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Ecological Risk Assessment of Contaminants of Emerging Concern in Coastal Waters of Sharjah, United Arab Emirates

Lucy Semerjian[1,2], Salima Aissaoui[1], Abdallah Shanableh[1,2], Mohammad H. Semreen[3,4], Khaled Abass[1,2,4,5]
[1]Department of Environmental Health Sciences, College of Health Sciences, University of Sharjah
Sharjah, United Arab Emirates
lsemerjian@sharjah.ac.ae; aissa.salima@yahoo.fr; shanableh@sharjah.ac.ae; kabass@sharjah.ac.ae
[2]Research Institute of Science and Engineering, University of Sharjah
Sharjah, United Arab Emirates
[3]Department of Medicinal Chemistry, College of Pharmacy, University of Sharjah
Sharjah, United Arab Emirates
msemreen@sharjah.ac.ae
[4]Research Institute for Medical and Health Sciences, University of Sharjah
Sharjah, United Arab Emirates
[5]Research Unit of Biomedicine and Internal Medicine, Faculty of Medicine, University of Oulu
Oulu, Finland

Abstract – The current study assesses the ecological risks of contaminants of emerging concern in the coastal aquatic environment of Sharjah, United Arab Emirates receiving treated effluents from wastewater treatment plants. Twenty-one contaminants were detected in wastewater effluents, 23 in seawater, and 22 in sediments at concentrations varying between trace amounts to 1782 ng L^{-1}, (wastewater), 236.10 ng L^{-1} (seawater), and 60.15 ng g^{-1} (sediments). Imidacloprid, thiabendazole, and acetaminophen were identified as the most prevalent compounds in effluents, seawater, and sediments, respectively. Ecological risk assessment was conducted using the risk quotient methodology and for various trophic levels, including algae, crustacea (*Daphnia*), and fish. Most contaminants posed low risks; however, sulphathiazole presented a medium risk, and imidacloprid, ofloxacin, and isoproturon exhibited a high risk to aquatic life, with imidacloprid showing the highest risk quotient. Recorded outcomes reveal the priority contaminants of emerging concern as well as suggest the need for enhanced wastewater treatment processes to reduce the ecological risks associated with such emerging contaminants.

Keywords**:** Contaminants of emerging concern, ecological risk assessment, wastewater management, coastal ecosystems

1. Introduction

Contaminants of emerging concern (CECs) are a broad category of non-regulated compounds that primarily originate from varying sources such as domestic discharges, hospital effluents, industrial wastewaters, agricultural and aquaculture runoff, and landfill leachates [1]. Notably, municipal wastewater treatment plant (WWTP) effluents significantly contribute to the presence of emerging contaminants in water bodies [2-4]. Despite the fact that environmental concentrations of these micropollutants are low, many of them raise significant toxicological concerns [5] and may lead to adverse impacts on aquatic species and ecological imbalances [6]. Due to their consistent detection in environmental compartments and possible harmful properties, CECs impart an increasing global concern and are candidates for future regulation.

The assessment of CECs in marine ecosystems is particularly relevant due to direct discharges from WWTPs, as well as untreated wastewaters and rivers [7]. The relevance is further significant in contexts such as the Middle East and North Africa (MENA) region, where the marine environment is a major water resources in view of increasing reliance on seawater desalination [8]. In parallel, wastewater reuse is an important strategy for meeting the growing demand for water in water-stressed areas such as the MENA and the United Arab Emirates (UAE) and the reuse of wastewater necessitates the generation of effluents that meet the desired water quality standards.

To assess the potential threats posed by such emerging contaminants, numerous global organizations have formulated diverse environmental risk assessment guidelines aiming at evaluating the risks to both the environment and human health.

