Study of the occurrence, sources and distribution trends of emerging contaminants in the Saronikos Gulf and Elefsis Gulf, Greece, utilizing ion mobility tandem high resolution mass spectrometry

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Abstract: This study investigates the occurrence, distribution and ecological risk of emerging contaminants (ECs) and priority pollutants (PPs) in seawater and sediments of the Saronikos Gulf, and Elefsis Bay, Greece. The occurrence of more than 4,000 LC-amenable organic micropollutants was investigated through wide-scope target and suspect screening. A total of 171 analytes were detected, with pharmaceuticals identified as the most prevalent class. Semi-polar ECs with higher molar mass were determined exclusively in sediments near WWTPs, possibly due to their high logP values, reflecting their affinity for particulate matter. Additionally, seawater circulation was found to play a significant role in controlling the spatial distribution of ECs. Comparison with earlier studies suggests a shift in pharmaceutical usage by local population. Risk assessment revealed that PFAS exceeded annual average environmental quality standard values in 92% of seawater samples, whereas 20 ECs in seawater and 12 in sediments exceeded predicted no-effect concentrations, indicating potential adverse effects on marine biota.

Keywords: ion mobility spectrometry, wastewater, seawater, sediments, target/suspect screening

1. Introduction

Over the past years, emerging contaminants (ECs) have gained the wide interest of the scientific community, due to the possible risks they pose towards both human health and environmental ecological balance[1,2]. Wastewater treatment plants (WWTPs) have been highlighted as major sources of ECs, since the complete removal of ECs is yet to be achieved. It is reported that in WWTPs, removal efficiency varies in the range of 20-50%, 30-70%, and, in some cases, >90% during the primary, secondary, and tertiary treatment steps[3,4].

Following the release of ECs in the marine environment, biotic and abiotic processes take place, leading to their degradation, forming transformation products[5]. These compounds can potentially pose even greater adverse effects than parent substances towards human health. Sediments constitute a significant long-term repository for high lipophilicity ECs in the marine environment considering their high logP values[6].

Herein, a wide-scope target screening of more than 2,500 semi-polar to polar LC-amenable ECs from different chemical classes was conducted, by applying a novel analytical methodology utilizing liquid chromatography trapped ion mobility spectrometry tandem high-resolution mass spectrometry (LC-TIMS-HRMS). Additionally, a suspect screening was performed, covering a wide variety of surfactants. An ecological risk assessment was also conducted to prioritize detected chemicals risk-wise.

2. Materials and methods

In March 2023, a sampling campaign was conducted, collecting marine and wastewater samples obtained from both wastewater treatment plants (WWTPs) operating in the region. Upon reaching the lab, samples were immediately treated through generic sample preparation workflows, based on previously reported methods[7].

3. Results and discussion

A total of 171 analytes were detected in marine samples of the Saronikos Gulf and Elefsis Bay areas, 128 of which in seawater, while 70 in sediments. Regarding wastewater analysis, 189 compounds were determined in influents and 162 in effluents. Among them, 25 were solely detected in effluents, possibly due to transformation mechanisms of influent compounds during the cleanup process[8].

In general, more polar ECs were present in aqueous matrices, in contrast to the sediment layer, which is generally comparted by semi-polar lipophilic ECs with higher logP values. Literature suggests that semi- to nonpolar chemicals form aggregations with microplastics through sorption effects[9]. These aggregations continuously contribute to the formation of new sediment.

Overall, the environmental quality status of the study area was not determined to be heavily burdened by anthropogenic chemicals. Risk assessment performed in studied samples showed that only a small fraction of detected substances exceed annual average values of concentrations reported in EU legislation. Regarding PNEC values, a total of 20 compounds presented high-risk for studied seawater, while 12 compounds presented high-risk for sediments **(Tables 1&2)**.

Table 1. High-risk compounds in seawater samples

Analyte name	%FoD	PNEC exceedance	Max RQF
C12-LAS	15%	15% (n=2)	48.4
Nicosulfuron	8%	8% (n=1)	30.7
4-nitrophenol	15%	15% (n=2)	23.6
Fenbendazole	15%	15% (n=2)	15.7
C13-LAS	15%	15% (n=2)	11.4
Benzododecinium	100%	77% (n=10)	11.0
N-methyl dodecylamine	92%	23% (n=3)	4.35
Ibuprofen	46%	31% (n=4)	4.34
N,N-dimethyl dodecylamine	15%	15% (n=2)	3.09
Bisphenol AF	15%	15% (n=2)	2.98
2-phenylphenol	15%	8% (n=1)	2.42
Benzyl dimethyl tetradecyl ammonium	100%	8% (n=1)	2.00
BAC 14	15%	15% (n=2)	1.96
Octhilinone	15%	15% (n=2)	1.62
1-naphthol	15%	8% (n=1)	1.25
Thiabendazole	23%	8% (n=1)	1.13
Fluometuron	54%	8% (n=1)	1.10
Benzyl dimethyl hexadecyl ammonium	15%	8% (n=1)	1.08
BAC 16	8%	8% (n=1)	1.04
Dinoterb	92%	8% (n=1)	1.01

Table 2. High-risk compounds in sediment samples

Analyte Name	%FoD	PNEC exceedance	Max RQF
Perfluorooctane sulfonic acid (PFOS)	100%	100% (n=4)	586
Di-(2-ethylhexyl) phthalate (DEHP)	100%	100% (n=4)	471
Octhilinone	100%	100% (n=4)	1.95
2-phenethylamine	100%	75% (n=3)	3.51
Venlafaxine	75%	75% (n=3)	2.27
Methyl-pirimiphos	50%	50% (n=2)	9.11
Miconazole	75%	50% (n=2)	4.39
Nicotine	50%	50% (n=2)	15.9
Anabasine	50%	25% (n=1)	6.51
Fenbendazole	50%	25% (n=1)	1.59
Isoproturon	25%	25% (n=1)	1.75
Phorate-sulfone	25%	25% (n=1)	7.89

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