Abstract: The interest in UV filters’ occurrence in the environment has increased since they were recognized as “emerging contaminants” having potentially adverse impacts on many ecosystems and organisms. Increased worldwide demand for sunscreens is associated with temperature anomalies, high irradiance, and changes in the tourist market. Recently, it has been demonstrated that personal care products, including sunscreens, appear in various ecosystems and geographic locations causing an ecotoxicological threat. Our goal was to determine for the first time the presence of selected organic UV filters at four beaches in the central Pomeranian region in northern Poland and to assess their horizontal and vertical distribution as well as temporal variation at different locations according to the touristic pressure. In this pioneering study, the concentration of five UV filters was measured in core sediments dredged from four exposed beaches (Darłowo, Ustka, Rowy, and Czołpino). UV filters were detected in 89.6% of collected cores at detection frequencies of 0–22.2%, 75–100%, 0–16.7%, and 2.8–25% for benzophenone-1 (BP-1), benzophenone-2 (BP-2), benzophenone-3 (BP-3), and enzacamene (4-MBC), respectively. In terms of seasonality, the concentration of UV filters generally increased in the following order: summer > autumn > spring. No detectable levels of 3-BC (also known as 3-benzylidene camphor) were recorded. No differences were found in the concentration of UV filters according to the depth of the sediment core. During the summer and autumn seasons, all UV filters were detected in higher concentrations in the bathing area or close to the waterline than halfway or further up the beach. Results presented in this study demonstrate that the Baltic Sea coast is not free from UV filters. Even if actual concentrations can be quantified as ng·kg⁻¹ causing limited environmental threat, much higher future levels are expected due to the Earth’s principal climatic zones shifting northward.

Keywords: UV filters; benzophenones; emerging pollutants; sunscreen agents; beach sediments; exposed beaches; touristic pressure; Baltic Sea

1. Introduction

Seaside ecotone contamination is a common phenomenon caused by the presence of various substances, mainly from anthropogenic sources. In recent years, more attention has been paid to personal care products (PCPs) described as “emerging contaminants”. The presence of PCPs in the environment is considered a serious problem as their original forms and bioactive metabolites can be released into the aquatic environment continuously. Releasing PCPs can occur directly during a bath or recreation in water reservoirs when PCPs formerly applied onto the skin are rinsed off. Indirect sources are insufficiently treated domestic and urban wastewaters discharged into rivers, lakes, and oceans, domestic wastewater from washing and bathing with PCPs as well as wastewater...
from their production. Another problem is also related to PCPs leaching out from carelessly emptied packaging [1–3].

One of the most commonly used classes of PCPs is sunscreen agents, which constitute the majority of body care cosmetics. Since the International Agency for Research on Cancer (IARC) classified solar radiation (UV-B and UV-A) as human carcinogens [4], UV-filters containing creams, balms, and suntan lotions have been recommended by dermatologists as an effective means to protect the skin from excessive UV radiation, simultaneously preventing it from sun damage, premature aging, and skin cancers [5]. According to the, the estimated number of units of sunscreen sold worldwide in 1998 was 521 million, while the estimated volume of UV filters in them was 9.2 million tons [6]. It fits with other estimations from the beginning of the 21st century that approximately 10 million tons of UV filters are delivered and purchased annually on the global market [7]. However, current and forecasted data indicate the global sunscreen cream market was 8250 million US$ in 2018 and is expected to be 11,710 million US$ by the end of 2025, growing at a compound annual growth rate of 5.1% between 2019 and 2025. Assuming only 5% annual growth of the volume of UV filters from 1998, the currently estimated volume reaches 26.9 million tons. Increased frequency of holidays in sunny climates and outdoor leisure activities are resulting in the increased exposure of populations, especially those in temperate latitudes. Due to the pathways mentioned above, a huge amount of sunscreen agents is released into the environment, both on a global and local scale. Based on surveys carried out among Swiss sunbathers, it was estimated that during a single tourist season about 224 kg of ethylhexyl methoxycinnamate (EHMC), 152 kg of octocrylene (OC), 145 kg of 4-MBC, 122 kg of avobenzone (BMDM), and 77 kg of BP-3 was released into Lake Zürich [8]. Based on the estimated annual production of sunscreens and their average use in one application, it is calculated that 16,000–25,000 tons of sunscreen agents are used annually in tropical countries, 4000–6000 tons of which are released into water containing coral reefs [7]. Some researchers have estimated that about 1874 kg of EHMC, 1249 kg of OC, 1015 kg of BMDM, and 625 kg of BP-3 enter the Gulf of Mexico from all counties on the coast of Texas annually [9]. However, all authors suggest that the above estimates may differ from the real values due to the growing numbers of sunbathers who use sunscreens. Environmental changes, such as the depletion of the stratospheric ozone layer and shifting of climate zones, resulting in increased sun exposure [10], facilitate worldwide UV filter use. Even ubiquitous parts-per-trillion concentrations of UV filters detected in various environmental compartments inform the range of environmentally relevant concentrations for future assessment on the potential impacts of UV filters on marine species, i.e., coral reefs [11].