Notably, the European Medicines Evaluation Agency (EMEA) and the US Food and Drug Administration (FDA) have proposed a comprehensive approach utilizing a combination of measured environmental concentrations (MECs) and predicted no-effect concentrations (PNECs). This approach is integral to both environmental risk assessment (ERA) and human health risk assessment (HHRA) [9-11]. The quotient between predicted or measured contaminant concentrations in water and their PNECs assists in inferring the likelihood of adverse effects from exposure to one or more contaminants [12]. The current study aims to provide quantitative information on CEC loads discharged into the local aquatic environment through WWTPs or water reuse, and to evaluate the possible risks of the recorded CEC concentrations on the receiving aquatic environment. The risk quotient (RQ) serves as one of the most useful and convenient tools for the characterization of potential ecological risk of CECs in the aquatic environment. To the best of our knowledge, limited information on such assessments is reported for the UAE and MENA regions [9, 13-17], thus the significance of the current study in filling the existing knowledge gap, informing proper decisions to relevant stakeholders, and assisting in formulating proper regulatory and mitigation frameworks to protect marine environment and safeguard environmental health.

2. Methodology
2.1. Study Area and Sample Collection
Throughout Dec 2021 to Oct 2022, a total of 224 wastewater effluent, seawater, and sediment samples were collected and analysed for 25 CECs, including pharmaceuticals and personal care products (PPCPs), pesticides, and hormones. The wastewater effluent samples were collected from the effluent pipe ends at the central Sharjah wastewater treatment plant. Seawater and sediment samples were collected along the coastline of Sharjah, UAE namely extending from Al Heera Beach to Al Khan Beach. All wastewater and seawater samples were collected in 1 L clean plastic bottles, sealed, labeled properly, and stored in coolers (4–6◦C) until further transport within adequate maximum holding times. Sediment samples were collected into clean sealable plastic bags, labeled, and stored properly in coolers (4–6◦C). The authors extensively detail the sampling locations and the methodologies implemented for data collection in their preceding paper [2].

2.2. Sample Analysis and Instrumentation
Waters Acquity H-Class ultra-performance liquid chromatography (UPLC) - tandem triple-quadrupole mass spectrometer (Xevo-TQD) (Waters, Milford, USA) equipped with an electrospray ionization source was used to for the analysis of 25 target CECs (Table 1). Proper quality control and assurance measures were adopted throughout sample collection, preparation and analysis as detailed in [2].

2.3. Ecological Risk Assessment
The ecological risk assessment was conducted in accordance with the Technical Guidance Document on Risk Assessment of the European Union [18] using the "worst-case scenario" approach. The assessment considered standard aquatic toxicity organisms representing three distinct trophic levels, encompassing algae, invertebrates (*Daphnia*), and fish. RQs for aquatic organisms were determined by calculating the ratio between the measured MEC and the PNEC for each specific chemical (Eq. 1). The MEC represents the highest CEC concentration observed in effluents, seawater and sediments during the sampling period. The PNEC was estimated using the lowest values of acute EC50 (concentrations causing adverse effects to 50% of individuals exposed in a bioassay) or LC50 (lethal concentration, killing 50% of the organisms) divided by a default assessment factor (AF) (Eq. 2). An AF of 1000 was applied due to the availability of at least one short-term EC50 or LC50 from each of the three assessed trophic levels [10]. Toxicological data were obtained from the literature.

$$(RQ) = MEC/PNEC \tag{1}$$

$$PNEC = (EC50 \text{ or } LC50)/AF \tag{2}$$

RQ > 1 indicates high risk, 0.1 < RQ < 1 indicates medium risk, and RQ < 0.1 indicates low risk [18].

2.4. Statistical Analysis

GraphPad Prism (version 8.0.1 for Windows, GraphPad Software, USA) was used for all statistical analyses. Normality Normality of data was tested by the Shapiro–Wilk test. Values below the limits of detection were replaced by half of the limit of detection [19].

3. Results and Discussion

3.1. CEC Concentrations in Investigated Matrices

The current study sheds light on the prevalence and potential environmental implications of CECs across various environmental matrices in Sharjah, namely WWTP effluents, seawater and sediments.

