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A RELATIONSHIP BETWEEN CHLOROPHYLL AND DISSOLVED SUBSTANCES IN COASTAL WATERS OF SOUTH BALTIC SEA – ANTHROPOGENIC AND NATURAL INFLUENCES

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Abstract: The objectives of this study were to indicate the relationship between chlorophyll levels, dissolved metal group minerals and phosphates in the studied area of the Central Polish Coastal Waters and to relate these data to the influence of the terrestrial environment. In 2020, in the Central Polish Coastal Waters (PLB990002), which is a special area for the protection of birds, tests were carried out on the concentrations of chlorophyll, phosphates, dissolved microelements: zinc, cobalt, nickel and iron, and electrolytic conductivity. For the analysis of dissolved microelements, a graphite cuvette version of atomic absorption spectrophotometer (AAS-GF) was used. Chlorophyll and phosphates were studied using UV-VIS spectrophotometer. The concentrations obtained in coastal sea water in the spring after the wintering of waterfowl and in the autumn were compared. Microelement and phosphate concentrations were higher in spring than in autumn. The relationship between the level of chlorophyll and phosphates and the tested microelements in coastal waters was demonstrated, and the results were linked to the possible sources of these chemical substances, such as wintering of birds, tourism, municipal and port management. It was also observed that the upwelling effects occurred in the study area, which significantly influenced changes in the chemical composition of sea water.

Keywords: Baltic Sea, coastal water, phosphorus, chlorophyll, metals

1. INTRODUCTION

The Baltic Sea is a semi-enclosed, shelf, North European inner sea. It is characterized by its shallow depth. The average depth of the Baltic Sea is 56 meters. The maximum depth is 459 m - the Landsord depth (Urbański & Węsławski, 2008). The average salinity of the Baltic Sea is low and variable in the horizontal plane. Decreases from west to east as the influence of rivers flowing into the sea increases. The lowest salinity is observed in the northern part of the Baltic Sea in the Gulf of Bothnia. The waters of the Baltic Sea are fed by highly saline oceanic waters only through a system of straits (Fabisiak, 2008), these are the Skagerrak, Kattegat and narrow straits - the Sund, Great Belt and Little Belt (Urbański & Węsławski, 2008). Water exchange with the neighboring North Sea is limited and intermittent (Fabisiak, 2008). The total exchange of Baltic Sea waters with well-oxygenated and high-salinity Atlantic Ocean waters takes about 25 to 35 years. The average salinity of the Baltic Sea is approximately five times lower than that of Atlantic Ocean waters (Fabisiak, 2008).

The heavy metal pollution of the Baltic Sea mainly includes material delivered by rivers, estuarine lakes from inland, seaports and area pollution (HELKOM, 1993; Szefer, 2002; Trojanowski & Antonowicz, 2011). Industry directly pollutes seawaters by discharging wastewater into the sea and indirectly by discharging it into rivers that carry it to the sea. Also, the emission of fumes, smoke, dust and gases into the atmosphere and their subsequent deposition in the sea is significant. The level of pollution from inland also includes municipal economy, transportation and agriculture). Environmental disasters, exploitation of mineral resources of the seabed (Fabisiak, 2008) and seaports are also a major threat to the marine environment (Fabisiak, 2008; Ispas et al., 2020). Natural biogeochemical cycles of matter between abiotic and biotic zones of aquatic and terrestrial ecosystems result in the movement of matter and periodic accumulation of pollutants. For example, waterfowl leave droppings on the shore, which then dissolve in the water. In some areas, this represents a significant source of nutrients (Ligęza, 2008, Klimaszek et al., 2014; Shatova et al., 2017) and also metals (Jaspers et al., 2004; Espejo et al., 2014; Shatova et al., 2017; Sparaventi et al., 2021) for the aquatic environment.

The presented research was conducted in the coastal waters of the Baltic Sea in the areas of Darłowo, Ustka, Rowy and Czołpino. Central Polish Coastal Waters (PLB990002) is a special bird protection area established to protect avifauna and their habitats. It stretches 200 km from the tip of the Hel Peninsula to the Pomeranian Bay (Meissner, 2010). It includes three Natura 2000 areas and a section of about 15 km located in the area of the Slovinski National Park (Bielecki et al., 2022).

The aim of this study was to indicate the relationship between chlorophyll *a* level, dissolved metal group minerals and phosphates during spring and autumn in the studied area of the Baltic coastal waters and to relate these data to the influence of the environmental pollutions.

