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Occurrence and assessment of emerging contaminants adsorbed onto microplastic debris in the Macaronesia region

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ABSTRACT

The occurrence and accumulation of microplastics in the aquatic environment has becomes a global problem. These microplastics can adsorb on their superficies other hydrophobic organic chemicals surrounding and act as vectors for the transport of these contaminants and transfer to organisms. This study presents the first coordinated comprehensive three-year spatial-temporal assessment of the occurrence and distribution of emerging contaminants adsorbed on microplastic debris collected from 32 beaches across of Macaronesia (Canary Islands, Madeira, Azores, and Cabo Verde).

Two types of microplastic debris (pellets and fragments) were analysed for 34 contaminants using previously established analytical procedures. These included twelve UV filters (UVFs) and UV stabilizers (UVSs) commonly added to personal care products; thirteen steroid hormones and nine pharmaceutical compounds. Concentrations were typically in the nanograms per gram range, obtaining highest concentrations for UV compounds, followed by hormones and, in much lower concentration, pharmaceuticals, possibly due to their hydrophilic nature. The most frequently detected compounds of each family were octocrylene (UVFs), levonorgestrel (hormones) and caffeine (pharmaceuticals) found in 69.12 %, 36.65 % and 29.89 % of the samples, respectively.

This study presents a unique multi-archipelago dataset revealing unexpected contamination patterns including significant high concentrations of UV compound even on uninhabited and protected beaches such as Achados Beach (Santa Luzia, Cabo Verde), suggesting the influence of long-range oceanic transport.

The findings underscore the ecological risks posed by key pollutants like octocrylene associated with plastics in insular ecosystems. This baseline data is crucial to inform mitigation strategies, including the regulation of UV filters in coastal and marine environments.

1. Introduction

First plastic material was invented in the middle of the 19th century and since then, the plastic production and consumption have increased rapidly. In 2020, global plastics production reached 370 million tonnes, and in Europe, plastics production almost reached 58 million tonnes

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(Plastics Europe, 2021). The characteristics of plastics (durability and resistance to degradation) are major contributors to the widespread plastic pollution. A significant amount of them ends up as waste in the oceans, where it will persist and accumulate. Without waste management infrastructure improvements, the cumulative quantity of plastic waste available to enter the ocean from land is predicted to increase by an order of magnitude by 2025 (Jambeck et al., 2015). The distribution of plastics in the marine environment is governed by hydrodynamic processes and ocean currents and related to the density, morphology, and type of polymer, in addition to abiotic factors (light, temperature, air) and biotic factors (organisms) (Phuong et al., 2022).

The fragmentation of these waste plastics gives a rise to microplastics (MPs). The presence of MPs debris in the marine environment is widely documented and they are present worldwide (Woodall et al., 2014; Wang et al., 2020). MPs debris can enter and be dispersed in coastal marine environments from the land through wastewater treatment plant discharges, uncontrolled landfills and atmospheric transportation (Liu et al., 2019; Mora and Matthaei, 2020).

MPs pose a risk to marine organisms. These organisms ingest these particles by various pathways such as filtration, confusion with feed and trophic transfers due to ingestion. The consumption of MPs has shown to have negative effects on marine organisms through a reduction in fecundity, hindered mobility, decreased feeding rates, decreased growth and survival, clogging of both digestive and gastrointestinal tracts, leading to internal perforations, and in some instances, death. In 2015, it was reported that at least 690 marine species were exposed to MPs ingestion (Gall and Thompson, 2015). The consequences and extent of this MPs debris intrusion into food webs are relatively unknown.

Due to the diversity in sizes, shapes, and textures of MPs debris, other chemical pollutants present in surrounding media may be adsorbed on their superficies, and act as a vector for the transport for these other contaminants and transfer these pollutants to organisms, that means they have the chance to bioaccumulate. The adsorption and desorption process on microplastics are significantly influenced by environmental variables such as pH, salinity, organic matter and particulate matter (Yu et al., 2019).

There is an extensive list of marine organisms which have experienced adversities (and for some, death) from the effects of microplastic marine litter and the toxicity of contaminants associated with these debris. It is also possible that these pollutants were transferred to the organism, altering the endocrine system, with the possibility of biomagnification in the trophic levels (Yu et al., 2022; He et al., 2023).

Emerging contaminants such as steroid hormones and UV filters represent a significant threat to aquatic ecosystems due to their ability to interfere with the hormonal systems of wildlife, causing reproductive and developmental disorders. Their high lipophilicity promotes bioaccumulation in various marine organisms, where they can induce harmful effects such as coral bleaching and other physiological disruptions. These compounds are persistent in the environment and capable of biomagnification through the food web. (He et al., 2021; Hodge et al., 2025).

Recent studies confirm that microplastics can release adsorbed contaminants under the physiological conditions of marine organisms' digestive tracts. This process is particularly relevant for hydrophobic organic compounds. For example, Benzophenone-3 exhibited measurable desorption in simulated gastrointestinal fluids, influenced by enzymatic activity (Cui et al., 2021). More strikingly, experiments with 17β-estradiol and ethinylestradiol report desorption rates above 40 % from seawater-incubated microplastics (Lu et al., 2021). This potential for desorption highlights the ecological relevance of the contaminants associated with microplastics.

Therefore, it is essential to determine what chemical pollutants and what concentrations are associated with MPs debris. In order to develop an appropriate understanding of pollution associated of chemical contaminants adsorbed on MPs debris in marine environment, are needed an adequate methodology to determine their concentration. These organic contaminants can be extracted from MPs by different extraction techniques, such as liquid–solid extraction, washing, maceration, shaking, soaking, and Soxhlet extraction. These traditional extraction techniques require large amounts of organic solvent and time consuming. As alternative to these conventional extraction methods the Ultrasound-assisted extraction (UAE) and accelerated solvent extraction (ASE) allow reduce the overall extraction time and volume solvent used, while maintaining comparable effectiveness. After extraction, additional treatment steps such as drying, purification, and preconcentration using solid-phase extraction may be necessary (Hong et al., 2017; Santana et al., 2021a; Jiménez et al., 2021).

Although Gas Chromatography with Mass Spectrometry detection (GC–MS) is one of the most widely used separation and detection techniques for priority organic pollutants (POPs), some authors have developed Liquid Chromatography methods coupled with Mass Spectrometry (LC-MS) to separate and determine other organic pollutants, such as emerging contaminants adsorbed on plastics and microplastics (MPs) debris (Santana et al., 2021a; Jiménez et al., 2021).

The presence of organic pollutants adsorbed on MPs samples has been reported in different locations worldwide. Most of available data correspond to POPs (Mai et al., 2018; Camacho et al., 2019; Chen et al., 2019; Capriotti et al., 2021). They have been measured in MPs taken in both open ocean and coastal areas. However, there are not enough data available about the emerging organic pollutants such as hormones, pharmaceutical compounds and UV filters and stabilizers, which adhere to the hydrophobic surface of MPs debris.

In the Macaronesia region, MPs are becoming an increasingly significant problem (Cardoso and Caldeira, 2021). Recent studies have shown that the beaches in this region contain high levels of MPs, which can have serious consequences for marine life and human health (Gola et al., 2021; Barceló et al., 2023; Pham et al., 2023). The Macaronesian archipelagos, located in the eastern North Atlantic Ocean, provide a strategic setting for investigating the transport and fate of microplastics and associated contaminants. Their location within the North Atlantic subtropical gyre, combined with the influence of mesoscale oceanographic dynamics, such as Canary Current and the easternmost branch of the Azores Current, exposes them to the accumulation of litter transported over long distances. These islands serve as natural observatories for assessing how oceanographic currents influence the distribution and accumulation of microplastics and associated pollutants (García-Regalado et al., 2024; Rodrigues et al., 2024).