Raised public awareness connected with the global consumption of UV filters is due to their potentially dangerous impact on human health and the environment. After application to the sunbather’s body, UV filters penetrate skin barriers and are transported by the blood throughout the organism [12–15]. In the case of BP-3, octinoxate (OMC), OC, and 4-MBC, some negative effects on the human endocrine system were found [15–18]. Based on numerous analyses, the hormonal activity of certain UV filters (BP-1, BP-2, BP-3, benzophenone-4 (BP-4), homosalate (HMS), OC, EHMC, BMDM, 4-MBC, OMC) and their harmful impact on fertility and reproduction were proven [19,20]. Once washed off the skin through water recreation activity or bathing, UV filters are directly (sea, river, lake) or indirectly (sewage treatment plants) released into environmental compartments. As an effect, their presence and accumulation in the environment, particularly in the aquatic ecosystem [1,21], have become an indisputable fact. Although there was no analysis of biota done in this study in Table S1 (Supplementary Materials), the occurrence of UV filters in the tissues of fresh and saline water, fish, mussels, crustaceans, sea mammals, and birds is presented, while in Table S2 (Supplementary Materials) the UV filters content in saline, freshwater, and sediment samples is summarized. The purpose of the data presented in Table S1 was to prove that living organisms are impacted by the pollutants present in their natural habitats.

Although UV filters are commonly observed in the ng·g⁻¹ d.w. or ng·L⁻¹ range, they are present in many organisms or areas (Tables S1 and S2, Supplementary Materials). Several UV filters are
blamed for inhibition of oogenesis, egg production, releasing of mature oocytes and the loss of secondary sexual characteristics, inhibition of spermatogenesis, loss of mating behavior, cessation of reproduction in males in the fathead minnow \textit{(Pimephales promelas)} [19], growth inhibition in algae \textit{Scenedesmus vacuolatus} [22], or harmful effects toward coral reef areas [7,23–26] and other marine systems [17,18,27–30].

As mentioned above, broad studies have been conducted on the harmful effects of UV filters on living organisms or their distribution in most touristic locations around the world [11,30–33]; however, only a few studies have focused on the occurrence of UV filters in riverine run-offs and waters of the German Baltic Sea [34] or surface sediments collected from the Skagerrak and Kattegat straits [35] and some rare pieces of evidence concern freshwater reservoirs located in central Poland [36], but according to our best knowledge, there is a lack of any information concerning the Polish part of the coast. Therefore, the aims of this work were (1) to determine for the first time the presence of selected organic UV filters at four beaches in the central Pomeranian region in northern Poland, (2) to study both the horizontal and vertical distribution of UV filters along with the distance from the waterline, and (3) to assess the spatiotemporal variation of UV filters at different locations according to the touristic pressure. This study is the first field campaign accomplished in the Polish coastal ecosystem, which in comparison with Spain, France, the Mediterranean, or the Caribbean, is not particularly recognized as extraordinarily attractive for tourists, but it is very unstable and ecologically fragile due to the closed nature of the Baltic Sea basin.

2. Materials and Methods

2.1. Beach Description

The study was carried on an 80 km long section of the coast, between 82 and 252 km of the Polish sea border managed by the Maritime Office in Słupsk, where the widest and the most beautiful and attractive sandy beaches are located, offering a variety of touristic activities (Figure 1).
The four beaches were chosen based on the level of tourist pressure. Samples were collected in Darłowo (54°25' N/16°24' E) on the eastern side of the harbor canal, in Ustka (54°34' N/16°51' E) on the eastern side of the mouth of the Slupia River, in Rowy (54°39' N/17°03' E) on the eastern side of the harbor canal, and Czołpino (54°43' N/17°14' E). All beaches are exposed, however, they differ in terms of the degree of touristic pressure in the following order: Ustka > Darłowo > Rowy > Czołpino. Ustka, Darłowo, and Rowy are attractive touristic sites, however, it seems that Ustka is the most popular due to direct railway and the variety of bus connections with the majority of Polish cities. Moreover, Ustka is connected with other cities by a road of national status (DK21) while Darłowo and Rowy by local ones. It leads to an almost tenfold increase in the average number of citizens in Ustka during the summer holidays in comparison to the rest of the year. Based on information from 2012, the regular number of citizens in Ustka is around 16,300, while during the high season it increases up to 120,000. A similar trend, however, of a lower scale is observed in Darłowo and Rowy. The regular number of citizens in Darłowo and Rowy is 13,400 and 400, respectively, while during the summer it increases up to 30,000 and 15,000 tourists, respectively. The beach located in Czołpino is a part of the Słowiński National Park, which is registered on the World List of Biosphere Reserves, and due to very limited tourist activity could be recognized as a reference location.