2. MATERIAL AND METHODS

2.1. Studied area

Selected information on the studied areas is presented below:

Darłowo – a city in the area of which a seaport with the function of a fishing port is located. It is a recreational city. The seaport is the mouth of the Wieprza River into the Baltic Sea.

Ustka - a city with a seaport. It is a spa and tourist destination (Trojanowski et al., 2011). The port is the mouth of the Słupia River.

Rowy - a settlement with a seaport. Fishing ships are stationed here. It is also a recreational area with a village status. The eastern part of the beach in Rowy is located within the Slovinski National Park. The harbor is the mouth of the Łupawa River.

Czołpino - a small settlement located within the Slovinski National Park. There is no port in this settlement. The beach is open to tourists, who can get to it on foot. However, tourist traffic here is low (Trojanowski et al., 2011) compared to the other surveyed beaches.

Central Polish Coastal Waters (PLB990002). It is an important wintering site for waterbird species such as ducks and divers (Bielecki et al., 2022). It is estimated that the number of birds wintering in the area reaches 200,000 - 250,000 (Meissner, 2010, Bielecki et al., 2022). In Table 1 was presented the numbers of birds wintering in the area. According to the current 2022, Natura 2000 Standard Data Form, six species are protected: *Alca torda*, *Cepphus grylle*, *Clangula hyemalis*, *Larus argentatus*, *Melanitta fusca*, *Melanitta nigra* (Bielecki et al., 2022).

Table 1. Numbers of birds wintering in the area of the Central Polish Coastal Waters (Bielecki et al., 2022 [A]; Meissner, 2010 [B])

name	systematic name	number
Long-tailed duck	*Clangula hyemalis*	90000 – 120000[B]
Velvet scoter	*Melanitta fusca*	14000 – 20000[B]
Euroepan herring gull	*Larus argentatus*	8000 – 15000[B]
Common scoter	*Melanitta nigra*	5000 – 8000[B]
Black guillemont	*Cepphus grylle*	1500 i więcej[A]
Razorbill	*Alca torda*	500 – 1000[B]
Red-throated diver	*Gavia stellata*	100 – 500[B]
Black-throated diver	*Gavia arctica*	200 – 500[B]

In the study area, it is worth noting the occurrence here of anadromous fish such as *Salmo salar* and *Salmo trutta m. trutta,* which spawn in the rivers of Polish Pomerania (Bartel, 2000), such as the Wieprza, Słupia, Łupawa and Łeba. *Salmo salar* is an Atlantic species and occurs, among others, in the catchment area of the Baltic Sea (Radtke et al., 2017; Bernaś et al., 2009). On the other hand, an extremely rare species, *Cottus poecilopus,* occurs in the Łupawa River basin in a tributary of the Rokicianka River (Radtke et al., 2005). *Phocoena phocoena* and *Halichoerus grypus*, which are subject to species protection, appear at the Polish beaches (Dziubecki & Pisarczyk, 2014).

2.2. Sampling

The study area included the coastal waters of the Baltic Sea of four coastal locations: Darłowo, Ustka, Rowy and Czołpino (southern Baltic) (Figure 1). Four sampling stations were placed in each location. In the towns where there are seaports, i.e. Darłowo, Ustka and Rowy, the sampling stations were placed 2 on each side of the seaport exit to the sea. In the town of Czołpino where there is no canal port, the sampling stations were distributed along the shore. Water samples were taken in the spring and autumn of 2020 in polyethylene containers. Seawater samples were collected by wading in coastal water. Samples for the determination of metals were collected into chemically clean containers, digested in nitric acid (V) and rinsed with the first portion of water at the sampling station. Samples for metal determination were filtered on PTFE syringe filters with a diameter of 0.22 μm.

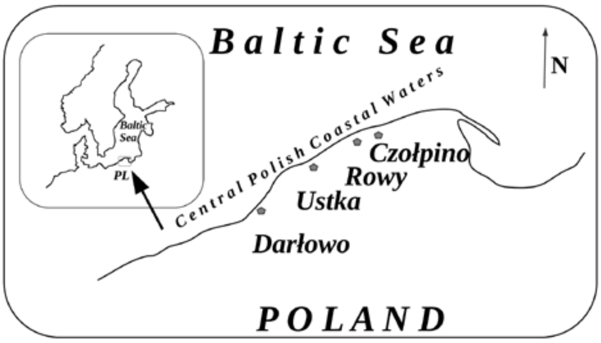

Figure 1. Location of Darłowo, Ustka, Rowy and Czołpino on the Polish Baltic Sea coast. On the upper – left of figure was presented contour map of northern Europe with the Polish Baltic Sea coast under study.