In the present study, three families of contaminants were examined. Nine pharmaceutical compounds belonging to different therapeutic groups (antineoplastic, anticonvulsant, stimulant, anti-hypertensive, lipid regulator and antibiotic compounds); twelve UV filters (UVFs) and UV stabilizers (UVSs) added to sunscreens or other sun care products and thirteen steroid hormones from four different classes: oestrogens, androgens, progestogens and glucocorticoids. These three families of emerging organic pollutants have a wide range of physicochemical and toxicological properties, and some of these compounds are endocrine disruptors and even carcinogenic. These contaminants are continuously released into the environment due to the limited disposal rate in wastewater treatment plants and are of great concern due to their persistence and bioaccumulation.

The aim of the present study was to evaluate the presence and concentration of the previously mentioned contaminants adsorbed on MPs debris collected from Macaronesia beaches. The samples consisted of pellets and fragments, and also included other types of MPs such as fibres, lines and particles associated with biofilms. Extractions and determination were carried by ultrasound-assisted extraction and ultra-high-performance liquid chromatography tandem mass spectrometry (UAE-UHPLC-MS/MS). The data presented in this article may be useful for further research on microplastic pollution and their associated chemical compounds. This study offers a unique opportunity to explore contaminant distribution of contaminants in the Macaronesian archipelagos, which is situated within key oceanic current systems. The

presence of plastic-associated pollutants in such isolated environments underscores the need to integrate chemical contamination into global assessments of marine debris movement.

2. Experimental

2.1. Material and reagents

LC-MS grade methanol (MeOH), HPLC grade MeOH, LC-MS grade water, formic acid, acetic acid and ammonia were purchased from Panreac Química (Barcelona, Spain).

Twelve UV compounds (six UVFs and six UVSs), thirteen steroid hormones and nine pharmaceutical compounds were obtained from Sigma-Aldrich (Madrid, Spain). Table 1 shows the compounds, the IUPAC name, the chemical structure and the CAS number, of each family.

Stock solutions of UV compounds were prepared in acetone at 250 $\mu g \cdot mL^{-1}$, stock solutions of hormones and pharmaceutical compounds were both prepared in methanol at 10 $\mu g \cdot mL^{-1}$, and all stored in amber bottles at −5 °C in the dark. Working standards solutions were prepared daily from each mixture.

2.2. Instrumentation

To extract all analytes from microplastics samples a ultrasound bath (VWR, Barcelona, Spain) was used. The determination of the compounds was carried out using two different equipment, and in each nitrogen was used as the desolvation gas and argon was employed as the collision gas. UV compounds and pharmaceutical compounds were determined with an ACQUITY UPLC system equipped with a triple quadrupole detector (TQD) and electrospray ionisation (ESI) interface controlled by the MassLynx Mass Spectrometry software and consisting of a Binary Solvent Manager, a 2777 autosampler and a column manager from Waters Chromatography (Barcelona, Spain). To separate the analytes an ACQUITY UHPLC Waters BEH C18 column (50 × 2.1 mm and 1.7 μm particle size) at 35 °C was used.

The mobile phase for UV compounds consisted of water (A) and methanol (B), both with 0.1 % formic acid at a flow rate of 0.3 $mL \cdot min^{-1}$. The gradient started with 25%A and was decreased to 0 % until 3 min. Then it was left with 0%A and 100%B for 2 min and was increased to 25%A for another minute. Finally, it was left at 25%A and 75%B (initial conditions) to equilibrate for 1 min, which achieved the separation of analytes in 7 min. The ESI parameters for mass spectrometry detection were cone voltage at 30 V, capillary voltage at 4 kV, radio frequency lens voltage at 1 V, extractor voltage at 2 V, source and desolvation temperatures at 150 °C and 450 °C, respectively, cone gas flow at 50 $L \cdot h^{-1}$ and desolvation gas flow at 500 $L \cdot h^{-1}$.

The mobile phase for pharmaceutical compounds was water (A) and methanol (B), both with 0.5 % acetic acid at a flow rate of 0.3 $mL \cdot min^{-1}$. The gradient began with 90%A for 0.56 min. Then, decreased to 40%A until 3.83 min and decreased again to 10%A until 6.93 min. It remained in these conditions until 7.42 min and finally increased to 90%A until 9 min. The optimum detection parameters were cone voltage 40 V, capillary voltage 3.5 kV, radio frequency lens 0.2 V, extractor voltage at 1 V, source and desolvation temperatures at 120 °C and 450 °C, cone gas flow at 50 $L \cdot h^{-1}$ and desolvation gas flow at 500 $L \cdot h^{-1}$.

Determination of hormones was carried out using an ACQUITY UPLC system equipped with a triple quadrupole detector (Xevo TQD) and electrospray ionisation (ESI) interface controlled by the MassLynx Mass Spectrometry software and consisting of a Quaternary Solvent Manager, a Sample Manager FTN and a column manager from Waters Chromatography (Barcelona, Spain), to separate analytes a Kinetex EVO C18 column (50 × 2.1 mm and 1.7 μm particle size) was used.

The mobile phase consisted of ultrapure deionized water (A) with 0.1 % ammonia and methanol (B) at a flow rate of 0.4 $mL \cdot min^{-1}$. The gradient started with 80%A 20%B and decreased to 40%A from 1.5 min to 2.75 min, after that it decreased to 25%A until 6 min, which then increased to 80%A until 6.5 min to reach the initial conditions. The ESI parameters for mass spectrometry detection were cone voltage at 60 V, capillary voltage at 3.5 kV, radio frequency lens voltage at 2.5 V, extractor voltage at 3 V, source and desolvation temperatures at 150 °C and 600 °C, respectively, cone gas flow at 50 $L \cdot h^{-1}$ and desolvation gas flow at 1000 $L \cdot h^{-1}$.

2.3. Extraction procedure by ultrasound assisted extraction

The extractions of the three families of compounds from microplastics were optimised in previous published research. Santana et al. (2021c) optimised UV filters extraction using 3 mL of methanol and 30 min of ultrasound; Guedes et al. (2021) optimised hormone extraction using 4 mL of methanol and 30 min of ultrasound; and Santana et al. (2021b) optimised pharmaceuticals extraction using 7.5 mL of methanol and 10 min of ultrasound. Extraction and analytical protocols were applied as previously validated for each compound group (Santana et al., 2021b, c; Guedes et al., 2021). These included QA/QC measures such as spike-recovery experiments (recoveries between 71 and 112 %), and method detection limits ranging from 0.01 to 1.6 ng/mL. No modifications were made to the validated methods in this study.

Briefly, 300 mg ± 30 mg of MPs samples were placed in 10 mL glass vials, followed by the addition of methanol up to the optimised volume. The mixture was then subjected to ultrasound-assisted extraction (UAE) under optimised conditions for each pollutant family. After extraction, the solvent was evaporated under a nitrogen stream, and the residue was reconstituted in 1 mL of methanol. Finally, the extract was transferred to a chromatographic vial for analysis using the UHPLC-MS/MS system. All analyses were performed in triplicate (n = 3).

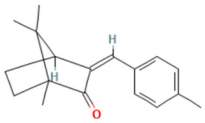
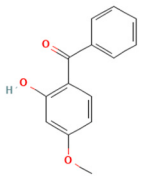
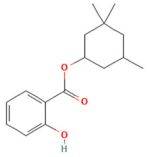
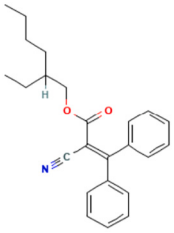
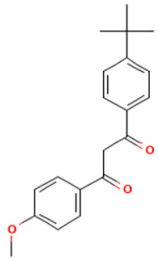
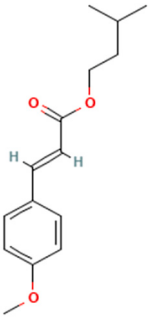
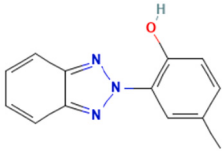
2.4. Sampling

This study was undertaken in four archipelagos of Macaronesia, located in the North Atlantic: Canary Islands, Madeira, Azores and Cabo Verde. The Canary archipelago is located about 100 km off the West African mainland encompassing eight islands. Administratively, the archipelago is divided into two provinces: Santa Cruz de Tenerife and Las Palmas. The Madeira archipelago is situated <500 km North from the Canary Islands. It is composed of seven islands, but two are inhabited. The Azores is the northernmost group with nine islands, located about 1500 km West from Lisbon, Portugal. The Cabo Verde archipelago has ten islands. These islands are between 600 and 850 km west of Cap-Vert, the westernmost point of continental Africa.