2.2. Sand Core Sampling

Sand samples from the beaches were collected seasonally (spring, summer, and autumn) in 2017 along a transect perpendicular to the shoreline (Figure 2).

![Figure 2. Location of sampling sites and presentation of the horizontal profile of one of the beaches.](image-url)

The spatial distribution of UV filters in the sand was assessed by sampling at four distances along the horizontal transect of the beach: site S1 was located approximately 3 m offshore, at a depth of about 1 meter underwater; site S2 was situated at the waterline (the boundary between the beach and the sea); site S3 was around halfway up the beach, 30 m from the shore, while the most distant site S4 was a sheltered place among dunes, about 60–70 m away from the shore. The same analogical sampling procedure as in Ustka and Czołpino was applied before by others for biological studies [37] and in Ustka, Czołpino, and Puck for seasonal distribution of metals and microbial enzymatic activity assessment [38,39]. Sand core samples were taken with a hand-operated Morduchaj-Boltowski sampler (length 30 cm, inner diameter 15 cm). The sand cores, 15 cm long, were collected in three replicates and divided into 3 sections in the field (0–5 cm, 5–10 cm, 10–15 cm). Altogether 432 samples were collected (4 beaches × 3 seasons × 4 sites × 3 depths × 3 replicates). The samples were placed in polyethylene
bags and put in a special container at a temperature not exceeding 8 °C and then transported to the laboratory, where they were subjected to chemical analysis. Because in this survey we were particularly focused on location, seasonality, distance from the waterline, and core depth, seawater samples were not analyzed due to the significant momentary variability of water composition caused by large undulation along the part of the coast subjected to research.

2.3. Sample Pretreatment and Analytical Methods

Sample preparation was done according to the slightly modified procedure of Jeon et al. [40]. A 10 g sample of air-dried sediment was extracted with 5 mL MeOH (Sigma-Aldrich Fluka for HPLC, purity ≥ 99.9%) using ultrasonic-assisted extraction (30 min). Air drying was used to avoid the thermal decomposition of organic compounds. Consecutively, the sample was centrifuged (5500 rpm), decanted, and vaporized to dryness in the N2 flux and then reconstructed in MeOH to 0.25 mL. Five selected UV filters were determined using a UHPLC system (Shimadzu LC Workstation, Japan) equipped with an LC-2AD pump (Shimadzu, Japan) and diode array detector SPD-M20A DAD (Shimadzu, Japan). Some characteristics, such as the name, symbol, chemical formula, chemical structure, and analytical wavelength of the studied filters are summarized in Table 1.

Details on the UHPLC-DAD analytical procedure followed for UV filter quantification were as follows: analytical column: NUCLEOSIL®100-5 C18 (250 mm × 4.6 mm; 5 µm); mobile phase: MeOH/H2O 70:30 v/v; isocratic elution; mobile phase flow: 1 mL/min; sample volume: 20 µL; temperature: 35 °C; pressure: 140 bar; data collection time: 13 min.
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Table 1. The name, symbol, chemical formula, structural formula, type of UV radiation protection, average content in cosmetics, octanol-water partition coefficient, and analytical wavelength.

| Compound (Abbreviation) /Systematic Name /CAS No | Chemical Formula | Chemical Structure | UV Protection | Average Content in Cosmetics ¹ | Log Kow | Amax (nm) |
|-----------------------------------------------|------------------|--------------------|---------------|------------------|---------|----------|
| Benzophenone-1 (BP-1) /2,4-dihydroxybenzophenone /131-55-6 | C₁₃H₁₀O₃ | | UV-A | up to 10% according to country | 3.15 | 290 |
| Benzophenone-2 (BP-2) /2,2',4,4'-tetrahydroxybenzophenone /131-55-5 | C₁₃H₁₀O₅ | | UV-A | up to 10% according to country | 2.78 | 285 |
| Benzophenone-3 (BP-3) /2-hydroxy-4-methoxybenzophenone /131-57-7 | C₁₄H₁₂O₃ | | UV-A | 6% [41] | 3.79 | 287 |
| Enzacamene (4-MBC) /[(3E)-1,7,7-trimethyl-3-[4-methylphenyl]methylene]-2-norbornanone /36861-47-9 | C₁₈H₂₂O | | UV-B | 4% | 4.95 | 300 |
| 3-benzylidene camphor (3BC) /1,7,7-trimethyl-3-(phenylmethylene) bicyclo[2.2.1] heptan-2-one /15087-24-8 | C₁₇H₂₀O | | UV-A | use prohibited in UE [42] | 5.37 | 289 |

