

**DIFFERENCES OF CHEMICAL COMPONENTS  
IN BEACHES SEDIMENTS WITH DISSIMILAR ANTHROPOPRESSURE**

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**Abstract**

The investigations of the chemical composition of sands were conducted on the beach in Ustka and Człopino. The Ustka is a typical tourist town and Człopino is located in the Slovinski National Park away from urban or rural areas. The beach sediments in Ustka contain much more organic matter, nitrogen and phosphorus compounds as well as calcium carbonate than analogous deposits in Człopino. The effect of sea water was manifested in the high content of organic matter in places having permanent contact with sea water. The content of the organic matter increased together with the depth of settlements in these places. However more organic matter in surface layers was observed in regions more distant from the sea, because penetration of organic matter into the sediments is possible during precipitation. The concentration of ammonia nitrogen in the analyzed beach deposits increased with depth, what probably results from the lower oxygen content in deeper layers. It was confirmed that organic matter in sands of the beach in Człopino is of natural origin, while in Ustka it is primarily of anthropogenic origin.

**Key words:** organic matter, nitrogen, phosphorus, sand, beach

**INTRODUCTION**

Processes taking place in the coastal zone of a sea are a highly complex function of interactions of the lithosphere, hydrosphere, atmosphere and economic activity of man, with which tourism and recreation are also connected. In the Baltic, as well as other seas, both wave motion and changes in water levels occurring in the coastal zone have a significant effect on all hydrodynamic processes, since depending on changes in the sea level and the character of wave motion, wave energy may be discharged on the beach at a relatively big distance from the coastline (Musielak et al.

2005). In such a case we deal with the movement of debris in the coastal zone or at the far end of the beach. This results in a direct destruction of the seashore and its base (Pempkowiak 1997). Moreover, different types of pollutants reach the coastal zone. They may be taken onto the beach both from the sea (marine transport) and the land (municipal sewage, industrial effluents and agricultural sewage) and the atmosphere (rainfall, dustfall, industrial gases). Inflow of all nitrogen and phosphorus forms, both as mineral salts and different organic compounds, results in deep biocenotic transformations which have been observed for years now, first as progressing eutrophication of the sea and partly also intoxication of the plant and animal life (Żmudziński 1990), as well as changes the biochemical composition of beach deposits. The mechanism of these changes has not been thoroughly clarified to date, either in terms of its biology or chemistry. Water currents transporting the Baltic waters in the Polish zone are parallel in terms of their direction. This is also promoted by the dominant westerly winds. Sewage and pollutants introduced to the sea are brought primarily by the Vistula and Oder rivers and rivers of Central Pomerania. They accumulate in the coastal zone and to a lesser degree are transported deep into the sea. It was estimated that approx. 90% sea pollution comes from inland sources and the other 10% is brought by water transport, the atmosphere and disturbance of the sea bottom during exploration when searching for mineral resources (Andrulewicz 1994). Studies on the potential reduction of the load of pollution discharged into sea waters in the area of Central Pomerania were conducted by Korzeniewski (1978) in the years 1955-1976. Later these studies were continued by Trojanowski et al. (2001, 2007).

The aim of the presented investigations was to:

- compare sandy sediments in terms of the chemical composition of two beaches differing in their tourist and recreation traffic load and the effect of conurbations;
- investigate changes in the chemical composition of sediments at the vertical section of the beach to a depth of 15 cm and at the horizontal section of the inner and outer beaches to the dunes in order to determine the effect of marine and land factors and determine the penetration of pollutants reaching with sea water deep into the sand on the beach.

## **MATERIALS AND METHODS**

### **Area of study**

Chemical analyses of sandy sediments were conducted in the Polish coastal zone of the Baltic Sea on two beaches differing in terms of the degree of anthropopressure. One of the beaches was located in Ustka, while the other was situated in the Slovinski National Park near Człopino. Both beaches are found in the north-western part of the Pomorskie province.

The municipal beach in Ustka is exposed to the strong eutrophication effect of the Słupia River and the town. At the same time it is an attractive recreation area and a resort for the inhabitants of the Pomerania region and numerous tourists coming from all over Poland.

In turn, the location of the beach in Czolpino in an area covered by legal protection by itself indicates that in contrast to the Ustka beach it remains under a relatively slight impact of anthropogenic factors. This results from the very low population density of this region, poor agricultural management and at the same time it is a section of the Polish coastline very rarely visited by tourists. This region is one of the least polluted in the Polish coastal waters zone and as such it meets one of the selection criteria of marine protected areas (Andrulewicz and Wielgat 1995).

The slope in both beaches is approx.  $9^\circ$  and their mean width is approx. 40 m. They are enclosed by a belt of small dunes overgrown with vegetation and the main component of these beaches is quartz sand. They are tideless beaches, with periodically occurring strong wave motion. The highest water temperatures in their region are recorded in August, while minimum temperatures are found in February, with potential water freeze-up.

Dune beaches account for 95.8% coastline in that region. Their width ranges from 30 to 80 m. The front dunes are 5-15 m in height (Uściniowicz and Zachowicz 1991). Lithodynamic processes in that coastal zone have been poorly investigated; however, accumulation processes predominate here, limiting the destructive effect of sea waves.

## Sampling

Analyses of sediments were conducted in the years 2006-2008. In each of the investigated beaches in the profile perpendicular to the coastline a transept was established, on which four sampling stations were located (Fig. 1):

- station 1 – located in the sea approx. 1.5 m from the coastline at a depth of approx. 0.5 m;
- station 2 – located on the coastline, at the boundary between the beach and the sea;
- station 3 – located at a middle distance of the beach;
- station 4 – it was established at the dune, at a location most distant from the coastline.

