Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.883801

52 (2014) 3819–3831
May

The influence of anthropogenic factors on organic matter content changes in chosen beach ecosystems

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Received 20 February 2013; Accepted 11 September 2013

ABSTRACT

Sandy sediments coming from two beaches being under the various anthropopressure were analyzed. The first beach was situated in Ustka, while the other one on the terrain of The Słowiński National Park. The general content of organic matter (OM), proteins, lipids, carbohydrates, chlorophyll *a*, and organic carbon were determined. The content of a biopolymeric organic carbon, values of a food index, and a coefficient of aging of the OM were estimated. Research was conducted with intervals for three months. It was established that human activity impacts on the concentration of analytes in the ecosystem of a seaside beaches. Their higher concentration was observed on the beach under more intensive anthropopressure. The results of the analysis of variance proved that the content of chemical parameters depends on the economic and tourist activity, the season of the year, and the impact of sea water. The stations situated at the central part of the beach are characterized by larger concentration of proteins, lipids, and carbohydrates rather than those that those who are not under the direct impact of the sea. The concentration of carbohydrates were characterized by the highest percentage contribution, while proteins by the lowest. Uncharacterized fraction of the organic carbon was higher in Ustka, while the food index in Czołpino. This suggests anthropogenic origin of the OM on the beach in Ustka and natural origin in Czołpino. At the sediments, there were comparable coefficients of the ageing of the OM.

Keywords: Sediments; Beach; Organic matter; Proteins; Lipids, Carbohydrates; Chlorophyll *a*

1. Introduction

Nowadays, sea coast due to the presence of specific climate and unusual natural values and health benefits is used intensely for tourism and recreation as well as economic purposes. Thus, both coastal waters and seaside beaches have to be clean taking into consideration the chemical and biological pollution in order to reach a high standard [1]. In many countries, intensive investigations of the sanitary conditions of seaside ecosystems are conducted.

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Presented at the 11th Scientific Conference on Microcontaminants in Human Environment. 25–27 September 2013, Wisla, Poland
Organized by Department of Chemistry, Water and Wastewater Technology,
Faculty of Environmental Engineering and Biotechnology, Czestochowa University of Technology

Such research has been conducted in Poland for about 50 years [2–6]. Buczkowska [7] was the pioneer of studies on Poland's Baltic coast pollution. In the fifties of the twentieth century, she conducted the research concerning the quality of coastal waters of the Gdańsk Gulf. The research was widened by Korzeniewski and Korzeniewska [2,8] who investigated the western part of the Baltic coast, from Jarosławiec to Mielno. They were the first to notice that the sanitary assessment of seaside ecosystems should not only regard the quality of coastal waters, but also the seaside beaches.

The sea coast is a place of the co-operation of processes taking place in lithosphere, hydrosphere, atmosphere, and also a place of man's economic activity [9]. The self-purification processes of sea waters are considerably much smaller than those of fresh waters. This is related to about 20% smaller content of oxygen in sea waters in comparison with fresh ones [10,11]. That is why nitrification processes in sea water are considerably slower, and also bacteria survivability from the groups of *Escherichia Coli* and *Salmonella* increases [12]. Large quantities of sea and land water that flows through beach sands are filtered by them. Therefore, the beach makes up a specific purgative filter, protecting land ecosystems from penetration of pollution coming from the sea [13]. At the same time, the filtration leads to excessive accumulation of organic matter (OM), pollutants, and toxic substances in the beach sediments [14,15]. Among them, petroleum compounds and heavy metals are the most dangerous [16]. Another problem is that not the whole OM kept in sediments is mineralized by micro-organisms [17,18]. The excessive inflow of pollutants to beaches also influences benthos organisms living there [19]. This results in excessive development of the allochthonous bacteria and inhibiting of the development of autochthonous ones. These changes cause a progressive eutrophication and the intoxication of the world of plants and animals and consequently a transformation of natural biocenosis [20].

The presented work aimed at:

- defining the influence of anthropopresure on the content of organic substances in sediments of two different beaches;
- obtaining information about the quantity of labile organic compounds being the measure of the potential food accessible to consumption for the benthos; and
- estimating the alimentary quality and the age of the OM contained in the studied sediments and their changes throughout one year.

2. Material and methods

2.1. Research site

The samples of beach sediments for chemical investigations were collected on two beaches of Polish coast of Baltic Sea (Fig. 1). First of the studied beaches was situated in Ustka on the eastern side of the mouth of river Słupia. The other one was in The Słowiński National Park in the region of Czołpino. Ustka and Czołpino are two localities situated in northern Poland. Both are characterized by beautiful, sandy beaches. However, the beaches differ considerably in terms of the influence of anthropogenic factors, which affects the content and distribution of the studied chemical parameters in them.

Ustka (54˚42N, 16˚52E) is a port town, situated in the northern part of Poland, in the Pomeranian province. The beach in Ustka is situated near the municipal agglomeration where the Słupia River flows into the Baltic Sea. A big sea harbor is situated nearby. The superiority of western winds over this area results in pollutants movement from the harbor and the river along the studied beach and their accumulation in the sand. This contributes to the fact that the beach in the neighborhood of Ustka is under a big influence of anthropogenic factors. The beach is by the open sea, and the material found on the coast, there is mainly fine-grained and susceptible to transportation along and across the shore [5]. This beach is classified as narrow—up to 30 m width (according to Zawadzka's classification [21]. Low dunes [22] occur on its background. The advantages of the beach are its location, forests in the neighborhood, and the air rich in iodine. That is why the beach in Ustka possesses the status of health resort and is well-known as a seaside spa and used intensely for tourism and recreation purposes throughout the year.