¹ term “cosmetics” means UV filters containing creams, balms, and suntan lotions only.

Note:
2.4. Quality Assurance and Quality Control

To acquire the correct retention times, the standards of BP-1, BP-2, BP-3, 3-BC, and 4-MBC purchased from Sigma-Aldrich Fluka (purity 98%) were analyzed separately and then the calibration curves were acquired for a mixture of standard solutions at concentration ranges from 0.001 to 10.000 µg·L\(^{-1}\). The curves were determined for six different concentration measurements repeating each injection three times. Stock standard solutions were prepared in MeOH (Sigma-Aldrich Fluka for HPLC, purity ≥ 99.9%) containing 1 g·L\(^{-1}\) of each compound. From these standards, working standard mixtures containing each compound were prepared daily in MeOH. Within the studied concentration range, the calibration curves were linear (\(r^2 \geq 0.9991\)) and hence fit the EU directive for confirmatory methods [43], which require a correlation coefficient higher than 0.9980. The limit of detection (LOD) was calculated as three times the signal-to-noise ratio (\(S/N = 3\)), and the limit of quantitation (LOQ) was calculated as 10 times the signal-to-noise ratio (\(S/N = 10\)). The calibration curve parameters and detection limits are given in Table 2.

Table 2. The calibration curve parameters and detection limits of five UV filters.

| Compound                                      | Correlation Coefficient \((r^2)\) | LOD \((S/N = 3)\) \(\mu g\cdot L^{-1}\) | LOQ \((S/N = 10)\) \(\mu g\cdot L^{-1}\) |
|-----------------------------------------------|-----------------------------------|------------------------------------------|------------------------------------------|
| Benzophenone-1 (BP-1)                        | 0.9999                            | 0.010                                    | 0.033                                    |
| Benzophenone-2 (BP-2)                        | 0.9991                            | 0.025                                    | 0.083                                    |
| Benzophenone-3 (BP-3)                        | 0.9999                            | 0.035                                    | 0.116                                    |
| 3-Benzylidene camphor (3-BC)                 | 0.9999                            | 0.030                                    | 0.099                                    |
| 3-(4-Methylbenzylidene)-camphor (4-MBC)      | 0.9997                            | 0.030                                    | 0.099                                    |

2.5. Statistical Procedures

In the initial stage of the research, it was planned to assess the effect of four independent factors (location, seasonality, distance from the waterline, and core depth) on UV filter concentration values, and this is why the multiway ANOVA was carried out, although some crucial constraints were not fulfilled (i.e., Gaussian data distribution, homogeneity of variance between comparing groups of samples). Since in some cases the lack of data occurred because of concentrations below LOD, a comprehensive comparison (concerning all possible combinations of independent factors) using a multi-way ANOVA technique was not possible. This is why ANOVA was consciously applied only as a preliminary step to recognize if any significant differences could be expected, while final statistical testing was accomplished using the non-parametric Mann–Whitney U test for two-group comparison and Kruskal–Wallis test for multiple-group comparison. In the case of all combinations with the depth of the core as an independent factor, none of statistical significance was obtained using multi-way ANOVA, and this is why the comprehensive comparison was limited to three independent factors (location, seasonality, distance from the waterline) combined only in logical variants. When a positive Kruskal–Wallis test result was obtained it was integrated with a Kruskall–Wallis multiple comparison test. All tests were calculated at \(p = 0.05\) using Statistica 13.3 (TIBCO Statistica Inc., Palo Alto, CA, USA).