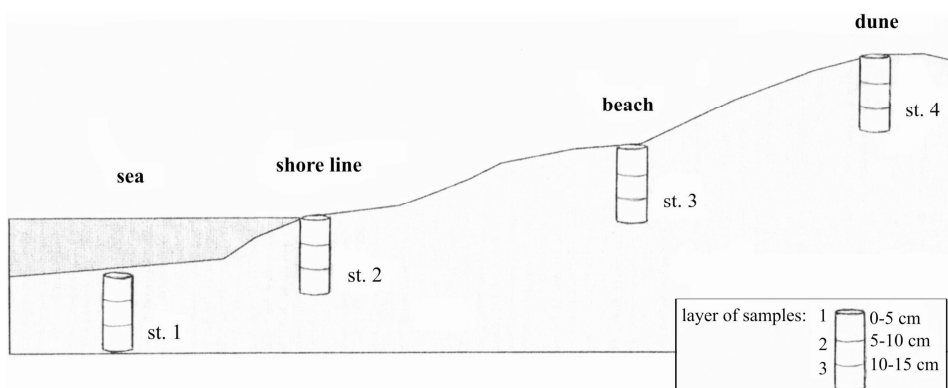


Fig. 1. Location of sampling stations on the beach

Sand samples were collected four times a year, in the characteristic seasons. From each station samples were collected at three different points using a hand corer with a diameter of 5 cm. Collected sand cores were divided horizontally into three sections, i.e. 0-5 cm, 5-10 cm and 10-15 cm, which were placed in glass containers. Such collected samples were transported to a laboratory in a container with ice, in which temperature did not exceed 4°C, next some samples, which were not immediately analyzed, were frozen at the laboratory and their complete chemical analysis was performed within 2 weeks.

### **Chemical analysis**

In the analyzed samples of sandy sediments the determined parameters included moisture content and contents of organic matter, total nitrogen, ammonia nitrogen, total phosphorus, organic phosphorus and phosphate phosphorus as well as calcium and carbonates. Determinations were performed following the methodology given in Standard Methods (1992). Determinations of ammonia nitrogen and total and phosphate phosphorus were performed using a UV-1202 spectrophotometer by SHIMA-DZU.

Grain size measurements in the tested sands were taken using dried sand (at a temperature of 80°C) of a known weight, which was sieved through a set of sieves with mesh size ranging from 0.06 to 2.00 mm.

## **RESULTS AND DISCUSSION**

Grain size analysis of sands from beaches in Ustka and Czołpino indicates a predominance of fine-grained sands. However, sands of the compared beaches differ. On beaches in Ustka sands with grain diameter of 0.06-0.15 and 0.16-0.25 mm predominate, while in Czołpino it is sands with a diameter of 0.26-0.30 mm (Fig. 2). A similar predominance of fine sand was reported by Musielak et al. (2005), who investigated a section of the beach between Dźwirzyno and Mrzeżyno, as well as that by Serpa et al. (2007), conducted on sandy deposits in a lagoon of the Ria Formosa (Portugal). At the coast of south-eastern China sand with a much smaller grain diameter predominates (Hou et al. 2007).

Certain differences in grain size distribution of sands were observed both within the beach in Ustka and in Czołpino. On both beaches with a growing distance from the sea the content of sands with grain size of 0.16-0.25 mm increased (from 34.5% at station 1 to 48.8% at station 4) and in Czołpino with a diameter of 0.26-0.30 mm (from 57.8% at station 2 to 73.6% at station 4). On the latter beach sand from station 1 significantly differed from sands from the other stations. At station 1 sand with a diameter of 0.16-0.25 mm (58.3%) and 0.06-0.15 mm (32.2%) predominates. Content of sand with a diameter of 0.26-0.30 mm was on average 0.2%. Sand with this diameter predominated at the other stations, where it exceeded 50%.

Humidity of beach sediments was similar at both compared beaches and also changed in a similar manner. In terms of mean values for the entire period of analy-

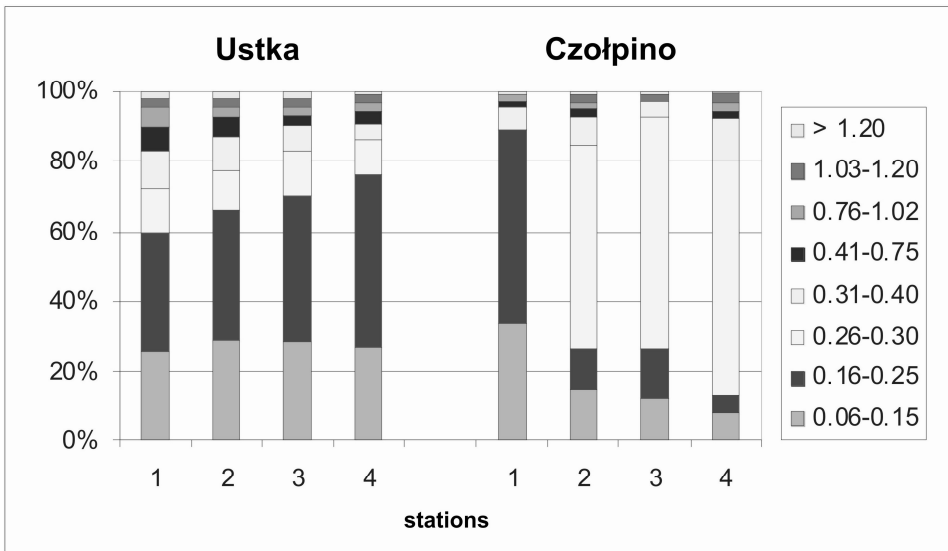


Fig. 2. Granulometric of sand sediments from Ustka and Czołpino beaches. The sizes of sand grains were passed in mm

sis and for a layer of 0-15 cm, at stations 1 humidity was approx. 20%, at stations 2 it was approx. 14%, and – as it could have been expected – it decreased with an increasing distance from water, reaching the values of approx. 3% at stations 3 and 4. A slightly higher humidity of sands in the Czołpino beach results probably from the predominance of sand with a higher grain diameter.

