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Distribution of Nine Organic UV Filters along the Shore Next to the Harbor Canals in the Middle Pomeranian Region (Northern Poland)

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Abstract: Spatiotemporal changes in the concentration of UV filters were investigated along the shore according to increasing distance from breakwaters, from the shoreline, as well as according to seasonality in three locations of different anthropogenic pressures, involving those from cosmetic products being released during touristic activity. Nine organic UV filters (benzophenone-1 (BP-1), benzophenone-2 (BP-2), benzophenone-3 (BP-3), octocrylene (OCR), 4-methoxy benzylidene camphor (4-MBC), ethylhexyl methoxycinnamate (EHMC), ethylhexyl salicylate (EHS), homosalate (HMS), and butyl methoxydibenzoylmethane (BMDM)) were determined in core sediments, and the range of determined concentrations above the limit of quantification was between 19.2 ng·kg^{-1} d.w. (HMS) and 539.5 µg·kg^{-1} d.w. (4-MBC). Unexpectedly, contrary to the level of anthropogenic pressure, the concentrations of four (BP-1, BP-2, BP-3, OCR) UV filters decreased in the following order: Darłówko > Ustka > Rowy. Higher concentrations of BP-1, BP-2, BP-3, and OCR were determined in spring than in summer and autumn. The maximal concentration of HMS and EHMC/EHS was found in the summer and in the autumn, respectively. BMDM was determined occasionally only in two samples collected in Ustka. The higher maximal concentration range of all UV filters was determined in core sediments taken from the eastern (539.5 µg·kg^{-1} d.w.) rather than from the western (11.3 µg·kg^{-1} d.w.) parts of the beaches. According to increasing distance from the breakwaters, higher concentrations of UV filters were determined in sites located up to 100 m away in all locations and seasons. Spatial variation in the concentration of UV filters was observed in profiles perpendicular to the water line. Typically, higher concentrations were determined at sites having contact with water, although incidentally, high concentrations were also noticed at sites located further into the beach. The Polish coast of the Baltic Sea is not free from organic UV filters, and expectations concerning the abundance of UV filters in a given location are far from recorded data due to the impact of hydro-technical treatments (i.e., stony and wooden breakwaters, artificial reefs, nourishment) and coastal littoral drift.

Keywords: breakwaters; emerging contaminants; littoral drift; sand sediments; UV filters

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1. Introduction

A total of 30% of worldwide coasts are sandy coasts. Sandy beaches are fragile to various natural processes such as waves, wind, storms, sea currents, rising sea levels, and climate change [1]. However, the most important factor that impacts their ecosystem is anthropogenic activity, including the construction and expansion of ports, tourism infrastructure, and inappropriate coast development [2–8]. In addition, existing harbor structures change coastal flow hydrodynamics and sediment transport in the nearshore zone [7,9]. Sandy shores are often eroded and coastlines are shifting inland [5,7], causing a decline in tourist value and increasing the vulnerability of inland areas to flooding [9,10]. Numerous hydro-technical activities are conducted (e.g., artificial nourishment with sand,

and construction of detached and submerged breakwaters) [11] to avoid negative chaps and protect the sea coast.

Nearshore areas are impacted by anthropogenic contaminants released to the sea through river load or tourism. The environmental fate of contaminants depends on their physicochemical properties (e.g., water solubility, octanol/water partition coefficient (Log K_{ow}), solid–liquid distribution) [12]. The main characteristic that determines the fate of hydrophobic organic compounds in water reservoirs is the sorption ability into sediments. It depends on interactions between organic matter and hydrophobic centers of molecules [13] and could be modified by local hydrodynamics. During intensive waves, sediments might be resuspended and comped down on the beach or migrate from the release site to remote locations due to sea currents, such as local littoral drift [12,13].

In recent years, more attention has been paid to "emerging contaminants" (ECs) which are not subject to standards and regulations by environmental monitoring [14]. ECs consist of about 20 classes of pollutants such as pharmaceuticals, personal care products (PCPs), surfactants, pesticides, plasticizers, endocrine disruptors (EDCs), etc. [12,15]. PCPs constitute skin care cosmetics such as sunscreens, suntan lotions, premature aging creams, makeup, and hair care products. Organic UV filters classified as PCPs [14] belong to the ECs list. Increased use of UV filters is associated with awareness of the negative impact of solar radiation (e.g., skin damage, photoaging) and skin cancer prevention [15–17]. Direct sources of UV filter release to the marine environment are seaside tourism and water recreation [17–19], while the indirect source is insufficiently treated municipal sewage [20–22] and river transport [23]. Most of the organic UV filters are characterized by a high octanol-water partition coefficient (log $K_{ow} > 4$) and tend to accumulate in sediments and living organisms [24–26].

Although organic UV filters' presence is reported in seawater [22,27–29], rivers [30–32], lakes [25,33,34], and marine sediments [23,35,36], beach sediments are often overlooked in UV filter research. To our best knowledge, only a few studies touch on this issue [37–42]. Unfortunately, most of them tend to focus only on a few compounds, which makes an overall concentration comparison difficult. However, studies concerning UV filters' abundance in beach sediments can be an important source of information concerning the environmental state of the marine environment. Analytical data derived from the sand core analysis are crucial to study UV filters' accumulation in sediments [13]. As mentioned above, due to hydrophilicity, UV filters tend to accumulate in the sediments; however, they can be remobilized through natural (e.g., storms, waves, tidal currents) or anthropogenic (e.g., dredging, nourishment) processes [43]. Once remobilized, UV filters can be transported by sea currents or coastal littoral drifts over long distances reaching even the Arctic region [44,45] or protected coastal areas [42,46]. This is why sediments can be considered a reservoir of accumulated contaminants that pose a threat to marine biota [47].

As mentioned above, UV filters are commonly detected in the seas and oceans. However, little research has been conducted on their presence in the Baltic Sea basin. Besides some preliminary records confirming the abundance of UV filters in beach sediments from Darłówko, Ustka, Rowy, and Czołpino [42], there is still a scientific gap concerning the organic UV filters' presence in the area of the Polish coast of the Baltic Sea. Omitting referenced research [42], there is still a lack of information on seasonal variability, coastal transport, and local spatial variation of organic UV filters due to the hydrodynamic processes in the vicinity of the rivers' mouths and harbor canals equipped with breakwaters. Therefore, the current study aimed to assess the distribution of nine organic UV filters along the shore next to harbor canals in three locations along the Polish part of the Baltic Sea coast. The common feature of all locations is the presence of a port canal dividing the beaches into the western and eastern parts. The specific aims were (i) to assess the spatiotemporal variability of selected UV filters in beach sediments in Darłówko, Ustka, and Rowy, (ii) to assess changes in UV filters' concentration in samples taken from the western and eastern parts of the beach separated by a harbor canal protected by breakwaters, and

(iii) to study the distribution of UV filters in beach sediments along a transect perpendicular to the shoreline.

2. Materials and Methods

The study area covered an 80 km section of the Polish coast, between the 82nd and 252nd km of the Polish sea border (Figure 1).

