3

Synthetic Chelating Agents in the Aquatic Environment: Effect on the Growth of Phytoplankton[1]

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1. Introduction

Major commercial applications of chelators include the pulp and paper, textile, metal, photographic, cosmetic and detergent industry.The substitution of polyphosphates in P-free washing products with complexing agents such as nitrilotriacetic acid (NTA), sodium citrate, sodium carboxymethyltartonate (CMT) and recently co-polymeric carboxylic acids and inorganic builder Zeolite type A enabled the elimination of phosphates [6, 18]. However, domestic and industrial discharges brought about a dramatic increase of concentration of new organic compounds capable of metal chelation for instance (amino polycarboxylates as low-MW: NTA, EDTA or high-MW as co-polymers acrylic acids, acrylic/maleic acids) in the environment, especially in the coastal waters where most of non-degradable matter is finally introduced.

Industrial processes such as photography development, boiler descaling and water softening represent main sources of nitrilotriacetic acid [3]. At research laboratories, NTA as well as other synthetic agents chelating metals are specifically used to study the iron metabolism. For instance, in order to prevent precipitation of insoluble trace metals, especially iron, bacterial and algal growth media are commonly supplemented with either EDTA or NTA [1, 11, 12].

NTA has been shown to be a very strong chelating agent and has been implicated in promoting mobilisation of metals [6, 18]. Little is known, however, about the environmental impact of NTA.

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[1] The investigations were carried out within the framework of the research programme of the Institute of Oceanology PAS, Sopot

Modern interest in polycarboxylic acids (PCA) as detergent constituents has largely been directed towards their use as co-builders and enhancing antiredeposition and dispersant factors.

The polycarboxylates used in detergents and cleaning agents are mostly homopolymers of acrylic acid or copolymers of acrylic and maleic acid with a high density of anionic carboxylate groups. However the introduction and wide application of synthetic polymers such as PCAs can have implications for the aquatic biota.Little is known about the function of the ligands in marine environment.

Most PCAs have a carbon backbone molecular structure and are poorly biodegradable under normal conditions [5]. There is very little literature concerning the behaviour and environmental fate of polycarboxylates.

The universal use of P-free detergents causes a necessity to study the effects of these chemicals upon biological subjects in various parts of the environment.

Little information is available regarding the effects of interaction between plycarboxylate and heavy metals in the environment.

According to recent findings [19] the detergent ingredient, Zeolite A - Polycarboxylic Acid (PCA), may have played a role in exacerabiting the mucilage phenomenon, observed in the Northen Adriatic Sea, after the introduction of phosphorous free detergents. On the other hand experimental study of Monti et.al., [14] has not revealed any evident causal relationship between the presence of Zeolite A - PCA system and the formation of mucous aggregates [14].

The paper deals with the results of studies on the influence of polycarboxylates, on the growth of phytoplanktonic cells under iron-deficient culture conditions.The study present findings from two species green algae – *Chlorella kessleri* and *Scenedesmus microspina* and two species of cynanobacteria – *Synechocystis aquatilis* and *Gleocapsa minor* – in order to shed light on the function of the synthetic chelators – polycarboxylates in the aquatic environment.

2. Materials and methods

An axenic cultures of the green algae *Scenedesmus microspina* (Martens and Pankov) (B2-76) was isolated from the Baltic Sea (Culture Colection of the Institute of Oceanology, PAS, Sopot) and *Chlorella kessleri* (H-1901) as well as a xenic culture of cyanobacterium *Chroococcus minor* Kutzing (A-101) and *Synechocystis aquatilis* (Sauvageau) (A-801) were obtained from the Collection of Autrophic Organisms (Prague). These cultures were used in the study as test organisms. These organisms are common in water of the Gulf of Gdańsk and Puck Bay and are important components in the food chain [16, 20].