The concentration of organic matter in the analyzed beach sediments was almost two times lower in Czołpino ( $2.02 \text{ mg g}^{-1}$ ) than in Ustka ( $4.99 \text{ mg g}^{-1}$ , Table 1). A similar content of organic matter was observed by Urban-Maling and Opaliński (2001) in sands of the beach in Sopot (the Gdańsk Bay), as well as Hou et al. (2007) on the

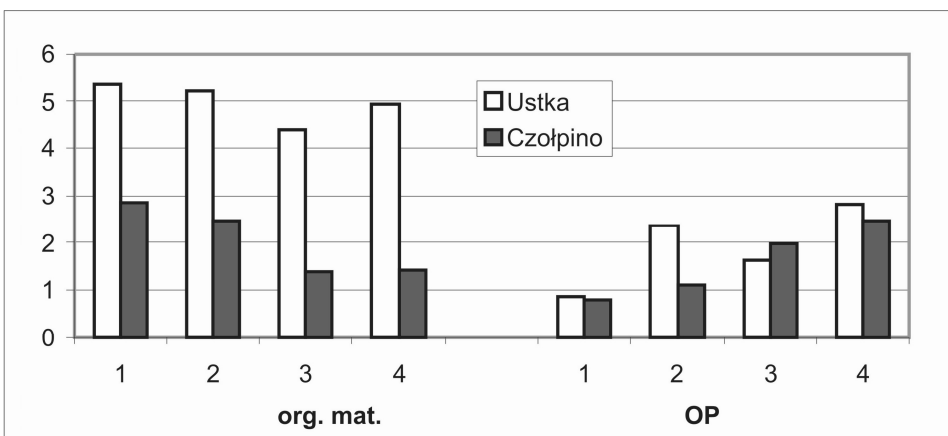


Fig. 3. Contents of organic matter and organic phosphorus ( $\mu\text{g g}^{-1} \text{ d.m.}$ ) in sands of Ustka and Czołpino beaches

Table 1

Seasonal changes of the concentration of chosen components in the sands of beaches in Ustka and Czolpino.  
Concentrations were passed  $\mu\text{g g}^{-1}$  d.m., only organic matter was passed in  $\text{mg g}^{-1}$  d.m.

Parameters	Spring		Summer		Autumn		Winter		Ustka			Czolpino		
	Ustka	Czolp.	Ustka	Czolp.	Ustka	Czolp.	Ustka	Czolp.	x*	Range	SD	x*	Range	SD
Org. mat.	5.72	2.50	5.65	2.48	4.44	1.47	4.00	1.62	4.99	3.29-7.89	0.83	2.02	0.48-3.73	0.12
T-N	148.8	135.9	160.5	151.2	206.5	168.6	226.9	149.7	185.6	8.8-442.0	32.4	151.4	72.4-260.2	26.3
NH <sub>4</sub> -N	9.11	13.20	12.69	9.63	15.06	10.08	16.15	9.96	13.13	0.39-0.02	3.01	10.72	4.27-16.84	2.12
T-P	8.29	4.49	7.84	6.76	8.32	6.51	8.06	7.08	8.13	0.68-6.16	1.44	6.21	0.67-14.99	1.05
PO <sub>4</sub> -P	5.61	3.46	6.41	4.93	6.50	4.64	6.37	5.47	6.20	0.36-5.71	1.22	4.62	0.20-11.81	0.92
OP	2.67	1.03	1.43	1.83	1.92	1.87	1.69	1.61	1.93	0.25-6.31	0.12	1.59	0.21-4.98	0.11
Ca	104.6	68.0	126.4	102.1	162.8	122.0	224.6	148.6	154.6	31.3-82.1	31.6	110.1	19.4-225.4	20.5
Carbonate	140.1	89.6	161.3	135.3	220.5	161.8	302.9	197.1	206.2	52.9-96.1	28.1	146.0	27.9-321.0	21.4

coast of China. Differences between contents of this matter in beach sands in Ustka and Czołpino were statistically significant ( $p < 0.05$ ). The biggest differences were observed at stations 3 and 4 (Fig. 3), where organic matter content in Ustka was almost three times bigger. This region of the beach is most exposed to the impact of terrestrial factors, primarily that of human activity, through its intensive use for recreation purposes. In the course of beach use connected with tourist traffic and recreation several foodstuffs, cosmetics, disinfectants, all types of packaging, etc. reach the beach sediments. This problem was presented in their studies by Jędrzejczak (1999) and Węśławski et al. (2000).

Taking into consideration the cross-section of the beach, both in beach sediments from Ustka and Czołpino, the biggest amounts of organic matter were recorded at stations 1 and 2 (Fig. 3), i.e. in the area of the beach, which is most exposed to the effect of sea water. Waves and tides deposit many organic substances onto the beach (Ramaiah and Chandramohan 1992, Asmus and Asmus 2000). The primary source of organic matter, which accumulates in the sea coastal zone, includes assimilates released by phytoplankton and phytobentos, products lixiviated and washed from seaweeds, animal excreta, mainly of macro- and meiofauna, dead plant and animal remains as well as the runoff of organic substances from land (Vahteri et al. 2000, Mudryk 2004). Koop and Griffiths (1982) calculated that approx. 70% of this organic matter introduced to the ecosystem of sandy beaches is mineralized by bacteria.

Table 2 presents changes in the concentration of organic matter at the vertical section of the analyzed sediments. Both in Ustka and in Czołpino in beach sediments a reduction of organic matter concentration was observed with the increasing distance from the deposit surface. Only at station 1 and partly at station 2 these concentrations were uniform, and in Czołpino they were even higher in the deeper layers than in the surface ones. However, differences between individual layers are not sta-

Table 2  
Concentration of selected chemical components in the surface layers of beach sands of Ustka and Czołpino

Layer (cm)	0-5		5-10		10-15	
	Ustka	Czołpino	Ustka	Czołpino	Ustka	Czołpino
Beach						
Org. Mat. (mg g <sup>-1</sup> )	5.48	2.20	4.90	2.03	4.60	1.82
T-N (μg g <sup>-1</sup> )	161.3	140.8	187.1	149.4	208.5	163.9
NH <sub>4</sub> -N (μg g <sup>-1</sup> )	10.69	8.13	13.71	9.65	15.41	12.68
T-P (μg g <sup>-1</sup> )	7.03	5.19	7.60	5.98	9.80	7.43
PO <sub>4</sub> -P (μg g <sup>-1</sup> )	4.78	3.61	5.75	4.47	8.06	5.79
OP (μg g <sup>-1</sup> )	2.25	1.58	1.70	1.51	1.71	1.64
Ca (μg g <sup>-1</sup> )	142.9	97.7	155.1	107.8	166.6	124.9
Carbonate (μg g <sup>-1</sup> )	192.5	137.3	215.1	148.4	216.8	160.5