Czołpino (54˚34N, 17˚14E) is located in the Pomeranian province. Local beaches rank among the largest and best cared for beaches in Poland. They are completely wild. They lie on the terrain of the Słowiński National Park, are under protection, so are considerably less subject to the influence of man's activities. Also, sparse population and limited movement in the summer period results in a smaller inflow of pollutants. The shallow of Czołpino, situated about 10 m from the shore, is a characteristic feature of this section of the coast. Strong sea currents and intensive wave motion that occur in this area are responsible for pollutants movement, and these in turn for creating dunes and cliffs characteristic for this section. Dune beaches reach the width from 30 to

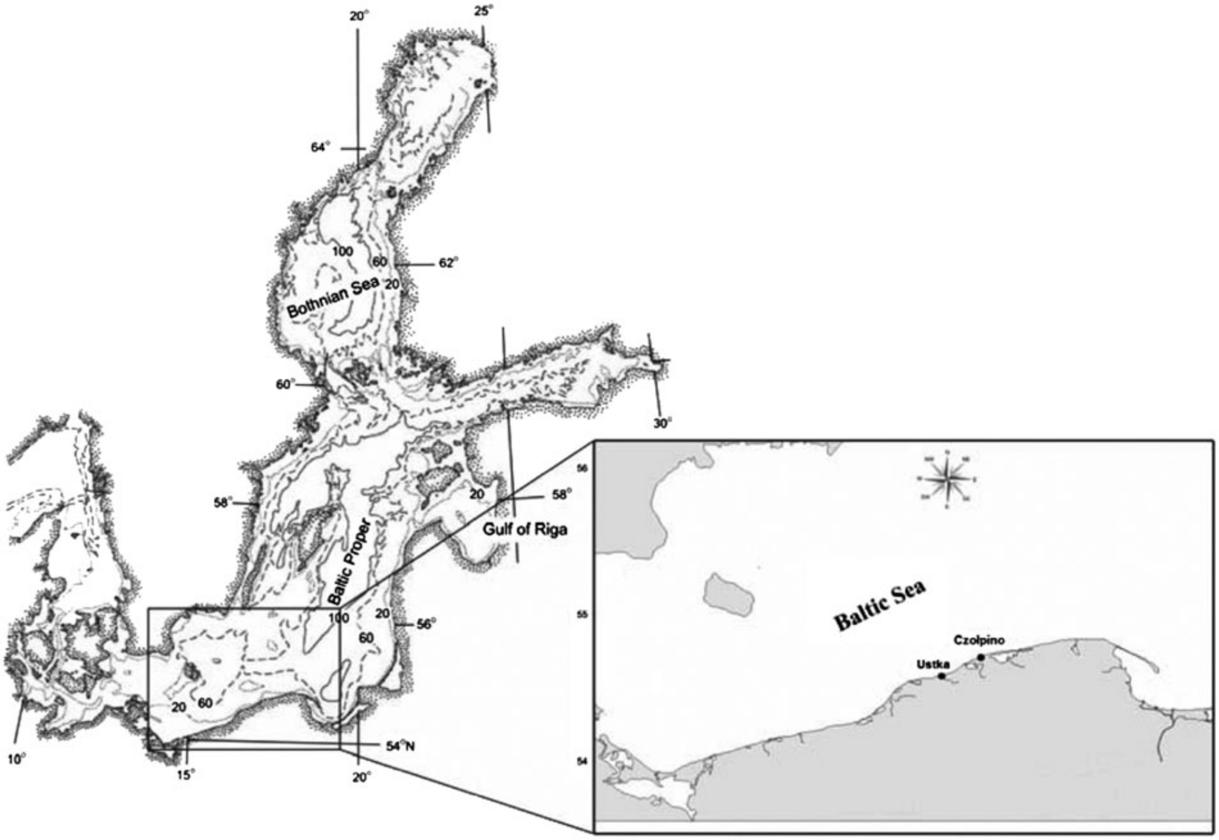

Fig. 1. Location of the two beaches studies on the north coast of Poland.

even 80 m. In this region, accumulation processes are prevailing, which limits fundamentally the abrasive activity of the sea.

2.2. Sediment sampling

The transect was marked on each of the studied beaches, in their transverse profile; on the transect, four sampling stations were marked (Fig. 2):

- *Station 1 (sea)*—3 m from the shore line deep into the sea (shallow station).
- *Station 2 (water)*—shore line (the border of the sea with the land)(swash/saturation).
- *Station 3 (beach)*—the center of the beach (resurgence/retention).
- *Station 4 (dune)*—near the dune neighboring directly with the beach (supratidal).

Investigations were conducted on the two beaches in years 2009–2010. Sampling was carried out with a Morduchaj—Bolkowski hand coring, dimensions: about 30 cm long and 15 cm wide, in following months: October (2009), January, April and July (2010). Sediment samples in 5 cm layers were collected from the depth 0–5 cm and 10–15 cm in three replicates. The samples of sand were placed in a special container of a temperature not exceeding 8°C and transported to the laboratory, where they were subjected to chemical analysis.

2.3. Methods of chemical analysis

Each sediment sample was mixed, and subsamples were analyzed for the content of OM, organic carbon, proteins, lipids, carbohydrates, and chlorophyll *a* (Chl *a*) as well as water. All subsamples were frozen at −10°C until further processing, except those for water content analysis.

Water content was determined from the difference between the mass of the fresh sand sample and the mass of the sand sample dried (in the temperature 85°C) to the solid mass.

The OM was determined gravimetrically as the loss during calcination. It was estimated by delimitation of the difference between the mass of the sample dried earlier, and the mass of the sample calcinated in a muffle furnace (in the temperature of 450–500°C) to the solid mass. The sample was previously flooded with 10% chloride acid in order to remove carbonates.

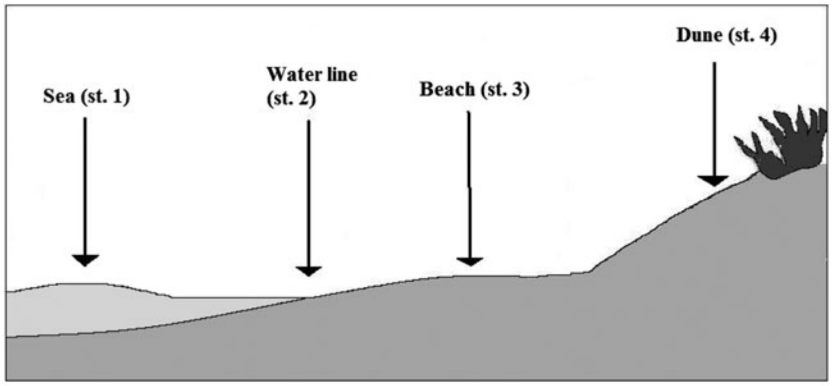

Fig. 2. Location of sampling stations.