The cultures were grown under iron deficient conditions, on modified synthetic media according to Kratz and Mayers, [9] for cyanobacterium and Bristol's medium (BBM) for green algae [8, 21]. Na2-EDTA was excluded from media and the medium pH was adjusted to 7.5 with 1M KOH. To remove iron contamination from the culture glassware, all culture flasks were rinsed with 3M HCl and, finally, with deionised water.

Such poor in iron medium was gained by passing through an activated Chelex-100 Na^+ ion exchange resin (BioRad) to reduce trace metal background and contamination.

The inoculum of algae and cyanobacteria were incubated for ten days in the modified medium and was washed every day with fresh modified medium before the experiments. In this manner, iron was removed from the cell surface [8].

The initial inoculum for green algae (S*cenedesmus microspina, Chlorella kessleri*) and cyanobacteria (*Synechocystis aquatilis and Gleocapsa minor*) was $3\cdot10^{-5}$ mg cm^{-3} of chlorophyll-a.

The cultures were incubated under continuous illumination at an intensity of 50 Wm^{-2} and temp. 20±1°C.

Aqueous solutions of the following organic substances were used in the experiment polycarboxylates (PCAs) in the form of Sakalan CP5p, co-polimer of maleic-acrylic acid Mw=70.000 (BASFA) and nitrilotriacetic acid (NTA) (Sigma). Concentrations of PCAs in the medium were from $1\cdot10^{-7}$ to $2\cdot10^{-6}$ $mole\cdot dm^{-3}$. NTA as trisodium salt $N(CH_2CO_2Na)_3\times H_2O$ was dissolved in deionized water at the final concentration of 10^{-4} $mole\cdot dm^{-3}$. Stock solution of NTA diluted with basal medium to the desired concentrations in the range from 10^{-7} to $5\cdot10^{-5}$ $mole\cdot dm^{-3}$.

The iron solutions were prepared using Titrisol (1 g $FeCl_3$ in 15% HCl) from Merck.

Organic compounds and iron were added to the cultures in different combination. The cultures without organic compounds PCA, NTA and iron served as the control samples.

Flasks containing 50 cm^3 of medium were inoculated in clean laminar flow cabin ensuring sterile conditions. All incubations were carried out at constant temperature (19±0.1°C); light was provided by cool white fluorescent bulbs (14 h light: 8 h dark cycle) with photosynthesis photon flux density of 112 $\mu Em^{-2}\cdot s^{-1}$ (Revco Diurnal Chamber).

The amount of chlorophyll *a* in the tested organisms was a measure of the growth of phytoplankton cells. After 10 days of incubation, the cultures were filtered through Whatman GF/C filters and chlorophyll-*a* content was measured according to modified method of Strickland and Parsons [2, 22]. Each experimental variant was repeated at least nine times. Cultures of green algae were periodically checked for bacterial or other contamination. Axenic status was confirmed after inoculation of medium and after 10 days incubation cultures with and without tested organic compounds. Liquid cultures were visually inspected for contamination using a phase contrast microscope. Bacterial counts (colony forming units, cfu) were determined also using the nutrient agar plate (NA) dilution method. Bacteria could not be detected in various media, both solid and liquid, nor ny epifluorescence microscopy and NA plate.

The statistical analysis of the results consisted in the evaluation of the statistically significant differences at $\alpha=0.05$ level [17].

3. Results

The results of experiments on the influence of high-MW copolymer acrylic/maleic acids (PCA) on the chlorophyll-a content measurements in *Chlorella kessleri* and *Synechocystis aquatilis* cultures are shown in Figures 1-2.

After 10 days incubation, under iron-deficient culture conditions, concentration of chlorophyll a in control samples was greater (4-10 times) in comparison to initial chl a content in cultures, respectively green algae and cyanobacteria.

The chlorophyll-a content of *C.kessleri* cells and *S.aquatilis* strains was larger when polycarboxylates were present in the medium. The stimulation was PCA-concentration dependent under experimental conditions. It appears that the presence of polycarboxylates, water soluble synthetic polymers, in the medium at concentration from $1\cdot10^{-7}$-$4\cdot10^{-7}$mol$\cdot$dm^{-3}, resulted in an increase in chlorophyll-a content in the population of both *C.kessleri* cells and *S.aquatilis* by 20-150% and 20 to 200% respectively, as compared with the control sample.

