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ORIGINAL PAPER

Wastewater treatment plant efficiency and contaminant levels in a Mediterranean coastal area: a comprehensive inventory and assessment

P. Merdy[1] · F. Delpy[1] · G. Baratto[2] · E. Plessis[2] · Y. Lucas[1]

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Abstract
The contamination of estuarine and coastal waters raises the question of risk assessment, management and remediation, all of which require a good knowledge of the contamination present. Most studies focus on specific species in samples from a given site, but few examine the presence of multiple contaminants at once. Here we considered 7 nonmetallic inorganics, 32 metals and metalloids, 4 chlorobenzenes, 16 PAHs, 8 PCBs, 34 organochloride pesticides and 239 other pesticides or pesticide metabolites, 12 pharmaceuticals and 2 others, in sea water, sediments, and in urban wastewater before and after treatment. Our study sites included a reference station, a harbor, a coastal bay and a treated wastewater outlet plume. Our results provide insight into the current contamination levels and the efficiency of the wastewater treatment plant for a wide range of contaminants. Although some organic contaminants remained at concentrations above the limit of reporting in the treated water, the dilution effect in the plume was sufficient to bring most of the organic contaminants studied below detectable levels, except for 17α-ethinylestradiol, which was the most commonly detected contaminants. This finding underscores the insufficient reduction of endocrine disruptors by current wastewater treatment.

Keywords Persistent compounds · Trace metals · Pharmaceuticals · Coastal waters · WWTP effluents · Mass load

Introduction

Coastal marine environments face significant impact from human activities, as they receive and concentrate numerous anthropogenic pollutants. The coastal zone, acting as a buffer between the land and the ocean, plays a critical role in providing various ecosystem services (Lu et al. 2018). Consequently, conserving this zone becomes imperative to ensure the sustainable utilization of marine resources (ICSU-ISSC 2015). Contaminants found in the coastal zone can originate either directly from the marine environment or more commonly, they are transported from the continental environment (Riechers et al. 2021), particularly from large rivers and the surrounding coastal areas. Depending on the specific type of contaminant, local sources may exert greater influence, primarily due to the high population density and urban development in coastal regions (Creel 2003; Nicolau et al. 2012; Merkens et al. 2016). The contaminants that tend to accumulate or transit in coastal regions encompass chemicals, metal, metalloids, nutrients, oil, microplastics, and plastics (Riechers et al. 2021). These contaminants can emanate from diffuse, non-point sources or localized, point sources, and their contamination can manifest as either sporadic or long-term occurrences.

Within the realm of chemical micropollutants, pesticides and pharmaceuticals stand out as major concerns (Fent et al. 2006). Notably, pesticides like glyphosate, a non-selective herbicide extensively employed by farmers and gardeners, pose a significant risk off runoff into watersheds and groundwater through soil infiltration (Daouk et al. 2015; Dollinger 2016). The concentrations of glyphosate in surface waters can, in the most severe cases, reach the mg L^{-1} range, while they typically reside in the µg L^{-1} range in rivers and ng L^{-1} in seawater (Annett et al. 2014; Bento et al. 2021; Feltracco et al., 2021). However, the prevalence of glyphosate

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✉ P. Merdy
merdy@univ-tln.fr

[1] Université de Toulon, Aix Marseille Univ., CNRS, IM2NP, 83041 Toulon Cedex 9, France

[2] Véolia Eau, Var Provence Méditerranée, Rue Des Oliviers - Le Pouverel, La Garde (83), France

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in aquatic environments is frequently underestimated due to its degradation into aminomethylphosphonic acid (AMPA), which can reach concentrations surpassing those of glyphosate by more than fourfold (Bento et al. 2021).

Pharmaceuticals compounds, including antibiotics, analgesics, and nonsteroidal anti-inflammatory drugs, have been identified in seawater by dedicated studies (Gaw et al. 2014; Puckowski et al. 2016; Madikizela et al. 2020). Despite growing awareness of the potential impact of these drugs on aquatic organisms, current regulations do not account for their release into the environment, whether directly or through wastewater treatment plant (WWTP) effluents. In Europe, the regulatory framework for medicinal products is outlined in Directive 2001/83/EC, which lacks provisions addressing the discharge of these substances into the environment. In contrast, guidelines specifying permissible limits exist for most potentially toxic metals and metalloids. While veterinary pharmaceuticals can be directly released into the environment, the majority of human medicine products pass through WWTPs. However, the effectiveness of WWTPs in removing these pharmaceuticals varies significantly depending on the specific compound (Strenn et al. 2004).

In Europe, the main approach to reducing the presence of micropollutants in the environment is to implement reductions, or bans, on their use upstream of rivers or WWTPs. The Water Framework Directive (CEC 2000) aims to achieve a "good" ecological and chemical status for water bodies. The chemical status assessment is based on the analysis of 45 priority substances, encompassing 24 pesticides and only three pharmaceuticals, while the ecological status assessment involves 177 molecules (EU-CDI 2013). However, this list, established nearly a decade ago, falls short of reflection the advancements in understanding micropollutants and their evolving sources.

Chemicals also fall within the purview of the European REACH regulation, designed to establish a harmonized system for the registration, evaluation, and authorization of chemical substances at the European level (Williams et al. 2009). Currently, this framework does not encompass pharmaceutical substances, although their inclusion is under investigation.

Scientists engage in research efforts aimed at informing and shaping regulatory frameworks, often with the support and encouragement of government agencies. In 2009, the NORMAN's Bioassay Working Group was established with the mission of fostering information exchange, method and tool validation, and project coordination related to the assessment of emerging environmental compounds (INERIS 2018). These substances fall outside the scope of routine monitoring programs in Europe, and there remains limited understanding of their behavior, fate, and (eco)toxicological impacts. To address these concerns, the OSPAR convention binds its signatory nations to identify environmental threats and collaboratively undertake effective measures against the most hazardous substances in marine environments. The European Parliament voted on 5/10/2023 for a proposal for a Directive specifically addressing urban wastewater treatment.

It is therefore crucial to ehance our comprehension of contaminants in the environment and to translate this knowledge into regulatory actions. While individual studies on specific contaminants are essential to decipher their behavior and impacts, a holistic understanding of all potential contaminants within a given area becomes crucial, especially when assessing the cumulative effects of multiple contaminants on aquatic ecosystems (Relyea 2009; Saaristo et al. 2018; Petersen et al. 2014). To this end, we conducted an inventory of potential contaminants in the coastal waters and sediments of a Mediterranean coastal agglomeration characterized by a wide array of activities. Our analysis targeted a large number of potential contaminants on the same site, which is innovative: 10 nonmetallic inorganic parameters, 32 dissolved metals, 5 chlorobenzenes, 19 PAHs, 10 PCBs, 40 organochlorine pesticides, 242 non-organochlorine pesticides, 1 PBBs, and 12 pharmaceuticals. To evaluate the influence of wastewater treatment plants (WWTPs) on the coastal environment, we conducted sampling at both the WWTP entrance and exit, as well as in the sea near the WWTP outlet. Furthermore, we conducted sediment analysis in addition to surface water analysis at three distinct sampling stations, recognizing the tendency of certain organic compounds to adsorb to solid particles.