The sampling was conducted quarterly from July 2020 to August 2023 across 32 beaches: 21 beaches in the Canary Islands archipelago (Fig. 1A), 7 beaches in the Madeira archipelago (Fig. 1B), 1 beach in the Azores (Fig. 1C) and 3 beaches in Cabo Verde (Fig. 1D). In total, 302 samples were collected consisting of 190 samples of fragments and 112 samples of pellets. At each site, samples were collected during each campaign, allowing seasonal variability to be assessed and ensuring the representativeness of the data. Table 2 shows the locations and characteristics of all beaches. It is important highlight that the selection of beaches was subject to both environmental and logistical factors. In the case of the Azores, only one beach (Porto Pim) was included due to logistical constraints, difficult access, and a lower density of microplastic debris, making regular sampling campaigns unfeasible. However, this beach was sampled quarterly over a three-year period, enabling the detection of seasonal trends despite the limited spatial coverage.

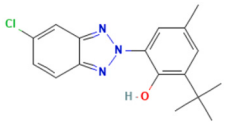
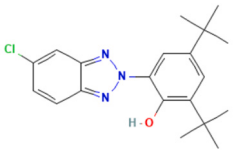
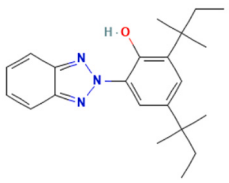
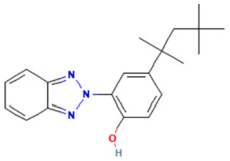
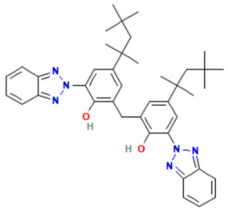
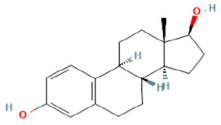
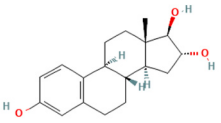
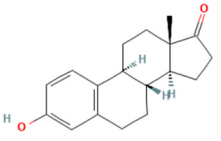
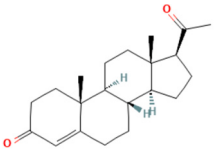
For this study, only microplastic pellets and fragments were selected for analysis, as they were the most abundant forms found across all sampled beaches and have been widely reported to exhibit higher sorption capacities due to their surface characteristics. Polymer characterization (e.g., via FTIR) was not conducted in this study because this analysis was already performed on the same sampling network within the IMPLAMAC project (Pham et al., 2023), which revealed that over 95

Table 1
List of analysed compounds, chemical structure and CAS Number. Values obtained from Pubchem database (https://pubchem.ncbi.nlm.nih.gov).

Family	Abbreviation	Compound	Chemical structure	CAS number
UV filters	4-MBC	4-Methylbenzylidene camphor		36861-47-9
	BP-3	Oxybenzone		131-57-7
	HMS	Homosalate		118-56-9
	OC	Octocrylene		6197-30-4
	BMDBM	Butyl methoxydibenzoylmethane		70356-09-1
	IMC	Isoamyl p-methoxycinnamate		71617-10-2
	UV-P	2-(Benzotriazol-2-yl)-4-methylphenol		2440-22-4

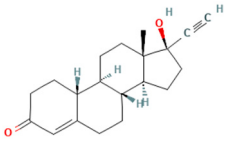
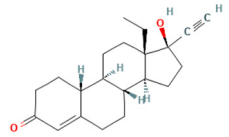
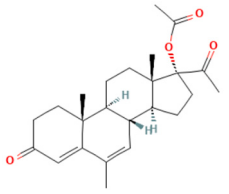
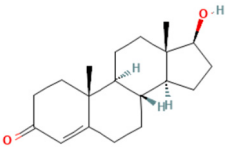
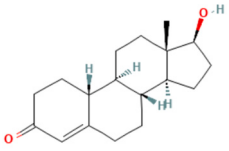
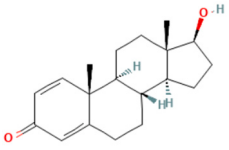
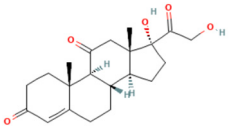
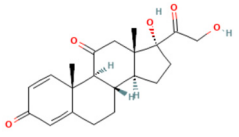
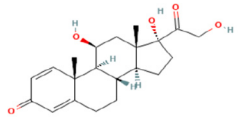
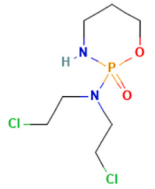
(*continued on next page*)

Table 1 (*continued*)

Family	Abbreviation	Compound	Chemical structure	CAS number
	UV-326	2-Tert-butyl-6-(5-chlorobenzotriazol-2-yl)-4-methylphenol		3896-11-5
	UV-327	2,4-Ditert-butyl-6-(5-chlorobenzotriazol-2-yl)phenol		3864-99-1
	UV-328	2-(Benzotriazol-2-yl)-4,6-bis(2-methylbutan-2-yl)phenol		25973-55-1
	UV-329	2-(Benzotriazol-2-yl)-4-(2,4,4-trimethylpentan-2-yl)phenol		3147-75-9
	UV-360	2-(Benzotriazol-2-yl)-6-[[3-(benzotriazol-2-yl)-2-hydroxy-5-(2,4,4-trimethylpentan-2-yl)phenyl]methyl]-4-(2,4,4-trimethylpentan-2-yl)phenol		103597-45-1
Hormones	E2	17β-Estradiol		50-28-2
	E3	Estriol		50-27-1
	E1	Estrone		53-16-7
	PRO	Progesterone		57-83-0

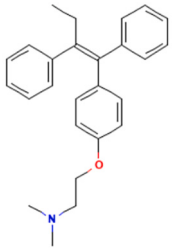
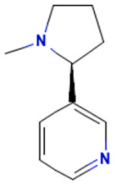
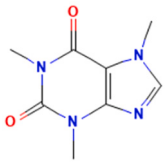
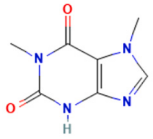
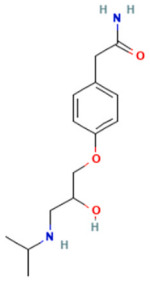
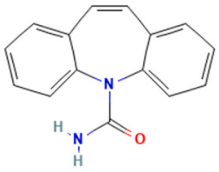
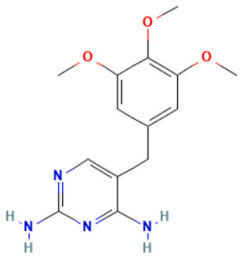
(*continued on next page*)

Table 1 (*continued*)

Family	Abbreviation	Compound	Chemical structure	CAS number
	NORET	Norethisterone		68-22-4
	NOR	Levonorgestrel		797-63-7
	MGA	Megestrol acetate		595-33-5
	TES	Testosterone		58-22-0
	NAN	Nandrolone		434-22-0
	BOL	Boldenone		846-48-0
	COR	Cortisone		53-06-5
	PRD	Prednisone		53-03-2
	PRDNL	Prednisolone		50-24-8
Pharmaceuticals	CP	Cyclophosphamide		50-18-0

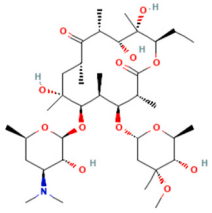
(*continued on next page*)

Table 1 (*continued*)

Family	Abbreviation	Compound	Chemical structure	CAS number
	TAM	Tamoxifen		10540-29-1
	NIC	Nicotine		54-11-5
	CAF	Caffeine		58-08-2
	PRX	Paraxanthine		611-59-6
	ATL	Atenolol		29122-68-7
	CMZ	Carbamazepine		298-46-4
	TMP	Trimethoprim		738-70-5

(*continued on next page*)

Table 1 (*continued*)