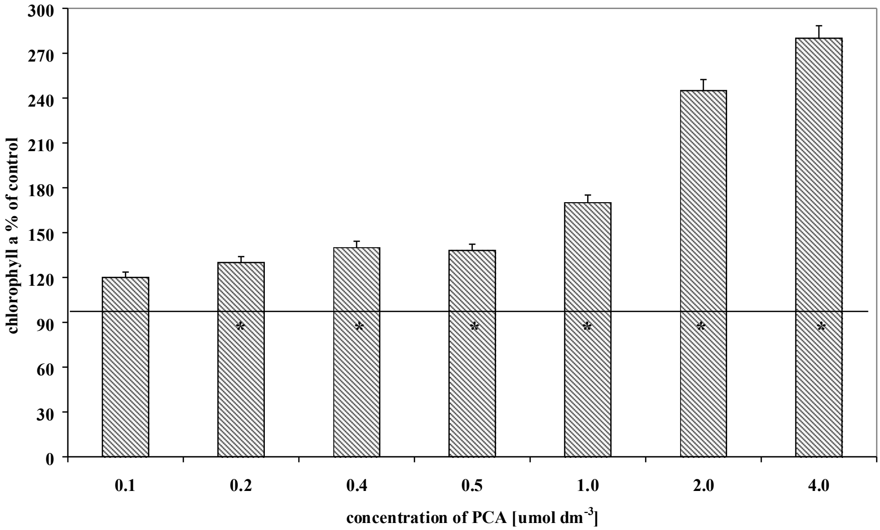

Fig. 1. Concentration of chlorophyll *a* in populations of *Chlorella kessleri* cultivated under iron-deficient conditions ($Fe<10^{-7}$ mol·dm^{-3}) in the presence of high-MW copolymer polycarboxylates; Control = 100%: cultures without of PCA, data of chl a represent mean of number of 9 replicates. Error bars represent standard deviations; * differ significantly from the results of a control based on Student's t-test at $\alpha = 0.05$

Rys. 1. Stężenie chlorofilu *a* w populacjach *Chlorella kessleri* hodowanych w warunkach niedoboru żelaza ($Fe<10^{-7}$ mol·dm^{-3}) w obecności wielkocząsteczkowych polikarboksylowych kopolimerów;; Kontrola = 100%: kultury bez PCA, dane chl a reprezentują średnią z 9 powtórzeń. Wąsy błędów reprezentują odchylenia standardowe; * różnią się znacząco od wyników kontroli w oparciu o test t-Studenta przy $\alpha = 0,05$