tistically significant ( $p < 0.05$ ). Especially small differences were recorded for the beach in Czołpino. The pattern of organic matter in the vertical profile of deposits is influenced by several factors. The most significant of these is the degree of oxygenation, deposit particle size and water flow velocity. The higher the concentration of oxygen, the better the conditions for microbial growth. Moreover, oxygenation regulates processes of changes and energy transfer from the detritus to the consumers. Since the surface layers of sediments are most oxygenated, it is in these layers that the biggest amounts of organic matter are found. On the other hand, organic matter together with water is filtered to the deeper layers, with the infiltration process occurring much easier in places with a continuous water inflow. A similar phenomenon was observed by Incera et al. (2003). At stations more distant from the sea water the process of organic matter transfer into the sediments is possible only during precipitation, thus deeper layers are poorer in this nutrient. Only at stations 1 and 2, where infiltration is facilitated by flooding with sea waves, organic matter content in deeper layers is also high. A significant role of sea water filtration by sands on their physical and chemical properties was stressed in their study by Levin et al. (2001). Seasonal changes have a similar effect on contents of organic matter in sands of both beaches (Table 1). In autumn and winter the concentration of organic matter was much lower than in spring and summer. Serpa et al. (2007) also observed similar dependencies. This is understandable, since in autumn and winter life processes of organisms living in beach sands are inhibited, and first of all decomposition and mineralization processes of organic matter take place. In turn, in spring and summer higher temperatures promote enhanced vegetation, which rate considerably exceeds the rate of the mineralization process. However, it needs to be stressed that mineralization of organic matter to inorganic nutrients, which are next transported to sea water and sand, is a very important biological function of marine ecosystems of sandy beaches.

Sandy sediments contain nitrogen being a component of organic and inorganic matter. Typically the content of the inorganic nitrogen form in beach sands is much lower than that of the organic nitrogen form (Trojanowski et al. 2007). Sands of analyzed beaches contained different forms of total nitrogen (T-N), (Table 1). Mean content of nitrogen compounds was higher in Ustka ( $185.6 \mu\text{g g}^{-1}$ ) in comparison to Czołpino ( $151.4 \mu\text{g g}^{-1}$ ). The difference between these values was statistically significant ( $p < 0.05$ ). When comparing T-N content in sands of these beaches at individual stations (Fig. 4) it needs to be stressed that differences between analogous stations in Ustka and Czołpino were even bigger than between mean values. At stations 1 and 2 total nitrogen concentration was much higher in Czołpino than in Ustka. An even bigger difference in the concentration of this element was observed at stations 3 and 4, with this reservation that its bigger amount was recorded in beach sands in Ustka. However, both in Ustka and Czołpino its concentration increased with the growing distance from sea water. The direction of changes in concentrations of organic matter was opposite. This suggests that sandy deposits, having a direct contact with sea water, contain organic matter composed primarily of organic substances devoid of nitrogen, e.g. carbohydrates, fats, hydrocarbons. In turn, the closer it is to dunes, the bigger the amounts of organic substances containing nitrogen, such as protein, peptides, nucleic acids and amino acids. This suggests



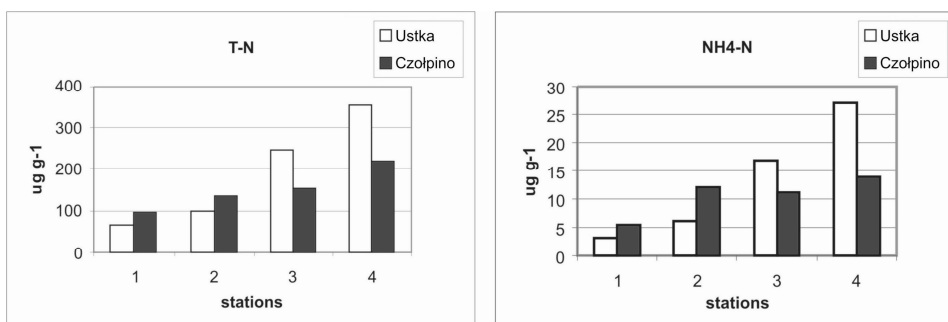


Fig. 4. Contents of total nitrogen and ammonia nitrogen ( $\mu\text{g g}^{-1}$  d.m.) in sands of Ustka and Czołpino beaches

that a considerable part of organic matter found in sands of the analyzed beaches, particularly in the region of sea water, is of anthropogenic origin.

Earlier studies also indicated that on beaches with high anthropopressure differences in the contents of total nitrogen in sands from different stations are much bigger than in case of beaches less frequented by people (Trojanowski et al. 2007). A much higher content of nitrogen (over  $400 \mu\text{g g}^{-1}$ ) was observed by Cividanes et al. (2002) in sands of beaches located in north-western Spain, as well as Hou et al. (2007) in sands of south-western coast of China.

As it results from Table 2, differences between the mean content of total nitrogen in individual analyzed layers of beach sand are smaller than between stations. Particularly small differences were observed in Czołpino at stations 3 and 4. In most cases, both in Ustka and Czołpino, differences between layers in terms of total nitrogen content were statistically non-significant ( $p < 0.05$ ). On both beaches in a 0-5 cm layer the level of total nitrogen was the lowest (on average Ustka  $161.3$ , Czołpino  $140.8 \mu\text{g g}^{-1}$ ), and the deeper the layer, the higher the amount, reaching in the 10-15 cm layer values of  $208.5$  and  $163.9 \mu\text{g g}^{-1}$ , respectively. In this case also the direction of changes in organic matter contents was opposite to that for total nitrogen content, i.e. the deeper into the layers, the lower the amounts of organic matter and the higher the amounts of nitrogen compounds. This means that the closer to the surface, the bigger the proportion of organic substances devoid of nitrogen in organic matter. However, it needs to be stressed that in Ustka an increase in the concentration of total nitrogen in sand with depth was not always observed. The highest concentration in the 5-10 cm layer was recorded twice and it was observed once in a 0-5 cm layer.