Family	Abbreviation	Compound	Chemical structure	CAS number
	ERY	Erythromycin		114-07-8

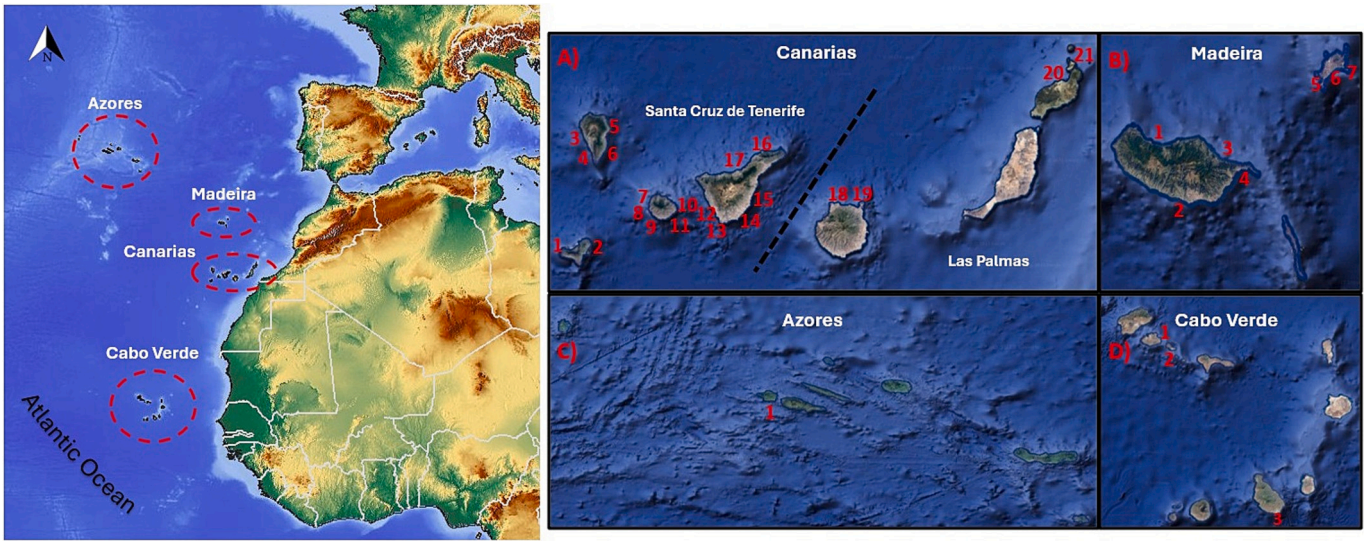


Fig. 1. Location of the beaches studied in the Canary Islands, Madeira islands Azores islands and Cabo Verde islands (obtained from Google Earth).

% of microplastics were composed of polyethylene and polypropylene. Therefore, the current study focused specifically on assessing the occurrence and concentrations of adsorbed emerging contaminants.

The recollection protocol was: sampling was conducted above the high tide line, where sand samples were systematically collected. At each beach, 50 × 50 cm^2 quadrats were selected, with a 25-meter separation between quadrats to ensure spatial coverage, for beaches exceeding 500 m in length, a 100-meter interval between quadrats was employed. The upper 5 cm layer of sand was extracted using a stainless-steel spatula with a defined blade length corresponding to a depth of 5 cm, ensuring consistency across all sampling points. Microplastic extraction from sand was conducted using a dry sieving procedure. After isolation, microplastics were classified by morphology (fragments and pellets).

3. Results

This study is part of a long-term monitoring campaign in the Macaronesia region aimed at determining the presence and distribution of emerging contaminants adsorbed onto microplastics collected along the coasts of this region. Although polymer composition is known to influence the adsorption behaviour of hydrophobic contaminants such as UV filters, this study did not include a detailed characterization of microplastic polymer types. Environmental weathering processes, such as prolonged UV exposure, biofouling, and chemical degradation, can significantly alter the surface properties of microplastics, potentially reducing the relevance of pristine polymer identity in determining adsorption capacity under real environmental conditions. Temporal patterns were assessed during data analysis, but no significant or consistent seasonal differences were observed in contaminant concentrations across the sampled beaches. As a result, data were aggregated to better reflect spatial distribution patterns across the region.

After three years of sampling, the comparison of concentration distributions across the archipelagos revealed a consistent trend: UV compounds exhibited the highest median concentrations, followed by hormones and, lastly, pharmaceuticals (Fig. 2). This pattern, observed across multiple sampling sites and campaigns, supports the proposed ranking. All analysed samples consisted of 300 ± 30 mg of microplastics and were processed using the same extraction and analytical procedures. This standardized approach ensures the comparability of concentration data across regions. Although most concentrations were below 1000 ng/g, certain UV filters and stabilizers, such as OC (5167.45 ng/g), UV-328 (4746.11 ng/g) and UV-360 (4438.36 ng/g), showed exceptionally high values, particularly in the Canary Islands and Cabo Verde. In contrast, only one hormone, levonorgestrel, exceeded this threshold, while no pharmaceutical compound reached 1000 ng/g, with paraxanthine being the most concentrated (974.70 ng/g). These results suggest that UV compounds may have a higher affinity for microplastics, likely due to their hydrophobic nature.

Fig. 2 reveals different trends in the distribution and variability of contaminants among the studied areas in Macaronesia region. UV compounds (blue) dominate across all regions, consistently exhibiting the highest median concentrations compared to hormones and pharmaceuticals. This prevalence is particularly pronounced in Cabo Verde, where median concentrations of UV compounds exceed 10^2 ng/g, and also in Santa Cruz de Tenerife- Canary Islands, where several samples showed UV levels above 10^3 ng/g, considering most of them as outliers in the boxplot graph. Such high concentrations suggest a strong influence of tourism activities, particularly the extensive use of sunscreen products, which are known to leach UV compounds into the marine environment (Cadena et al., 2019).

To assess whether any archipelago displayed significantly different

Table 2
List of beaches in the Macaronesia region.