3. Results and Discussion

A summary of concentration ranges, mean concentration with standard deviation value, and detection frequencies for all UV filters investigated according to location and seasonality is detailed in Tables 3 and 4, respectively.
Table 3. Concentration range (ng·kg\(^{-1}\) d.w.), mean concentrations (ng·kg\(^{-1}\) d.w.), and detection frequencies (%) for UV filters in the core sediments of the Darłowo, Ustka, Rowy, and Czołpino beaches (n.d.—not detected).

| Location  | UV Filter | Range     | Mean  | S.D.  | Detection Frequency (%) |
|-----------|-----------|-----------|-------|-------|-------------------------|
|           |           |           |       |       |                         |
| Darłowo   | BP-1      | <LOD-52.5 | 21.0  | 16.1  | 19.4                    |
|           | BP-2      | 27.3-977.0| 273.6 | 249.0 | 100                     |
|           | BP-3      | <LOD-74.2 | 63.3  | 10.3  | 16.7                    |
|           | 3-BC      | n.d.      | 0     | 0     | 0                       |
|           | 4-MBC     | <LOD-132.1| 73.9  | 32.5  | 25.0                    |
| Ustka     | BP-1      | <LOD-5.4  | 5.4   | 2.8   | 2.8                     |
|           | BP-2      | 17.0-782.7| 267.7 | 241.9 | 100                     |
|           | BP-3      | <LOD-25.6 | 25.6  | 2.8   | 2.8                     |
|           | 3-BC      | n.d.      | 0     | 0     | 0                       |
|           | 4-MBC     | <LOD-67.3 | 67.3  | 2.8   | 2.8                     |
| Rowy      | BP-1      | n.d.      | 0     | 0     | 0                       |
|           | BP-2      | <LOD-704.5| 233.7 | 208.6 | 75.0                    |
|           | BP-3      | n.d.      | 0     | 0     | 0                       |
|           | 3-BC      | n.d.      | 0     | 0     | 0                       |
|           | 4-MBC     | <LOD-71.3 | 71.3  | 71.3  | 2.8                     |
| Czołpino  | BP-1      | n.d.      | 0     | 0     | 0                       |
|           | BP-2      | <LOD-729.6| 387.5 | 207.3 | 81.2                    |
|           | BP-3      | <LOD-25.6 | 25.6  | 2.1   | 2.1                     |
|           | 3-BC      | n.d.      | 0     | 0     | 0                       |
|           | 4-MBC     | <LOD-133.0| 84.5  | 25.4  | 18.8                    |

Table 4. Concentration range (ng·kg\(^{-1}\) d.w.), mean concentrations (ng·kg\(^{-1}\) d.w.), and detection frequencies (%) of UV filters in core sediments collected in spring, summer, and autumn, 2017 (n.d.—not detected).

| Season  | UV Filter | Range     | Mean  | S.D.  | Detection Frequency (%) |
|---------|-----------|-----------|-------|-------|-------------------------|
|         |           |           |       |       |                         |
| spring  | BP-1      | n.d.      | 0     | 0     | 0                       |
|         | BP-2      | <LOD-329.8| 119.4 | 96.4  | 93.7                    |
|         | BP-3      | n.d.      | 0     | 0     | 0                       |
|         | 3-BC      | n.d.      | 0     | 0     | 0                       |
|         | 4-MBC     | n.d.      | 0     | 0     | 0                       |
| summer  | BP-1      | <LOD-52.5 | 15.0  | 11.7  | 33.3                    |
|         | BP-2      | <LOD-1474.3| 393.9 | 444.6 | 93.7                    |
|         | BP-3      | <LOD-74.2 | 55.7  | 18.7  | 18.7                    |
|         | 3-BC      | n.d.      | 0     | 0     | 0                       |
|         | 4-MBC     | <LOD-132.1| 72.7  | 33.1  | 20.8                    |
| autumn  | BP-1      | n.d.      | 0     | 0     | 0                       |
|         | BP-2      | <LOD-729.6| 387.5 | 207.3 | 81.2                    |
|         | BP-3      | <LOD-25.6 | 25.6  | 2.1   | 2.1                     |
|         | 3-BC      | n.d.      | 0     | 0     | 0                       |
|         | 4-MBC     | <LOD-133.0| 84.5  | 25.4  | 18.8                    |