The concentration of total nitrogen changed in the analyzed sands with a change in the seasons of the year. Its highest concentration was observed in autumn and winter, while the lowest in spring and summer (Table 1). These differences were particularly evident in sands of the beach in Ustka, where they are statistically significant ( $p < 0.05$ ). Cividanes et al. (2002) in the sands of Spanish beaches also in the spring recorded the lowest concentration of this element, whereas in the summer they observed its very high concentration. The lower concentration of nitrogen compounds in spring and summer could have been caused by the higher mineralization rate of organic matter, as a consequence formed inorganic nitrogen forms are more readily

filtered into deeper parts of beach sediments. This would also explain higher nitrogen concentrations in the 10-15 cm layer.

Total nitrogen in the sediments of sandy beaches contains ammonia nitrogen ( $\text{NH}_4\text{-N}$ ), which – as it results from literature data (Korzeniewski 1978, Trojanowski et al. 2007) – is found at a considerably higher proportion in relation to the other forms of inorganic nitrogen. In case of the analyzed sands ammonia nitrogen constituted from 4 to 8% total nitrogen in Ustka, and it was slightly higher in Czołpino, i.e. from 5 to 10%. Such a low proportion of ammonia nitrogen in the total nitrogen pool may indicate two factors. One may be slow mineralization of organic nitrogen compounds, while the other – high requirement for this form of nitrogen by organisms living in beach sands. Bigger amounts of this nitrogen form were recorded in sands of the Ustka beach (on average  $13.13 \mu\text{g g}^{-1}$ , Table 1) than in Czołpino ( $10.7 \mu\text{g g}^{-1}$ ), but the differences were not statistically significant ( $p < 0.005$ ). It needs to be stressed that the range of fluctuations in concentration values both for total nitrogen and ammonia nitrogen was over two times bigger for the beach in Ustka than for the beach in Czołpino. Probably in the latter beach there are more stable conditions, it is less exposed to changing conditions, particularly anthropogenic conditions.

Ammonia nitrogen concentration in the analyzed sediments increased with a growing distance from the sea (Fig. 4). On the beach in Czołpino mean concentration of ammonia nitrogen ranged from 5.5 (station 1) to  $14.0 \mu\text{g g}^{-1}$  (station 4), while in Ustka it was from 3.2 to  $27.1 \mu\text{g g}^{-1}$ , respectively. In Ustka differences in  $\text{NH}_4\text{-N}$  content between stations were statistically significant ( $p < 0.05$ ), whereas in Czołpino the concentration of this nitrogen form at stations 2-4 was significantly higher than at station 1. The concentration of ammonia nitrogen in sands from stations 1 and 2 in

Table 3

The coefficients of correlation between the chemical components of beach settlements (TN – total nitrogen,  $\text{NH}_4\text{-N}$  – ammonia nitrogen, TP – total phosphorus,  $\text{PO}_4\text{-P}$  – phosphate phosphorus, OP – organic phosphorus,  $\text{CO}_3^{2-}$  – carbonate)

*	Org.mat	TN	$\text{NH}_4\text{-N}$	TP	$\text{PO}_4\text{-P}$	OP	Ca	$\text{CO}_3^{2-}$	
Org.mat	*	0.479	0.398	0.566	0.556	0.302			C Z O Ł P I N O
TN	0.133	*	0.587	0.782					
$\text{NH}_4\text{-N}$	0.08	0.896	*	0.587					
TP	0.065	0.766		*	0.966	0.592			
$\text{PO}_4\text{-P}$	0.093			0.908	*	0.407	0.302		
OP	0.003			0.246	0.044	*			
Ca					0.249		*	0.953	
$\text{CO}_3^{2-}$							0.970	*	
	U S T K A								*

Czołpino was almost two times higher than in sands from Ustka from analogous stations. In turn, at stations 3 and 4 an opposite situation was observed. It seems that the content of  $\text{NH}_4\text{-N}$  in sands of the analyzed beaches depends mainly on the concentration of total nitrogen.