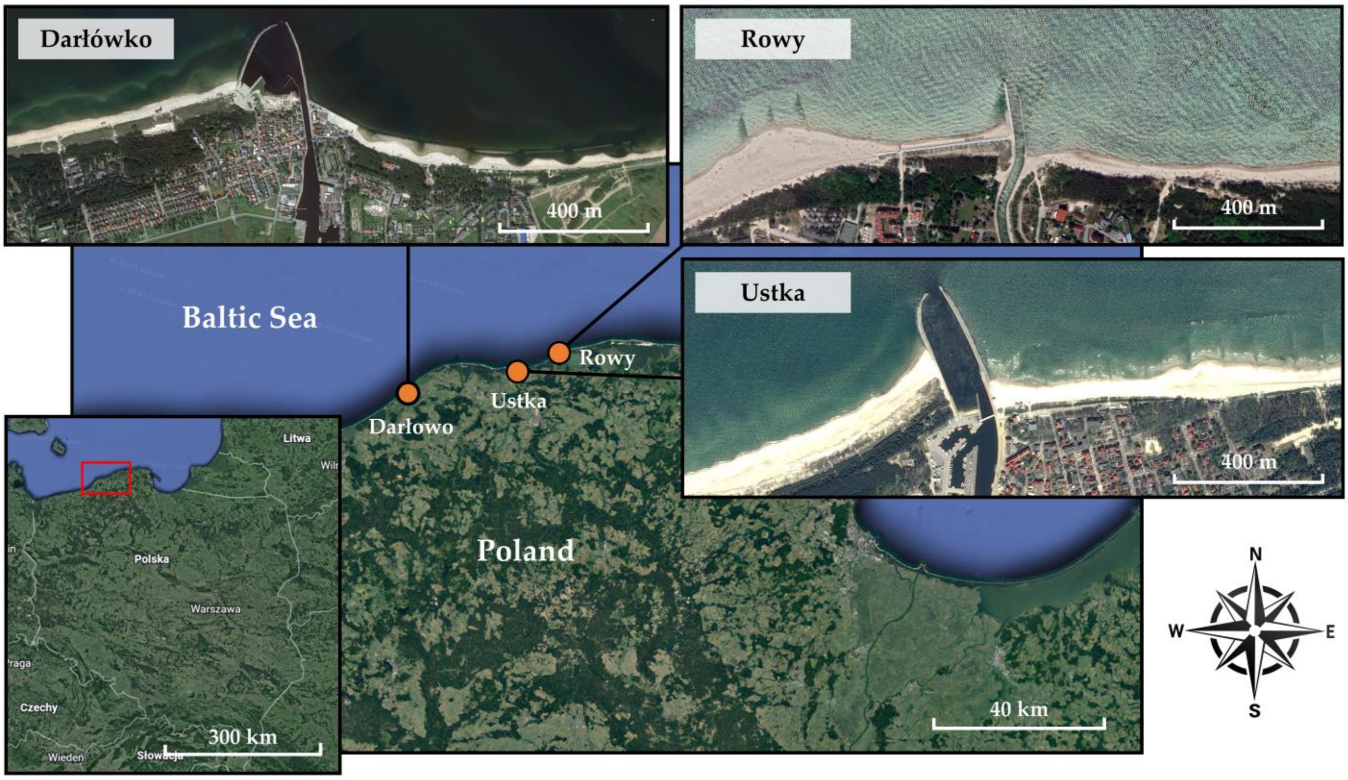

Figure 1. Location of a research area.

2.1. Beach Description

The study was carried out on sandy beaches located in Darłówko (54°25′ N/16°240′ E), Ustka (54°340′ N/16°510′ E), and Rowy (54°39′ N/17°03′ E). All beaches are classified as exposed, non-tidal, and characterized by high touristic pressure in the following order: Ustka > Darłówko > Rowy [42,48]. Ustka is a very popular tourist destination in summer and off-season due to its health resort status [48]. Darłówko and Rowy are popular summer resorts, characterized by a lower level of tourist pressure in the off-season [49]. However, Darłówko is slightly more visited than Rowy due to easy access via a road of national status. In all locations, beaches are divided by the local river estuary into eastern and western parts. Because strong, western winds prevail on the Polish coast, harbor entrances are protected by concrete breakwaters.

The entrance to the port in Darłówko is protected by two breakwaters of a length of around 300 m each. Additionally, a series of parallel, detached, stony breakwaters were built to protect the eastern part of the beach. After a section of detached stony breakwaters, the beach is protected by a series of more than 20 perpendicular wooden breakwaters built to decrease wave energy.

The main entrance to the port in Ustka is protected by two breakwaters of a length of around 250 m each. The eastern part of the beach is additionally protected by a series of wooden constructions perpendicular to the beach. Moreover, directly after them (at a distance of around 200 m from the shoreline), the underwater, stony artificial reef of around 850 m in length and 30 m in width was created. A reef consists of 4 sections of around 200 m in length each.

The main entrance to the port in Rowy is protected by two tiny breakwaters of around 100 m in length, while an artificial reef of 850 m in length is located at the western part of the beach. Moreover, to protect the western beach in Rowy, a triad of wooden breakwaters of around 60 m each is located at a distance of around 300 m from the western breakwater. None of the additional breakwaters were created on the eastern part of the beach. Detailed satellite images of constructions present in each location with their approximate dimensions are presented in Figure 2.

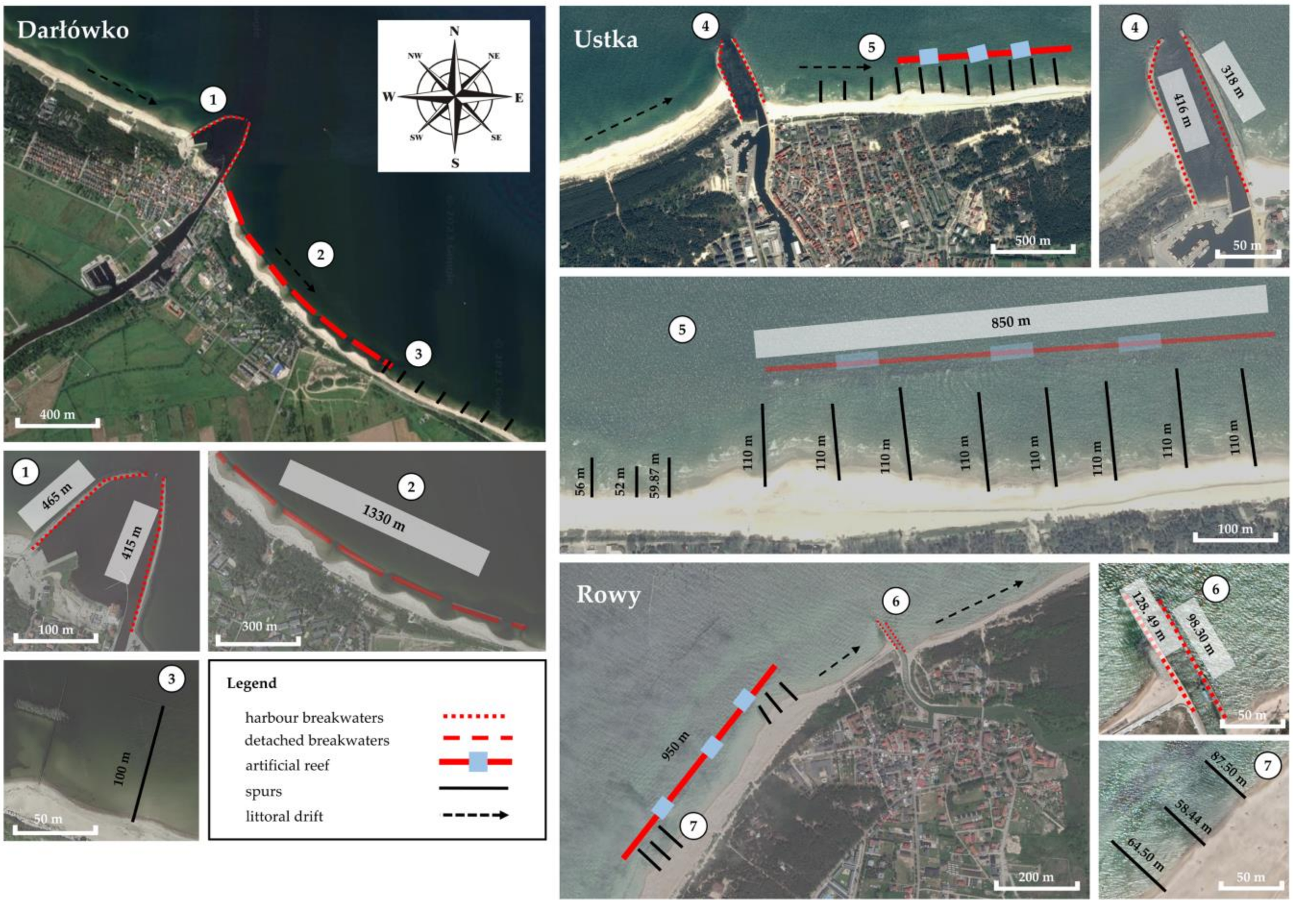

Figure 2. The length and location of the harbor breakwaters (1,4,6), detached breakwaters (3,7), artificial reefs (5), and spurs (2) in Darłówko, Ustka, and Rowy as well as the direction of the littoral drift.

Despite many protective constructions, sandy beaches in Darłówko and Ustka are impacted by a very strong waterfront causing substantial abrasion of the coast. To protect the beauty and uniqueness of beaches against abrasion, numerous hydro-technical treatments, including restoration and nourishment [11], are conducted periodically.