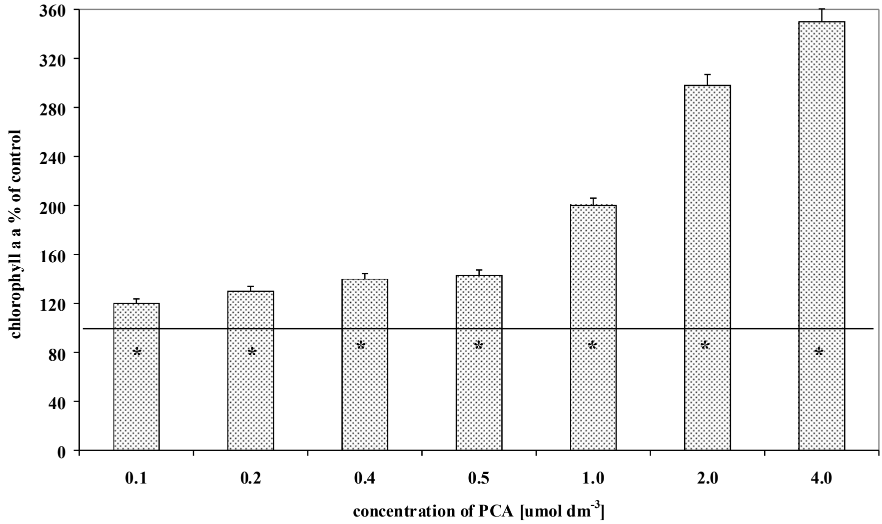

Fig. 2. Concentration of chlorophyll *a* in populations of *Synechocystis aquatilis* cultivated under iron-deficient conditions ($Fe<10^{-7}$ mol·dm^{-3}) in the presence of high-MW copolymer polycarboxylates; Control = 100%: cultures without of PCA, data of chl a represent mean of number of 9 replicates. Error bars represent standard deviations;* differ significantly from the results of a control based on Student's t-test at $\alpha = 0.05$

Rys. 2. Stężenie chlorofilu *a* w populacjach *Synechocystis aquatilis* hodowanych w warunkach niedoboru żelaza ($Fe<10^{-7}$ mol·dm^{-3}) w obecności wielkocząsteczkowych polikarboksylowych kopolimerów; Kontrola = 100%: kultury bez PCA, dane chl a reprezentują średnią z 9 powtórzeń. Wąsy błędów reprezentują odchylenia standardowe; * różnią się znacząco od wyników kontroli w oparciu o test t-Studenta przy $\alpha = 0{,}05$

The effect of iron and PCA on chlorophyll-a content in *Chlorella kessleri* and *Synechocystis aquatilis* cultures is shown in Tables 1 and 2.

The addition of iron ($1.4\cdot10^{-7}$ mol·dm^{-3}) and polycarboxylates in low concentrations ($1\cdot10^{-7}$-$4\cdot10^{-7}$mol·dm^{-3}) to the cultures caused ~60-110% growth stimulation of both phytoplankton species in comparison to the control sample. Addition of PCA in presence of iron at concentration ($1.4\cdot10^{-7}$ mol·dm^{-3}) increased production of chlorophyll a 30-70% as compared with the cultures exposed to iron only, at the same concentration.

Table 1. Concentration of chlorophyll *a* in populations of *Chlorella kessleri* cultivated in the presence of iron and high-MW copolymer polycarboxylates; Control: cultures without of Fe and PCA,* data of chl a represent mean of number of 9 replicates , σ - SD, ** differ significantly from the results of a control based on Student's t-test at $\alpha = 0.05$

Tabela 1. Stężenie chlorofilu *a* w populacjach *Chlorella kessleri* hodowanych w obecności żelaza i wielkocząsteczkowych polikarboksylowych kopolimerów; Kontrola: kultury bez Fe i PCA, * dane chl a reprezentują średnią z 9 powtórzeń. σ – odchylenie standardowe, ** różnią się znacząco od wyników kontroli w oparciu o test t-Studenta przy $\alpha = 0{,}05$

Concentration			
PCA $[mol \cdot dm^{-3}]$	FeIII $[mol \cdot dm^{-3}]$	Chlorophyll *a*	
		$[mg \cdot dm^{-3}]^{*} \pm \sigma$	% of control
0,0	0.0	0.120 ± 0.004	100
0,0	$1.4 \cdot 10^{-7}$	0.168 ± 0.004**	140
$1 \cdot 10^{-7}$	$1.4 \cdot 10^{-7}$	0.204 ± 0.006**	170
$2 \cdot 10^{-7}$	$1.4 \cdot 10^{-7}$	0.228 ± 0.010**	190
$4 \cdot 10^{-7}$	$1.4 \cdot 10^{-7}$	0.240 ± 0.020**	200

Table 2. Concentration of chlorophyll *a* in populations of *Synechocystis aquatilis* cultivated in the presence of iron and high-MW copolymer polycarboxylates; Control: cultures without of Fe and PCA,* data of chl a represent mean of number of 9 replicates, σ - SD,** differ significantly from the results of a control based on Student's t-test at $\alpha = 0.05$