Materials and methods

Sample site description

Located on the French coast of the Mediterranean Sea, the Toulon Bay is bordered by a metropolis of about 450,000 inhabitants. The site has been subjected to various human activities (e.g., intense maritime traffic, commercial, military port and marina, urban, industrial and agricultural discharges) resulting in high contamination of organometallic compounds (mono-, di- and tributyltin), organic (PAHs, PCBs, pesticides, pharmaceuticals, etc.) and metals (mercury, copper, lead, cadmium, etc.) whether in the water column or in sediments. Six sampling stations were chosen, distributed inside and outside the Toulon Bay (Fig. 1, Table 1), representative of the main environmental situations observed in the area. At each station, water was sampled at 1 m depth. The REF station is a point of reference, situated upstream of Toulon with regard to the liguro-provençal current, therefore the closest point relatively protected from the anthropogenic impacts that affect the Toulon area. The Plume1, Plume2 and

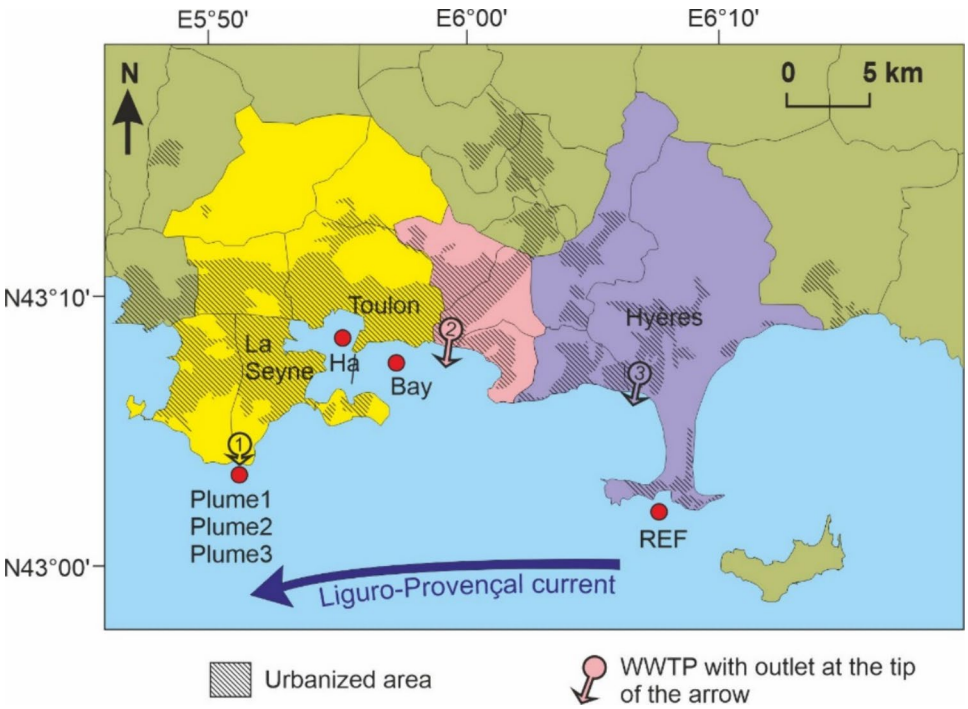

Fig. 1 Location of the sampling points. Each colored area refers to a different wastewater treatment plant. 1: Amphitria WWTP

Plume3 stations are located in the treated water discharge plume of the Amphitria WWTP, which has a capacity of 500×10^3 Population Equivalent (PE) for a reference flow of 86×10^3 m^3 d^{-1}. The Plume1 station is vertical to the outlet located at a depth of 6 m, the Plume2 and Plume3 stations are located 150 m and 300 m, respectively, downstream in the plume. Two other WWTPs with a capacity of 106×10^3 and 122×10^3 PE treat the wastewater of the metropolis (Fig. 1). The Bay station is located in the middle of the Toulon Bay. The Ha station (Harbour station) is located within the protected port area, shielded from the waves by a dyke which limits water exchanges with the outer part of the bay. The port area has a depth of less than 20 m and a multi-contaminated sediment (Tessier et al. 2011; Pougnet et al. 2014).

Sampling

The samples at sea were taken 1 m below the surface using a NISKIN-type sampling bottle. Temperature, salinity, pH, dissolved oxygen, redox potential, turbidity and chlorophyll of seawater were measured in situ at sampling time using a multiparametric probe (Hydrolab DS5). Various procedures were carried out immediately after sampling, depending on the type of analysis required. For dissolved organic carbon (DOC), 10 mL of water was filtered through a 0.45 µm nitrocellulose syringe filter pre-rinsed with 10% HNO_3 nitric acid, then stored at 10 °C in a 15 mL centrifuge tube, to which 100 µL of 1 M NaN_3 (sodium azide) was added to prevent microbial activity until analysis. For ions, 10 mL of water was filtered through the same type of syringe filter, then collected in a 15 mL centrifuge tube and stored at −20 °C until analysis. For metals, 40 mL of water was filtered through the same type of syringe filter, then collected in a 50 mL centrifuge tube, acidified with 200 µL of 70% HNO_3 nitric acid and stored at 10 °C until analysis. For organic molecules, 2 L of water was taken in a glass bottle, then stored at 10 °C until analysis.

Wastewater was sampled at the Amphitria WWPT (station 1 on Fig. 1). Raw sewage (RS) and treated wastewater (TWW) were sampled upstream and downstream, respectively, of the WWTP to assess the % of abatement for the targeted chemicals. RS and TWW were sampled twice, once in July 2017 and again in February 2018, to investigate possible differences between summer, with high tourist load, and winter. The July 2017 sampling took place during a dry period, with more than 30 days without rain, whereas the February 2018 sampling occurred after approximately 50 mm fell over the area in the preceding 10 days. Annual species fluxes to the sea were calculated using the average TWW concentrations from the two sampling, with a concentration of 0 assigned when a species concentration was below the Limit of Reporting (LOR). The average annual volume of TWW was 18.6×10^6 m^3.

Sediment samples were collected using a Van Walt stainless steel weighted grab. After collection, they were oven dried at 45 °C then sieved at 2 mm.

Table 1 List of elements or compounds analyzed.