The organic carbon (TOC) was measured by Tiurin's method [23].

The proteins (PRT) were determined according to the method described by Markwell et al. [24]. For this purpose, the protein was extracted with the use of 1 M solution of NaOH, from the sand powdered in the mortar. After filtration, the extract was treated sequentially with mixtures of solutions according to the methodology and heated in water bath (70˚C). After the solution was cooled, the content of the protein was determined with a SHIMADZU spectrophotometer UV-1202 (length of the wave 650 nm) in relation to distilled water.

Carbohydrates (CHO) were analyzed by Dubois et al. method [25]. The weighed samples of sand were treated with nitrogen acid (V), taking advantage of reducing properties of saccharides, which in alkaline environment reduce nitrate groups to amino groups, and themselves oxidize aldehyde groups to carboxyl groups. Amino acid derivatives that are formed have an orange color. The intensity of color depends on the quantity of carbohydrates that are reduced in the sample.

The method of lipid (LIP) determination according to Zöllner and Kirsch [26] consists in the extraction of lipids from the studied samples with the use of chloroform–methanol mixture. After the lipids were extracted and the sample itself was filtrated and washed with a mixture of chloroform and methanol, the solvents were vaporized in water bath. Concentrated sulfuric acid was added to the studied sample (VI) after vaporization. Then the whole was heated mildly, after which it was cooled, and finally the solution of vanillin was added. As a result a liquid of a pink color was formed. The absorption of the solution in relation to distilled water was measured at the length of wave 530 nm, with a SHIMADZU spectrophotometer UV-1202.

The Chl *a* was determined from wet sand, according to the method described by Lorenzen [27]. For this purpose, chlorophyll was extracted from the measured quantity of the sand with 90% acetone. Then, after draining off the extract and measuring the volume, the absorption was marked on a SHIMADZU spectrophotometer UV-1202, at the lengths of waves: 665 and 750 nm, and the content of chlorophyll was calculated according to the formula:

$$\text{Chl } a\,(\text{mg m}^{-3}) = (A_{665} - A_{750})26.7 \times v/V \times L$$

where A—absorption; v—volume of the extract; V—volume of the container; L—width of the container.

Apart from that the equivalent of organic carbon in individual compounds was calculated, by applying appropriate conversion factors (0.40—carbohydrates, 0.49—proteins, and 0.70—lipids) according to Danovaro and Fabiano [28]. The biopolymeric carbon (BPC) contained in OM of studied sediments was also marked [29], adding up the organic carbon contained in proteins, lipids, and carbohydrates. The uncharacterized fraction of organic carbon (COM) calculated from the difference between total organic carbon (TOC) and biopolymeric organic carbon (BPC) was also defined (TOC—BPC). From the BPC:TOC ratio, the food factor of OM for benthos in sands of the studied beaches was estimated, whose value was defined in percentage. The coefficient of OM ageing was also estimated basing on PRT:CHO ratio [30].

2.4. Statistical analysis

The statistical analysis of obtained results was carried out in STATISTICA 8 program. The two-way analysis of variance ANOVA was applied for comparing averages. The correlation coefficient was calculated for examining statistical relationship of two variables.

3. Results and discussion

The chemical composition of beach sands shows the actual role of sediments in the filtration of sea water and retaining a number of various substances, therefore it reveals the state of degradation of seaside ecosystems, including beaches. It is also a very important factor defining the quality of the OM, and thus its usefulness as the food for micro-organisms living on the beach [31–34].

The research conducted in Ustka and Czołpino shows that anthropopressure has a great influence on the content of studied chemical components in beach sediments. Fig. 3 and Table 1 represent the content of individual chemical parameters in beach sediments of studied beaches. The larger content of studied parameters in beach sediments coming from Ustka is connected with the man's economic and recreational activity. The presence of municipal agglomeration, sea harbor, mouth of the river, and tourist use of the beach result in considerably more OM gathering in sediments there. The average content of OM in the sands of the beach in Ustka (5.15 mg g^{-1}) was 2.5 times larger than in the sands of the beach in Czołpino (1.93 mg g^{-1}). The range of its concentration in Ustka oscillated from 3.53 to 9.98 mg g^{-1} and in Czołpino from 0.52 to 3.68 mg g^{-1}. Both on the beach in Ustka and in Czołpino, the sediments which were in continuous contact with sea water (St. 1 and 2) contained considerably more OM than the sediments that were distant from the water line (St. 3 and 4). The differences between them were statistically significant ($p < 0.001$, Table 2). The more significant differences were observed in Czołpino, where the concentration of OM in the sediments on the stations more distant from the sea water was twice smaller than on the remaining two stations. Seasons of the year exerted a significant influence on the OM content in studied sands (Fig. 3). This is particularly clear in the case of Czołpino. The concentration of this component was significantly higher in vegetative periods (spring, summer) than in non-vegetative periods. Only in Ustka, on stations distant from the sea water (retention and supratidal) no significant changes in the content of the OM (Fig. 3) were noticed throughout the year.

Those results confirmed earlier investigations conducted on beaches in Sopot and Czołpino [35], showing a significant anthropogenic influence on the chemical composition of beach sediments. A similar influence of anthropopressure on the chemical composition of beach sediments was shown by Fabiano et al. [29] and Defeo et al. [9].

The concentration of the TOC in studied sands in Ustka fluctuated in range 2.03–5.74 mg g^{-1}, at average content of 2.96 mg g^{-1}, and in Czołpino 0.30–2.11 mg g^{-1} and the average value of 1.23 of mg g^{-1} (Table 1). The observed changes in the concentration of TOC on both beaches, both in the cross-section of the beach and during a year, were similar as the concentration of OM is regarded (Fig. 3).