	Beach	Island	Location	Orientation	Length (km)	Characteristics	Tourist intensity
A) 1	Arenas Blancas	El Hierro	27° 46′ 00″ N 18° 07′ 18″ W	East	0.500	Remote virgin beach, white sand, no services	Low
A) 2	Timijiraque	El Hierro	27° 46′ 13″ N 17° 54′ 52″ W	East	0.350	Practically virgin, volcanic sand, remote	Low
A) 3	Tazacorte	La Palma	28° 39′ 00″ N 17° 56′ 49″ W	West	0.375	Close to a port, volcanic sand, WWTP in the vicinity	High
A) 4	Puerto Naos	La Palma	28° 35′ 11″ N 17° 54′ 41″ W	West	0.120	Volcanic sand, WWTP in the vicinity	High
A) 5	Nogales	La Palma	28° 45′ 32″ N 17° 44′ 21″ W	Northeast	0.450	Secluded virgin beach, volcanic sand, no services	Low
A) 6	Los Cancajos	La Palma	28° 39′ 09″ N 17° 45′ 37″ W	Northeast	0.624	Semiurban beach, volcanic sand, water sports, WWTP in the vicinity	High
A) 7	Playa del Inglés	La Gomera	28° 06′ 01″ N 17° 20′ 50″ W	West	0.310	Volcanic sandy beach, services	Low
A) 8	La Calera (Valle Gran Rey)	La Gomera	28° 05′ 41″ N 17° 20′ 32″ W	West	0.450	Largest sandy beach on the island, close to the port, WWTP in the vicinity	Medium
A) 9	Vueltas	La Gomera	28° 04′ 57″ N 17° 19′ 54″ W	South	0.100	Sandy beach, semiurban, close to the port	Medium
A) 10	La Cueva	La Gomera	28° 05′ 27″ N 17° 06′ 20″ W	Southeast	0.350	Quiet sandy beach, close to the port, services	Medium
A) 11	San Sebastián	La Gomera	28° 05′ 15″ N 17° 06′ 46″ W	Southeast	0.950	Volcanic sand, close to the port, services	High
A) 12	El Puertito	Tenerife	28° 06′ 45″ N 16° 46′ 04″ W	Southwest	0.160	Volcanic-sandy beach in a small cove, low water renewal rate, WWTP in the vicinity	Medium
A) 13	Diego Hernández	Tenerife	28° 06′ 31″ N 16° 45′ 40″ W	Southwest	0.200	Sandy virgin beach, difficult to access, WWTP in the vicinity	Low
A) 14	La Tejita	Tenerife	28° 01′ 54″ N 16° 33′ 23″ W	South	1.000	Quite sandy beach, windy, water sports	Medium
A) 15	Playa Grande	Tenerife	28° 09′ 09″ N 16° 25′ 54″ W	North	0.310	Sandy beach, easy access, WWTP in the vicinity	Medium
A) 16	Almáciga	Tenerife	28° 34′ 16″ N 16° 12′ 12″ W	North	0.300	Beach of volcanic sand and rocks, easy access	Low
A) 17	Playa Jardín	Tenerife	28° 24′ 46″ N 16° 33′ 33″ W	Northwest	2.000	Urban beach, volcanic sand, services, WWTP in the vicinity	High
A) 18	Vagabundos	Gran Canaria	28° 08′ 40″ N 15° 35′ 47″ W	North	0.450	Volcanic-sandy and rocky beach, water sports	Medium
A) 19	Las Canteras	Gran Canaria	**28° 08′ 42″ N 15° 25′ 54″ W**	West	3.100	Urban sandy beach, protected by a natural barrier, services	High
A) 20	Famara	Lanzarote	28° 06′ 56″ N 13° 33′ 22″ W	Northwest	6.000	Sandy beach, water sports, services	Medium
A) 21	Lambra	La Graciosa	29° 16′ 45″ N 13° 29′ 44″ W	Northeast	0.600	Virgin beach, white sand, windy, no services	Low
B) 1	Seixal	Madeira	32° 49′ 20″ N 17° 06′ 11″ W	Northeast	0.200	Volcanic sand, easy access, close to the port	Low
B) 2	Formosa	Madeira	32° 38′ 30″ N 16° 57′ 26″ W	Southwest	0.200	Volcanic sand, rocks, services	High
B) 3	Maiata	Madeira	32° 46′ 03″ N 16° 49′ 16″ W	Northeast	0.500	Volcanic sand, water sports, services	Medium
B) 4	Prainha	Madeira	32° 44′ 34″ N 16° 42′ 57″ W	South	0.100	Volcanic sand, limited access, services	Low
B) 5	Ponta da Calheta	Porto Santo	33° 01′ 29″ N 16° 22′ 47″ W	Southeast	0.400	Sandy beach, services	High
B) 6	Fontinha	Porto Santo	33° 03′ 26″ N 16° 20′ 06″ W	Southeast	0.400	Sandy beach, services	High
B) 7	Docas	Porto Santo	33° 03′ 45″ N 16° 18′ 32″ W	South	0.400	Sandy beach, services	High
C) 1	Porto Pim	Faial	38° 31′ 29″ N 28° 37′ 32″ W	West	0.500	Volcanic sandy beach, easy access, water sports	Medium
D) 1	Praia Grande	Sao Vicente	16° 36′ 24″ N 24° 52′ 38″ W	North	0.500	Sandy virgin beach, no services	High
D) 2	Praia dos Achados	Santa Luzia	16° 45′ 09″ N 24° 42′ 27″ W	North	4.000	Sandy virgin beach, protected area	Low
D) 3	Quebra Canela	Santiago	14° 54′ 23″ N 23° 31′ 01″ W	Southeast	0.200	Sandy beach, easy access, services	High

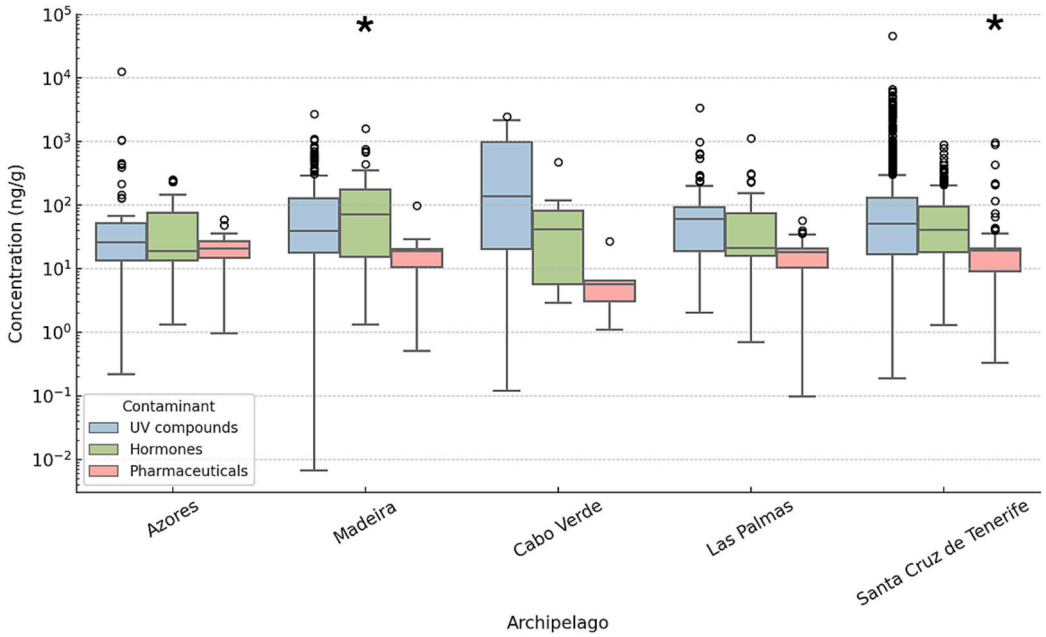


Fig. 2. Concentrations of the three families of compounds studied in studied areas.
Asterisks (*) indicate archipelagos with mean concentrations significantly different from the rest of the dataset for that compound family ($p < 0.05$, one-way ANOVA).

concentrations of each compound family compared to the rest, a one-way ANOVA was performed for each case. Specifically, for each family, the mean concentration in a given archipelago was compared against the combined data from all other archipelagos. The analysis revealed that Madeira exhibited significantly higher concentrations of hormones than the rest ($p < 0.001$), and Santa Cruz de Tenerife showed significantly elevated levels of pharmaceuticals compared to the other archipelagos ($p = 0.0048$). In contrast, no significant differences were detected among archipelagos for UV compounds.

Regarding the relative composition across the 32 surveyed beaches in the Azores, Cabo Verde, Madeira, and Canary Islands archipelagos, distinct patterns in the distribution of UV compounds, steroid hormones, and pharmaceuticals are observed Fig. 3. UV compounds were the predominant contaminant across most beaches, with values exceeding 75 % in several locations, including Porto Pim (Azores), Achados (Cabo Verde), and Playa Jardín (Santa Cruz de Tenerife– Canary Islands).