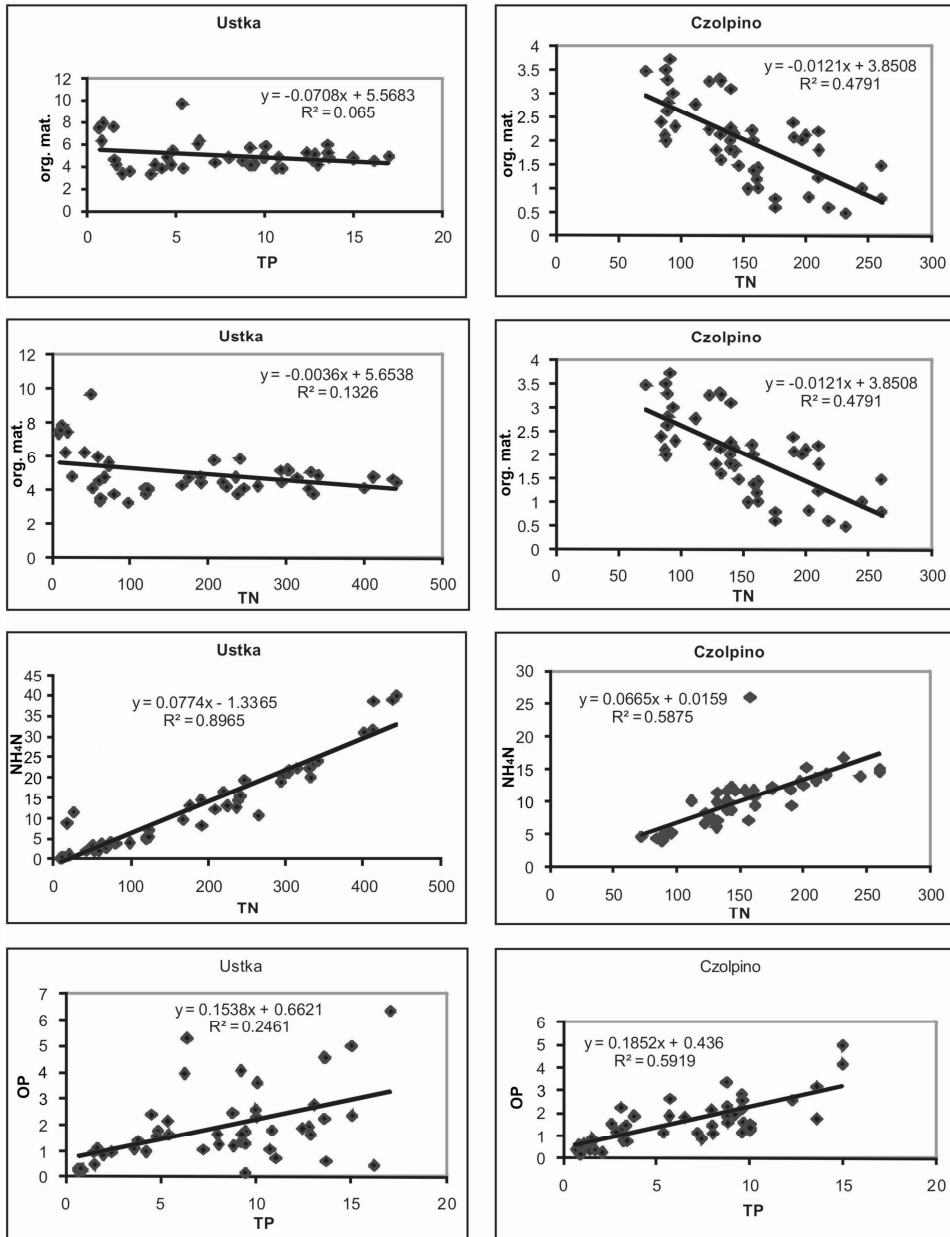


Fig. 5. Correlation coefficients between concentration of respective parameters in beach sands from Ustka and Czołpino

Generally, the content of ammonia nitrogen in sandy sediments of both analyzed beaches increased with depth (Table 2). Probably this is caused by a much lower amount of oxygen in deeper layers. This promotes mineralization of organic matter towards formation of ammonia. Differences between neighbouring layers were statistically non-significant, whereas between the 0-5 and 10-15 cm layers they were significant ( $p < 0.05$ ).

In the course of a year observed differences between concentrations of  $\text{NH}_4\text{-N}$  in the analyzed sands of Czołpino were slight (Table 1), while in Ustka more marked differences were recorded. In autumn and winter concentration of this form of nitrogen in Ustka was approx.  $15.5 \mu\text{g g}^{-1}$ , while in spring and summer it was by 3-6  $\mu\text{g g}^{-1}$  lower. Similarly, in that period a lower concentration of ammonia nitrogen in sands of the coastal zone (stations 3 and 4) were recorded by Korzeniewska and Korzeniewski (1976). In spring and summer enhanced development of organisms results in a higher consumption of ammonia nitrogen than in other seasons of the year.

Observed changes in concentrations of this components in sands of Ustka were consistent with changes in total nitrogen concentration, characterized by a high correlation coefficient  $r = 0.896$  ( $n = 48$ ,  $p < 0.05$  – Table 3, Fig. 5). A lower value was recorded for the correlation coefficient describing this dependence for the Czołpino beach ( $r = 0.587$ ,  $n = 48$ ,  $p < 0.05$ ). This suggests that processes of decomposition and mineralization of organic matter containing nitrogen take place in the analyzed beach deposits mainly in the direction of ammonia nitrogen formation. This is consistent with observations reported by other researchers (Nishio et al. 1983).

Mean content of total phosphorus (T-P) in beach sediments in Ustka was  $8.13 \mu\text{g g}^{-1}$  and it was higher than in Czołpino by  $6.21 \mu\text{g g}^{-1}$  (Table 1). The difference between these concentrations was statistically significant ( $p < 0.05$ ). A much lower concentration of this element in beach sands was observed earlier (Trojanowski et al. 2007, Mudryk 2004). For comparison, more total phosphorus was recorded in sands from a lagoon of the Ria Formosa in Portugal (Serpa et al. 2007). Similarly as concentra-

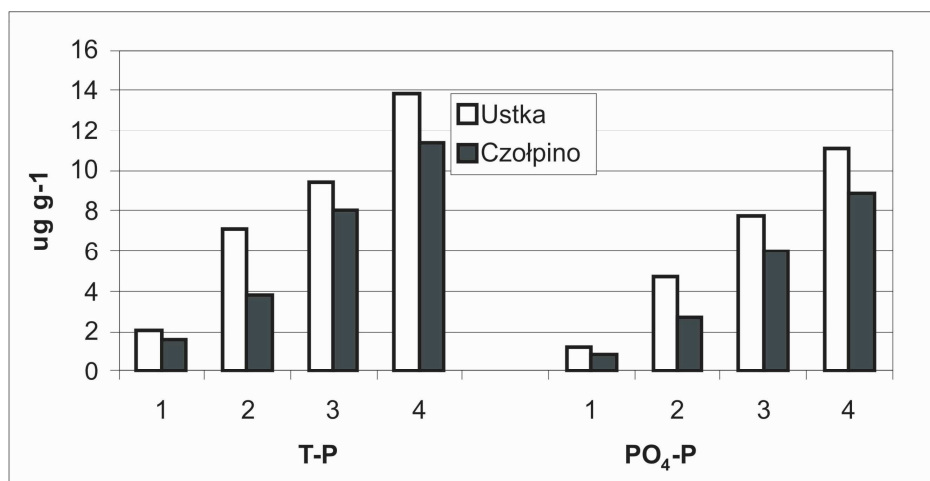


Fig. 6. Contents of total phosphorus and phosphate phosphorus ( $\mu\text{g g}^{-1}$  d.m.) in sands of Ustka and Czołpino beaches