The concentration of lipids, proteins, carbohydrates, and Chl *a* was significantly higher (Table 1) in the sands of the beach in Ustka than of the beach in Czołpino (Table 2, $n = 64$, $p < 0.001$). The average concentration of lipids (LIP) in beach sediments in Ustka was 344.7 μg g^{-1} at the minimum value of 59.1 μg g^{-1} (in winter) and maximum 730.2 μg g^{-1} (in summer). The concentration of lipids in beach sediments coming from Czołpino was significantly smaller (251.1 μg g^{-1}) and it fluctuated from 59.4 (in winter) to 574.2 μg g^{-1} (in summer).

Land factors (touristic and recreation) have an essential influence on the content of lipids and carbohydrates in studied beach sediments. This is clearly visible on the beach in Ustka, where their concentration is considerably larger on the stations that are distant from the line of water (St. 3 and 4) than on stations being under pressure of sea water (Fig. 3, Table 1). On station 1 the content of lipids and carbohydrates in sediments under sea water, on both beaches (lipids about 85 μg g^{-1}, carbohydrates about 360 μg g^{-1}), was several times lower than on the remaining stations.

The concentration of proteins (PRT) in the studied beach sediments was significantly lower than concentration of lipids and carbohydrates (Table 1). Their average content in Ustka amounted to 182.2 μg g^{-1}, and in Czołpino 127.7 μg g^{-1} (Table 1). As in the case of lipids, the range of concentration values of proteins and carbohydrates in beach sediments in Ustka was larger (proteins—from 58.1 to 361.9 μg g^{-1}, carbohydrates—from 157.6 to 1342.2 μg $g^{-1)}$ than in Czołpino (proteins—from 14.6 to 238.5 μg g^{-1}, carbohydrates—from123.9 to 758.6 μg g^{-1}). As far as the content of PRT in sediments of Ustka was similar in the cross-section of the beach, in Czołpino the sediments from stations being in the contact with sea water (St. 1 and 2) contained in the average about 40% more proteins than sediments from the remaining two stations. The largest differences were found in autumn, when the concentration of protein was three times larger on the two first stations (Fig. 3(b)).

The content of carbohydrates (CHO) in the studied sediments was higher than proteins and lipids (in Us-

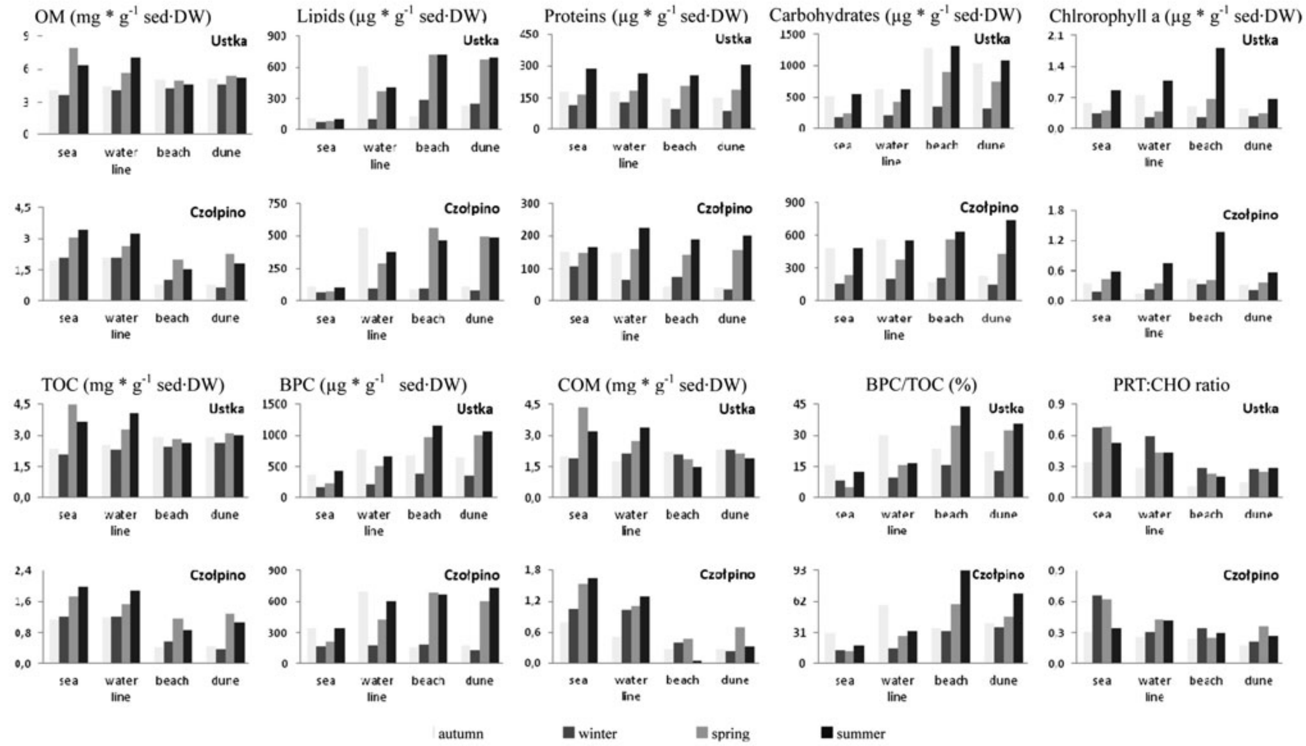

Fig. 3. Temporal changes in the concentrations of organic matter (OM), chlorophyll a, carbohydrates, lipids, proteins, TOC, BPC, COM, food factor of organic matter (BPC:TOC), and protein to carbohydrate ratio (PRT:CHO) with station (distance) and season.

tka—average $652.4\,\mu g\,g^{-1}$, in Czołpino—$374.3\,\mu g\,g^{-1}$, Table 1). The concentration of carbohydrates in Czołpino which was observed in sands from individual stations was similar but significant differences were observed in Ustka (Fig. 3).