Four of the five UV filters were detected in the core sediments with various frequencies. Besides 3-BC, with a lack of detection events, the lowest general detection frequency was observed for BP-3, while the highest for BP-2. In general, the average concentration decreased as follows: BP-2 > 4-MBC > BP-3 > BP-1. BP-2 and 4-MBC were detected at all sites and were present at the highest concentrations compared to the other two UV filters, with quantitative levels ranging from 10.2 (Rowy\(_{spring}\)) to 1474.3 (Rowy\(_{summer}\)) ng·kg\(^{-1}\) d.w. and 26.4 (Darłowo\(_{summer}\)) to 133.0 (Rowy\(_{autumn}\)) ng·kg\(^{-1}\) d.w., respectively.
An average value for BP-2 and 4-MBC was 296.2 ng·kg⁻¹ d.w. (with average concentration per site ranging from 233.7 ng·kg⁻¹ d.w. to 414.0 ng·kg⁻¹ d.w.) and 78.3 ng·kg⁻¹ d.w. (with average concentration per site ranging from 67.3 ng·kg⁻¹ d.w. to 85.5 ng·kg⁻¹ d.w.), respectively. The next highest UV filter concentration was for BP-3 with the average concentration per site below the LODs to 63.3 ng·kg⁻¹ d.w. (Darłowo). Both BP-1 and BP-3 were detected at three out of four sites. No traces of BP-1 and BP-3 were found in Czołpino, which could be recognized as a reference station. No detectable levels of 3-BC were recorded for core sediments at all sites. To our knowledge, this study is the first report of UV filter appearance in beach sediments from the Polish part of the Baltic Sea coast. Although BP-2 and 4-MBC most commonly are observed in the ng·kg⁻¹ d.w., and occasionally in the µg·kg⁻¹ d.w., their presence is confirmed and can be used as reference data for future assessments and investigations.

Although some of UV filters have been reported to cause significant environmental threat [7,18,23,24,44], reporting of UV filter abundance in beach sediments is rare and only a few studies have examined their occurrence and profiles in these kind of environmental samples [45–48]. Moreover, many authors focus only on selected compounds, which is reasonable due to frequent changes in legal acts specifying the conditions for using UV filters in PCPs. This is why a comprehensive comparison of the results obtained in this study with other data is difficult, and this is also why the current study is of high importance. Of the five examined UV filters, the most commonly reported organic UV filters in beach sand were BP-3 and 4-MBC with a concentration typically in the ng·g⁻¹ d.w. range (<LOQ-1.0 ng·g⁻¹ d.w. (BP-3) and <LOQ-2.0 ng·g⁻¹ d.w. (4-MBC) [45]; <LOD-10.2 ng·g⁻¹ d.w. (3-BC) and 4.9-16.2 ng·g⁻¹ d.w. (4-MBC) [46]; <LOD-33 ng·g⁻¹ d.w. (3-BC) and 0.066-206 ng·g⁻¹ d.w. (4-MBC) [47]; n.d.-6.2 ng·g⁻¹ d.w. (3-BC) and n.d.-333 ng·g⁻¹ d.w. (4-MBC) [48]) (Table S2, Supplementary Materials). As ensues from the reported data, the concentration of BP-3 and 4-MBC determined in core sediments collected on the Polish coast is much lower than in Maspalomas [46] and on the western Spanish coast [48]. Generally, it fits the expectations concerning the beach sediments and their correlation with the scale of touristic pressure. It seems that the highest concentrations of 3-BC and 4-MBC found in Poland could be comparable to those reported for Portugal and Mallorca [47]. Although 4-MBC is still approved in PCPs in Europe [49], it is barely used nowadays [50,51], and this is probably why it was figuratively detected in Polish beach sand (19 samples, mean 78.3 ng·kg⁻¹ d.w.). It generally fits with the results presented by the researcher who did not determine 4-MBC in any sample collected close to the initial part of the Polish coast [35].

Since BP-2 was the most frequently found, its concentration in sand sediments collected in Darłowo, Ustka, Rowy, and Czołpino according to seasonality and distance from the waterline as well as to the depth of the sand core is detailed in Figures 3 and 4, respectively, while the statistical differences according to location, season, and distance are summarized in Table S3 (Supplementary Materials).