Twenty-one CECs were identified in the WWTP effluents as summarized in Table 1, with imidacloprid emerging as the predominant contaminant, exhibiting the highest mean concentration (1782 ng L^{-1}). Detection frequencies revealed a subset of CECs, including imidacloprid, ofloxacin, metoprolol, ciprofloxacin, thiabendazole, acetamiprid, and sulphapyridine, respectively as the most frequently measured pollutants in the effluent samples. The findings reveal a partial capability of the conventional WWTP in removing such recalcitrant contaminants which may lead to their potential discharge into the receiving environments. Findings also underscore the need for advanced treatment strategies and highlights the potential risk of environmental exposure. In fact, recorded outcomes resonate well with previous studies from Sharjah whereby a diverse array of CECs was identified in both the influents and effluents of the WWTP, encompassing antibiotics, analgesic/antipyretic medicines, anti-asthma agents, antipsychotics, antihistamines, antifungals, hormones, insecticides, pesticides, and personal care products [4]. Additionally, the prevalence of high antibiotic levels in treated wastewaters is consistent with broader regional and international studies. Mheidli et al. revealed antibiotics as the most frequently detected therapeutic class, followed by analgesics and anti-inflammatory medications in the MENA region [10].

As for the marine environment, twenty-three CECs were detected. Imidacloprid, caffeine, ciprofloxacin, and ofloxacin were among the compounds exhibiting the highest concentrations. In a related context, Ali et al. reported the presence of 13 different PPCPs in Saudi coastal water samples collected from various points at the Red Sea. Metformin, diclofenac, acetaminophen, and caffeine were the most frequently occurring PPCPs [20]. Similar findings were reported by Pico et al., identifying diclofenac, caffeine, and paracetamol as dominant PPCPs [21]. Results from current study revealed the correlation between the presence of CECs in the marine environment and the discharge of treated wastewater, as reported by Moreno-González et al. [22]. In the investigated seawater samples, the maximum concentrations were closely associated with inputs from Sharjah WWTP effluents. However, contaminant levels were lower in seawater compared to wastewater effluents. Dilution factors and degradation processes, including adsorption, photolysis, and biodegradation, likely contributed to the recorded levels of CECs in the marine environment. Sediment analysis revealed the presence of 22 out of 25 contaminants, with acetaminophen and imidacloprid frequently detected. The concentrations of some contaminants, particularly acetaminophen and isoproturon, were higher in sediments compared to the water phase, indicating potential additional sources beyond WWTP discharges.

As indicated by Ouda et al., monitoring of CECs in seawater within the MENA region is notably scarce, with approximately 40% of reviewed studies investigating CEC concentrations in both groundwater and seawater [8].

Table 1: CEC concentrations in Sharjah WWTP effluents (ng/l), seawater (ng/l) and sediments (ng/g).

CEC	**Wastewater**		**Seawater**		**Sediment**	
	mean± SD	RSD%	mean± SD	RSD%	mean± SD	RSD%
Acetaminophen	0.32±0.35	108.93	0.91±1.09	119.99	9.13±7.98	87.36
Nicotinic acid	1.42±1.85	129.92	1.02±1.05	102.82	0.92±0.85	92.25
Carbendazim	1.23±2.36	191.89	0.31±0.008	168	0.05±0.52	15.38
Caffeine	248.48±488.40	196.54	50.38±90.07	178.76	1.77±2.02	113.96
Thiabendazole	2.52±0.59	23.69	0.58±0.55	94.69	0.05±0.001	3.58
Biotin B7	BDL	-	1.04±1.99	190.43	BDL	-
Sulphapyridine	19.12±12.97	67.86	1.47±1.68	114.29	3.81±7.47	196.07
Sulfadiazine	34.52±8.94	197.78	1.01±1.93	190.16	8.69±10.16	116.86