Tabela 2. Stężenie chlorofilu *a* w populacjach *Synechocystis aquatilis* hodowanych w obecności żelaza i wielkocząsteczkowych polikarboksylowych kopolimerów; Kontrola: kultury bez Fe i PCA, * dane chl a reprezentują średnią z 9 powtórzeń. σ – odchylenie standardowe, ** różnią się znacząco od wyników kontroli w oparciu o test t-Studenta przy $\alpha = 0{,}05$

Concentration			
PCA	FeIII	Chlorophyll *a*	
$[mol \cdot dm^{-3}]$	$[mol \cdot dm^{-3}]$	$[mg \cdot dm^{-3}]^{*} \pm \sigma$	% of control
0,0	0,0	$0{,}32 \pm 0{,}03$	100
0,0	$1{,}4 \cdot 10^{-7}$	$0{,}42 \pm 0{,}01$**	130
$1 \cdot 10^{-7}$	$1{,}4 \cdot 10^{-7}$	$0{,}51 \pm 0{,}02$**	160
$2 \cdot 10^{-7}$	$1{,}4 \cdot 10^{-7}$	$0{,}58 \pm 0{,}04$**	181
$4 \cdot 10^{-7}$	$1{,}4 \cdot 10^{-7}$	$0{,}69 \pm 0{,}02$**	210

The results also shown, that polycarboxylates PCA stimulate the growth of cyanobacteria *S.aquatilis* to a much larger extent than green algae *Chlorella*.

The results of experiments on the influence of low-MW polycarboxylate as nitrilotriacetic acid (NTA) on chlorophyll *a* concentration in cultures of *Scenedesmus microspina* and *Chroococcus* minor are presented in Fig. 3-4.

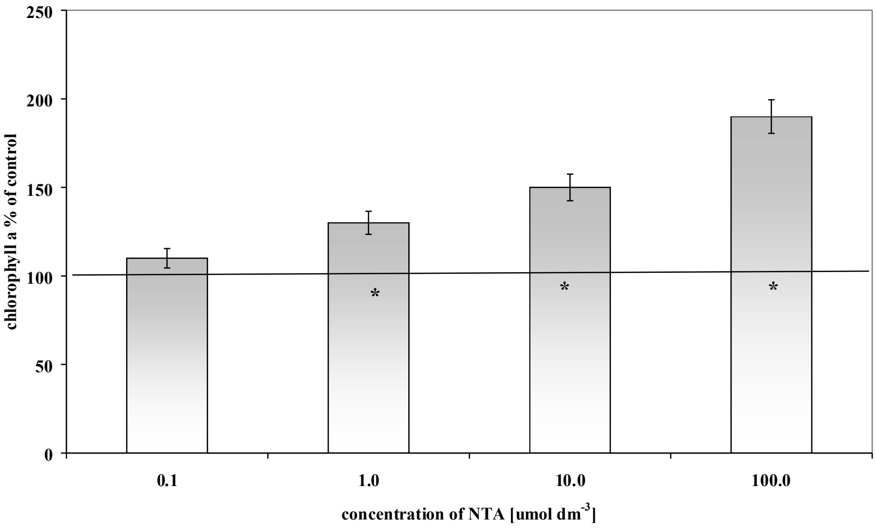

Fig. 3. Concentration of chlorophyll *a* in populations of *Scenedesmus microspina* cultivated under iron-deficient conditions ($Fe<10^{-7} mol \cdot dm^{-3}$) in the presence of low-MW polycarboxylate-NTA; Control = 100%: cultures without of NTA, data of chl a represent mean of number of 9 replicates. Error bars represent standard deviations. * differ significantly from the results of a control based on Student's t-test at $\alpha = 0.05$