Non metallic species											
Ammonia and ammonium ions as N (PHO)	0.040 mg/L			Ammonia and ammonium ions as N (SPC)	0.040 mg/L			Fluoride	0.200 mg/L		
Nitrates	2.00 mg/L			Nitrites	0.040 mg/L			Orthophosphate as P	0.010 mg/L		
Sulphate as SO_4^{2-}	5.00 mg/L										
Dissolved metals											
Ag	1.0 µg/L	Bo	10.0 µg/L	Fe	2.0 µg/L	Mo	1.0 µg/L	Se	1.0 µg/L	V	5.0 µg/L
Al	5.0 µg/L	Ca	0.005 mg/L	Hg	0.01 µg/L	Na	0.03 mg/L	Sn	1.0 µg/L	Zn	2.0 µg/L
As	1.0 µg/L	Cd	0.5 µg/L	K	0.015 mg/L	Ni	3.0 µg/L	Sr	1.0 µg/L		
Ba	1.0 µg/L	Co	0.5 µg/L	Li	1.0 µg/L	P	0.05 mg/L	Te	5.0 µg/L		
Be	0.2 µg/L	Cr	5.0 µg/L	Mg	10 µg/L	Pb	1.0 µg/L	Th	0.5 µg/L		
Bi	1.0 µg/L	Cu	1.0 µg/L	Mn	0.5 µg/L	Sb	1.0 µg/L	Ti	5.0 µg/L		
Chlorobenzenes											
1.2.3.5- &1.2.4.5-Tetrachlorobenzene	0.004 µg/L			1.2.3.4-Tetrachlorobenzene	0.002 µg/L						
Hexachlorobenzene (HCB)	0.002 µg/L			Pentachlorobenzene	0.002 µg/L						
PAHs											
Naphthalene	0.005 µg/L			Fluoranthene	0.001 µg/L			Benzo(k)fluoranthene	0.001 µg/L		
Acenaphthylene	0.001 µg/L			Pyrene	0.001 µg/L			Benzo(a)pyrene	0.001 µg/L		
Acenaphthene	0.001 µg/L			Benz(a)anthracene	0.001 µg/L			Indeno(1.2.3.cd)pyrene	0.001 µg/L		
Fluorene	0.001 µg/L			Chrysene	0.001 µg/L			Dibenz(a.h)anthracene	0.001 µg/L		
Phenanthrene	0.001 µg/L			Benzo(b)fluoranthene	0.001 µg/L			Benzo(g.h.i)perylene	0.001 µg/L		
Anthracene	0.001 µg/L										
PCBs											
PCB 28	0.001 µg/L		PCB 101	0.001 µg/L		PCB 138	0.001 µg/L		PCB 180	0.001 µg/L	
PCB 52	0.001 µg/L		PCB 118	0.001 µg/L		PCB 153	0.001 µg/L		PCB 194	0.001 µg/L	
Organochlorine pesticides											
2.4-DDD	0.002 µg/L		Dichlobenil	0.002 µg/L		Hexachlorobutadiene	0.002 µg/L				
2.4-DDE	0.002 µg/L		Dieldrin	0.002 µg/L		Hexachloroethane	0.002 µg/L				
2.4-DDT	0.002 µg/L		Endosulfan sulfate	0.005 µg/L		Isodrin	0.002 µg/L				
4.4`-DDD	0.002 µg/L		Endrin	0.002 µg/L		Methoxychlor	0.005 µg/L				
4.4`-DDE	0.002 µg/L		Heptachlor	0.002 µg/L		Mirex	0.002 µg/L				
4.4`-DDT	0.002 µg/L		Heptachloroepoxide-cis	0.005 µg/L		Oxychlordane	0.005 µg/L				
Alachlor	0.005 µg/L		Heptachloroepoxide-trans	0.005 µg/L		Pentachlorotoluene	0.002 µg/L				
Aldrin	0.002 µg/L		Hexachlorocyclohexane Alpha	0.002 µg/L		Telodrin	0.002 µg/L				
alpha-Endosulfan	0.002 µg/L		Hexachlorocyclohexane Beta	0.002 µg/L		trans-Chlordane	0.003 µg/L				
beta-Endosulfan	0.002 µg/L		Hexachlorocyclohexane Delta	0.002 µg/L		Trans-Nonachlor	0.003 µg/L				
cis-Chlordane	0.005 µg/L		Hexachlorocyclohexane Epsilon	0.002 µg/L							
cis-Nonachlor	0.002 µg/L		Hexachlorocyclohexane Gamma	0.002 µg/L							
Pesticides											
1-(3.4-Dichlorophenyl) urea (DCPU)	0.05 µg/L		2-amino-N-(isopropyl) benzamide	0.05 µg/L		2-Chloro-2.6-diethylacetanilide	0.05 µg/L		Chlorotoluron-desmethyl	0.05 µg/L	
Acetamiprid	0.05 µg/L		Azoxystrobin	0.05 µg/L		Carfentrazone-ethyl	0.05 µg/L		Cybutryne (Irgarol)	0.05 µg/L	
Acetochlor	0.05 µg/L		BAM	0.05 µg/L		Chlorbromuron	0.05 µg/L		Cymoxanil	0.05 µg/L	
Acibenzolar-S-methyl	0.05 µg/L		BDMC	0.05 µg/L		Chlorfenvinphos	0.05 µg/L		Cyprazine	0.05 µg/L	
Aclonifen	0.05 µg/L		Benalaxyl	0.05 µg/L		Chloridazon	0.05 µg/L		Cyproconazole	0.05 µg/L	
Alachlor	0.05 µg/L		Bendiocarb	0.05 µg/L		Chloridazon-desphenyl	0.05 µg/L		Cyprodinil	0.05 µg/L	
Aldicarb	0.05 µg/L		Bentazone methyl	0.05 µg/L		Chlorotoluron	0.05 µg/L		Cyromazine	0.05 µg/L	

Table 1 (continued)