The concentration of the Chl *a* showed significant statistical differences in the studied sediments (Table 2, $p < 0.001$) between both beaches and it varied depending depended on the position from which samples were taken. The average concentration of the Chl *a* $0.617\,mg\,g^{-1}$ carried out in sands of Ustka (Table 1) was higher than in sands from the beach in Czołpino ($0.427\,mg\,g^{-1}$). At both beaches and content of Chl *a* increased in the summer as it moves away from the sea. The highest value was observed at station 3 (Fig. 3).

Due to the anthropogenic factors, the sediments from the beach in Ustka are characterized by the larger content of the OM which includes more carbohydrates, protein, and lipids as well as Chl *a*, than analogous sediments from Czołpino. The concentration of these components of the OM was in the range of values described for other coastal sea areas (Table 3). Wide range in literature data result from climatic, hydrographic, and anthropogenic differences. The unquestionable cause of the difference in the biochemical composition of sediments from Ustka and Czołpino is both land factors as well as marine one. Trojanowski et al. [5] showed considerably higher concentration of chemical parameters in sea water in the region of Ustka than in Czołpino. It results from this, that sediments coming from the beach in Ustka accept and accumulate larger quantities of pollutions coming from both the sea and the land, than sediments coming from the beach in Czołpino.

The results showed some clear changes in the content of the OM along the location of the research station. Its source in beach sediments is both, firstly—the sea water which filtering through the sand leaves in it the contained OM, and secondly—land factors (municipal pollutions, surface flowing, and wind), but mainly the people who plot on the beach a lot of materials which include organic substances [36]. The second source causes the accumulation of the OM in the area of the beach not having the contact with sea water or this contact is occasional. Most OM accumulated on the stations where sea water that has the direct influence on beach sediments. Misic and

Table 1
The contents of chemical organic parameters in beach sand of Ustka (U) and Czołpino (C) (OM, organic matter; TOC, total organic carbon; LIP, lipid; CHO, carbohydrate; PRT, protein; Chl *a*, chlorophyll *a*; BPC, biopolymeric carbon; COM, uncharacterized fraction of organic carbon)

Parameters	Unit	Location	Stations				X^*	$x_{min.}$	$x_{max.}$	SD
			Sea	Water line	Beach	Dune				
OM	mg g^{-1}	U	5.52	5.30	4.69	5.07	5.15	3.53	9.98	1.29
		C	2.55	2.52	1.28	1.37	1.93	0.52	3.68	0.87
TOC	mg g^{-1}	U	3.17	3.04	2.70	2.91	2.96	2.03	5.74	0.74
		C	1.46	1.45	0.74	0.78	1.23	0.30	2.11	0.50
LIP	μg g^{-1}	U	86.3	368.53	466.83	457.19	344.70	59.10	730.20	251.81
		C	83.4	330.72	300.47	289.84	251.08	59.40	574.20	198.48
CHO	μg g^{-1}	U	371.3	467.05	965.94	796.66	650.24	157.60	1,342.20	331.40
		C	340.3	424.80	399.13	388.01	388.06	123.88	758.60	190.33
PRT	μg g^{-1}	U	185.1	187.54	174.99	181.16	182.19	58.11	361.88	71.99
		C	142.1	149.86	111.61	107.21	127.70	14.63	238.49	63.37
Chl *a*	μg g^{-1}	U	0.557	0.618	0.897	0.396	0.617	0.073	1.354	0.314
		C	0.387	0.350	0.628	0.346	0.427	0.071	2.161	0.362
BPC	μg g^{-1}	U	299.6	536.68	798.90	727.47	590.66	152.94	1,196.22	306.40
		C	264.1	474.85	424.67	410.63	393.55	108.59	768.30	228.25
COM	mg g^{-1}	U	2.87	2.51	1.90	2.19	2.37	1.18	5.53	0.81
		C	1.20	0.98	0.31	0.37	0.84	0.08	1.75	0.48
BPC:TOC	%	U	10.31	18.06	29.68	24.62	20.67	3.56	50.40	11.31
		C	19.02	24.25	53.82	49.59	31.21	10.95	90.33	21.48
PRT:CHO		U	0.55	0.43	0.20	0.23	0.35	0.11	0.76	0.18
		C	0.48	0.35	0.28	0.25	0.34	0.12	0.74	0.15

X^* - the average content.

Fabiano [37] and Incera et al. [38] observed similar changes. Only in the case of protein, the values did not correlate with their results which showed its bigger content in the part of the beach not having the contact with sea water. The cause of this diversity can be the difference in species composition of micro-organisms living on the beach and what is connected with this use of different material as food. Between these two areas of the beach the very clear difference concerning the content of OM was found on the beach in Czołpino regardless the time of the year. However, an analogous difference was observed in Ustka only in spring and summer period. The intensive use of the beach in Ustka inflicts that the OM level in the part of the beach which is not flooded by sea water changes to a small degree throughout the year.

The chemical composition of the studied beach sediments was subject to clear seasonal changes and the observed changes of studied parameters were similar throughout the year (Fig. 3). Their highest chemical content was found in summer, and the lowest in winter. These changes were in conformity with the vegetative periods of organisms living in the shore zone of the sea. Essential seasonal differences were not observed only in the case of lipids on station 1. The observed differences concerning the concentrations of these components throughout the year were statistically essential in the majority of the remaining compounds (Table 2, $p < 0.001$). Therefore, the concentration of particular parameters in beach sediments is strictly connected with the time of the year which corresponds with the results of different researchers [20,32,38]. The content of labile forms (proteins, lipids, and carbohydrates) of the OM is related to the development of micro-organisms and organisms living in coastal waters and sediments. That is why, most often, the highest concentration occurs in the months of their biggest activity. Most of the OM and its studied components were found in sediments in spring and summer months. Cividanes et al. [30], who observed the largest concentration of carbohydrates and lipids in spring and summer months obtained similar results. Only protein studied by them occurred in great number in winter. However, Fabiano et al. [32] noted down the maximum content of carbohydrates and protein in spring and lipids in autumn. Undoubtedly in the case of the studied beaches, on one hand, it is connected with the lively life activity of beach organisms and on the other hand, especially on the beach in Ustka, with widely developed tourist and recreational traffic in these months. The attention should also be paid to high concentration of