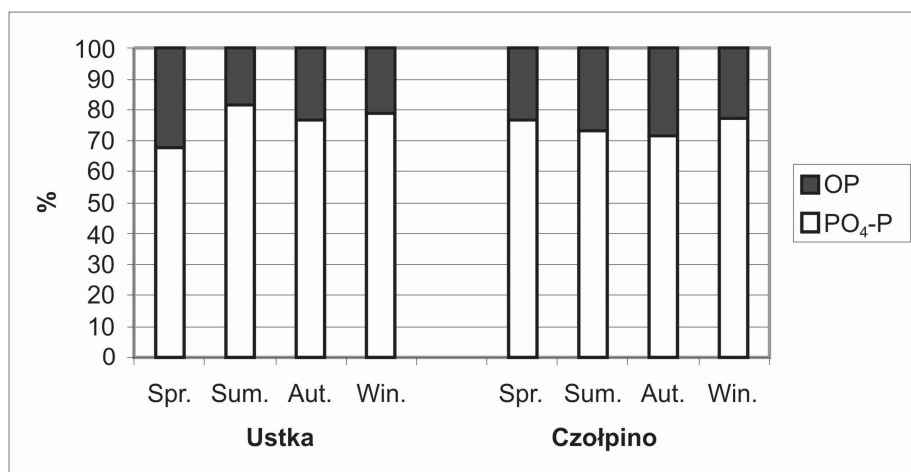


Fig. 7. The part of organic phosphorus and phosphate phosphorus in total phosphorus in the sands of Ustka and Czolpino beaches

tions of nitrogen compounds, the concentrations of phosphorus compounds in analyzed sands increased with the decreasing distance to dunes (Fig. 6). In sands of the Ustka beach mean concentration of total phosphorus increased from 2.1 (station 1) to 13.9  $\mu\text{g g}^{-1}$  (station 4), while in Czolpino it was from 1.6 to 11.3  $\mu\text{g g}^{-1}$ , respectively. A similar trend was found for changes in phosphate contents (PO<sub>4</sub>-P) from 1.2 to 11.3  $\mu\text{g g}^{-1}$  in Ustka and from 0.8 to 9.0  $\mu\text{g g}^{-1}$  in Czolpino. Also organic phosphorus (OP) content in the analyzed sands increased with the growing distance from sea water (Fig. 3). Mean proportion of phosphate phosphorus in total phosphorus in analyzed sands was approx. 73% (Fig. 7). This means that organic phosphorus constituted a smaller proportion in total phosphorus. However, this proportion changed depending on the sampling site. In places where sand had more contact with sea water the proportion of organic phosphorus increased. For this reason in those places the proportion of organic and inorganic phosphorus was 50% each. At station 2 the proportion of PO<sub>4</sub>-P was already much higher and amounted to approx. 70%. In turn, at stations most distant from the sea this form of phosphorus constituted over 80% total phosphorus. The farther from the sea water, the less organic matter was recorded in sands of analyzed beaches, and thus also fewer microorganisms, and as a consequence probably lower consumption of phosphates formed in the process of mineralization of organic substances. The same reasons may have caused an increase in the concentration of phosphate phosphorus in the analyzed sands with depth (Table 2). In Ustka mean concentration of PO<sub>4</sub>-P increased from 4.8  $\mu\text{g g}^{-1}$  in the 0-5 cm layer to 8.1  $\mu\text{g g}^{-1}$  in the 10-15 cm layer, while in Czolpino it was from 3.6 to 5.8  $\mu\text{g g}^{-1}$ . Also the content of total phosphorus increased with depth, while that of organic phosphorus decreased. On both beaches the dependence between the concentration of total phosphorus and phosphate phosphorus in the analyzed sands was characterized by very high correlation coefficients (Ustka  $r^2=0.908$ , Czolpino  $r^2=0.966$ ,  $n=48$ ,  $p<0.05$  – Table 3). In turn, the dependence between the content of total phosphorus and organic phosphorus in sands of the Ustka beach was non-

significant ( $r^2=0.246$ ), while in Czołpino this dependence was characterized by a correlation at an average level ( $r^2=0.592$ ,  $n=48$ ,  $p<0.05$  – Fig. 5). Thus the difference results probably from the different type of organic matter observed in the compared beaches. This is confirmed by correlation coefficients between contents of organic matter and contents of individual forms of nitrogen and phosphorus (Table 3, Fig. 5). In case of the Ustka beach these coefficients were statistically non-significant, while in Czołpino it was the opposite – they were significant in all cases. This means that organic matter in beach sands in Czołpino is probably of natural origin, while in Ustka it is mainly of anthropogenic origin.

Differences between concentrations of individual forms of phosphorus in sands of the analyzed beaches in the course of a year were statistically non-significant ( $p<0.05$ ). However, seasonal changes in these concentrations on the compared beaches are slightly different (Table 1). In Czołpino the lowest concentrations of the three forms were recorded in the spring period, amounting to  $4.5 \mu\text{g g}^{-1}$  (T-P),  $3.5 \mu\text{g g}^{-1}$  ( $\text{PO}_4\text{-P}$ ) and  $1.0 \mu\text{g g}^{-1}$  (OP), and they were by almost two times lower than in Ustka in the same period, where it was  $8.3$ ,  $5.6$  and  $2.7 \mu\text{g g}^{-1}$ , respectively. In turn, in Czołpino the highest values of  $7.1 \mu\text{g g}^{-1}$  (T-P) and  $5.5 \mu\text{g g}^{-1}$  ( $\text{PO}_4\text{-P}$ ) were recorded in winter. However, the differences between concentrations of total phosphorus in summer, autumn and winter in Czołpino were slight, thus it may be assumed that they are at an identical level of approx.  $6.8 \mu\text{g g}^{-1}$ . In turn, the predominance of the mineralization process of organic matter containing phosphorus over biochemical processes of the formation of this matter in winter results in the highest concentrations of phosphates and the low concentration of organic phosphorus. This is also confirmed by the highest values of the TP : OP ratio in winter and spring (Table 4). This also means that in spring the rate of mineralization is comparable with that in winter. However, the highest concentration of total phosphorus in Ustka was observed in autumn and spring (over  $8.0 \mu\text{g g}^{-1}$ ), that of phosphate phosphorus in autumn ( $6.5 \mu\text{g g}^{-1}$ ), while that of organic phosphorus – in spring ( $2.7 \mu\text{g g}^{-1}$ ). Biochemical processes of formation of organic phosphorus compounds on that beach were most intensive in spring. This is manifested by the lowest value of the TP : OP ratio (3.10, Table 4) and the highest concentration of organic phosphorus. In contrast, mineralization processes predominated in the summer period (TP : OP = 5.48).