In the case of distance from the waterline as an independent factor, detailed inspection of Figures 3 and 4 suggested that the concentrations determined in S1 and S2 are generally higher than in S3 and S4. Moreover, in the majority of combinations, BP-2 concentrations determined in S3 and S4 were pretty comparable, and this is why the four distances from the waterline were merged in S1–2 and S3–4, dividing the beach for two areas: with (S1–2) and without (S3–4) direct contact with seawater. An additional reason for such merging was to avoid unreachable statistical significance due to the decreasing sample size, particularly in Rowy and Czołpino.
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As ensues from Table S3 (Supplementary Materials), BP-2 median concentration in beach sediments \((n = 27–36\) sites per location) was statistically comparable in three of the four locations \((198.6–210.5\ ng·kg\textsuperscript{-1}·d.w.)\) and slightly decreased in Czołpino \((141.5\ ng·kg\textsuperscript{-1}·d.w.)\). It suggests that BP-2 concentration does not fully correlate with the magnitude of touristic pressure, which in Ustka...
is far more intensive than in Darłowo and Rowy during the summer holiday peak. Moreover, some preliminary assumptions concerning Czołpino were slightly different from reality. It was assumed that beach sediments collected in Czołpino should be free from UV filters since it is located in the area of Słowiński National Park. Direct release of UV filters in this part of the coast is problematic since sunbathing in Czołpino is restricted and tourist activity is limited only to walking along the seashore due to limited access to the park area. This is why other phenomena might be responsible for the presence of BP-2 and traces of 4-MBC in beach sediment in Czołpino. Although the Baltic Sea has no noticeable permanent currents, many climatological analyses made in the southern Baltic area have detected prevailing winds from western directions, particularly from WSW, WNW, and W [52]. It causes slight, seasonal western sea currents, and hence, part of the load of pollutants released in the areas of Darłowo, Ustka, and Rowy can be transported and deposited easterly along the coastal zone by longshore littoral drift. We suppose that the longshore littoral drift of meridian direction in the coastal zone of the southern Baltic may be responsible for pollution spreading along the coast.

The artificial origin of UV-filters and their occurrence correlation with tourism was confirmed by seasonal assessment. The BP-2 median concentration in the spring (72.3 ng·kg\(^{-1}\) d.w.) was significantly lower than in the summer (141.5 ng·kg\(^{-1}\) d.w.) and the autumn (433.0 ng·kg\(^{-1}\) d.w.) (Figure 3, Table S3, Supplementary Materials). A similar pattern was observed for 4-MBC. 4-MBC was not found in core sediments collected in the spring, while its presence was confirmed in around 20% of collected samples in the autumn and summer with concentrations rising to 72.7 and 84.5 ng·kg\(^{-1}\) d.w., respectively (Table S3, Supplementary Materials). Even in the case of BP-1 and BP-3, the highest detection frequencies were observed in the spring with a lack of detection in the summer. The results observed in our study are well supported by the results presented by others who observed a higher concentration of organic UV filters in water reservoirs in the summer [23,51,53]. Mutual effects of two independent factors (location vs. season) revealed significant seasonal differences in BP-2 median concentration in Rowy and Czołpino. In Rowy, BP-2 concentration determined in the spring was tenfold and sixfold lower than that determined in the summer and the autumn, respectively. Although a similar magnitude of seasonal BP-2 concentration differences was observed in Czołpino, some important differences in the pattern of seasonal BP-2 variability were observed among all four investigated beaches. It seems that maintaining the general increasing trend, lower magnitudes of seasonal differences of BP-2 concentration were observed in Darłowo and Ustka. This is probably connected with the activity of biological wastewater treatment plants (WWTPs) operating in two of the four investigated locations. The water utilized by tourists passes through WWTPs for treatment before re-entering Wierprza (in Darłowo) and Słupia (in Ustka) rivers, which directly enter the Baltic Sea on the west side of the respective sampling sites. Based on many worldwide pieces of evidence [2,53–60], WWTPs have difficulty treating organic UV filters due to their low water solubility, high lipophilicity, and a high organic carbon-water partition coefficient. As an effect, they can be only partially removed from sewage, and hence, UV filters are usually present both in influents as well as effluents of WWTPs. Although an increase in UV filters in the WWTP effluent of more than 25% during the summer was reported by others [56], in the current case biological WWTPs operating in Darłowo and Ustka could be recognized as buffer facilities which compensate the increase of touristic pressure and decrease the release of UV filters in the central Pomeranian region during the summer holidays. The extreme seasonal changes in BP-2 concentration in Rowy and Czołpino are observed because none of WWTPs are operated in these locations.

The status of Czołpino as a reference station was partially supported by the results of BP-2 median concentration comparison between locations, however, limited to the specific season (Table S3, Supplementary Materials). Among the four investigated locations the lowest BP-2 concentration in the spring and the summer was determined in core sediments collected in Czołpino. At the end of the touristic season, BP-2 concentration was comparable in core sediments from all locations, which proves that pollutants released into the coastal zone of the marine environment could be comparatively scattered along the exposed part of the coast.
As mentioned above, the UV filters are characterized by relatively low water solubility and high lipophilicity (Table 1) and this is why they have the highest degree of impact in the bathing zone of the beach (in our case the merged S1–2 section). The UV-filter concentrations in core sediments from offshore or nearshore sites were significantly different ($p < 0.001$) in all of the touristic beaches (Darłowo, Ustka, Rowy). Water recreation as a dominant source of UV filters in touristic locations was shown by the difference in median BP-2 concentrations collected in offshore/nearshore sites in Darłowo (493.0 ng·kg$^{-1}$ d.w.), Ustka (394.6 ng·kg$^{-1}$ d.w.), and Rowy (474.8 ng·kg$^{-1}$ d.w.) compared to Czołpino (250.1 ng·kg$^{-1}$ d.w.). Generally, the median BP-2 concentration in the merged S1-2 sites was almost tenfold higher (445.6 ng·kg$^{-1}$ d.w.) than in sites located deeper into the dunes (merged S3-4).