2.3. Chemical and physical analyses

Seawater samples were mineralised using *suprapur®* nitric acid (V). Metals Zn, Ni, Cu and Co were analysed using an atomic absorption spectrophotometer AAS iCE 3000 Series with electromagnetic excitation with Thermo Scientific's Graphite Furance GFS module and Thermo Flex 900 cooling kit. Zinc was analysed at 213.9 nm, nickel at 232.0 nm, iron at 248,3 nm and cobalt - 240.7 nm wavelength. Deionised water obtained from a Hydrolab HLP 10UV apparatus was used as a blank. Inorganic Ventures standards were used for the preparation of calibration curves.

Electrolytic conductivity (EC) was determined by potentiometric method using a CX - 501 conductivity meter (Elmetron, Poland), water pH was determined using a Combined Meter Mi 805 (Martini Instruments) and dissolved oxygen was determined using a Mi 605 (Martini Instruments). Water temperature was tested directly in situ using an electronic thermometer.

Phosphate concentration (P-PO_4 - phosphate phosphorus) was determined using the ascorbic acid method (APHA, 1992). Chlorophyll *a* (chl *a*) concentration was determined after extraction of samples on a vacuum pump filtration set-up using filters. The obtained samples were then extracted in acetone and analysed using a spectrophotometer (Jeffery & Hamphrey, 1975) Hitachi U-5100 UV - VIS.

2.4. Statistical analyses

Statistical analyses were carried out in the Statistica ver. 13 software, including: basic statistical parameters such as median, mean, standard deviation, calculated: Shapiro – Wilka test (study of the type of distribution of variables), U Mann – Whitney test and Spearman - r correlation. A multivariate cluster analysis of the relationships between the parameters under study (Ward's method, Euclidean distance) was also performed.

3. RESULTS

3.1. Chlorophyll *a*, phosphate phosphorus and dissolved oxygen

In Figures 2 and 3 were presented the dynamics of changes in chlorophyll *a*, phosphate phosphorus, dissolved oxygen and dissolved metal forms. In Table 2 was presented data on water reaction, electrolytic conductivity and temperature (T). The highest concentrations of chlorophyll *a* were observed in spring near Darłowo, while in autumn the concentration of chlorophyll *a* was comparable in all studied areas.

Table 2. Comparison of pH mean levels, electrolytic conductivity [mS] and water temperature [ºC] in spring and autumn 2020 in Baltic coastal waters (± standard deviation).

season	parameter	Darłowo	Ustka	Czołpino	Rowy	all locations
s		6.87	7.11	7.36	7.50	7.21
p	pH	±0.11	±0.10	±0.09	±0.01	±0.26
r		12.32	12.56	12.34	12.42	12.41
i	EC	±0.48	±0.06	±0.06	±0.07	±0.24
n		12.60	14.58	14.08	13.20	13.61
g	T	±0.08	±0.10	±0.10	±0.14	±0.79
a		7.13	7.65	7.70	7.60	7.52
u	pH	±0.30	±0.12	±0.03	±0.23	±0.29
t		14.07	14.09	13.84	12.68	13.67
u	EC	±0.20	±0.06	±0.11	±1.25	±0.83
m		16.50	17.45	17.43	16.43	16.95
n	T	±0.08	±0.06	±0.10	±0.10	±0.51