2.2. Sampling

The scientific literature lacks a universal method that should be used for sampling beach sediments. Some authors omit the description of the method used [37–39], while some present only pieces of information, such as the material of the used spatula [50]. To assure repeatability of the sampling procedure in other domains, in this study, sampling was accomplished according to guidance on sampling techniques for qualitative, chemical, and biological assessment PN-ISO 10381-2:2007 [51]. Sand samples were dredged seasonally (spring, summer, autumn) in 2019 and 2020 from the beaches located on both sides of the breakwaters (named further as the western and eastern sides). In both directions, 3 horizontal transects were marked out at a distance of 50, 100, and 500 m (Figure 3A). Each time, four cores were taken in a transect perpendicular to the shoreline: S1 was located in the sea, around 3 m from the waterline, S2 was located at the waterline, S3 was situated halfway up the beach, around 30–35 m distance from the shore, and S4 was a sheltered place among the dunes, around 60–70 m away from the shore (Figure 3B). Sampling along a transect is in agreement with the recommendation presented by others [52]. Core sand samples were taken using a stainless steel Morduchaj-Boltowski core scoop (30 × 15 cm) (Figure 3C).

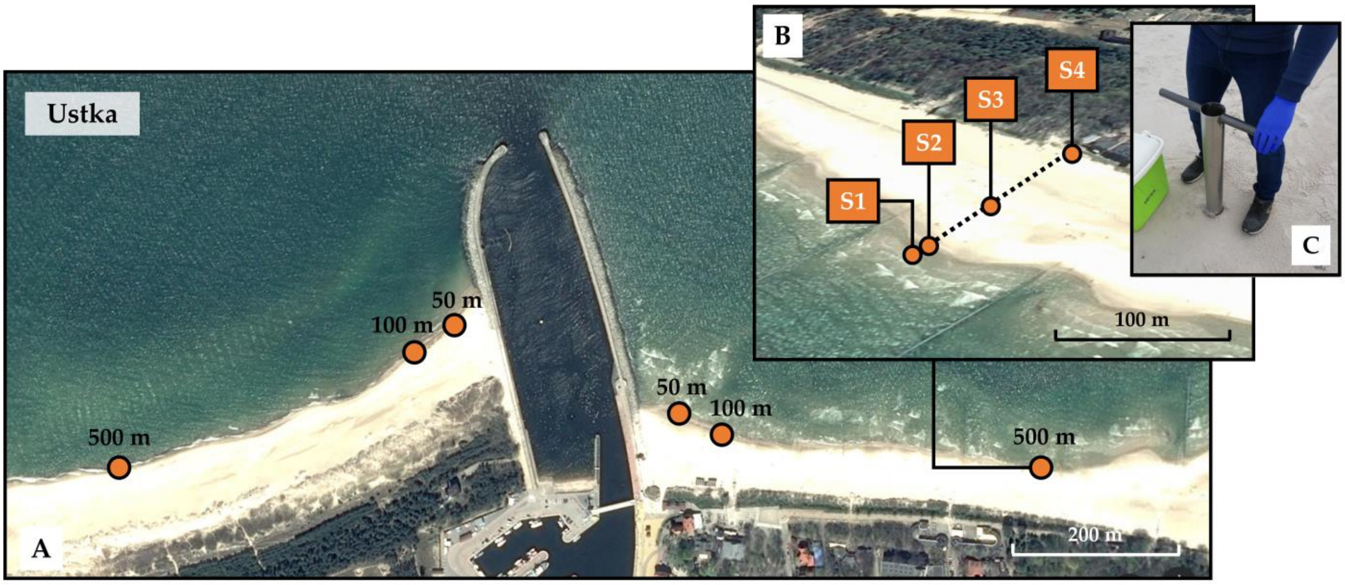

Figure 3. Distances (**A**) and sampling sites in a horizontal profile (**B**) on the example of the beach in Ustka using a core scoop (**C**).

Surface sediments from 0–5 cm depth were collected for analysis because none of the statistical variations according to the depth of the cores were found in previous studies [42]. Sand samples were placed in polyethylene bags and transported to the laboratory in portable refrigerators at a temperature of 4 °C. The analogical sampling procedure was applied in previous studies conducted in this area [42,49,53]. As mentioned above, sandy beaches are unstable in a longer time perspective, and this is why sampling recommended as suitable to geospatial assessment was replaced by sampling enabling long-term monitoring. For the interpolations typically required in soil-related surveys, variograms computed on fewer than 50 sampling spots are of little informational value, and at least 100 spots are needed [54]. This is the reason why geospatial maps requiring a relatively stationary system and using interpolation techniques, such as Kriging [55], were substituted by heat maps.

2.3. Sample Preparation and Analytical Methods

Analytical standards (purity > 98%) of nine organic UV filters (BP-1, BP-2, BP-3, 4-MBC, OCR, EHMC, EHS, HMS, and BMDM) were purchased from Merck (Darmstadt, Germany). The main characteristics of the studied UV filters are summarized in Table S1 (Supplementary Materials).

Sand sample preparation was performed according to a slightly modified procedure of Jeon et al. [56] and Astel et al. [42], shown in Figure 4.

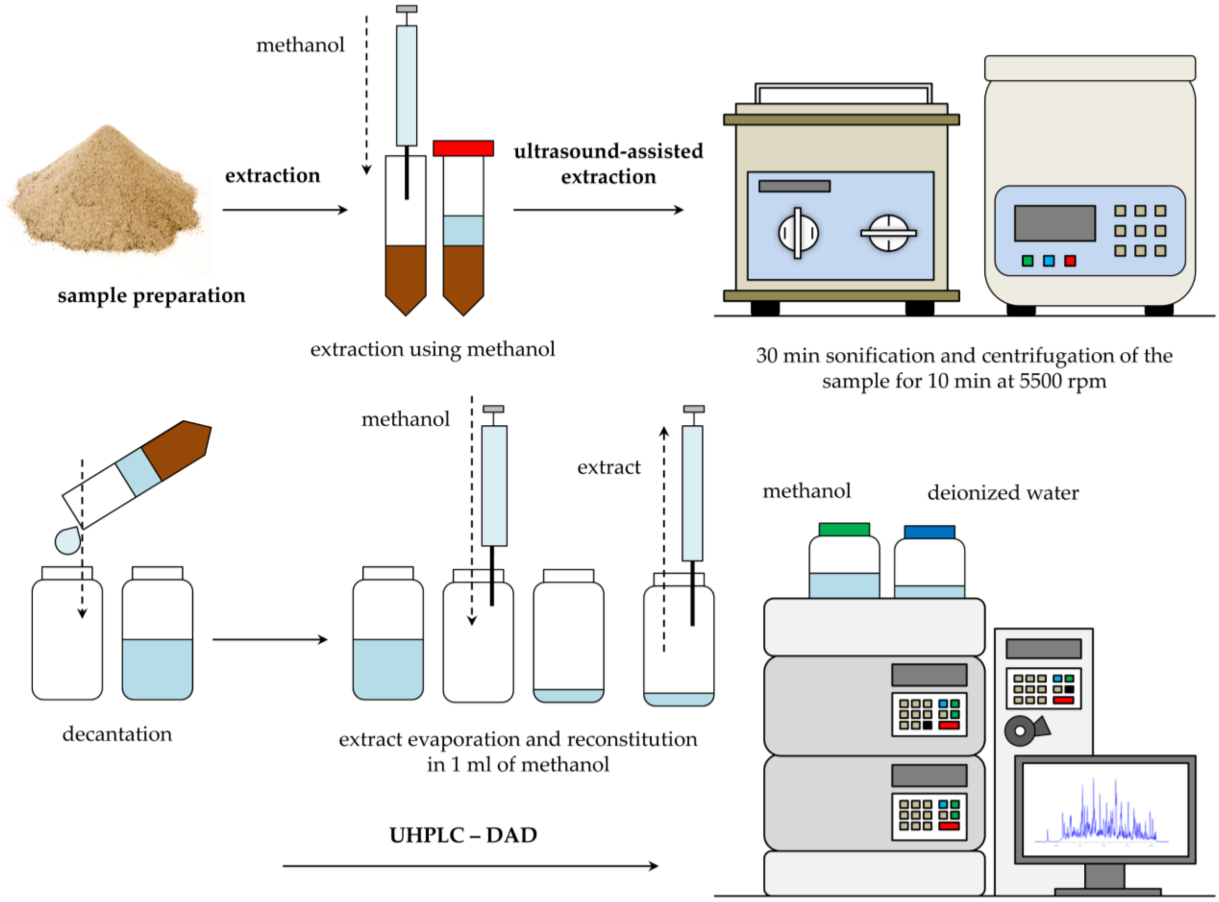

Figure 4. Schematic diagram of sample preparation and UV filter extraction.