None of distance-based differences in BP-2 concentration were observed between cores collected more than 30 m from the shore (S3 and S4). Limited access of waves along the transect perpendicular to the waterline in the direction of the dunes minimizes the spreading of UV filters along this transect. Moreover, some other dispersion phenomena could be observed in the direction of the sea. In Ustka and Rowy, the maximal BP-2 concentration peak was observed in S2, which was the boundary between the beach and the sea (being at the same time the place where the waves dispersed their energy), compared to in S1, which was an offshore site (Figure 4). According to the site-specific characteristic of the bathing zone (i.e., the slope of the seabed), the water movement could disperse the UV filters beyond their initial releasing points. These findings are in agreement with those reported by others who found decreasing BP-3, EHMC, and HMS concentrations with increasing distance from the shoreline at two beaches in the US Virgin Island [55]. Analogical patterns of differences along the transect perpendicular to the waterline were discovered using a combination of seasons and distances as independent factors. The UV filter concentrations in core sediments from offshore or nearshore sites were significantly different ($p < 0.001$) in all examined seasons (Table S3, Supplementary Materials). Both assessments confirm the source of UV filters involving recreational activities with beach and nearshore water recreation.

In the final step of data analysis an assessment of UV filters distribution in vertical profiles of four Polish beaches was done (Table S3, Supplementary Materials). The content of the studied filters in core sediments does not change significantly in the vertical profile of the beach (Figures 3 and 4). This suggests that in the case of UV filters the filtration along the sand does not play as important role as in the case of metals and their enrichment in the upper layers is not observed. The comparable content of UV filters in the three examined core layers is probably due to the frequent washing by the waves as well as the limited interaction between silica-based sand and highly lipophilic organic substances.

4. Conclusions

The study reported the presence of five selected UV filters in the core sediments collected in the central Pomeranian region on four beaches of various touristic pressure, expanding the current state of knowledge concerning the abundance of one of the PCP classes in the southern Baltic Sea. The measured concentrations were far lower than reported for other touristic areas, such as Maspalomas or the western part of the Spanish coast, however, they are of environmental interest due to the northward shift of the climatic zones and increasing popularity of central Europe as a touristic destination. Benzophenone-2 and 3-(4-Methylbenzylidene)-camphor were mostly observed in the highest peak of the summer holidays (the summer and the autumn), while Benzophenone-1 was occasionally found in the summer at a concentration range of ng·kg$^{-1}$. No evidence suggesting the presence of 3-benzylidene camphor was found. The concentration of BP-1, BP-2, BP-3, and 4-MBC fluctuates significantly by location, level of public access, season, and distance from the waterline. In the core sediments collected in the three exposed touristic beaches and one reference beach, organic UV filters were quantified in much higher concentrations in the bathing zone (offshore or nearshore sites) than beyond it suggesting that sediments collected more than 30 m from the shore could be impacted by UV filters only during heavy storms. Some traces of two out of five examined UV filters found in the reference station located in the area of the national park with limited access suggest that pollutants
released in a location of significant touristic pressure can spread along the coast via meridian transport caused by even slight currents. The environmental concentration of UV filters evidenced in the current study causes limited environmental threat, however, should be further monitored due to the closed, unstable, and fragile characteristics of the Baltic Sea basin.

**Supplementary Materials:** The following are available online at [http://www.mdpi.com/2073-4441/12/11/3024/s1](http://www.mdpi.com/2073-4441/12/11/3024/s1), Table S1: An occurrence of the selected UV-filters in organisms living in marine and freshwater habitats (d.w.—dry weight, l.w.—lipid weight, n.d.—not detected, OD-PABA—2-ethylhexyl 4-(dimethyloamino) benzoate, BP-4—benzophenone-4, IMC—3-methylbutyl-(2E)-3-(4-methoxyphenyl)-acrylate) [61–66]. Table S2: UV-filters content in saline and freshwater samples [8,23,31,35,44–48,53–55,63,67–77]. Table S3: Statistical assessment of UV-filters concentration according to four independent factors: location, season, distance and core depth as well as their mutual combinations.

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