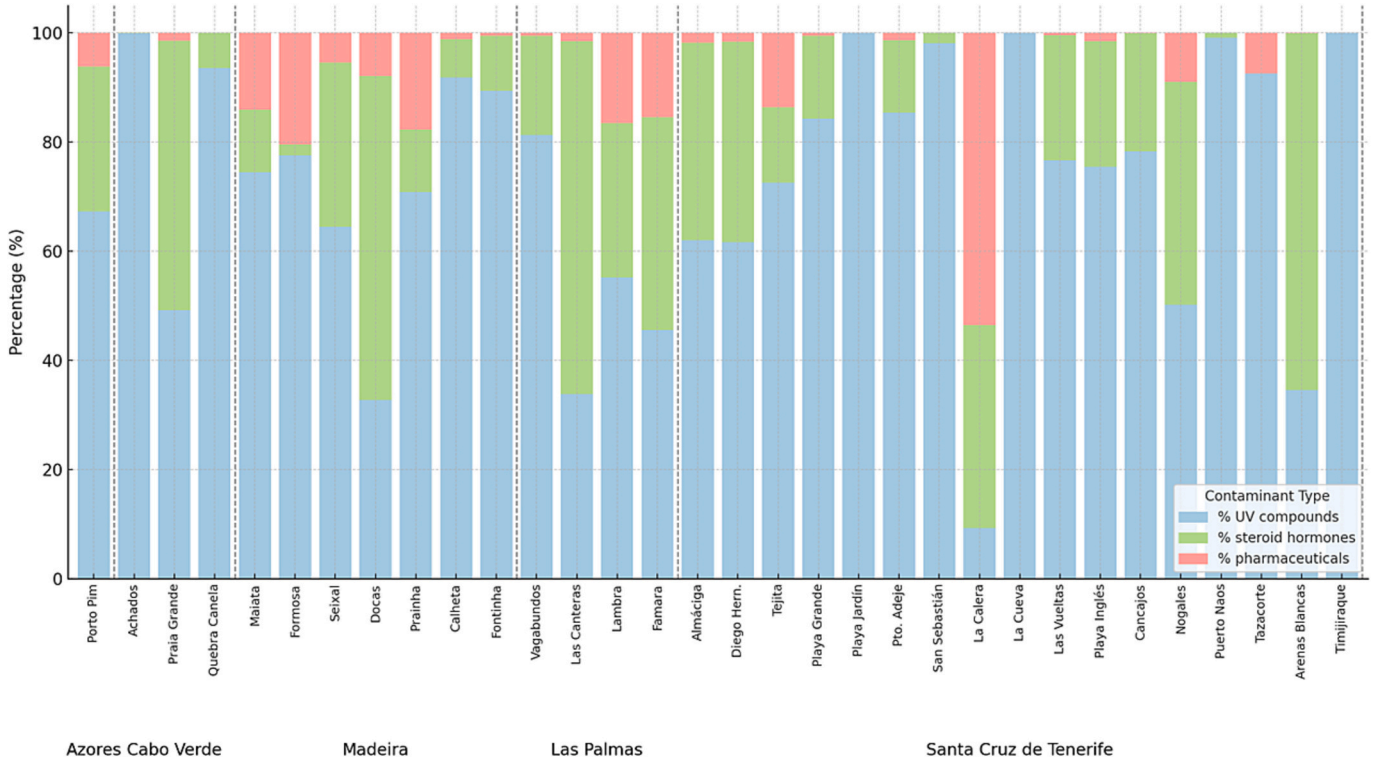


Fig. 3. Relative detection frequency of detected contaminants in the surveyed beaches.

Conversely, steroid hormones and pharmaceuticals contributed relatively lower proportions, although certain beaches, such as Las Canteras (Las Palmas-Canary Islands) and La Calera (Santa Cruz de Tenerife-Canary Islands), exhibited higher percentages of these contaminants. Notably, Madeira showed the most balanced distribution among the three contaminant types, with sites such as Docas having approximately 59 % steroid hormones and 7.92 % pharmaceuticals. This distribution contrasts with the dominance of UV compounds in beaches like Achados, where over 99 % of the contaminants were belong to this family. Such variability highlights potential differences in contamination sources and environmental retention mechanisms across the regions.

The presence of pharmaceuticals, although generally minimal, was markedly higher at La Calera (53.58 %) and Formosa (20.42 %), suggesting localized anthropogenic inputs potentially linked to wastewater discharge or untreated sewage.

Overall, the data suggest that UV compounds are the primary contributors to contamination in the studied beaches, reflecting the widespread use of sunscreen and related personal care products in touristic regions.

3.1. UV compounds

Fig. 4 presents the average concentration (bars) and detection frequency (dotted line) of UV compounds quantified in microplastics. UV-327 and UV-360 exhibited the highest average concentrations, at 564.19 and 598.10 ng/g, respectively. The rest of UV compounds were below 400 ng/g. Although detected in fewer than 15 % of samples, their elevated concentrations and known toxicity—including endocrine-disrupting effects and environmental persistence—make them a cause for concern at the ecosystem level. In contrast, octocrylene (OC) was the most frequently detected compound, found in nearly 70 % of the samples.

These results are aligned with other studies such as Camacho et al. (2019), where it was reported the significant presence of UV compounds in microplastic samples. Similarly, Cadena et al. (2019) also noted a correlation between tourist activity and the presence of these compounds, suggesting that beaches with higher tourist visitation rates are hotspots for UV compounds. The elevated detection frequency of octocrylene aligns with this hypothesis, as its widespread use in sunscreens makes it a key contributor to contamination in tourist-heavy areas.

However, this justification does not apply to the case of Achados beach. Located on Santa Luzia Island, an uninhabited and protected area with restricted access and minimal tourism. Achados is not subject to direct contamination from tourism. Instead, the high accumulation of debris on this beach is likely due to ocean currents, which transport waste from other regions. This hypothesis is supported by previous research which demonstrated that prevailing currents in the region—such as the Canary and North Equatorial Currents—play a key role in shaping microplastic accumulation patterns across Macaronesian beaches (Pham et al., 2023).

3.2. Steroid hormones

Fig. 5 illustrates the average concentration and detection frequency of hormones quantified in microplastics. The compounds with the highest average concentrations were estriol (E3), levonorgestrel and estradiol (E2) with concentrations of 222.11, 188.93 and 174.40 ng/g, respectively. All other hormones were below 62 ng/g. Levonorgestrel was the most frequently detected hormone, appearing in almost 37 % of the samples, followed by testosterone and progesterone, which were found in approximately 20 % of samples.

The notable differences between concentration and detection frequency suggest variations in the environmental behaviour of these compounds. For example, while E3 exhibited the highest concentration, its detection frequency was relatively low (15.38 %). This could indicate localized sources of contamination. These steroid hormones likely originated from human pharmaceutical use and wastewater discharge, introducing biologically active compounds into marine environments. Their presence on microplastics may enhance both their transport and persistence in coastal ecosystems. Furthermore, many of these hormones are known endocrine disruptors, posing risks to aquatic organisms by interfering with reproductive and developmental processes.

Previous research shows that hormones can efficiently be adsorb onto microplastics. For example, Hu et al. (2020) studied the influence of microplastics and the adsorption for E2 indicating that the increase of microplastics items in the soil reduces the presence of E2 in the soil. Similarly, Días et al. (2023), results proved high efficiency of adsorption of sex hormones (testosterone and progesterone) onto microplastics in different aquatic matrices. These findings align with the observed data and the study of Guedes et al. (2021) that showed similar concentrations of these contaminants also in microplastics from beaches of Canary

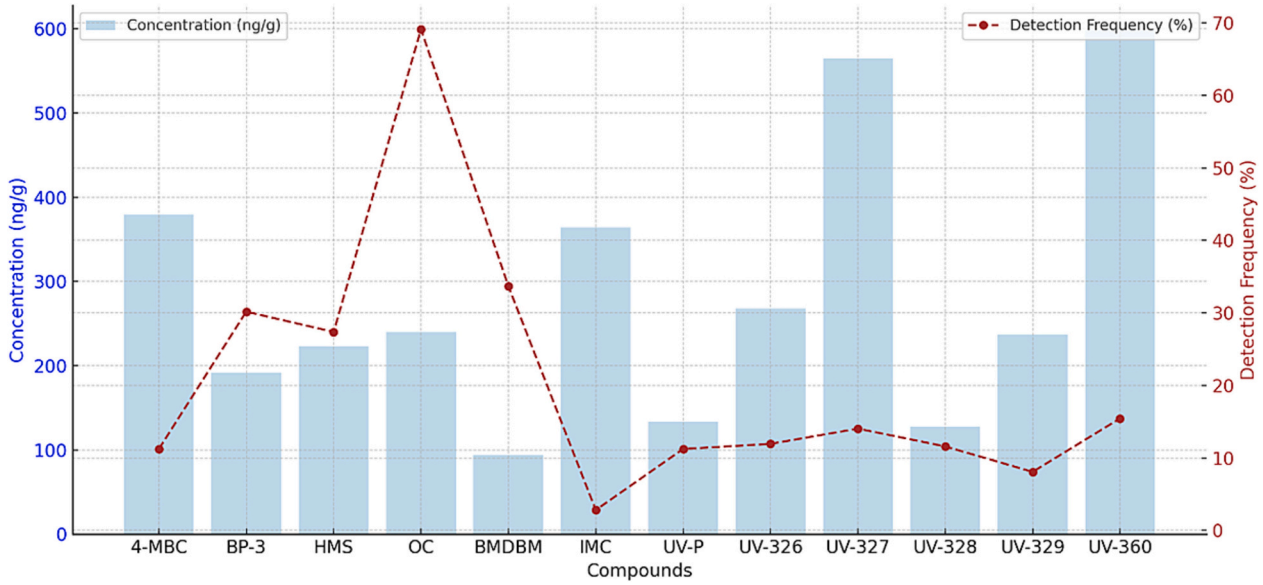


Fig. 4. Average concentrations (blue bars) and detection frequency (red dotted line) of UV compounds adsorbed on microplastics. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