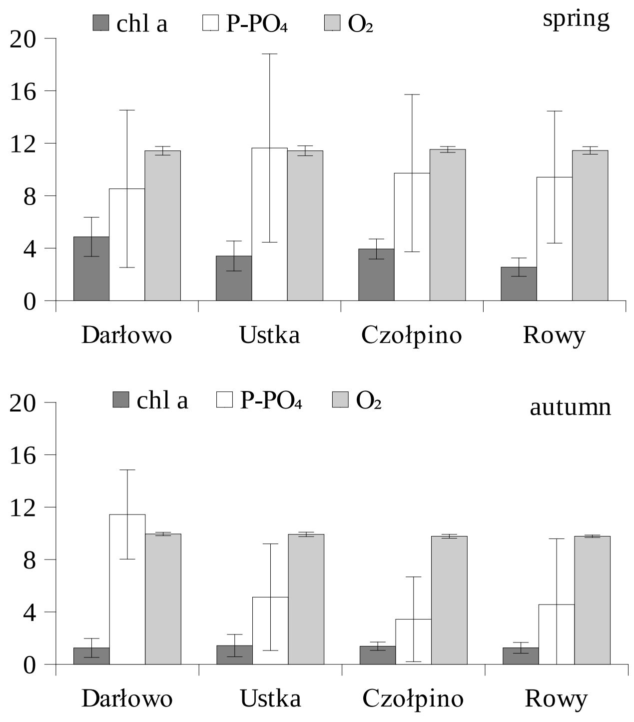

Figure 2. Concentrations of chlorophyll *a*, phosphate phosphorus [μg dm^{-3}] and dissolved oxygen [mg dm^{-3}] in spring and autumn 2020 on Baltic coastal waters area

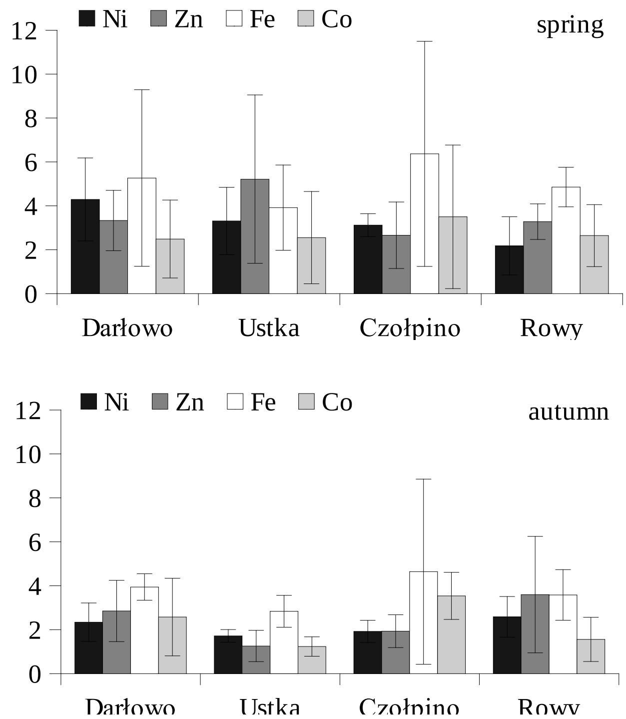

Figure 3. Concentrations of dissolved forms of metals: zinc, cobalt, nickel and iron [μg dm^{-3}] in spring and autumn 2020 on Baltic coastal waters area

The highest concentrations of phosphorus were observed in spring in Ustka and in autumn in Darłowo (Figures 2 and 3). The mean concentration of phosphate phosphorus from all investigated areas in spring was about 60% higher than in autumn (Figure 4). Dissolved oxygen concentration was comparable in the horizontal plane in the studied areas, while its concentration in spring was about 15% higher than in autumn (Figure 4).

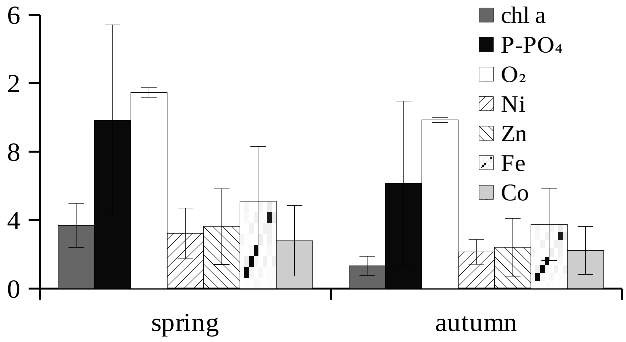

Figure 4. Comparison of chlorophyll *a*, phosphate, nickel, zinc, iron, cobalt [μg dm^{-3}] and dissolved oxygen [mg dm^{-3}] concentrations obtained in spring and autumn from all study areas

3.2. Heavy metals

The concentrations in seawater of the heavy metals studied during the spring period form the following descending series: Fe > Zn > Ni > Co, while in autumn: Fe > Zn > Co > Ni. Concentrations of nickel and zinc were about 50% higher in spring than in autumn, also higher concentrations in spring were observed for iron by 35% and by 25% for Co (Figure 4). The highest Ni concentrations were observed in spring in Darłowo, while in autumn high Ni concentrations were observed in Darłowo and Rowy. The highest Zn concentrations were found in spring in Ustka, while in autumn in Rowy. The highest concentrations of Fe and Co were observed in spring and autumn in Czołpino (Figure 3).