Pesticides							
Aldicarb sulfone	0.05 µg/L	Bifenox	0.05 µg/L	Chloroxuron	0.05 µg/L	DEET	0.05 µg/L
Ametryn	0.05 µg/L	Bitertanol	0.05 µg/L	Chlorpropham	0.05 µg/L	Desmetryn	0.05 µg/L
Amidosulfuron	0.05 µg/L	Boscalid	0.05 µg/L	Chlorpyrifos	0.05 µg/L	Diazinon	0.05 µg/L
Amitrole	0.1 µg/L	Bromacil	0.05 µg/L	Chlorpyrifos-methyl	0.05 µg/L	Dichlofenthion	0.05 µg/L
AMPA	0.05 µg/L	Bromophos-ethyl	0.05 µg/L	Chlorsulfuron	0.05 µg/L	Dichlormid	0.05 µg/L
Atraton	0.05 µg/L	Cadusafos	0.05 µg/L	Clodinafop	0.05 µg/L	Dichlorvos	0.05 µg/L
Atrazine	0.05 µg/L	Carbaryl	0.05 µg/L	Clomazone	0.05 µg/L	Dicrotophos	0.05 µg/L
Atrazine-2-hydroxy	0.05 µg/L	Carbendazim	0.05 µg/L	Clomeprop	0.05 µg/L	Diethofencarb	0.05 µg/L
Atrazine-desethyl	0.05 µg/L	Carbetamide	0.05 µg/L	Clothianidin	0.05 µg/L	Difenacoum	0.05 µg/L
Atrazine-desisopropyl	0.05 µg/L	Carbofuran	0.05 µg/L	Coumaphos	0.05 µg/L	Difenoconazole	0.05 µg/L
Azinphos-ethyl	0.05 µg/L	Carbofuran-3-hydroxy	0.05 µg/L	Crimidine	0.05 µg/L	Difenoxuron	0.05 µg/L
Azinphos-methyl	0.05 µg/L	Carboxin	0.05 µg/L	Cyanazine	0.05 µg/L	Diflubenzuron	0.05 µg/L
Pesticides							
Diflubenzuron	0.05 µg/L	Imazamox	0.05 µg/L	Neburon	0.05 µg/L	Pyribenzoxim	0.05 µg/L
Diflufenican	0.05 µg/L	Imazethapyr	0.05 µg/L	Nicosulfuron	0.05 µg/L	Pyrimethanil	0.05 µg/L
Dimefuron	0.05 µg/L	Imidacloprid	0.05 µg/L	Nuarimol	0.05 µg/L	Pyriproxifen	0.05 µg/L
Dimethachlor	0.05 µg/L	Indoxacarb	0.05 µg/L	Omethoate	0.05 µg/L	Quinclorac	0.05 µg/L
Dimethenamid	0.05 µg/L	Iprodione	0.05 µg/L	Oxadixyl	0.05 µg/L	Quinmerac	0.05 µg/L
Dimethoate	0.05 µg/L	Iprovalicarb	0.05 µg/L	Oxamyl	0.05 µg/L	Quinoxyfen	0.05 µg/L
Dimethomorph	0.05 µg/L	Isoproturon	0.05 µg/L	Paclobutrazol	0.05 µg/L	Quizalofop	0.05 µg/L
Diuron	0.05 µg/L	Isoproturon-desmethyl	0.05 µg/L	Paraoxon-ethyl	0.05 µg/L	Rimsulfuron	0.05 µg/L
Diuron desmethyl (DCPMU)	0.05 µg/L	Isoproturon-monodes-methyl	0.05 µg/L	Paraoxon-methyl	0.05 µg/L	Sebuthylazine	0.05 µg/L
Epoxiconazole	0.05 µg/L	Isopyrazam	0.05 µg/L	Parathion-ethyl	0.05 µg/L	Secbumeton	0.05 µg/L
EPTC	0.05 µg/L	Kresoxim-methyl	0.05 µg/L	Penconazole	0.05 µg/L	Sethoxydim	0.05 µg/L
Ethiofencarb	0.05 µg/L	Lenacil	0.05 µg/L	Pencycuron	0.05 µg/L	Simazine	0.05 µg/L
Ethion	0.05 µg/L	Linuron	0.05 µg/L	Pendimethalin	0.05 µg/L	Simazine-2-hydroxy	0.05 µg/L
Ethofumesate	0.05 µg/L	Malaoxon	0.05 µg/L	Phorate	0.05 µg/L	Simetryn	0.05 µg/L
Ethoprophos	0.05 µg/L	Malathion	0.05 µg/L	Phosalone	0.05 µg/L	Spiroxamine	0.05 µg/L
Fenamiphos	0.05 µg/L	Mandipropamid	0.05 µg/L	Phosmet	0.05 µg/L	Sulfosulfuron	0.05 µg/L
Fenarimol	0.05 µg/L	Mecarbam	0.05 µg/L	Phosphamidon	0.05 µg/L	Tebuconazole	0.05 µg/L
Fenhexamid	0.05 µg/L	Mefenpyr-diethyl	0.05 µg/L	Picloram	0.05 µg/L	Tebuthiuron	0.05 µg/L
Fenoxaprop	0.05 µg/L	Mesosulfuron-methyl	0.05 µg/L	Picoxystrobin	0.05 µg/L	Teflubenzuron	0.05 µg/L
Fenoxycarb	0.05 µg/L	Mesotrione	0.05 µg/L	Pirimicarb	0.05 µg/L	Terbuthylazine	0.05 µg/L
Fenpropidin	0.05 µg/L	Metalaxyl (isomers)	0.05 µg/L	Pirimiphos-ethyl	0.05 µg/L	Terbuthylazine-desethyl	0.05 µg/L
Fenpropimorph	0.05 µg/L	Metamitron	0.05 µg/L	Pirimiphos-methyl	0.05 µg/L	Terbuthylazine-desethyl-2-hydroxy	0.05 µg/L
Fensulfothion	0.05 µg/L	Metazachlor	0.05 µg/L	Pretilachlor	0.05 µg/L	Terbuthylazine-hydroxy	0.05 µg/L
Fenuron	0.05 µg/L	Metconazole	0.05 µg/L	Primisulfuron-methyl	0.05 µg/L	Terbutryn	0.05 µg/L
Fipronil	0.05 µg/L	Methabenzthiazuron	0.05 µg/L	Prochloraz	0.05 µg/L	Thiabendazole	0.05 µg/L
Florasulam	0.05 µg/L	Methamidophos	0.05 µg/L	Prodiamine	0.05 µg/L	Thiamethoxam	0.05 µg/L
Fluazifop	0.05 µg/L	Methidathion	0.05 µg/L	Profenofos	0.05 µg/L	Thifensulfuron-methyl	0.05 µg/L
Fluazifop-butyl (isomers)	0.05 µg/L	Methiocarb	0.05 µg/L	Promecarb	0.05 µg/L	Thiobencarb	0.05 µg/L
Flusilazole	0.05 µg/L	Methomyl	0.05 µg/L	Prometon	0.05 µg/L	Thiophanate-methyl	0.05 µg/L
Flutolanil	0.05 µg/L	Methoxyfenozide	0.05 µg/L	Prometryn	0.05 µg/L	Triadimefon	0.05 µg/L
Fonofos	0.05 µg/L	Metobromuron	0.05 µg/L	Propachlor	0.05 µg/L	Triadimenol	0.05 µg/L
Foramsulfuron	0.05 µg/L	Metolachlor (isomers)	0.05 µg/L	Propamocarb	0.05 µg/L	Tri-allate	0.05 µg/L

Table 1 (continued)

Pesticides							
Furathiocarb	0.05 µg/L	Metoxuron	0.05 µg/L	Propanil	0.05 µg/L	Triasulfuron	0.05 µg/L
Glufosinate ammonium	0.1 µg/L	Metribuzin	0.05 µg/L	Propaquizafop	0.05 µg/L	Triazophos	0.05 µg/L
Glyphosate	0.05 µg/L	Metribuzin-desamino	0.05 µg/L	Propazine	0.05 µg/L	Tribenuron-methyl	0.05 µg/L
Haloxyfop	0.05 µg/L	Metsulfuron-methyl	0.05 µg/L	Propham	0.05 µg/L	Tricyclazole	0.05 µg/L
Haloxyfop-methyl (isomers)	0.05 µg/L	Molinate	0.05 µg/L	Propiconazole	0.05 µg/L	Trifloxysulfuron-sodium	0.05 µg/L
Hexaconazole	0.05 µg/L	Monocrotophos	0.05 µg/L	Propoxur	0.05 µg/L	Trifluralin	0.005 µg/L
Hexazinone	0.05 µg/L	Monolinuron	0.05 µg/L	Propoxycarbazone-sodium	0.05 µg/L	Triflusulfuron-methyl	0.05 µg/L
Hexythiazox	0.05 µg/L	Monuron	0.05 µg/L	Propyzamide	0.05 µg/L	Triforine	0.05 µg/L
Imazalil	0.05 µg/L	Napropamide	0.05 µg/L	Prosulfocarb	0.05 µg/L	Triticonazole	0.05 µg/L
Imazamethabenz-methyl	0.05 µg/L	Naptalam	0.05 µg/L	Prothioconazole	0.05 µg/L		
Others							
PBB 153		0.002 µg/L		Octachlorostyrene		0.003 µg/L	
Pharmaceuticals							
Carbamazepine		0.01 mg/L		17β-oestradiol (E2)		0.0003 µg/L	
Clorofibric acid		0.01 mg/L		17α-ethinyloestradiol (EE2)		0.00003 µg/L	
Clarithromycin		0.001 µg/L		Ibuprofen		0.01 mg/L	
Diclofenac		0.01 mg/L		Paracetamol		0.01 mg/L	
Fluoxetin		0.0002 µg/L		Propanolol		0.01 mg/L	
Gemfibrosil		0.01 mg/L		Tamoxifen		0.005 µg/L	