Rys. 3. Stężenie chlorofilu *a* w populacjach *Scenedesmus microspina* hodowanych w warunkach niedoboru żelaza ($Fe<10^{-7}$ $mol \cdot dm^{-3}$) w obecności niskocząsteczkowego kwasu polikarboksylowego NTA; Kontrola = 100%: kultury bez NTA, dane chl a reprezentują średnią z 9 powtórzeń. Wąsy błędów reprezentują odchylenia standardowe; * różnią się znacząco od wyników kontroli w oparciu o test t-Studenta przy $\alpha = 0,05$

The addition of NTA water solution (0.1 to 100 $\mu mole \cdot dm^{-3}$ final concentrations) to medium resulted in an increase of chlorophyll *a* content in the population of green algae *S. microspina* by 30-100% compared to the control sample. In the case of cyanobacterium *C. minor*, the presence of nitrilotriacetic acid caused an increase of the amount of chlorophyll *a* by 60-900%, compared to control cells.

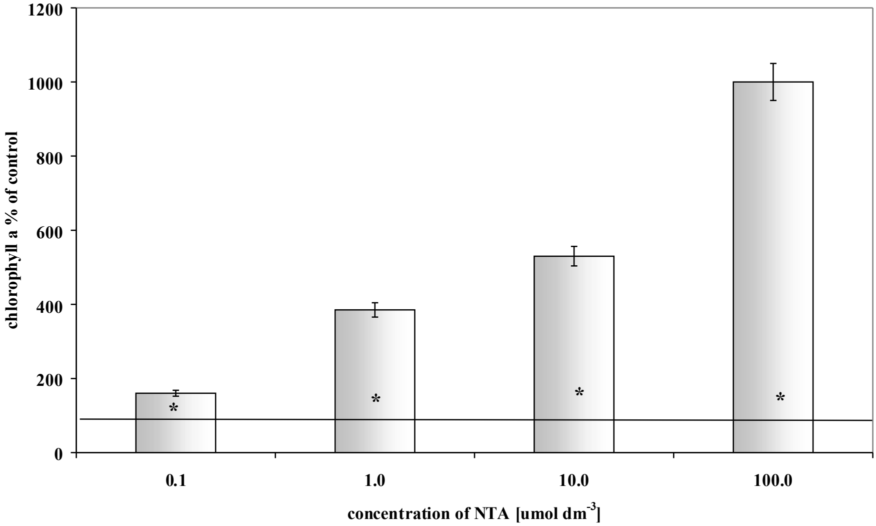

Fig. 4. Concentration of chlorophyll *a* in populations of *Gleocapsa minor* cultivated under iron-deficient conditions (Fe <10^{-7} mol·dm^{-3}) in the presence of low-MW polycarboxylate NTA; Control = 100%: cultures without of NTA, data of chl a represent mean of number of 9 replicates. Error bars represent standard deviations. * differ significantly from the results of a control based on Student's t-test at α = 0.05

Rys. 4. Stężenie chlorofilu *a* w populacjach *Gleocapsa minor* hodowanych w warunkach niedoboru żelaza (Fe<10^{-7} mol·dm^{-3}) w obecności niskocząsteczkowego kwasu polikarboksylowego NTA; Kontrola = 100%: kultury bez NTA, dane chl a reprezentują średnią z 9 powtórzeń. Wąsy błędów reprezentują odchylenia standardowe; * różnią się znacząco od wyników kontroli w oparciu o test t-Studenta przy α = 0,05

4. Discussion

Agricultural, domestic and industrial discharges have caused a drastic increase of organic substances capable of forming chelates with heavy metals in the environment, especially in the coastal zone where most of the poorly degradable compounds are introduced.

As primary production agents the green and blue-green algae are an important link of the aquatic food chain and are suitable for ecotoxicological tests with substances present in an aqueous environment. Chlorophyll-a is photosynthetic pigment that serves as a measurable parameter for all phytoplanktonic production.

The chlorophyll a production response of *C.kesslerii* or *S.aquatilis* (in control sample) indicates that cyanobacteria and green algae may be production of siderophores, ferric iron-chelating agents, under iron-deficient culture conditions. Siderohores function as iron-specific ligands which aid in the solubilization and assimilation of FeIII in environments where availability of iron acts to limit growth [8].

