	8	48	8	3	580	0.1
Ibuprofen	0.30	0.9	9375	3	3000	15	3 000
Triclosan	<LOQ	-	-	-	-	-	-
17α ethynl	3.67	4587500	3058333	1835000	-	-	1223
Estradiol	<LOQ	-	-	-	-	-	-
Progesterone	<LOQ	-	-	-	-	-	-
Testosterone	<LOQ	-	-	-	-	-	-
RQmix	4.32	4587509	3067 764	1835011	3003	596	4223
Wastewater Effluent							
Acetaminophen	<LOQ	-	-	-	-	-	-
Carbamazepine	0.93	26	155	27	9	1860	0.4
Ibuprofen	4.3	14	134 375	43	43000	215	43000
Triclosan	0.13	214	308	461	60	0.03	0.02
17α ethynl	16.60	20750000	13 833333	8300000	-	-	5533
Estradiol	<LOQ	18750	1000	1000	-	-	0.7
Progesterone	0.01	10000	1428	-	-	-	-
Testosterone	<LOQ	-	-	-	-	-	-
RQmix	21.97	20779004	13970599	8301531	43069	2075	48534

Notation: RQ: risk quotient; RQmix: risk quotient mixture; LOQ: limit of quantification; mg/L: milligram per litre.

4. Conclusion

The aim of the study was to assess the environmental risks of emerging contaminants in dams and wastewater effluent in the city of Bloemfontein, South Africa. Individual emerging contaminants in dams and effluents showed the potential to cause high acute and chronic ecological risks during spring season. Moreover, the substance mixture risks was also above the acceptable level for both acute and chronic toxicity. The results demonstrate that aquatic species may be adversely affected by these contaminants. This study constitute the initial contribution for a better understanding of emerging contaminants risks on aquatic ecosystems and will help in pollution control, protection of aquatic ecosystem and local community. Some limitations of this study include the fact that few contaminants were targeted and lack of toxicity data for some contaminants. Moreover, the risk assessment values such as the predicted non-effect concentration are based on currently available data and may change as more reliable data become available.

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