For each of them is given the limit of reporting (LOR). The elements or compounds marked in blue had a concentration higher than the LOR for at least one of the samples analyzed

Chemical analysis

Phosphates were analyzed by spectrophotometry (SHIMADZU®, UV-1800) according to the method of Murphy and Riley (1962), with the modifications of Strickland and Parsons (1972) (dl 0.02 µM). All other analysis were performed in the certified laboratory ALS Czech Republic, Prague, using the following methods: NH_3 and NH_4^+ by discrete spectrophotometry; F^-, NO_3^-, NO_2^- and SO_4^{2-} by ion liquid chromatography; major cations Ca, P, K and Na by atomic emission spectrometry with inductively coupled plasma; other dissolved metals (excepting Hg) and metalloids by mass spectrometry with inductively coupled plasma; Hg by atomic fluorescence spectrometry; clarithromycin and fluoxetine by high-performance liquid chromatography; tamoxifen, 17β oestradiol and 17α-ethinyloestradiol by gas chromatography-mass spectrometry; octachlorostyrene, chlorobenzenes, PAHs, PCBs, organochlorine pesticides, trifluralin, PBB163 by gas chromatography-tandem mass spectrometry; all other pesticides by liquid chromatography-tandem mass spectrometry with prior derivatization for amitrole, AMPA, glufosinate ammonium and glyphosate. Sediment total analysis was performed on the < 2 mm fraction. Organics in the sediments were analyzed on a water extract at the solid/liquid ratio of 1/10 of the pulverized sample. The analyzed species are listed on Table 1.

Results and discussion

This article discusses the concentration data for substances with concentrations above the limit of reporting (LOR) for at least one of the samples. The set of results can be consulted in the supplementary data.

From wastewater to WWTP plume at sea

Inorganic species did not show significant differences between the two sampling periods (see Table 2). Nitrates and nitrites were absent in the WWTP inlet but present at the outlet due to nitrification of the ammonia produced by organic matter mineralization in the treatment process. Sulfates levels may also increase as a result of the oxidation of sulfides present in the raw sewage during the treatment process. Both N and P compounds were dispersed in the plume, but their concentrations were below the limit of reporting

Table 2 Nonmetallic inorganics and metals in the raw sewage (RS), the treated wastewater (TWW) and in the TWW plume at sea.

Chemical species	Feb. 2018 sampling			Jul. 2017 sampling					
	RS	TWW	Abatement	RS	TWW	Abatement	Plume 1	Plume 2	Plume 3
Nonmetallic inorganics									
NH_3 and NH_4^+ as N (mg L^{-1})	65.3	50.5	23%	64.5	5	92%	0.301	<LOR	<LOR
Nitrates (mg L^{-1})	<LOR	10.2	nd	<LOR	163	nd	<LOR	<LOR	<LOR
Nitrites (mg L^{-1})	<LOR	3.2	nd	<LOR	2.17	nd	<LOR	<LOR	<LOR
Orthophosphate as P (mg L^{-1})	6.21	1.57	75%	5.68	2.05	64%	0.018	<LOR	<LOR
Sulfate (mg L^{-1})	287	345	-20%	379	363	4%	2780	2830	2810
Metals									
Al (µg L^{-1})	53.5	<LOR	nd	51	<LOR	nd	<LOR	<LOR	<LOR
Ba (µg L^{-1})	32	14	56%	32	14.9	53%	<LOR	<LOR	<LOR
Be (µg L^{-1})	<LOR	<LOR	nd	<LOR	<LOR	nd	<LOR	4.02	4.72
B (µg L^{-1})	586	638	-9%	682	596	13%	3960	3950	4160
Ca (mg L^{-1})	116	140	-21%	134	145	-8%	419	461	413
Cu (µg L^{-1})	<LOR	3	nd	<LOR	<LOR	nd	47.3	<LOR	<LOR
Fe (µg L^{-1})	55.3	156	-182%	208	37.6	82%	146	77.6	131
Hg (µg L^{-1})	<LOR	<LOR	nd	<LOR	0.113	nd	<LOR	<LOR	<LOR
K (mg L^{-1})	69.3	64.6	7%	77.2	74.7	3%	485	508	496
Li (µg L^{-1})	26.7	25.6	4%	30.9	29.5	5%	164	162	185
Mg (mg L^{-1})	142	146	-3%	162	167	-3%	1430	1360	1350
Mn (µg L^{-1})	41.1	76.6	-86%	607	421	31%	21.8	19.6	21.6
Na (g L^{-1})	1.1	1.0	3%	1.4	1.4	-5%	11.9	11.4	11.8
P (mg L^{-1})	6.1	1.73	72%	5.52	1.9	66%	<LOR	<LOR	<LOR
Se (µg L^{-1})	13.1	<LOR	nd	<LOR	<LOR	nd	<LOR	<LOR	<LOR
Sr (µg L^{-1})	1190	1200	-1%	1430	1430	0%	9120	8580	8670
Zn (µg L^{-1})	11.5	11.5	0%	<LOR	17	nd	92.2	89	162

LOR limit of reporting, *nd* non defined

at the second point of the plume, indicating the absence of eutrophic conditions. Metals and metalloids fell within the expected range at both inlet and outlet of the WWTP. However, higher concentrations of Fe, Ca, and Mn in TWW compared to RS could be attributed to the use of flocculants during the treatment process. In the plume, concentrations of Fe and Zn increased, indicating concentrations in the seawater higher than the typical values of approximately 0.03 and 0.4 µg L^{-1}, respectively (Bruland et al. 2014). Beryllium was not detected in sewage, TWW, or the first sample of the plume (Plume1), but it was found in the Plume2 and Plume3 samples at a concentration higher than the predicted no effect concentration (PNEC), which was evaluated at 0.08 µg L^{-1} (Assoumain and Salomon 2020). This non-radioactive metal is highly toxic and is classified as a category 1 carcinogen by the European Union. It can be generated by rock weathering or coal burning and can be found in various products such as cosmetics, electronic products, alloys, and ceramics use by various industries, including nuclear weapons, aeronautics, and coal mining. It can be found in manufacture goods like electronic compounds, alloys or ceramics, but beyond specialized industrial sites its occurrence in the environment is primarily associated with the alteration of rocks or the combustion of coal. However, further studies are required to fully interpret these observations.