Table 2
Summary of three-way Anova of protein (PRT), carbohydrate (CHO), lipid (LIP), chlorophyll a (Chl *a*), organic matter (OM), biopolymeric carbon (BPC), total organic carbon (TOC), uncharacterized fraction of organic carbon (COM), PRT:CHO and BPC:TOC

	PRT		CHO		LIP		Chl *a*		OM		BPC		PRT:CHO		TOC		COM		BPC:TOC	
Source of variation	*F*	*p*	*F*	*p*	*F*	*p*	*F*	*p*	*F*	*p*	*F*	*p*	*F*	*p*	*F*	*p*	*F*	*p*	*F*	*p*
Location	34.8	***	884.5	***	506.1	***	7.8	*	857.9	***	8.2	*	0.279	ns	728.5	***	657.4	***	155.6	***
Season	82.2	***	1,948.3	****	1,663.5	***	6.7	***	46.7	***	903.5	***	20.383	***	31.7	***	27.0	***	91.1	***
Distance	0.5	ns	1,161.5	***	2,118.5	***	11.3	***	23.3	***	454.4	***	49.604	***	11.4	***	21.3	***	107.8	***
Location × season	5.5	**	55.5	***	37.7	***	3.2	*	2.7	ns	9.7	***	2.348	ns	6.7	***	6.1	***	13.6	***
Location × distance	0.1	ns	1,94.5	***	119.6	***	7.2	***	4.1	*	47.5	***	1.849	ns	0.7	ns	0.5	ns	12.2	***
Season × distance	1.0	ns	72.5	***	195.8	***	2.8	**	6.3	***	39.4	***	2.619	*	10.2	***	10.3	***	11.1	***
Location × season × distance	1.3	ns	13.3	***	11.3	***	4.7	***	5.3	***	6.0	***	1.406	ns	2.7	*	2.6	*	3.2	**

ns-no significant.
*Significance level of $p < 0.05$ ($n = 64$).
**Significance level of $p < 0.01$ ($n = 64$).
***Significance level of $p < 0.001$ ($n = 64$).

Table 3
Comparison of components OM concentration from different flats and beach areas (TOC, total organic carbon; LIP, lipid; CHO, carbohydrate; PRT, protein; Chl *a*, chlorophyll *a*)

Location	TOC $mg\,g^{-1}$	CHO $\mu g\,g^{-1}$	PRT $\mu g\,g^{-1}$	LIP $\mu g\,g^{-1}$	Chl *a* $\mu g\,g^{-1}$	Source
Marseille, Franse	1.84–15.8	870–4,120	480–2,620	10–660	0.01–6.0	Fichez [44]
Bay of Mont-Saint-Michel (France)	0.9–13.6			30–200		Meziane et al. [45]
Ionian and Aegean seas	0.4–8.7	1,230–2,510	72–165	58–196	0.04–6.3	Danovaro et al. [31]
Ligurian sea (Zoagli)	1.95–29.1	128–669	45–67	117–214	1.95–3.96	Fabiano et al. [32]
Barraña (Galicia, Spain)		30–670	40–4,100	50–1,480		Cividanes et al. [30]
Iberian Peninsula (Spain)		4–1,783	37–4,160	1–190		Incera et al. [38]
Ligurian sea (NW Mediterranean)	2.1–8.3	7.2–283.1	5.0–287.2	3.2–366.1		Fabiano et al. [29]
Baltic sea (Poland)	0.3–5.7	124–1,342	14.6–362	59–730	0.07–2.16	Present study

carbohydrates in autumn. This concentration resulting probably from the smaller pace of the decompositions of these compounds in comparison to protein. There is greater demand for proteins [39]. In this period of time, under the influence of anthropogenic factors, the level of carbohydrates on stations 3 and 4 in Ustka was over twice higher than on stations being in the continuous contact with sea water (Fig. 3). However, the opposite situation was observed in Czołpino.

On the basis of the liable content and easily degradable fraction of the OM (protein, lipids, and carbohydrates), the approximate values of BPC, the COM, the food index (BPC:TOC), and the coefficient of OM ageing (PRT:CHO) [29,30,38] were estimated. The values of the above mentioned-parameters in beach sediments were presented in Table 1. The BPC is significantly higher on the beach in Ustka (591 $\mu g\,g^{-1}$) than on the beach in Czołpino (394 $\mu g\,g^{-1}$). But BPC in Ustka constitutes only about 20% of TOC, and in Czołpino over 32%. The fraction of the BPC defines the alimentary base for consumers living in the sediments. The obtained data represent the quantitative composition of the OM in studied beach sediments. The concentration of the BPC in beach sediments of Ustka and Czołpino is considerably higher than the concentration this component in beach ecosystems of The Ligurian sea [29,32,40] but similar as on the beaches of the northwest coast of Spain [30,38].

The longer distant from the sea, the more mean content of BPC in studied sediments increased on both beaches. Rodil et al. [34] observed similar dependence. Only in spring, the violent fall of the level of this form of organic carbon was observed particularly clear in Czołpino in sediments from stations 3 and 4. The smallest level of this parameter on stations 1 and 2 was observed in winter and spring, and the highest in autumn and summer. Incera et al. [38] observed, similarly as on the beaches studied by us, the largest content of BPC in part of the beach (St. 3) with the slight contact with sea water. The percentage participation of this fraction of carbon in organic carbon on this station was on average 30% on the beach in Ustka and 57% in Czołpino. According to Fabiano et al. [32] such value of the participation this result allows to rate our studied sediments oligotrophic. He thinks that the passage from the eutrophic environment to the oligotrophic one can cause the increase of the concentration of the biopolymeric fraction of the carbon that is why the quality of the food increases. However, it should be remembered that the concentration of carbohydrates and the biopolymeric fraction can be revalued because the decomposition of carbohydrates is connected with souring and the partial hydrolysis of complex organic compounds and geopolymers which can react with various reacting substances [41].