3.3. Salinity, pH and temperature of water

Throughout the study area, water pH was lower in spring than in autumn, as were electrolytic conductivity and water temperature. In the study areas, water pH was lowest in Darłowo in spring and autumn. Electrolytic conductivity in spring was comparable in the studied areas, while in autumn in Darłowo and Ustka it was about 15 % higher than in Rowy, where it was the lowest.

3.4. Statistical interpretation

Using the Mann-Whitney U test, statistically significant differences were found between the spring and autumn seasons for chlorophyll *a* ($p < 0.001$), dissolved oxygen ($p < 0.001$), nickel ($p <$

0.05), water pH ($p < 0.01$), electrolytic conductivity ($p < 0.001$) and water temperature ($p < 0.001$).

In Figure 5 was presented a dendrogram showing the correlations between the parameters in question. Two clusters are distinguished in the dendrogram. Cluster A groups together the following parameters: water temperature, electrolytic conductivity and water pH. Cluster B groups the following parameters: Fe, Zn, P - PO_4, Co, Ni, O_2 and chlorophyll *a*.

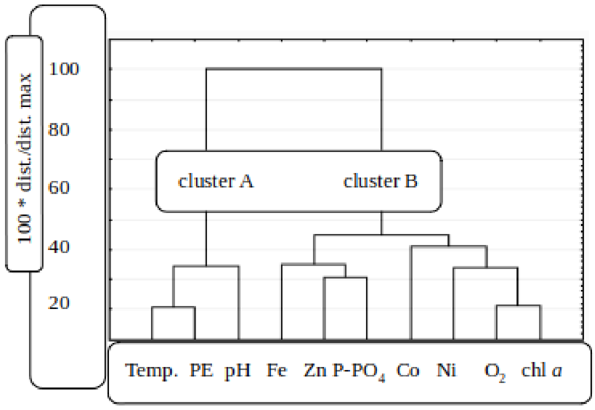

Figure 5. Dendrogram showing multivariate cluster analysis of the relationships between the parameters under study (Ward's method, Euclidean distance)

A Spearman - r rank correlation analysis was performed between the parameters studied. The most important statistically significant (n=32) correlations include: P-PO_4 - chl *a*, O_2 - chl *a*, P-PO_4 - O_2, Zn - Ni, Zn - Fe. Negative correlations were also found between: pH - chl *a*, pH - P-PO_4, chl *a* - EC, chl *a* – temperature.

4. DISCUSSION

Beaches represent a specific area, which with its chemical composition may interfere to some extent with the chemical composition of the waters of the Baltic Sea coastal zone. The chemical composition of beaches may be modified by a number of factors, such as tourist traffic and animal habitation. The Polish coastal areas of the Baltic Sea are a wintering site for large numbers of birds (Meissner, 2010; Bielecki et al., 2022). Pollutants accumulated on beaches, including metals, biogenic substances of natural and anthropogenic origin are transported to the marine environment.

Studies conducted in Baltic coastal waters have identified likely factors modifying the levels of chlorophyll, phosphates and biologically important metals in coastal seawater. These are factors of anthropogenic and natural origin.

4.1. Natural sources of pollution

The studied coastal zone includes the Central Polish Coastal Waters Special Protection Area (PLB990002) (Bielecki et al., 2022). It is estimated that the number of birds wintering in the area reaches a sizeable number of 200 - 250 thousand (Meissner, 2010; Bielecki et al., 2022). Overwintering waterfowl leave feaces, food remains, eggshells, feathers and dead individuals on the beaches, which can be a source of biogenic substances (Stempniewicz et al., 2007; Ligęza, 2008; Klimaszek et al., 2014), as well as metals (Shatova et al., 2017; Sparaventi et al., 2021). Furthermore, the faeces of piscivorous birds contain significantly higher amounts of phosphates than those of herbivorous birds (Stempniewicz et al., 2007). However, fish for birds wintering on Polish beaches are only part of the food. Studies conducted on the Polish coast show that phosphate concentrations were higher in spring after the wintering period of birds than in autumn. Studies conducted in the Arctic by Stempniewicz et al., (2007) indicate a strong influence of bird faeces on the level of nutrients including phosphates in ocean water. Seabirds periodically occur in the Arctic in huge aggregations. During their breeding colonies, which last for several months, they provide significant amounts of nutrients - along with food caught from the sea onto land (Stempniewicz et al., 2007).