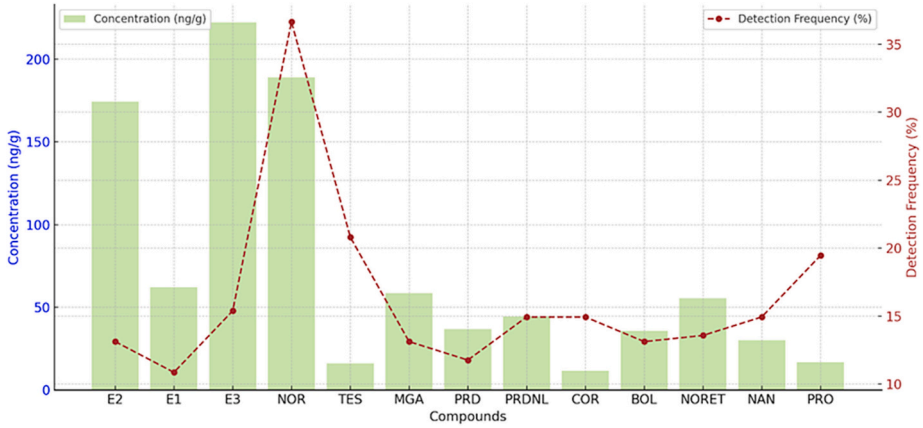


Fig. 5. Average concentrations (green bars) and detection frequency (red dotted line) of hormones adsorbed on microplastics. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Islands. In this study, levonorgestrel was also the most detected steroid hormone.

3.3. Pharmaceuticals

Fig. 6 shows that for the family of pharmaceutical compounds, the highest average concentrations were obtained for nicotine, atenolol and paraxanthine with concentrations that ranged from 31.44 to 37.03 ng/g. The rest of the pharmaceutical compounds were detected at concentrations below 20 ng/g. Caffeine and carbamazepine were the most frequently detected pharmaceutical compounds, appearing in 29.89 % and 27.83 % of the samples respectively. Notably, despite its relatively higher concentration, atenolol showed a remarkably low detection frequency (3.61 %), suggesting sporadic contamination.

These results align with previous findings that microplastics can adsorb pharmaceutical pollutants. Puckowski et al. (2020) after studying the adsorption of pharmaceuticals on the surface of microplastics suggested that microplastics influence to adsorb pharmaceuticals compounds may not be significant. On contrast, Razanajatovo et al. (2018) also studied the sorption of pharmaceuticals suggesting that adsorption of these compounds onto microplastics are positively related to their hydrophobicity. Since the pharmaceuticals studied here are predominantly hydrophilic, their relatively low concentrations in microplastics are consistent with this expectation.

3.4. Spatial distribution

Regionally, Cabo Verde stands out as a contamination hotspot for UV compounds, with concentrations significantly exceeding those observed in other archipelagos. This could be attributed to persistent oceanographic conditions that trap microplastics and their associated contaminants.

In other studied areas like Santa Cruz de Tenerife (Canary Islands) it was observed a broader distribution of contaminants, with relatively high levels of both UV compounds and hormones. In this case it was also studied the relation between the different pollutant families in order to infer potential contamination pathways. The correlation matrix presented in Fig. 7 determine the relationships between different contaminant families in the different Beaches of Santa Cruz de Tenerife area. Values close to 1 indicate a strong correlation, while values near 0 suggest little to no association of the concentrations of the different families. A strong positive correlation ($r = 0.66$) is observed in this area between UV compounds and hormones, suggesting that these contaminants may share similar sources or environmental behaviours. This could be

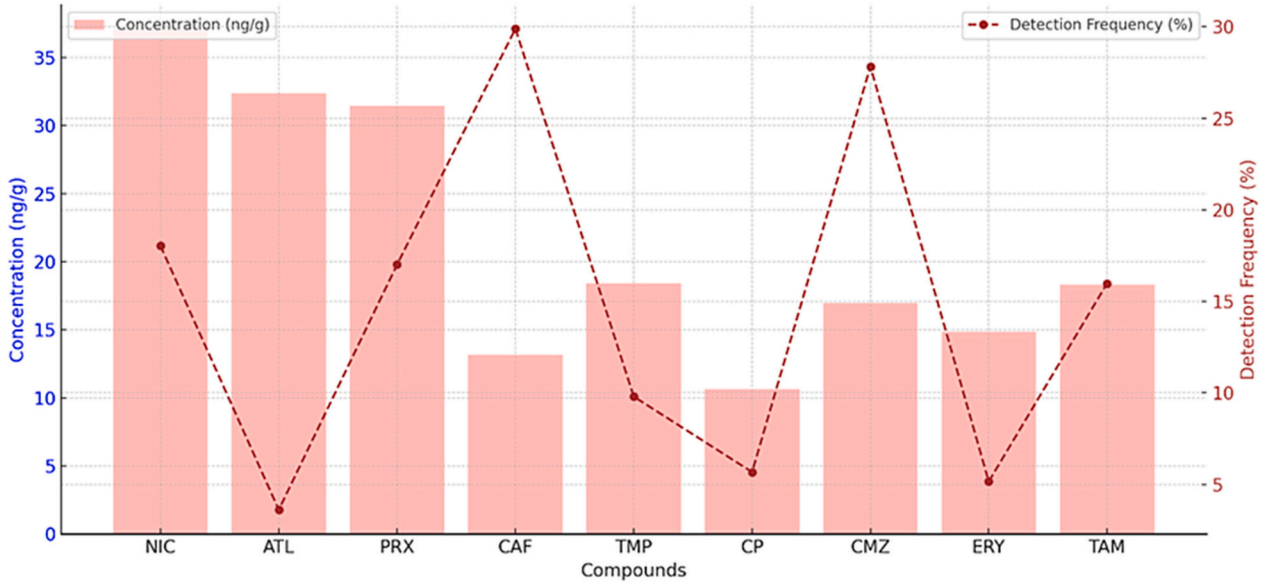


Fig. 6. Average concentrations (red bars) and detection frequency (red dotted line) of pharmaceuticals adsorbed on microplastics. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

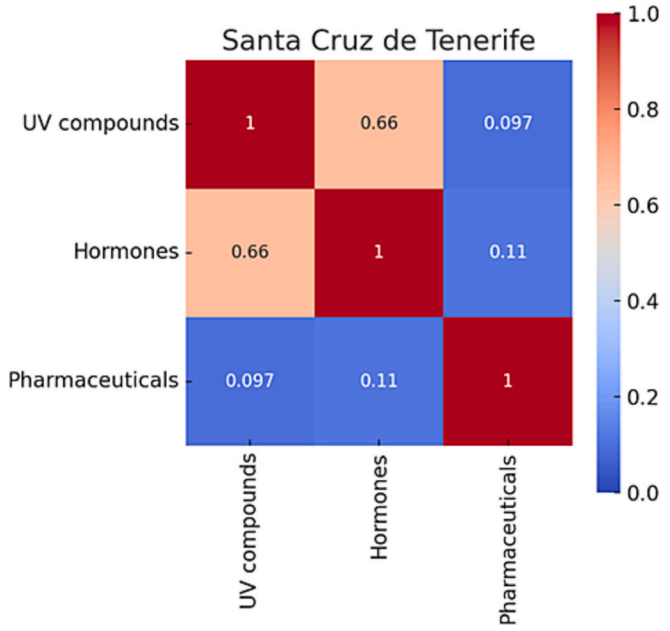


Fig. 7. Correlation matrix between contaminant families (UV compounds, hormones and pharmaceuticals) in Santa Cruz de Tenerife.

attributed to the combination of recreational activities and wastewater discharge pathways. However, pharmaceuticals show weak correlations with both UV compounds ($r = 0.097$) and hormones ($r = 0.11$), indicating a limited association between these contaminant families. The weak relationships may point to differences in how these contaminants are introduced into the environment, but it is important to highlight that this type of contaminants showed the lowest concentrations and detection frequencies of the three studied families.