To avoid the thermal decomposition of target analytes, air-drying of collected samples was used. An amount of 10 g of sample was extracted with 10 mL of MeOH (HPLC grade, purity $\geq$ 99.9%, Merck, Darmstadt, Germany) using ultrasonic-assisted extraction (30 min). Once extraction was accomplished, a sample was centrifuged (5500 rpm), decanted, vaporized to dryness, and reconstructed in MeOH to 1 mL.

UV filters were determined using a UHPLC system (Shimadzu LC Workstation, Kioto, Japan) equipped with an LC-2AD pump and a diode array detector SPD-M20A DAD. The analysis was performed using conditions similar to Peruch and Rath [57]: analytical column NUCLEOSIL®100-5 C18 (250 mm × 4.6 mm; 5 µm); mobile phase MeOH/H_2O 88:12 *v*/*v*; isocratic elution; mobile phase flow: 1 mL/min; sample volume: 20 µL; temperature: 20 °C; pressure: 147 bar. Data were acquired at 18 min in the wavelength range 230–360 nm.

2.4. Quality Assurance and Quality Control

To assure correct retention times, analytical standards were analyzed separately, and then the calibration curves were acquired for a mixture of standard solutions at concentrations ranging from 0.001 to 1000 µg·L^{-1}. The curves were determined for six different concentrations determined in triplicate. Stock standard solutions were prepared in MeOH containing 1 g·L^{-1} of each compound for daily validation. From these standards, working standard mixtures containing each compound were prepared daily. Within the studied concentration range, the calibration curves were linear ($r^2 \geq 0.9984$), fitting the EU directive [58] for confirmatory methods. The limit of detection (LOD) was calculated as 3 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, detection limits, and wavelength are summarized in Table S2 (Supplementary Materials).

2.5. Statistical Procedure

It was planned to assess the effect of several independent factors (location, seasonality, distance from the breakwater in western and eastern directions, and distance along a transect perpendicular to the shoreline) on UV filter concentration determined in core-sediment samples. This is why, primarily, multiway ANOVA was targeted as the most suitable statistical tool. However, due to the lack of fulfilling ANOVA's constraints (i.e., Gaussian data distribution (tested by the use of W Shapiro–Wilk's test), homogeneity of variance between comparing groups of samples (tested by the use of Fisher-Snedecor test)), comparison according to all combinations of independent factors was not possible. Because of this, statistical testing was accomplished using the non-parametric U Mann–Whitney test for two-group comparison and the Kruskal–Wallis test for multiple-group comparison. All tests were calculated at $p = 0.05$ using Statistica 13.3 (TIBCO Statistica Inc., Palo Alto, CA, USA).

3. Results

The concentration values of all investigated UV filters determined in sand samples are summarized in Tables 1 and 2. The results were arranged according to the location, direction relative to breakwaters, and season. In general, 432 sand samples were analyzed, and 34.5% of the determination results were above the LOQ.

Table 1. Basic statistics (ng·kg^{-1} d.w.) and detection frequency (%) of UV filters determined in core sediments according to direction relative to breakwaters (west—western beach, east—eastern beach) in Darłówko, Ustka, and Rowy (*n*—number of samples with concentration higher than LOQ).

UV Filter	Site	Direction	*n*	%	Mean	Median	Min	Max	Lower Quartile	Upper Quartile	S.D.
BP-1	Ustka	east	2	2.8	113.8	113.8	69.9	157.7	69.9	157.7	62.1
BP-2			72	100.0	171.9	148.4	74.2	1340.4	114.2	175.4	151.9
BP-3			13	18.1	173.8	40.8	28.3	667.2	36.8	246.2	220.2
OCR			30	41.7	1331.6	187.8	39.7	12,369.4	79.8	1730.0	2571.7
4-MBC			5	6.9	107,986.3	120.0	59.3	539,534.3	60.3	157.6	241,242.7
EHMC			11	15.3	90.9	74.4	28.9	295.4	50.4	93.4	74.1
EHS			66	91.7	778.0	444.6	43.7	2714.1	314.8	878.2	757.3
HMS			53	73.6	454.7	277.8	19.2	5888.8	187.2	381.2	904.8
BMDM			2	2.8	68,099.9	68,099.9	53,311.5	82,888.3	53,311.5	82,888.3	20,914.0
BP-1		west	2	2.8	74.9	74.9	29.0	120.9	29.0	120.9	64.9
BP-2			72	100.0	200.4	167.0	56.8	518.7	136.3	230.2	97.8
BP-3			9	12.5	79.6	69.9	33.5	141.8	49.4	98.2	37.7
OCR			17	23.6	610.4	304.0	27.0	2358.9	98.1	799.6	711.6
4-MBC			0	0.0							
EHMC			7	9.7	79.4	70.9	29.9	160.7	38.7	115.9	45.3
EHS			59	81.9	756.0	664.5	103.6	1966.3	382.4	1078.5	492.7
HMS			42	58.3	306.9	302.7	87.3	546.1	204.7	399.6	130.1
BMDM			0	0.0							
BP-1	Rowy	east	4	5.6	57.6	53.9	28.8	93.8	39.5	75.7	27.1
BP-2			71	98.6	3205.9	147.7	43.9	23,845.6	101.1	410.5	7273.4
BP-3			33	45.8	564.0	192.9	34.0	6821.4	83.6	734.9	1182.3
OCR			25	34.7	473.1	127.9	27.5	5789.1	61.3	308.1	1152.7
4-MBC			1	1.4	25.8	25.8	25.8	25.8	25.8	25.8	
EHMC			13	18.1	7679.0	101.3	40.2	98,704.2	75.6	121.9	27,349.7
EHS			46	63.9	571.9	488.1	59.1	1279.9	319.1	789.7	315.9
HMS			38	52.8	307.9	303.8	57.3	621.9	239.4	381.3	116.2
BMDM			0	0.0							
BP-1		west	3	4.2	48.6	29.7	25.4	90.8	25.4	90.8	36.6
BP-2			71	98.6	184.9	150.7	38.8	535.3	93.2	246.4	124.1
BP-3			14	19.4	131.5	122.9	43.2	285.8	83.9	155.6	71.8

Table 1. *Cont.*

UV Filter	Site	Direction	*n*	%	Mean	Median	Min	Max	Lower Quartile	Upper Quartile	S.D.
OCR			37	51.4	943.5	98.9	31.5	10,149.6	56.4	259.3	2250.0
4-MBC			0	0.0							
EHMC			11	15.3	354.7	82.3	40.7	2309.6	54.9	153.0	694.7
EHS			57	79.2	504.4	393.5	69.1	1566.6	182.2	739.9	401.2
HMS			41	56.9	280.6	280.4	32.8	648.9	154.9	363.3	136.4
BMDM			0	0.0							
BP-1	Darłowo	east	1	1.4	9845.7	9845.7	9845.7	9845.7	9845.7	9845.7	
BP-2			72	100.0	237.3	145.3	44.0	2781.1	112.6	178.3	355.5
BP-3			19	26.4	7966.8	103.3	25.8	137,090.5	46.9	241.3	31,340.9
OCR			41	56.9	2598.2	192.3	30.6	44,828.6	68.8	976.7	7753.3
4-MBC			4	5.6	11,063.5	942.0	45.1	42,324.9	297.1	21,829.9	20,847.7
EHMC			8	11.1	564.3	219.0	50.1	3040.0	132.5	360.9	1008.0
EHS			39	54.2	497.8	291.9	42.7	1386.4	191.7	901.2	403.7
HMS			24	33.3	457.2	268.2	46.4	3825.8	192.6	439.3	739.3
BMDM			0	0.0							
BP-1		west	0	0.0							
BP-2			71	98.6	231.3	172.2	63.0	1718.1	133.1	220.0	240.9
BP-3			16	22.2	78.5	66.5	25.1	147.9	52.4	103.6	37.3
OCR			37	51.4	1923.0	222.1	61.1	11,320.6	129.4	1518.2	3321.1
4-MBC			3	4.2	149.4	196.5	49.6	202.2	49.6	202.2	86.5
EHMC			10	13.9	295.7	72.2	41.2	1687.4	63.2	190.6	521.5
EHS			41	56.9	663.8	658.9	62.7	1657.7	396.4	948.0	361.6
HMS			28	38.9	360.1	331.6	31.2	875.3	174.8	489.0	221.4
BMDM			0	0.0							

Table 2. Basic statistics (ng·kg^{-1} d.w.) and detection frequency (%) of UV filters determined in core sediments collected in spring, summer, and autumn (*n*—number of samples with concentration higher than LOQ) in three Polish beaches located in the Middle Pomeranian region.