The availability of phosphates in seawater at the Polish coast in spring should translate into an increase in chlorophyll *a* level (indirectly phytoplankton biomass). Similar correlations were observed in studies of estuarine Lake Łebsko and coastal waters of the Baltic Sea located in the area of the Słowiński National Park (Antonowicz, 2018). Similarly, in ongoing studies of coastal waters, a positive correlation was found between chlorophyll and phosphates ($r = 0.35$, $p < 0.05$). This relationship was also confirmed using multivariate cluster analysis where both parameters appear in the same cluster (cluster B, Figure 5).

Bird faeces are also a source of metals such as Ni, Zn, Fe, Co. A study by Sparaventi et al., (2021) found high levels of Fe and Zn and lower levels of Co and Ni in bird faeces. It was also confirmed that these faeces were a source of the above-mentioned metals in coastal waters. This correlates with the data presented in this work.

A study by Shatova et al., (2017) also confirmed that metals such as Mn, Fe, Co, Ni, Cu and Zn present in waterbird faeces not only affected metal concentrations in the water, but also significantly affected phytoplankton growth.

Studies of Polish coastal waters have shown that mean concentrations of Ni, Zn, Fe, and Co were 25 to 50 % higher in spring than in autumn (Figure 4). Presumably, the deposition effect of chemical substances from bird faeces, feathers, spits, dead animals, such as metals and biogenic substances, is observed on the surveyed Polish beaches during winter. This matter then feeds into the coastal waters during the spring. The matter accumulating on the beaches is in a constant dynamic: the movement of winds moves it along with the sand and, at the same time, coastal waters wash up on the beaches with the waves (Trojanowski et al., 2011). In winter, decomposition processes are severely slowed down due to low temperatures. Sunlight accelerates the processes of mineralization of organic matter (Gebus-Czupyt & Wach, 2022). During the spring, organic matter, once supplied with the solar energy necessary for the reaction, is decomposed and mineralised, which consequently affects the levels of these components in coastal waters.

4.2. Anthropogenic sources of pollution

In parallel, a broad spectrum of human activities is a factor influencing metal pollution levels. Heavy metal contamination is mostly a result of industrial and urban human activity (Amraoui et al., 2015). Seaports provide metals such as Zn, Ni, Fe, Co (Szefer & Skwarzec, 1988; Szefer, 2002; Antonowicz et al., 2017). For water organisms the most available are dissolved forms of chemical components (Andrulewicz et al., 2008). These metals are commonly used in everyday objects, also brought by tourists to beaches such as packaging, metal objects. During their use, over long periods of time, tourists as well as the population living in the cities introduce metals into municipal waters as well as directly onto the beaches, which can cause an increase in their levels in the environment (Szefer, 2002). In addition to metals, biogenic substances are also delivered to waters as a result of port operations, municipal management, and river transport from inland (Mudryk et al., 2015). Rivers, through being localized in seaports in the estuaries, inject material into the Baltic Sea which comes largely from denudation and erosion and inland pollution. This material is sedimented near the mouth to the sea and partially transported into the depths (Perlinski et al., 2015).

In Polish coastal waters near harbors, the highest concentrations of Ni and Zn were observed. Santhiya et al., (2011), indicated that high concentrations of Ni, Cu, Pb and Zn in harbour pollution are mainly related to the presence of fishing ports and industrial pollution. Darłowo, Ustka and Rowy are seaports with a fishing port function. In contrast, the highest Fe concentrations were observed near Czołpino, where there is no port. This may be due to the fact that this is a forested area and geochemical studies have shown high Fe contents in forest soils in close proximity to the beaches (Lis & Pasieczna, 1995) which could be the source of this metal in coastal waters.