The largest seasonal difference in the content of BPC in the studied beaches was observed on stations 3 and 4. Concentration of BPC on these stations was four times higher in spring and summer than in autumn and winter in Czołpino. This probably results from the intensive development of beach organisms in vegetative seasons [42,43].

The COM was about three times higher in beach sediments from Ustka (average 2.37 $\mu g\,g^{-1}$, Table 1) than from Czołpino (0.84 $\mu g\,g^{-1}$). Clear differences between its concentration in sands from stations 1 and 2 can be seen in the case of this form of organic carbon and sands from stations 3 and 4. Particularly, large visible differences are in Czołpino. The counted content of the COM showed lower values than in sediments of sea coast of France [44] but similar to concentration of this fraction of organic carbon on Spanish beaches [30]. This fraction constitutes an index of quantity of hard decomposing OM [38]. In beach sediments of Ustka and Czołpino, the share of this fraction in the mass of organic carbon is large and amounts, respectively, to 80 and 62%. It means that the nutritious proprieties of the OM in sands from the beach in

Ustka are considerably worse than in Czołpino and on Spanish beaches [30]. The relation of content of BPC to the content of TOC (BPC:TOC) is often used as the food index of the OM i.e. the coefficient of its quality in relation to the potential food available for consumers [30,32,45]. Comparing in this respect the OM in the sediments of the beach in Ustka and in Czołpno then the nutritious quality of the OM is considerably better from Czołpino than in Ustka (Table 1) which coincides with the conclusion referring to the content of COM. Contents of carbohydrates and lipids have a significant impact on the value of this coefficient on studied beaches mainly. The high coefficients of the correlation between BPC:TOC and concentration CHO and LIP in studied sands (Ustka: $r_{CHO} = 0.94$, $r_{LIP} = 0.95$; Czołpino: $r_{CHO} = 0.91$, $r_{LIP} = 0.94$; Table 5) testify about this. The OM which was in the sediments of this part of the beach which does not have the constant contact with sea water (St. 3 and 4) in both studied ecosystems showed the highest values of the food index. It means that sea water plots to studied beach sediments the OM of the considerably worse alimentary quality because values of food index on stations 1 and 2 were twice lower. It also confirms the highest content of the unidentified fraction of the organic carbon on these stations. The seasonal change of the concentration of BPC which in spring and summer achieved maximum values on stations 3 and 4, then it was eaten away achieving the lowest values in autumn and winter. The lack of any correlation between the concentration of organic carbon and the value of the alimentary coefficient on the beach in Ustka (Table 5) should be taken into consideration. Meanwhile, the negative correlation exists between these parameters in Czołpino. This dependence shows that the high content of organic carbon is connected with the smaller demand on food which the OM constitutes. It is connected with Tenor and Hansena's [46] conclusion that only about 5–15% of detrital in sediments are generally accessible to consumption for the benthos. This dependence agrees with the observations accomplished by Fabiano et al. [32]. The possibility of the decomposition of the OM deposited in beach sediments is closely connected with this issue. It mainly depends on bacterial activity, physical extraction, and eating away by meiofauna [6,47].

The results showed that anthropopressure has the large influence on the chemical composition of beach sediments. It is testified by the fact that 72% of the OM in beach sediments from Ustka and 60% of the OM in beach sediments from Czołpino constitute different compounds than lipids, carbohydrates, and protein (Table 4). This is also reflected in measurements of COM. Its concentration is decidedly higher in Ustka. On both beaches, the OM plotted through sea water on two first stations contained the least percentage of lipids, carbohydrates, and protein (Ustka: St. 1—12%, St. 2—20%, Czołpino: St. 1—22%, St. 2—36%, Table. 4). However, in sands from the two remaining stations, the participation of these components in the OM was almost twice higher (Ustka: St. 3—35%, St. 4—29%, Czołpino: St. 3—63.3%, St. 4—57.1%). The obtained values show that the OM contained in beach sediments in Czołpino is richer in lipids, protein, and carbohydrates. In this respect, the largest differences between both beaches were observed in the central part of the beach (St. 3). As far as alimentary compounds are concerned, carbohydrates constitute the majority of OM—17 and 20% (respectively in sediments from Ustka and Czołpino). Protein constitute the smallest fraction of the OM in the amount of 4% on the beach in Ustka and 7% on the beach in Czołpino. Despite the smallest part of proteins in composition of OM, they show stronger directly proportional dependence with the OM than the carbohydrates or lipids (in Ustka $r = 0.42$, $p < 0.01$; in Czołpino $r = 0.29$, $p < 0.05$, Table 5).

The relation of the concentration of protein to the concentration of carbohydrates (PRT:CHO) describes aging of the organic material [30,41]. It is connected with the fact that protein are used much easier by bacteria than carbohydrates [29,39] and transformed easier in harder decomposing compounds. Higher values of PRT:CHO show on the presence of the alive OM or just created detrital [31]. However, the low

Table 4
The percentage part of the individual components of OM in beach sand of Ustka (U) and Czołpino (C) (LIP, lipids; CHO, carbohydrates; PRT, proteins; BPC, carbon of the biopolymeric fraction; COM, uncharacterized fraction of organic carbon)

Parameters	Location	Sea st. 1	Water line st. 2	Beach st. 3	Dune st. 4	Total
LIP	U	2	7	10	9	7
	C	3	13	23	21	13
CHO	U	7	9	21	16	17
	C	13	17	31	28	20
PRT	U	3	4	4	4	4
	C	6	6	9	8	7
ANDERE	U	88	80	65	71	72
	C	78	64	37	43	60
BPC	U	9	18	30	24	20
	C	18	33	60	53	38
COM	U	91	82	70	76	80
	C	82	67	40	47	62