Table 3 presents the concentrations of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). Out of the 16 PAHs examined, 15 were detected above the LOR. High concentrations of phenanthrene, fluoranthene, pyrene and chrysene were found in the samples from July, with values exceeding 0.02 µg L^{-1}. PAH concentrations in untreated wastewater exhibited a substantial increase in July 2017 compared to February 2018. Although forest fires occurred in the Toulon region before the sampling period in July 2017, it is challenging to ascertain how the generated PAHs could have entered the sewer system. A more plausible hypothesis involves a significant surge in backyard barbecues during the summer in the Toulon region, notably driven by the substantial rise in population associated with tourism. These barbecues emit PAHs, which may find their way into the sewer system through the washing of dishes and utensils. The WWTP demonstrated varying degrees of effectiveness in reducing PAH concentrations, with an abatement ranging from 32% (acenaphthene) to

Table 3 PAHS and PCBs in the raw sewage (RS), the treated wastewater (TWW) and in the TWW plume at sea.

Chemical species	Feb. 2018 sampling			Jul. 2017 sampling					
	RS	TWW	Abatement	RS	TWW	Abatement	Plume 1	Plume 2	Plume 3
PAHs (ng L^{-1})									
Naphtalene	34	<LOR	100%	<LOR	<LOR	nd	<LOR	<LOR	<LOR
Acenaphthylene	1.6	<LOR	100%	<LOR	<LOR	nd	<LOR	<LOR	<LOR
Acenaphthene	<LOR	<LOR	nd	3.4	2.3	32%	<LOR	<LOR	<LOR
Fluorene	5.6	<LOR	100%	7.1	3.3	54%	<LOR	<LOR	<LOR
Phenanthrene	15.5	<LOR	100%	32.6	7.3	78%	<LOR	<LOR	<LOR
Anthracene	<LOR	<LOR	nd	5.5	2.1	62%	<LOR	<LOR	<LOR
Fluoranthene	1.2	<LOR	100%	37.3	14.9	60%	<LOR	<LOR	<LOR
Pyrene	13.9	<LOR	100%	35.0	13.2	62%	<LOR	<LOR	<LOR
Benz(a)anthracene	2.6	<LOR	100%	16.4	8.4	49%	<LOR	<LOR	<LOR
Chrysene	6.9	<LOR	100%	24.3	15.3	37%	<LOR	<LOR	<LOR
Benzo(b)fluoranthene	3.9	<LOR	100%	15.2	7.0	54%	<LOR	<LOR	<LOR
Benzo(k)fluoranthene	1.8	<LOR	100%	10.0	4.3	57%	<LOR	<LOR	<LOR
Benzo(a)pyrene	2.6	<LOR	100%	9.2	3.3	64%	<LOR	<LOR	<LOR
Indeno(1.2.3.cd)pyrene	1.4	<LOR	100%	6.6	2.37	59%	<LOR	<LOR	<LOR
Benzo(g.h.i)perylene	2.5	<LOR	100%	7.7	2.7	65%	<LOR	<LOR	<LOR
PCBs (ng L^{-1})									
PCB 28	<LOR	<LOR	nd	14	1	90%	<LOR	<LOR	<LOR
PCB 138	1.8	<LOR	100%	<LOR	<LOR	nd	<LOR	<LOR	<LOR
PCB 153	1.7	<LOR	100%	<LOR	<LOR	nd	<LOR	<LOR	<LOR

LOR limit of reporting, *nd* non defined

78% (phenanthrene). In February, the raw sewage exhibited considerably lower concentrations compared to July, except for naphthalene and acenaphthylene. This discrepancy may account for the observed 100% abatement for all PAHs in February. As the plume extended, all PAH concentrations became diluted, dropping below the LOR at the very first point in the plume.

Out of the eight polychlorinated biphenyls (PCBs) analyzed, three were found at concentrations above the LOR but at low levels: PCB 28 was detected in July, while PCB 138 and 153 were detected in February (Table 3). PCB 28 exhibited a 90% abatement during wastewater treatment, while the other two were completely eliminated. At all plume sampling points, concentrations of all PCBs were below the LOR.

Regarding organochlorines and other pesticides, out of the 279 compounds analyzed, four exceeded the LOR in July 2017, and 15 exceeded it in February 2018 (Table 4). The higher number of compounds detected in February 2018 is likely due to heavy rainfall in the days preceding the sampling, resulting in the overflow of rainwater from agricultural areas into the sewer network. Pesticides have been detected in wastewater (Sutton et al. 2019; Budd et al. 2023), yet the mechanisms facilitating their entry into sewers remain inadequately characterized (Knight et al. 2023). In the context of the July 2017 and February 2018 samplings, a notable distinction lies in the heavy rainfall observed in the days leading up to the latter sampling. This precipitation may have triggered runoff from agricultural areas, causing an overflow into the sewer system and introducing professional herbicides like imazamox, propyzamide, or terbutryn. While most of these substances were present at low concentrations, three stood out: glyphosate, AMPA, and DEET. Glyphosate is the active herbicide ingredient in Roundup®, commonly used by both professionals and individuals. AMPA (aminomethylphosphonic acid) is one of its degradation residues. In raw sewage, concentrations of glyphosate and AMPA were higher in July 2017 compared to February 2018. This can be attributed to the intensive use of the herbicide during the period of vegetation growth, especially in areas where the separation between the stormwater network and the sewer network is not perfect. DEET (N, N-diethyl-3-methylbenzamide) is a widely used mosquito repellent. The higher concentration of DEET in raw sewage in July 2018 can be explained by its increased usage during the summer months.

The abatement of organochlorines and other pesticides ranged from 8% for acetamiprid (an insecticide) to 47% for propamocarb (a fungicide). The few negative abatements can be attributed to low concentrations near the detection limit, resulting in higher relative uncertainties. In the plume samples, all pesticide concentrations were below the LOR, except for AMPA in the Plume 1 sample.

Table 4 Organochlorine and other pesticides in the raw sewage (RS), the treated wastewater (TWW) and in the TWW plume at sea.

Chemical species	Feb. 2018 sampling			Jul. 2017 sampling					
	RS	TWW	Abatement	RS	TWW	Abatement	Plume 1	Plume 2	Plume 3
Organochlorine pesticides (µg L^{-1})									
Heptachloroepoxide-cis	0.164	< LOR	nd	< LOR	< LOR	nd	< LOR	< LOR	< LOR
Heptachloroepoxide-γ	0.0056	0.0046	18%	< LOR	< LOR	nd	< LOR	< LOR	< LOR
Pesticides (µg L^{-1})									
Acetamiprid	0.013	0.012	8%	< LOR	< LOR	nd	< LOR	< LOR	< LOR
AMPA	3.66	3.77	− 3%	12.9	9.28	28%	0.077	< LOR	< LOR
Boscalid	0.013	0.011	15%	< LOR	< LOR	nd	< LOR	< LOR	< LOR
DEET	1.05	0.795	24%	3.77	2.31	39%	< LOR	< LOR	< LOR
Diuron	0.012	0.014	− 8%	< LOR	< LOR	nd	< LOR	< LOR	< LOR
Glyphosate	0.50	0.40	20%	1.19	0.7	41%	< LOR	< LOR	< LOR
Imazamox	0.033	< LOR	100%	< LOR	< LOR	nd	< LOR	< LOR	< LOR
Imidacloprid	< LOR	0.054	nd	0.09	0.13	− 46%	< LOR	< LOR	< LOR
Propamocarb	0.099	0.053	47%	< LOR	< LOR	nd	< LOR	< LOR	< LOR
Propyzamid	0.014	0.020	− 15%	< LOR	< LOR	nd	< LOR	< LOR	< LOR
Terbutryn	0.051	0.056	10%	< LOR	< LOR	nd	< LOR	< LOR	< LOR

PNEC Predicted No Effect Concentration, *LOR* limit of reporting; nd: non defined

Among the 12 pharmaceutical substances analyzed, 10 were detected at concentrations above the detection threshold, exhibiting variable % of abatements between July 2017 and February 2018 (Table 5). Negative abatements can be attributed to low concentrations or fluctuations in the input of raw sewage into the WWTP. No definitive conclusion can be drawn for gemfibrozil because its PNEC is lower than the LOR.