4.3. Dynamic of salinity

During the study conducted, salinity levels (expressed by electrolytic conductivity levels) were higher in autumn than in spring (Table 2). In the coastal waters of the Baltic Sea, the phenomenon of elevating of the lower parts of more saline waters is observed. This phenomenon is called upwelling and is caused by the upwards flow of cold sea water from below the thermocline near the shore (Urbański & Węsławski, 2008). This is an important mechanism causing vertical mixing of seawater observed in the coastal waters of the Baltic Sea (Myrberg & Andrejev, 2003). The upwelling phenomenon occurs when the east wind blows along the shore ranging from north to south - easterly origins. This wind causes surface water to flow away from the shore and be replaced by cold water from below the thermocline. This phenomenon may last for several days or even several tens of days and disappears when the wind direction changes (Urbański & Węsławski, 2008). Waters from beneath the thermocline of the Baltic Sea often represent waters with significantly higher salinity than surface waters. These cold waters are also better oxygenated (Mohrholz et al., 2015). This would probably explain why, in the surveyed Polish coastal waters, higher oxygen levels were observed in autumn in 2020 (statistically confirmed, $p < 0.01$).

A Spearman - r rank analysis stated a negative statistically significant correlation between chlorophyll *a* and EC ($p < 0.01$). Also using cluster multivariate analysis, it was shown that chlorophyll *a* and EC occur in two distinct clusters (Figure 5). This rationale leads to the conclusion that a temporary increase in salinity (measured by EC) probably caused a decrease in chlorophyll *a* (expressing phytoplankton biomass). Similar responses of microorganisms in brackish waters were observed in studies of the nearby estuarine Lake Gardno. In such areas, the death of species not adapted to salinity changes occurs with its sudden changes, where they experience osmotic shock (Mudryk & Skórczewski, 2007).

Table 3. Comparison of Co, Fe Ni and Zn concentration data in the Baltic Sea and the Atlantic Ocean.

	Co	Fe	Ni	Zn	
Western Baltic Sea [µg l^{-1}]				1.21	Dippner & Pohl, 2004
Central North Sea [µg l^{-1}]			*0.5 – 1.5	*13.4 – 23	Fileman et al., 1991
NE Atlantic dissolved July inner [nM]	0.26 ± 0.06		4.1 ± 0.9	10.2 ± 2.3	Prego et al., 2013
NE Atlantic July inner particulate [nM]		17 ± 5	0.15 ± 0.09	0.52 ± 0.27	Prego et al., 2013
Baltic Sea SML [µg l^{-1}] dissolved				*0.2 – 5.8	Brügmann et al., 1992
German Bright SML [µg l^{-1}] total				10.2 – 20.5	Hardy & Cleary, 1992
Gotland [nmol kg^{-1}]			13.8 ± 21	14.1 ± 3.1	Kremling & Streu, 2000
Bornholm Sea [nmol kg^{-1}]			11.3 ± 0.8	10.8 ± 2.6	Kremling & Streu, 2000
Arkona [nmol kg^{-1}]			10.9 ± 3	16.5 ± 4.5	Kremling & Streu, 2000
Belt Sea [nmol kg^{-1}]			11 ± 1	14.1 ± 4	Kremling & Streu, 2000
Coastal sea water near Ustka [µg l^{-1}]			10.93 ± 2.16	< 20	Antonowicz et al., 2017
Baltic Sea, Baltic Proper [µg l^{-1}]	*0.03 – 0.235	*0 – 190	*0.59 – 1.63	*0.33 – 1.62	Pempkowiak et al., 2000
This study [µg dm^{-3}]	2.51 ± 1.76	4.43 ± 2.75	2.68 ± 1.27	3.02 ± 2.03	

* minimum and maximum value
± standard deviation

4.4. Comparison of concentrations metals in sea water

Table 3 presents data on concentrations of the studied metals in the Baltic Sea and the north-eastern part of the Atlantic Ocean cited from Fileman et al., (1991), Brügmann et al., (1992), Hardy & Cleary, (1992), Kremling & Streu, (2000), Pempkowiak et al., (2000), Dippner & Pohl, (2004), Prego et. al., (2013), Antonowicz et al., (2017). The collected data from Polish coastal waters correspond with those obtained by other authors, as presented in Table 3. In the case of Zn, concentrations in coastal waters were comparable to the background concentrations of 3 µg dm^{-3} according to Borg and Johansson (1989).

5. CONCLUSION

All the discussed anthropogenic factors: seaports, tourism, municipal management as well as of natural origin: faeces of birds overwintering on beaches and mixing of seawater influenced the relationships between nutrients, the studied heavy metals and chlorophyll in coastal waters.

In the studied coastal zone of the Baltic Sea, higher concentrations of trace elements and phosphates were observed in spring than in autumn, which indicates the accumulation of these substances during winter.

Further studies of the coastal zone are necessary to provide more information on whether these changes are cyclical and to better understand the circulation of these elements in adjacent marine and terrestrial environments.

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