UV Filter	Season	*n*	%	Mean	Median	Min	Max	Lower Quartile	Upper Quartile	S.D.
BP-1	spring	1	0.7	9845.7	9845.7	9845.7	9845.7	9845.7	9845.7	
BP-2		143	99.3	1668.8	157.0	38.8	23,845.6	104.8	195.2	5332.1
BP-3		49	34.0	3375.2	138.6	36.8	137,090.5	68.1	426.7	19,562.5
OCR		23	16.0	3145.6	84.0	30.6	44,828.6	43.4	1147.5	9485.0
4-MBC		4	2.8	11,063.5	942.0	45.1	42,324.9	297.1	21,829.9	20,847.7
EHMC		5	3.5	114.6	78.8	41.2	199.3	63.2	190.6	74.6
EHS		63	43.8	502.7	347.2	42.7	1966.3	180.1	732.3	425.1
HMS		48	33.3	308.5	234.9	31.2	3825.8	85.9	358.0	541.1
BMDM		0	0.0							
BP-1	summer	5	3.5	52.0	50.2	28.8	93.8	29.7	57.6	26.6
BP-2		142	98.6	175.4	133.9	42.7	2698.3	110.7	157.0	275.9
BP-3		36	25.0	216.6	61.6	25.1	3683.8	42.0	117.3	614.9
OCR		120	83.3	1565.1	273.4	27.0	19,610.4	116.8	1381.0	3150.8
4-MBC		1	0.7	25.8	25.8	25.8	25.8	25.8	25.8	
EHMC		45	31.3	282.7	87.7	28.9	3040.0	65.8	148.3	598.0
EHS		142	98.6	409.5	370.3	59.1	955.1	243.4	538.5	205.5
HMS		142	98.6	387.3	297.9	19.2	5888.8	216.8	412.1	564.2
BMDM		2	1.4	68,099.9	68,099.9	53,311.5	82,888.3	53,311.5	82,888.3	20,914.0
BP-1	autumn	6	4.2	82.3	80.4	25.4	157.7	29.0	120.9	51.9
BP-2		144	100.0	260.6	197.3	72.0	1225.0	139.9	365.4	173.5
BP-3		19	13.2	151.2	109.5	28.3	667.2	64.6	161.3	151.4
OCR		44	30.6	331.5	102.2	27.5	5845.1	66.3	182.3	968.8
4-MBC		8	5.6	67,547.5	138.8	49.6	539,534.3	59.8	199.4	190,711.5

Table 2. *Cont.*

UV Filter	Season	n	%	Mean	Median	Min	Max	Lower Quartile	Upper Quartile	S.D.
EHMC		10	6.9	9946.0	68.9	40.7	98,704.2	50.4	100.3	31,186.5
EHS		103	71.5	1046.8	984.1	51.0	2714.1	650.0	1279.9	606.0
HMS		36	25.0	318.0	339.7	31.1	648.9	229.6	395.4	134.9
BMDM		0	0.0							

Because BP-2, OCR, EHS, and HMS were the most frequently detected, their concentration in beach sediments collected in Darłówko, Ustka, and Rowy according to direction and distance from breakwaters as well as seasonality is detailed in Figures 5 and 6, respectively. To facilitate data interpretation, UV filters' concentrations determined in every location were normalized to unity, and discrete heat maps were created instead of geospatial plots, because of the reasons explained above. Based on heat maps, only some general interpretations concerning the spatiotemporal variation of UV filters in beach sediments in a single location (Figure 5), as well as the spatiotemporal variation of UV filters according to the direction from the harbor breakwaters (Figure 6), is possible; however, heat maps are not a suitable visualization for qualitative comparison of a measured UV filter's concentration values between locations. Instead of this, an analysis of the basic statistics according to the location of the beach, direction relative to the harbor breakwater, seasonality, and corresponding results of statistical tests presented in Table 3 is recommended.

Table 3. Statistical assessment of UV filter concentration according to three independent factors: location, season, and direction as well as their mutual combinations.

Compound	Categorized Variable	Number (n) of Concentrations above LOQ	Test Statistics	p-Value	K-W Multiple Comparison Test p-Value (Only Statistically Significant p Values Are Presented)
BP-2	location	Darłówko (n = 143) Ustka (n = 144) Rowy (n = 142)	K-W(H): 1.014	$p = 0.602$	
	location and direction	Darłówko $_{west}$ (n = 71) Darłówko $_{east}$ (n = 72)	M-W(U): 2092.0	$p = 0.061$	
		Ustka $_{west}$ (n = 72) Ustka $_{east}$ (n = 72)	M-W(U): 1881.0	$p = 0.004$	
		Rowy $_{west}$ (n = 71) Rowy $_{east}$ (n = 71)	M-W(U): 2208.0	$p = 0.203$	
	season	spring (n = 143) summer (n = 142) autumn (n = 144)	K-W(H): 55.126	$p < 0.001$	spring vs. summer $p = 0.009$ spring vs. autumn $p < 0.001$
	season and direction	spring $_{west}$ (n = 24) spring $_{east}$ (n = 24)	M-W(U): 244.0	$p = 0.370$	
		summer $_{west}$ (n = 24) summer $_{east}$ (n = 24)	M-W(U): 181.0	$p = 0.044$	
		autumn $_{west}$ (n = 23) autumn $_{east}$ (n = 24)	M-W(U): 225.0	$p = 0.197$	
	location and season	Darłówko $_{spring}$ (n = 48) Darłówko $_{summer}$ (n = 47) Darłówko $_{autumn}$ (n = 48)	K-W(H): 26.543	$p < 0.001$	Darłówko $_{spring}$ vs. Darłówko $_{autumn}$ $p < 0.001$