Table 5
Correlation analysis between environmental variables and biochemical compounds in Ustka (simple figures) and in Czołpino (thicking figures): protein (PRT), carbohydrate (CHO), lipid (LIP), chlorophyll *a* (Chl *a*), organic matter (OM), carbon of the biopolymeric fraction (BPC), protein to carbohydrate ratio (PRT:CHO), total organic carbon (TOC), uncharacterized fraction of organic carbon (COM), and food factor of organic matter BPC:TOC

	PRT	CHO	LIP	Chl a	OM	BPC	PRT:CHO	TOC	COM	BPC:TOC
PRT	1.00	0.66***	0.43**	0.69***	0.29*	0.60***	0.24	0.17	−0.02	0.50***
CHO	0.57***	1.00	0.86***	0.53***	−0.27	0.96***	−0.44**	−0.28	−0.54***	0.91***
LIP	0.32*	0.92***	1.00	0.14	−0.42**	0.95***	−0.52***	−0.33*	−0.61***	0.94***
Chl *a*	0.81***	0.31*	0.08	1.00	0.28	0.35*	0.16	0.17	0.08	0.23
OM	0.42**	0.27	0.20	0.17	1.00	−0.31*	0.59***	0.86***	0.82***	−0.47***
BPC	0.60***	0.88***	0.84***	0.40**	0.31*	1.00	−0.43**	−0.27	−0.56***	0.95***
PRT:CHO	0.02	−0.77***	−0.84***	0.21	−0.03	−0.60***	1.00	0.46***	0.55***	−0.48***
TOC	0.43**	0.27	0.20	0.17	1.00***	0.32*	−0.04	1.00	0.92***	−0.50***
COM	0.33*	0.05	−0.01	0.12	0.95***	0.12	0.12	0.95***	1.00	−0.75***
BPC:TOC	0.37**	0.94***	0.95***	0.17	0.04	0.85***	−0.83***	0.04	−0.17	1.00
N-PRT	1.00	0.57***	0.32*	0.81***	0.42**	0.60***	0.02	0.43**	0.33*	0.37**

*Significance level of $p < 0.05$ ($n = 32$).
**Significance level of $p < 0.01$ ($n = 32$).
***Significance level of $p < 0.001$ ($n = 32$).

relation of PRT:CHO expresses the old OM and that protein function as the factor limiting benthic consumption. As Incera et al. [38] show this relation can have values from below 0.1 to above 10. The average values of the analyzed relation were smaller than 1.0 in sediments studied by us, so they were situated in the bottom borders of the quoted scale. The obtained values were similar to those given by Fabiano and coworkers [29], but considerably smaller than the values given by Incera et al. [38] and Rodil et al. [34]. The low values of the relation of PRT:CHO in sediments on the studied beaches show that, mainly the old organic material is deposited there and protein is a factor limiting benthic consumption in these sediments. It first of all occurs in the part of the beach with a smaller contact with sea water (stations 3 and 4); however, sea water plots on stations 1 and 2 the persistently new organic material with still unconsumed protein. The oldest organic material was observed on both beaches in autumn which is after the period of intensive vegetation, when the demand on the protein was the highest. The coefficient of OM ageing (PRT:CHO) joins with the food factor closely (BPC:TOC). The high negative values of the coefficients correlation between these two parameters (Ustaka: $r = 0.85$; Czołpino: $r = 0.75$; Table 5) show this. In the studied beach sediments the older OM (lower values PRT: CHO) corresponds to higher value of the food factor, mainly because to a higher percentage content of carbohydrates and lipids.

The concentration of the Chl *a* showed low values in the studied sediments and it can be compared with the ones described by Hou et al. [48] on beaches of the China Sea and by Steele and Bairda [49] on Scottish beaches, however, they were lower than described by Fabiano et al. [32] in the Marconi Gulf. The content of the organic carbon in the chlorophyll *a* (C-Chl) determines the small part in the total carbon organic (C-Chl:TOC) (Ustka 2.4%, Czołpino 3.5%), which means that the participation of organisms containing the Chl *a* to create the OM is small on studied beaches. The part of chlorophyll carbon is also small in the labile organic material (BPC) (about 11%), which means that these organisms assure the benthic alimentary needs only in small degrees. It is confirmed by the weak correlation between the concentration of the Chl *a* and the concentration of BPC (Ustka: $r = 0.40$, Czołpino: $r = 0.35$, Table 5).

4. Conclusion

The results of the presented research prove the occurrence of the essential changes of the quantitative and qualitative concentrations of the OM in beach sediments in Ustka and in Czołpino, both in the time and in the space. The content liable forms of the OM were subjected to clear seasonal changes. These changes are related to micro-organisms and organisms living in coastal waters and sediments. That is why, most of the OM and its studied components were found in sediments in spring and summer months which are the months of the their biggest activity. Essential differences concerning the concentration of these substances which were observed in the lateral section of studied beaches resulted from the influence of land and sea factors. Sea water plotted the OM in which the share of carbohydrates, protein, and lipids was considerably smaller than in the OM in beach sediments not having the direct contact with sea water. It was also characterized by worse alimentary quality in relation to the benthos. It was shown in the dissertation that anthropopressure had a very large influence on the quantity, quality, and the composition of the OM in studied beach sediments. On the beach in Ustka, where the pressure of anthropogenic factors is considerably greater, the concentration of the OM and its individual components (the carbohydrates, protein, lipids, and Chl *a*) was considerably higher than in Czołpino. At the same time, the OM on the beach of smaller anthropopressure showed the considerably better alimentary quality. Mainly, the old organic material in which the protein is the factor limiting benthic consumption occurs on both beaches. And the participation of organisms contenting the Chl *a* in creating the OM is small on the studied beaches.

Research beaches are important. The choice of infilled (Ustka) and natural (Czołpino) beaches makes it possible to assess an impact of hydrotechnical actions on ecosystem of the beach. The completion of the study would help to answer the following question: whether the conducted actions targeted at improvement of the esthetics of the beaches mean at the same time introducing a huge amount of pollutants causing suppressing of self-purification processes.

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