Sulfamethoxazole	14.68±15.99	108.90	1.53±1.24	81.24	1.81±3.13	172.79
Sulfathiazole	0.89±1.68	188.81	0.22±0.35	156.36	0.93±1.59	171.05
Imidacloprid	944.05±592.38	62.74	142.12±85.91	60.45	0.35±0.20	56.21
Sulfamethazine	0.29±0.48	165.95	0.14±0.11	84.03	1.59±1.82	114.75
Triadimenol	0.10±0.11	105.88	-	-	-	-
17.hydroxyprogesterone	BDL	-	0.36±0.63	172.66	0.54±0.99	181.70
Ciprofloxacin	160.74±139.80	86.97	70.86±70.11	98.93	1.68±2.62	155.69
Danofloxacin	BDL	-	1.24±2.38	191.95	0.12±0.15	120.79
Ofloxacin	244.25±207.07	84.77	60.02±48.77	81.25	0.33±0.47	140.69
Amoxicillin	11.94±23.78	199.16	1.79±3.49	194.43	0.05±0.01	26.08
Risperidone	4.09±7.59	185.22	1.47±1.66	113.45	1.21±2.20	181.88
Erythromycin	1.28±1.84	143.32	0.44±0.45	104.34	0.05±0.01	31.07
Metoprolol	29.15±23.33	80.04	4.81±2.51	52.34	0.20±0.21	104.57
Acetamiprid	15.95±15.06	94.41	1.85±2.56	138.34	0.06±0.03	47.52
Isoproturon	0.48±0.87	179.45	2.47±4.48	195.95	15.07±30.05	199.33
Ampicillin	0.35±0.60	171.59	BDL	-	BDL	-
Cortisol (hydro- cortisol)	6.06±12.02	198.35	BDL	-	BDL	-

SD: Standard of deviation; **RSD (%):** Relative standard of deviation (%); **BDL:** Below detection limit

3.2. Ecological Risk Assessment of Investigated CECs

An ecological risk assessment was conducted to evaluate the environmental consequences of CECs in wastewater effluents, seawater, and sediments under study focusing on representative species within the food chain commonly employed in acute toxicity tests. The MECs utilized in our study were derived from actual maximum measurements of micropollutants in Sharjah WWTP effluents, seawater, and sediments. PNEC values were established by dividing LC50 or EC50 values of each emerging micropollutant, obtained from toxicological literature, by a safety factor of 1000.

Calculated RQ values, as depicted in Figure 1, varied across WWTP effluents, seawater, and sediments. For *Daphnia*, the RQ ranged from negligible to 35.64, 4.72, and 0.01 in WWTP effluents, seawater, and sediments, respectively. Similarly, fish exhibited RQ values from negligible to 11.04, 1.46, and 3.22, while algae showed RQs from negligible to 4.57, 0.6, and 1.39 in the respective environments.

Within WWTP effluents, imidacloprid triggered highest concern with RQ values of 4.57, 11.04, and 35.64 for algae, *Daphnia*, and fish, respectively. Ofloxacin followed closely with RQ values of 27.05 and 1.02 for algae and fish. Additionally, a medium effect on *Daphnia* was observed, with an RQ of 0.37. Medium impacts were also noted for sulphathiazole with RQ values of 0.26.

In seawater samples, imidacloprid again exhibited a high risk on fish and *Daphnia* (RQ = 1.46 and 4.72), with a medium effect on algae (RQ = 0.6). For ofloxacin, the marine environment revealed a high toxic effect on algae (RQ = 5.45) and medium effects on fish (RQ = 0.2). In addition, a medium effect of isoproturon on algae (RQ = 0.22) was recorded.

Sediment samples disclosed elevated toxicity levels for imidacloprid on fish and isoproturon on algae (RQ = 3.22 and 1.39), while sulfathiazole demonstrated a medium effect on algae. As expected, the highest risks were determined for wastewater effluents since the highest concentrations of CECs can be found in this matrix. However, even at low concentrations, CECs can promote high risk. Our findings highlight Imidacloprid as the most ecotoxic contaminant across the three sample matrices, with *Daphnia* being the most sensitive organism, followed by fish and algae.

Fig. 1: Ecological risks for detected CECs in wastewater effluent (A), seawater (B) and sediment (C) against algae, *Daphnia* and fish.

4. Conclusion

In the study, out of the investigated 25 target CECs, 21 CECs were present in effluent samples, 23 in seawater, and in sediment samples, with concentrations ranging from low ng L^{-1} up to 1782 ng L^{-1} in the effluents, up to 236.10 ng in seawater, and up to 60.15 ng g^{-1} in sediments., The RQ methodology has identified imidacloprid, ofloxacin, and isoproturon as posing elevated ecological risks, while sulphathiazole was classified to have a moderate-risk. there is a need to address the environmental risks associated with these emerging contaminants, particularly concerning their impact on aquatic ecosystems. Implementation of advanced wastewater treatment processes, adequate discharge measures, and continued environmental monitoring are recommended to mitigate ecological hazards.

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