Table 3. *Cont.*

Compound	Categorized Variable	Number (n) of Concentrations above LOQ	Test Statistics	p-Value	K-W Multiple Comparison Test p-Value (Only Statistically Significant p Values Are Presented)
		Ustka $_{spring}$ (n = 48) Ustka $_{summer}$ (n = 48) Ustka $_{autumn}$ (n = 48)	K-W(H): 20.134	$p < 0.001$	Ustka $_{summer}$ vs. Ustka $_{spring}$ $p = 0.002$ Ustka $_{summer}$ vs. Ustka $_{autumn}$ $p < 0.001$
		Rowy $_{spring}$ (n = 47) Rowy $_{summer}$ (n = 47) Rowy $_{autumn}$ (n = 48)	K-W(H): 14.517	$p < 0.001$	Rowy $_{summer}$ vs. Rowy $_{autumn}$ $p < 0.001$
OCR	location	Darłówko (n = 78) Ustka (n = 47) Rowy (n = 62)	K-W(H): 9.768	$p = 0.008$	Darłówko vs. Rowy $p = 0.008$
	location and direction	Darłówko $_{west}$ (n = 37) Darłówko $_{east}$ (n = 41)	M-W(U): 655.0	$p = 0.030$	
		Ustka $_{west}$ (n = 17) Ustka $_{east}$ (n = 30)	M-W(U): 255.0	$p = 0.990$	
		Rowy $_{west}$ (n = 10) Rowy $_{east}$ (n = 1)	M-W(U): 2208.0	$p = 1.000$	
	season	spring (n = 23) summer (n = 120) autumn (n = 44)	K-W(H): 22.130	$p < 0.001$	summer vs. spring $p = 0.007$ summer vs. autumn $p < 0.001$
	season and direction	spring $_{west}$ (n = 1) spring $_{east}$ (n = 8)	M-W(U): 0.0	$p = 1.000$	
		summer $_{west}$ (n = 23) summer $_{east}$ (n = 24)	M-W(U): 234.0	$p = 0.377$	
		autumn $_{west}$ (n = 13) autumn $_{east}$ (n = 9)	M-W(U): 50.0	$p = 0.593$	
	location and season	Darłówko $_{spring}$ (n = 9) Darłówko $_{summer}$ (n = 47) Darłówko $_{autumn}$ (n = 22)	K-W(H): 15.432	$p < 0.001$	Darłówko $_{summer}$ vs. Darłówko $_{spring}$ $p = 0.028$ Darłówko $_{summer}$ vs. Darłówko $_{autumn}$ $p < 0.002$
		Ustka $_{spring}$ (n = 3) Ustka $_{summer}$ (n = 33) Ustka $_{autumn}$ (n = 11)	K-W(H): 8.199	$p = 0.166$	
		Rowy $_{spring}$ (n = 11) Rowy $_{summer}$ (n = 40) Rowy $_{autumn}$ (n = 11)	K-W(H): 4.154	$p = 0.125$	
EHS	location	Darłówko (n = 80) Ustka (n = 125) Rowy (n = 103)	K-W(H): 6.762	$p = 0.034$	Ustka vs. Rowy $p = 0.033$
	location and direction	Darłówko $_{west}$ (n = 39) Darłówko $_{east}$ (n = 41)	M-W(U): 568.0	$p = 0.545$	
		Ustka $_{west}$ (n = 59) Ustka $_{east}$ (n = 66)	M-W(U): 1671.0	$p = 0.017$	
		Rowy $_{west}$ (n = 57) Rowy $_{east}$ (n = 46)	M-W(U): 1053.0	$p = 0.807$	
	season	spring (n = 63) summer (n = 142) autumn (n = 103)	K-W(H): 93.637	$p < 0.001$	autumn vs. spring $p < 0.001$ autumn vs. summer $p < 0.001$

Table 3. *Cont.*

Compound	Categorized Variable	Number (n) of Concentrations above LOQ	Test Statistics	p-Value	K-W Multiple Comparison Test p-Value (Only Statistically Significant p Values Are Presented)
	season and direction	spring $_{west}$ (n = 5) spring $_{east}$ (n = 3)	M-W(U): 0.0	$p = 1.000$	
		summer $_{west}$ (n = 24) summer $_{east}$ (n = 24)	M-W(U): 48.0	$p < 0.001$	
		autumn $_{west}$ (n = 12) autumn $_{east}$ (n = 12)	M-W(U): 66.0	$p = 0.751$	
	location and season	Darłówko $_{spring}$ (n = 8) Darłówko $_{summer}$ (n = 48) Darłówko $_{autumn}$ (n = 24)	K-W(H): 52.424	$p < 0.001$	Darłówko $_{autumn}$ vs. Darłówko $_{spring}$ $p < 0.001$ Darłówko $_{autumn}$ vs. Darłówko $_{summer}$ $p < 0.001$
		Ustka $_{spring}$ (n = 42) Ustka $_{summer}$ (n = 48) Ustka $_{autumn}$ (n = 35)	K-W(H): 18.547	$p < 0.001$	Ustka $_{autumn}$ vs. Ustka $_{spring}$ $p = 0.026$ Ustka $_{autumn}$ vs. Ustka $_{summer}$ $p < 0.001$
		Rowy $_{spring}$ (n = 13) Rowy $_{summer}$ (n = 46) Rowy $_{autumn}$ (n = 44)	K-W(H): 52.993	$p < 0.001$	Rowy $_{autumn}$ vs. Rowy $_{spring}$ $p < 0.001$ Rowy $_{autumn}$ vs. Rowy $_{summer}$ $p < 0.001$
HMS	location	Darłówko (n = 52) Ustka (n = 95) Rowy (n = 79)	K-W(H): 1.212	$p = 0.545$	
	location and direction	Darłówko $_{west}$ (n = 28) Darłówko $_{east}$ (n = 24)	M-W(U): 299.0	$p = 0.501$	
		Ustka $_{west}$ (n = 42) Ustka $_{east}$ (n = 53)	M-W(U): 1020.0	$p = 1.000$	
		Rowy $_{west}$ (n = 38) Rowy $_{east}$ (n = 41)	M-W(U): 692.0	$p = 0.396$	
	season	spring (n = 48) summer (n = 142) autumn (n = 36)	K-W(H): 9.256	$p = 0.01$	spring vs. summer $p = 0.01$
	season and direction	spring $_{west}$ (n = 4) spring $_{east}$ (n = 2)	M-W(U): 0.000	$p = 0.105$	
		summer $_{west}$ (n = 24) summer $_{east}$ (n = 22)	M-W(U): 176.0	$p = 0.054$	
		autumn $_{west}$ (n = 12) autumn $_{east}$ (n = 12)	M-W(U): 66.0	$p = 0.751$	
	location and season	Darłówko $_{spring}$ (n = 6) Darłówko $_{summer}$ (n = 46) Darłówko $_{autumn}$ (n = 0)	K-W(H): 0.000	$p = 1.0$	
		Ustka $_{spring}$ (n = 33) Ustka $_{summer}$ (n = 48) Ustka $_{autumn}$ (n = 14)	K-W(H): 1.373	$p = 0.503$	
		Rowy $_{spring}$ (n = 9) Rowy $_{summer}$ (n = 48) Rowy $_{autumn}$ (n = 22)	K-W(H): 19.370	$p < 0.001$	Rowy $_{spring}$ vs. Rowy $_{summer}$ $p = 0.001$ Rowy $_{spring}$ vs. Rowy $_{autumn}$ $p < 0.001$