Concentrations of clarithromycin, fluoxetine, 17β-estradiol, diclofenac, and carbamazepine in TWW exceeded their respective PNECs. However, in the plume, the dilution effect reduced the concentrations below the LOR and, consequently, below the PNEC for all of these substances, except for 17α-ethinylestradiol, which remained above the PNEC in all plume samples. The efficient removal of ibuprofen and paracetamol in the WWTP aligns with findings reported in the literature (Beausse 2004). The high

Table 5 Pharmaceuticals in the raw sewage (RS), the treated wastewater (TWW) and in the TWW plume at sea.

Chemical species	PNEC	Feb. 2018 sampling			Jul. 2017 sampling			Plume 1	Plume 2	Plume 3
		RS	TWW	Abatement	RS	TWW	Abatement			
Pharmaceuticals (µg L^{-1})										
Clarithromycin	0.13[(1)]	0.373	0.381	− 2 %	0.095	0.145	− 53 %	< LOR	< LOR	< LOR
Fluoxetine	0.012[(2)]	0.0606	0.0404	33 %	0.0041	0.0129	− 215 %	< LOR	< LOR	< LOR
17β-estradiol	0.0004[(3)]	0.0177	0.0001	99 %	0.0166	0.0019	89 %	< LOR	< LOR	< LOR
17α-ethinylestradiol	35 10^{-6}[(3)]	383 10^{-6}	256 10^{-6}	32 %	82 10^{-6}	116 10^{-6}	− 41 %	196 10^{-6}	98 10^{-6}	88 10^{-6}
Diclofenac	10[(4)]	2.04	2.06	− 1 %	1.104	1.261	− 14 %	< LOR	< LOR	< LOR
Carbamazepine	8[(5)]	nd	nd	nd	0.376	0.745	− 98 %	< LOR	< LOR	< LOR
Propanolol	0.0383[(6)]	0.362	0.355	2 %	0.127	0.1841	− 45 %	< LOR	< LOR	< LOR
Gemfibrozil	0.0043[(6)]	< LOR	< LOR	nd	0.08	< LOR	100 %	< LOR	< LOR	< LOR
Ibuprofen	7.1[(4)]	8.38	1.32	84 %	1.34	< LOR	100 %	< LOR	< LOR	< LOR
Paracetamol	13[(3)]	983.3	< LOR	100 %	< LOR	< LOR	nd	< LOR	< LOR	< LOR
Clofibric acid	21[(7)]	< LOR	< LOR	nd	< LOR	< LOR	nd	< LOR	< LOR	< LOR
Tamoxifen	0.081[(8)]	< LOR	< LOR	nd	< LOR	< LOR	nd	< LOR	< LOR	< LOR

PNEC Predicted No Effect Concentration, *LOR* limit of reporting, nd: non defined[(1)]: Bengtsson-Palme and Larsson 2016; [(2)]: Petrie et al. 2016; [(3)]: EU-CID 2018, Klaic and Jirsa 2022; [(4)]: Gamarra et al. 2015; [(5)]: Heye et al. 2019; [(6)]: Capolupo et al. 2018; [(7)]: Ferrari et al. 2003; [(8)]: Orias et al. 2015

concentration of paracetamol observed in the February 2018 sample may be attributed to a peak in influenza activity during that period (Bernard-Stoecklin 2018). The limited % of abatement of diclofenac and carbamazepine in the WWTP is consistent with previous studies (Zhang et al. 2008).

Table 6 presents the annual fluxes of species from the WWTP to the sea. While all potentially contaminating species, except for 17α-ethinylestradiol, were below the LOR in the WWTP plume, the annual fluxes carried by the TWW effluent could still have environmental implications. For instance, the fluxes of Cu and Zn from the WWTP are of comparable magnitude (27.9 and 265 kg per year, respectively) to those contributed by a small coastal river in the Bay of Toulon (7.5 and 42.3 kg per year as dissolved species and 88 and 401 kg per year as particulate species, respectively) (Nicolau et al. 2012). This highlights the potential impact of these metals in the marine environment.

Regarding organic micropollutants, their potential impact on human health can be attributed to both a high characterization factor and a substantial emitted mass (Aemig et al. 2021). Our findings address the lack of data regarding the latter parameter, i.e., the mass released into the environment, which is crucial for accurate machine learning-based modeling of environmental impacts (Servien et al. 2022).

Table 7 Nonmetallic inorganics, metals and organic species with at least one value above the LOR in sea stations and in the last TWW plume (Plume3), Jul. 2017 sampling.

Chemical species	LOR	Ha	Bay	REF	Plume3
Nonmetallic inorganics					
Sulfate (mg L^{-1})	5.00	2800	2840	2640	2810
Metals					
Be (µg L^{-1})	0.20	<LOR	6.09	<LOR	4.72
B (µg L^{-1})	10.0	4980	4130	3800	4160
Ca (mg L^{-1})	0.005	411	414	436	413
Fe (µg L^{-1})	2.00	<LOR	191	153	131
K (mg L^{-1})	0.015	489	501	509	496
Li (µg L^{-1})	1.00	166	179	152	185
Mg (mg L^{-1})	10.0	1420	1500	1390	1350
Mn (µg L^{-1})	0.5	18.2	17.7	20.6	21.6
Na (g L^{-1})	0.03	11.7	11.5	11.8	11.8
Sr (µg L^{-1})	1.00	8200	9530	8900	8670
Zn (µg L^{-1})	2.00	44.8	117	49.9	162
Organics (ng L^{-1})					
17α-ethinylestradiol	30 10^{-3}	69 10^{-3}	97 10^{-3}	443 10^{-3}	88 10^{-3}