Table 4  
The seasonal value changes of relation TP : OP in sands of beaches Ustka and Czołpino

Beach	Spring	Summer	Autumn	Winter	Year
Ustka	3.10	5.48	4.33	4.77	4.21
Czołpino	4.36	3.69	3.48	4.40	3.90

Beach sands in Ustka contained significantly ( $p<0.05$ ) more calcium and carbonate residues (on average  $154.6$  and  $206.2 \mu\text{g g}^{-1}$  – Table 1) than in Czołpino ( $110.1$  and  $146.0 \mu\text{g g}^{-1}$ ). Changes in the concentrations of both these nutrients were strongly correlated, as it is indicated by the very high correlation coefficients between them

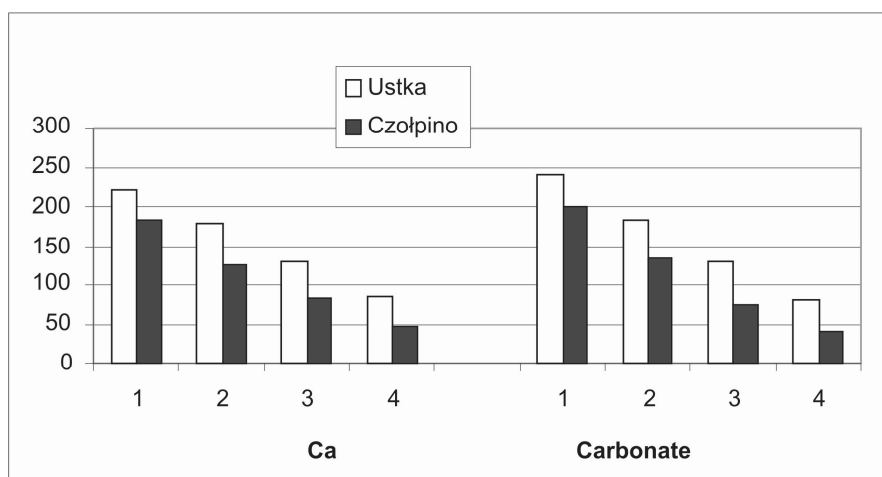


Fig. 8. Contents of calcium and carbonate ( $\mu\text{g g}^{-1}$  d.m.) in sands of Ustka and Czołpino beaches

(Ustka  $r^2=0.970$ , Czołpino  $r^2=0.953$ ,  $p<0.05$ ). This means that they are found in the analyzed sediments first of all in the form of calcium carbonate. Most probably they are remnants of shells, which primary component is calcium carbonate. This suggestion is confirmed by the highest content of calcium carbonate in places with the biggest contact of sand with sea water (station 1) in both analyzed beaches (Fig. 8). With the increasing distance from the sea its concentration decreased systematically. It was found that the differences in the concentrations of calcium and carbonate between stations are statistically significant ( $p<0.05$ ). In turn, no significant differences were observed between layers. There is only an upward trend for the contents of these nutrients with depth (Table 2), particularly evident in Czołpino.

## CONCLUSIONS

Both compared beaches differ in terms of three factors exposing them to pollution, i.e.:

1. the beach in Ustka is exposed to the effect of the town transporting onto the beach several different substances either by groundwater or through the atmosphere. In contrast, the beach in Czołpino is located in the Slovinski National Park away from urban or rural areas and thus it is not subjected to such impact;
2. the beach in Ustka is intensively used for tourist and recreation purposes not only in summer. In contrast, the beach in Czołpino is sporadically visited by tourists and it is only in the summer period;
3. the beach in Ustka is exposed to pollutants brought by the Słupia River, in that place flowing into the Baltic Sea. In contrast, the beach in Czołpino has contact with coastal waters of the Baltic Sea, in which pollution level is many times slower.

As a result of this impact beach sediments in Ustka contain much more organic matter, nitrogen and phosphorus compounds as well as calcium carbonate than analogous sediments in Czołpino. The effect of sea water was manifested in the high content of organic matter, which highest amounts were observed in places having permanent contact with sea water.

The concentration of ammonia nitrogen in the analyzed beach sediments increased with depth. This phenomenon, observed at all locations on the beaches, probably results from the lower oxygen content in deeper layers.

Beach sediments having permanent contact with sea waters contain bigger amounts of organic matter particularly in deeper layers (5-10 cm). Organic matter together with water is filtered into the sediments, with the mineralization process occurring much more readily in the surface layers. In the areas of the beach at a bigger distance from the sea water the process of penetration of organic matter into the sediments is first of all possible during precipitation, thus deeper layers are poorer in this nutrient.

Organic matter contained in sands of the beach in Czołpino is of natural origin, while in Ustka it is primarily of anthropogenic origin.

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## RÓŻNICE SKŁADNIKÓW CHEMICZNYCH W OSADACH PLAŻOWYCH O ODMIENNEJ ANTROPOPRESJI

### Streszczenie

Celem pracy było oszacowanie wpływu czynników antropogenicznych na skład chemiczny piasków z plaż w Ustce i Czołpinie. Ustka jest typową miejscowością uzdrowską i turystyczną, natomiast Czołpino leży na terenie Słowińskiego Parku Narodowego, z dala od miast i wiosek. Osady plażowe w Ustce zawierały znacznie więcej materii organicznej, związków azotowych i fosforowych oraz węglanu wapnia niż analogiczne osady w Czołpi-

nie. Wpływ wody morskiej na obydwu plażach odzwierciedlał się dużą zawartością materii organicznej w miejscach mających ciągły kontakt z wodą morską. Koncentracja tego składnika wzrastała tam wraz z głębokością. W rejonach plaży bardziej oddalonych od morza proces przenikania materii organicznej w głąb osadów jest natomiast możliwy przede wszystkim podczas opadów atmosferycznych, dlatego głębsze warstwy były uboższe w ten składnik. Prawdopodobnie ze względu na mniejszą zawartość tlenu w głębszych warstwach piasku koncentracja azotu amonowego w badanych osadach plażowych wzrastała wraz z głębokością. Stwierdzono, że materia organiczna zawarta w piaskach plaży w Czolpinie jest pochodzenia naturalnego, a w Ustce głównie pochodzenia antropogenicznego.