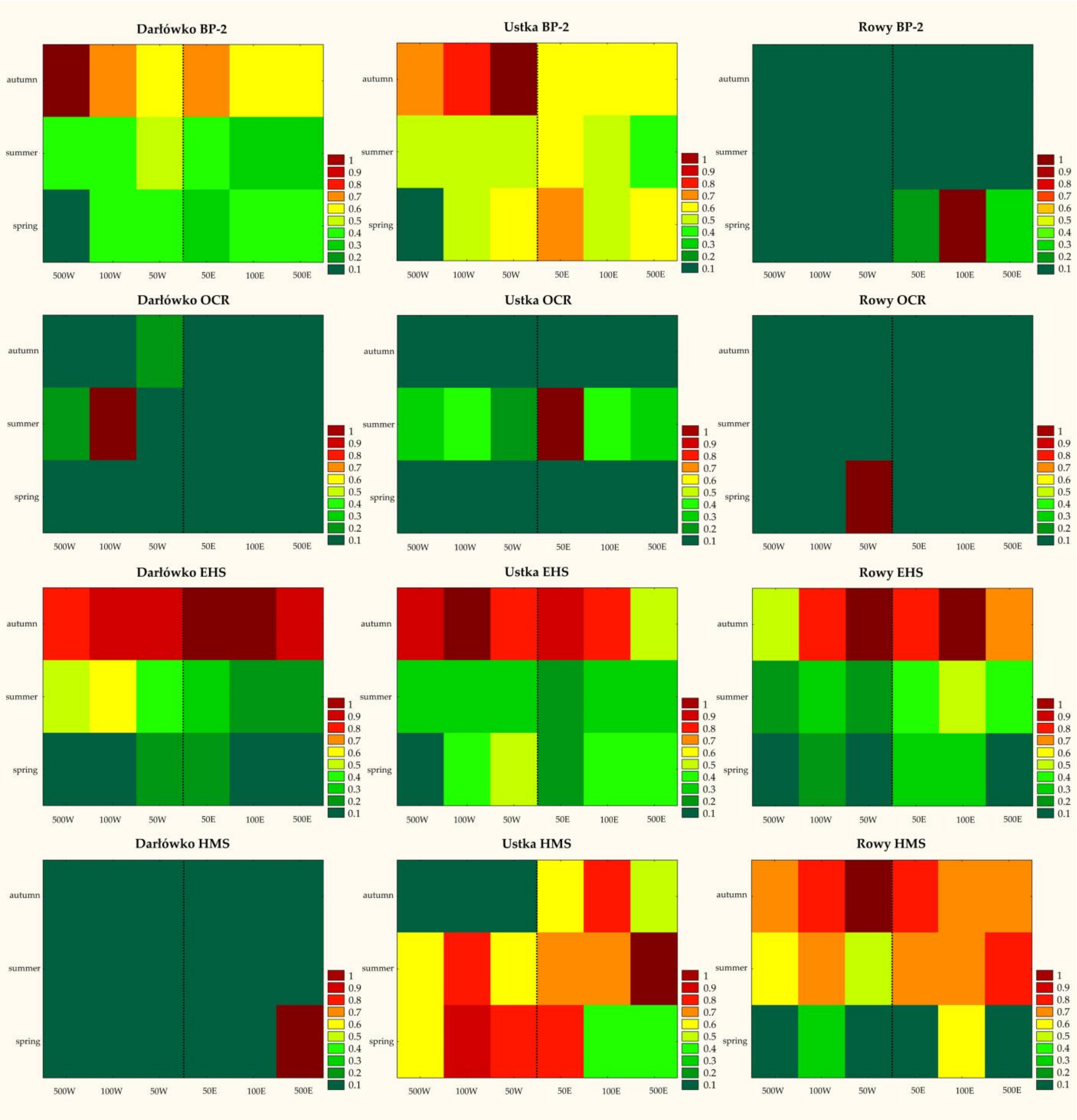

Figure 5. Heat map of normalized concentration (ng·kg^{-1} d.w.) of BP-2, OCR, EHS, and HMS determined in beach sediments collected in Middle Pomeranian beaches according to seasonality (spring, summer, autumn), direction (W—western, E—eastern), and distance relative to harbor breakwaters (50, 100, and 500 m, respectively).

In the case of all tested concentrations, possible differences according to a single categorized variable as well as their combinations were tested by the use of the Kruskall–Wallis test for multiple comparisons and the Mann–Whitney test for pair-wise comparisons, respectively.

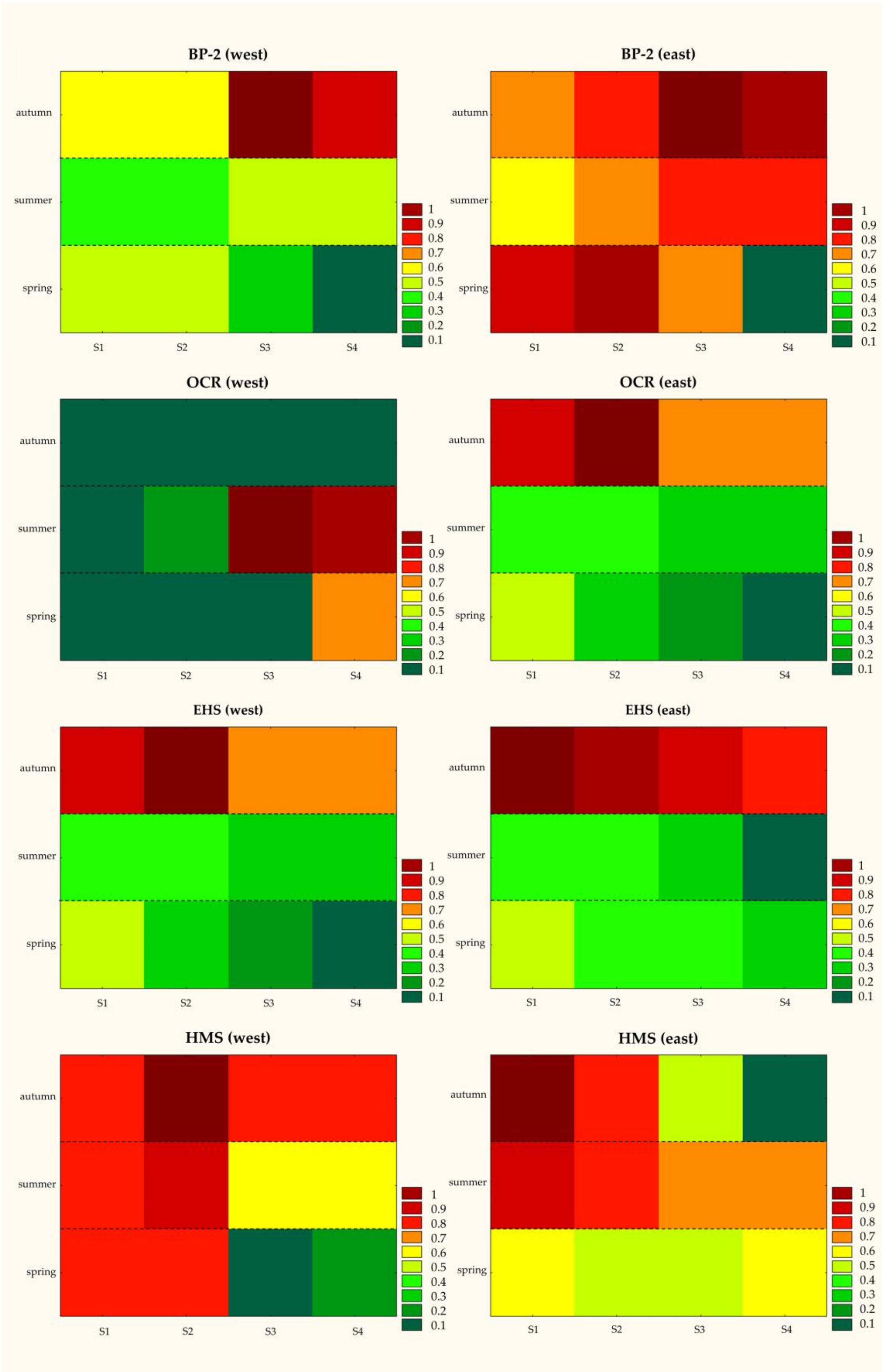

Figure 6. Heat map of normalized concentration (ng·kg^{-1} d.w.) of BP-2, OCR, EHS, and HMS in beach sediments collected in Darłówko, Ustka, and Rowy according to seasonality (spring, summer, autumn), direction (W—west, E—east), and distance from the shoreline along a perpendicular transect.

4. Discussion

Studied UV filters were detected in core sediments collected from western and eastern beaches in Darłówko, Ustka, and Rowy with various frequencies (Table 1). BMDM was determined occasionally only in two samples collected in Ustka. The highest detection frequency was observed for BP-2 (99.3%), while BMDM, BP-1, and 4-MBC were characterized by negligible detection frequency (0.46–3.0%). Observed extreme detection frequencies are partially in agreement with older records from this area [42]. The detection frequency of individual UV filters showed a descending trend: BP-2 > EHS > HMS > OCR > BP-3 > EHMC > 4-MBC > BP-1 > BMDM. In comparison with previous records [42], the detection frequency of BP-1 and 4-MBC have decreased in Darłowo and Rowy almost tenfold. The observed difference in detection frequencies is probably related to the chemical instability of molecules and their photodegradation. 4-MBC and EHMC undergo configurational isomerism and degradation under the influence of UV radiation [59,60]. In turn, the product of BP-3 degradation is BP-1, which consecutively degrades to BP-2 [61]. BMDM is highly unstable and rapidly photodegrades through the mechanism accelerated by BP-3 and EHMC [62]. Degradation patterns may have a significant impact on the occurrence of BP-2 in the marine environment. Negligible-to-moderate detectability of some UV filters, mainly 4-MBC (negligible) and BP-3 (moderate) may be additionally related to the restriction of their use in cosmetic products due to possible negative impacts on consumers [63,64] and the environment [65–68]. In 2017 and 2022, the European Commission introduced limitations on the maximum allowed concentration of BP-3 in cosmetics. Initially, the maximum concentration was reduced from 10% to 6% [69] and then to 5.5% [70]. Although no restrictions have been introduced for 4-MBC so far and it is still approved for use in the European Union, it is very rarely found in cosmetics [71]. Rare use of 4-MBC in cosmetics fits its only occasional detectability in beach sediments.