LOR limit of reporting, *nd* non defined

Table 6 Annual mass fluxes of species from the WWTP to the sea

Chemical species	kg y^{-1}	Chemical species	kg y^{-1}	Chemical species	kg y^{-1}
Nonmetallic inorganics		PAHs		Pesticides	
NH_3 and NH_4^+ as N	516×10^3	Acenaphthene	0.02139	Acetamiprid	0.112
Nitrates	1611×10^3	Fluorene	0.03069	AMPA	121
Nitrites	49.9×10^3	Phenanthrene	0.06789	Boscalid	0.102
Orthophosphate as P	33.6×10^3	Anthracene	0.01953	DEET	28,9
Sulfate	6584×10^3	Fluoranthene	0.13857	Diuron	0.130
Metals		Pyrene	0.12276	Glyphosate	10.2
Ba	269	Benz(a)anthracene	0.07812	Hexachlorocyclohexane-γ	0.043
B	$11,5 \times 10^3$	Chrysene	0.14,229	Imidacloprid	1,71
Ca	2651×10^3	Benzo(b)fluoranthene	0.06510	Propamocarb	0.493
Cu	27,9	Benzo(k)fluoranthene	0.03999	Propyzamid	0.186
Fe	1.80×10^3	Benzo(a)pyrene	0.03069	Terbutryn	0.521
Hg	1,05	Indeno(1.2.3.cd)pyrene	0.02204	Pharmaceuticals	
K	1295×10^3	Benzo(g.h.i)perylene	0.02511	Clarithromycin	4,89
Li	512	PCBs		Fluoxetine	0.496
Mg	2911×10^3	PCB 28	0.0093	17β-estradiol	0.017
Mn	4.63×10^3	Organochlorine pesticides		17α-ethinylestradiol	0.00346
Na	22.32×10^6	Heptachloroepoxide-γ	0.04278	Diclofenac	30.9
P	33.8×10^3			Carbamazepine	6,93
Sr	24.5×10^3			Propanolol	5,01
Zn	265			Ibuprofen	12,3

Seawater

Table 7 presents the results obtained from the Harbor (Ha), Toulon Bay (Bay), and reference (REF) stations, with a reminder for comparison of the most diluted WWTP plume station (PLUME3).

For nonmetallic inorganics and most metals (Table 6), the concentrations fell within the expected range for seawater. However, beryllium was observed at a high concentration in the Bay sample, although it remained below the limit of reporting (LOR) in the REF and Ha samples. This underscores the need for additional dedicated studies to better understand its occurrence. Iron and zinc concentrations were also significantly higher than their respective seawater solubility values, typically in the nanomolar range. These observations exceed what would be expected from colloidal aerosol deposition (Aguilar-Islas et al. 2010), highlighting the necessity for further investigations regarding these elements.

Among all the organic compounds analyzed (PAHs, PCBs, pesticides, and pharmaceuticals), only 17α-ethinylestradiol was found at levels exceeding the LOR. This was observed across all sea stations, including the reference station. This indicates that the studied area is relatively less impacted by organic contaminants compared to other heavily influenced coastal environments (Togola 2018; Kang et al. 2022; Wang et al. 2022). However, it is important to note that 17α-ethinylestradiol concentrations exceeded the PNEC of 35×10^{-3} ng L^{-1} at all sea stations. The presence of elevated concentrations at the reference station can be attributed to the transportation of WWTP effluents from small cities located east of Toulon by the liguro-provençal current, which flows from east to west. Although the recorded concentrations are in the lower range of those found in contaminated coastal areas like estuaries, lagoons, or semi-enclosed seas (Almeida et al. 2020), the observed values underscore the widespread contamination of coastal environments by this estrogen, which can potentially impact reproductive function and energy metabolism.

Sediments

Table 8 provides the concentrations of the species of interest in sediment samples that exceeded the limit of reporting (LOR), excluding iron which was not analyzed. The sediment samples collected beneath the WWTP plume exhibited comparable contents of elements (metals and metalloids). Only two elements, arsenic (As) and nickel (Ni), slightly exceeded the threshold effect level (TEL). The high manganese (Mn) content can be attributed to elevated concentrations in the plume. In comparison to the plume sample, the Ha sample had higher contents of chromium (Cr), copper (Cu), mercury (Hg), and lead (Pb), with Hg and Pb concentrations surpassing the probable effect level (PEL) and TEL, respectively. This indicates historical contamination of harbor sediments due to military activities since the Second World War (Tessier et al. 2011).

Table 8 Content of species of interest with at least one value above the LOR in the sediments

Chemical species	Plume1	Plume2	Ha	TEL	PEL
Metals (mg kg^{-1})					
Al	> 17,300	> 17,300	5570	/	/
As	14	14	8	7.2	41.6
Cr	22	22	12	52.3	160
Cu	13	10	33	18.7	108
Hg	0.023	nd	0.894	0.13	0.70
Li	48	56	9	–	
Mn	945	654	67	–	
Ni	24	26	9	15.9	42.8
Pb	11	7	32	30.2	112
Sr	69	198	521	/	
Ti	467	163	56	/	
V	22	23	16	/	
Zn	70	70	51	124	271

Fe was not analyzed. *TEL* Threshold effect level, *PEL* Probable effect level (Buchman 2008)

None of the organic compounds of interest were identified at concentrations above the LOR in the studied stations. This suggests that inputs from the WWTP, coastal rivers, and runoff are sufficiently dispersed or degraded to prevent accumulation in the sediments. Acidic compounds (such as aspirin, ibuprofen, ketoprofen, naproxen, diclofenac, indometacin) with pKa values ranging from 4.9 to 4.1, as well as clofibric acid and gemfibrozil, are expected to be primarily present in the water column before undergoing gradual degradation at their own rates. More hydrophobic compounds like 17β-estradiol are prone to adsorb onto mineral surfaces, but their detection was not observed in this study. This could be attributed to the limitations of the water extraction method chosen for assessing compound bioavailability, necessitating solvent extraction for further investigations.

Conclusion

The species of interest in this study, i.e. the species detected in at least one of the samples, included 7 nonmetallic inorganics, 32 metals and metalloids, 4 chlorobenzenes, 16 PAHs, 8 PCBs, 34 organochloride pesticides and 239 other pesticides or pesticide metabolites, 12 pharmaceuticals, and 2 other coumpounds.

The concentrations of nonmetallic inorganics, metals, and metalloids fell within the expected range in both raw sewage

at the WWTP inlet and treated wastewater at the WWTP outlet. Among the organic compounds, 13 PAHs, 3 PCBs, 14 pesticides and pesticide metabolites (including AMPA), and 9 pharmaceuticals were detected in raw sewage. Most of these species were also detected in treated wastewater. The abatement efficiencies were favorable for PCBs, ranging from 32 to 78% for PAHs, but less effective for pesticides and pharmaceuticals. However, in the treated wastewater plume at sea, the dilution effect led to concentrations of all organic compounds falling below the limit of reporting (LOR), and thus, in the case of pharmaceuticals, below their predicted no effect concentration (PNEC), except for 17α-ethinylestradiol. At the three offshore stations located far from the WWTP outlets, 17α-ethinylestradiol was the only organic compound of interest detected, and its concentration exceeded the PNEC. This finding underscores the insufficient reduction of endocrine disruptors by current wastewater treatment.

Furthermore, while the concentrations of contaminants were found to be low in the treated wastewater plume, the annual masses emitted by the WWTP could still have an environmental impact. In addition to pharmaceuticals, significant annual emissions were observed for AMPA, DEET, and glyphosate (121 kg y^{-1}, 30 kg y^{-1}, and 10 kg y^{-1}, respectively). Sediment analysis did not reveal any contamination related to the treatment plants, but the sediment in the port area exhibited contamination with Hg and Pb, likely associated with long-term military activities in the port.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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