On the other hand, Azores and Las Palmas (Canary Islands) beaches, exhibit the lowest concentrations across all contaminant types, with pharmaceuticals being nearly negligible. The limited contamination in Azores could be due to its lower population density and relatively low tourism pressure, reducing direct inputs of sunscreen-derived UV compounds and wastewater effluents. Similarly, the modest variability observed in Las Palmas suggests that local environmental and anthropogenic factors, such as wastewater management and coastal dynamics, may play a role in limiting contaminant accumulation.

When analysing the average concentrations of studied emerging pollutants across beaches, Achados (Cabo Verde), Vagabundos (Las Palmas-Canary Islands), Playa Grande, and Puerto Naos (Santa Cruz de Tenerife-Canary Islands) showed the highest values, all exceeding 1000 ng/g. In contrast, Madeira exhibited much lower concentrations, with values below 450 ng/g (Fig. 8). In the Azores, only one beach was studied (Porto Pim), which reported an average concentration of 660.89 ng/g. These results highlight substantial spatial variability in pollutant concentrations across the studied archipelagos. Notably, the elevated concentrations observed in Achados and Puerto Naos may be influenced by the limited number of samples analysed, which could affect the representativeness of these findings.

Several studies have identified beaches as "hotspots" based on the density of microplastic items per square meter. For example, Arenas Blancas beach was considered as a "hotspot" due to the presence of 559 microplastic items per square meter, while Playa Grande had 2971 items per square meter (Hernández et al., 2021; Álvarez et al., 2019), (both located in Santa Cruz de Tenerife-Canary Islands). However, despite this classification, Arenas Blancas did not exhibit high average concentrations of these emerging contaminants, whereas Playa Grande showed higher concentrations. This lack of a consistent relationship suggests that the adsorption of pollutants onto microplastics is influenced by multiple factors, including the chemical properties of the contaminants, environmental conditions, and the physical characteristics of the microplastics. Specifically, factors such as size, shape, and surface area, also play a key role in this process. Therefore, the variability in pollutants concentration cannot be explained solely by microplastic density, but is the result of a complex interaction between these factors.

4. Conclusions

Concerns regarding the impact of microplastics have grown significantly in recent years. This is increased by the ability of microplastics to act as carriers of emerging pollutants, increasing the negative impact on environmental health. In this study 302 samples of microplastic fragments and pellets were collected from 32 beaches in the Macaronesia region, between July 2020 and August 2023, and subsequently analysed.

The previous optimised UAE-UHPLC-MS/MS methods employed in

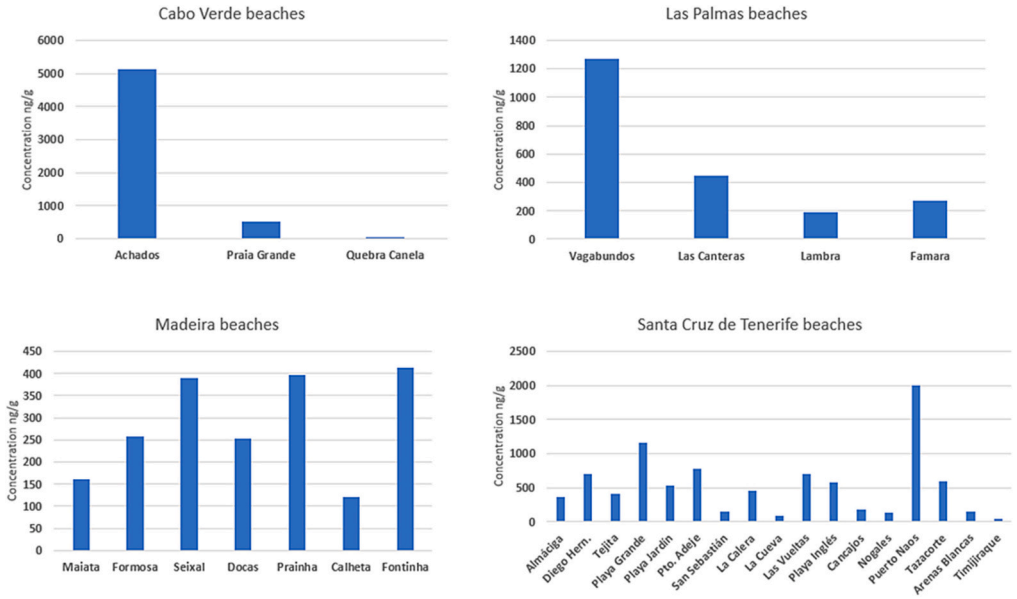


Fig. 8. Average concentration of total studied emerging compounds per total number of samples.

this study, allowed the identification of 12 UV compounds, including UV filters and UV stabilizers, 13 hormones and 9 pharmaceuticals in microplastic samples with satisfactory results. The highest concentrations were obtained for UV compounds, followed by hormones and lastly, pharmaceuticals. These results suggest that the adsorption of these contaminants onto microplastics is due to their hydrophobic nature.

Throughout the project, all target compounds were identified in at least some samples. Among the UV filters, octocrylene and butyl methoxydibenzoylmethane were the most frequently found, which were present in 69.12 % and 33.68 % of the samples, respectively. For the hormones, levonorgestrel was present in 36.65 % of the samples and testosterone in 20.81 %; and finally, from the pharmaceutical family, caffeine and carbamazepine were present in 29.89 % and 27.83 % of the samples.

Geographical patterns in contamination were observed across of these archipelagos. Cabo Verde and Santa Cruz de Tenerife (Canary Islands) presented the highest concentrations of UV compounds, while Madeira showed a more even distribution between the different contaminants. On the other hand, the Azores and Las Palmas (Canary Islands) showed the lowest concentrations, which may be related to lower tourist pressure and lower wastewater inputs.

Correlation analysis suggested that UV compounds and hormones may likely share similar sources and follow similar retention mechanisms as indicated by the correlation test, while pharmaceuticals show a weaker connection. This suggests differences on how they may enter the marine environment.

While this study did not assess ecological risk, the frequent detection of endocrine-active compounds such as octocrylene and levonorgestrel on microplastic debris underscores the need for future research addressing their potential desorption, bioavailability, and impact on marine organisms. Given that octocrylene is already under scrutiny in several jurisdictions due to its potential ecotoxicological effects, its high prevalence in coastal microplastics in Cabo Verde supports the need to consider its environmental management in the region.

Finally, this study provides an important information on the role of microplastics as carriers for emerging contaminants and their distribution in the Macaronesia region.

CRediT authorship contribution statement

Javier Pacheco-Juárez: Writing – original draft, Investigation, Data curation. **Zoraida Sosa-Ferrera:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Data curation, Conceptualization. **Rayco Guedes-Alonso:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Sarah Montesdeoca-Esponda:** Methodology, Investigation, Formal analysis. **María Esther Torres-Padrón:** Methodology, Investigation. **José Juan Santana-Rodríguez:** Writing – review & editing, Supervision, Conceptualization. **Cristopher Domínguez Hernández:** Investigation, Data curation. **Alicia Herrera:** Investigation, Data curation. **Mara Abu-Raya:** Investigation, Data curation. **Soledad Álvarez:** Investigation, Conceptualization. **Christopher K. Pham:** Investigation, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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