The concentration range of UV filters of the highest detection frequency ranged between 27.0 $ng \cdot kg^{-1}$ d.w. (OCR) and 44.83 $\mu g \cdot kg^{-1}$ d.w (OCR) (Table 1); however, the overall concentration range was between 19.2 $ng \cdot kg^{-1}$ d.w. (HMS) and 539.5 $\mu g \cdot kg^{-1}$ d.w. (4-MBC). In comparison to previous records [42], the mean concentration of BP-3 and BP-2 has increased roughly by the factors of 8–10 and 6, respectively. The concentration range of the most frequently determined filters is pretty close to concentrations determined in beach sediments reported in Spain (66 $ng \cdot kg^{-1}$–200.0 $\mu g \cdot kg^{-1}$ d.w.) [38] and in Portugal (30 $ng \cdot kg^{-1}$–373.0 $\mu g \cdot kg^{-1}$ d.w.) [39,40]. Surprisingly, the observation from the current study differs from the preliminary assumptions, suggesting higher differences in determined UV filter concentrations between Poland and Portugal or Spain due to incomparable tourist pressure in the Baltic Sea basin and the Iberian Peninsula's coasts. The Baltic Sea is characterized by a clear seasonality [66] with the most favorable weather conditions (averaged air temperature 20 °C) from mid-May to mid-September [72–74]. The lack of clear seasonality, higher insolation, as well as higher average air temperatures of 10–15 °C encourage tourists visiting the Spanish or Portuguese coast to apply sunscreens more often. In Iberian countries, UV filters are probably released to the marine environment almost constantly over time; however, their concentration in beach sediments is probably modified by factors different from those observed in Poland. Current results indicate that the accumulation of UV filters in sand sediment collected in the area of the Polish coast of the Baltic Sea is not fully correlated with the level of tourist pressure. It suggests that UV filters might be additionally released from indirect sources such as WWTPs that operate in Darłowo, Ustka, and Rowy [75–77]. According to scientific pieces of evidence, WWTPs insufficiently remove organic UV filters due to their lipophilic nature ($\log K_{ow} > 4$). Studies have reported incomplete removal of BP-1, BP-3, OCR, EHS, and HMS (33–99%) from wastewater [20,22] corresponding with concentrations' increase in the summer [32]. WWTPs in Darłówko, Ustka, and Rowy can be significantly overloaded in the summer due to population growth. The regular population of Ustka is about 16,000, while in summer it increases to over 100,000. In Darłówko and Rowy, the regular number of citizens is about 15,000 and 400, respectively. However, in the summer, it increases to 30,000 and 15,000, respectively [42]. Insufficiently treated water is discharged into the Wieprza (Darłowo), Słupia (Ustka), and Łupawa (Rowy) rivers, which enter into the Baltic Sea.

Based on the data presented in Table 1, it can be concluded that maximal concentrations of the majority of UV filters were determined in Darłówko and Ustka. It confirms previous records concerning UV filters' abundance detected in beach sediments collected in these locations [42]. However, obtained results do not fully correspond with touristic pressure. According to references, it declines in the following order: Ustka > Darłówko > Rowy [48]. As mentioned above, Ustka is more often chosen by tourists as a holiday destination than Darłówko. It should have a significant impact on the release of UV filters. However, higher total concentrations of UV filters were determined in the beach sediments collected in Darłówko. It is probably related to the presence of physical barriers limiting water exchange. The eastern beach in Darłówko has been secured with free-standing breakwaters in the form of stone islands. They limit water exchange between nearshore areas and an open sea [11]. A similar phenomenon explaining higher concentrations of UV filters in the area of Spanish-sheltered beaches compared to exposed ones was found by Sánchez Rodríguez et al. [28]. It enables us to conclude that the limited water exchange favors the accumulation of UV filters in the area of the beach in Darłówko.

Analyzing data on the seasonal variability of UV filter concentrations in beach sediments presented in Table 2 and Figure 5, higher concentrations were generally determined in spring and autumn. It is surprising because the highest concentrations of UV filters should be observed in the summer due to holidays [78,79]. However, based on data presented in Table 2, it is evidenced that UV filters are transported to the beach also prior to or after the summer season. In the area of the Polish sea coast, strong storm surges affect the seabed and the seashore [80] in spring and autumn. ECs accumulated in the bathing zone in the summer might be mobilized and deposited on the beach [25] as a result of intensive hydrodynamic processes. Moreover, due to the strong impact of the sea waves, hydro-technical treatments (with nourishment domination) are being carried out in the area of the Polish coast. Sediments for beach restoration are often collected by dredging the seaport basins and may contain ECs such as metals and organic chemicals [43,81,82] as well as UV filters previously immobilized in bottom sediments, in particular. Nourishment is often carried out before the tourist season [11]. However, in some locations (i.e., Ustka), nourishment is conducted before and after the holiday peak. Due to intensive hydro-technical treatments carried out in spring and autumn, the highest concentrations of UV filters are not observed in the summer. It enables us to conclude that nourishment might be a significant source of UV filters accumulated in beach sediments.

It was generally observed that UV filters are subject to coastal transport from the west to the east (Figure 5). It is consistent with western winds prevailing in the area of the Polish sea coast [80]. UV filters released in Darłówko, Ustka, and Rowy may be transported by the coastal littoral drift and deposited in zones along eastern directions with respect to spots of release. An explanation of the role of littoral drift in UV filter transport along the Polish coast was presented elsewhere [42]. As can be seen in Figure 5, port breakwaters disturb the course of the littoral drift. This results in disturbances in the transport of sediments, resulting in their accumulation on the updraft side (west) and erosion on the downdraft side (east), respectively [2,7,11]. According to distance from the harbor breakwaters as an independent factor, the UV filters' concentration was generally higher at sites located 50 and 100 m from the port breakwaters in all locations and seasons (Figure 5). This is due to the strong influence of morphodynamic processes. In the western part of the beach in Darłówko, Ustka, and Rowy, sediments are transported by littoral drifts toward the port breakwaters. Contaminated sediments are deposited in places of energy loss, which include sites located near the port breakwaters (100 and 50 m). On the other hand, UV filter-contaminated sediments carried by Wieprza (Darłówko), Słupia (Słupsk), and Łupawa (Rowy) rivers are released to the port canal, and through westerly-oriented sea currents, they can reach zones located far along the eastern direction.

Analyzing the variability of UV filters' concentrations according to the horizontal profile shown in Figure 6, a higher abundance of HMS can be observed in S1 and S2 in the summer. It is correlated with the intensity of the tourist activity in the bathing zone. Similar observations were reported by Bargar et al. [46] for BP-3, EHMC, and HMS. Due to high lipophilicity, washed-off UV filters are transported by waves toward the shore. Danovaro et al. [83] estimated that approximately 25% of sunscreens could be washed off the skin over a 20 min swim. On the other hand, in spring and autumn, variation in the concentration of UV filters is observed between sections S1–S2 (having contact with water) and S3–S4 (without contact with water). This is due to the fact that strong waves impacting the beach move marine sediments along the perpendicular transect of the beach and deposit them at sites far from the shore (S3–S4).

5. Conclusions

The study indicates the presence of nine organic UV filters (BP-1, BP-2, BP-3, 4-MBC, OCR, EHMC, EHS, HMS, BMDM) in the sediments of three Polish beaches. Obtained results ranged between 19.2 ng·kg^{-1} d.w. and 539.5 µg·kg^{-1} d.w. The determined concentrations were characterized by spatiotemporal variability. Higher concentrations were found in sediments collected from Ustka and Darłówko than Rowy and partially correspond to the beach protection and level of anthropogenic pressure at these locations. Assessment of seasonal variability showed that the highest concentrations of UV filters are not observed only in summer. This indicates that UV filters can be supplied to the environment throughout the year from indirect sources, e.g., WWTPs operating in the Darłówko, Ustka, and Rowy. Differences in concentrations were found between the western and eastern parts of the studied beaches. The measured concentration values were generally higher on the eastern than on the western parts of beaches in all locations and seasons. This is consistent with the level of anthropogenic pressure and coastal morphodynamics. Analyzing the variability of concentrations in the horizontal profile, generally higher concentration values were detected at sites located in the bathing zone (S1–S2). Incidentally, high concentrations were also found at sites located on the beach (S3–S4). The study also showed that UV filters are transported by littoral drift along the seashore from the west to the east. Therefore, UV filters can be transported to considerable distances from the source and become ubiquitous in the environment. Because obtained results were only partially consistent with previous studies conducted in the Middle Pomeranian region [42], further monitoring is desired to better understand the distribution of UV filters in the Polish coastal area.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/w15132403/s1, Table S1. The main characteristics of studied UV filters, Table S2. The calibration curve parameters and detection limits of five UV filters.

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