Polycarboxylates, when added to the growth medium of *Chlorella kessleri* and *Synechocystis aquatilis*, caused a strong growth-promoting effect on these phytoplankton cells at concentrations as low as 0.1 $\mu mol/dm^3$. Effect were strongly increased in concentrations varying in the range from $1\mu mol/dm^3$ to 4 $\mu mol/dm^3$.

The present studies showed that the addition of iron ($1.4\cdot10^{-7}$ $mol\cdot dm^{-3}$) and polycarboxylates in low concentrations ($1\cdot10^{-7}$-$4\cdot10^{-7} mol\cdot dm^{-3}$) to *Chlorella* and *Synechocystis* cultures caused a significant stimulation chlorophyll-a production (60-110%) of both phytoplankton species, in comparison to the control sample. Addition of PCA in presence of iron at concentration ($1.4\cdot10^{-7}$ $mol\cdot dm^{-3}$) also increased production of chlorophyll a 30-70% as compared with the cultures exposed to iron only, at the same concentration.

The results also shown, that polycarboxylates PCA stimulate the growth of cyanobacteria to a much larger extent than green algae. Therefore, the presence of synthetic polymers such as PCAs in estuarine and coastal waters may result in significant influence on the metabolism and growth of planktonic algae in marine environment.

The chemical speciation of trace metals in sea water, especially as a result of complexation by organic substances, has important effects on the biogeochemical cycling and biological activity of these metals. Organic complexation can markedly influence the availability of a metal to marine organisms, and reduce, eliminate or enhance its toxicity [12, 23].

Many authors have postulated that the interaction between organic matter and trace elements results in significant ecological consequences [13].

Modern interest in polycarboxylates as detergent constituents has largely been directed towards their use as co-builders, substitutes for polyphosphates, antiredeposition and dispersant factors. Most PCA have a carbon backbone molecular structures and are poorly biodegradable under normal conditions [5].

Another factor which must be taken into account when environmental implications at PCA use considered is chelation of heavy metals. In agreement with literature data, our results [7] show that, the biological activity of cobalt was considerably modified in the presence of PCA. Based on the results measurements of chlorophyll-a content and photosynthesis rates it was shown that polycarboxylates reduce the toxicity of cobalt in *Scenedesmus armatus* and *Synechocystis aquatilis* populations .

According to recent findings [19] the detergent ingredient, Zeolite A-Polycarboxylic Acid (PCA), may have played a role in exacerabiting the mucilage phenomenon, observed in the Northen Adriatic Sea, after the introduction of phosphorous free detergents. On the other hand experimental study of Monti et.al., [14] has not revealed any evident causal relationship between the presence of Zeolite A - PCA system and the formation of mucous aggregates [14].

Polycarboxylates show strong complexing properties toward heavy metals. There is a possibility, that PCA might effect algal growth by increasing the availability of limiting trace elements e.g. iron via chelation. This could be a tentative explanation of the results shown in Fig.1-2 and Tab.1 -2.

NTA, when added to the growth medium of *Scenedesmus microspina* and *Chroococcus minor* exerted a strong growth-promoting effect on these microorganisms. Nitrilotriacetic acid solutions, stimulated the growth of cyanobacterium *Chroococcus minor* to a much larger extent than in the case of green algae *Scenedesmus microspina*. The presence of NTA in estuarine and coastal waters is thus likely to have a significant and varying effect on the metabolism and growth of bacterial and phytoplankton cells in the marine environment. One important feature of the environment which may by affected is the succession of species. This requires a separate study.

Nitrilotriacetic acid has been shown to be a very strong chelating agent [6, 18]. Graneli and Edler [4] demonstrated the ability of NTA to chelate copper(II) in coastal waters thereby reducing toxicity due to by copper(II) and stimulating the growth of the toxic red tide dinoflagellate *Prorocentrum minimum* and diatom *Skeletonema costatum*.

However, the toxicity of copper to some organisms is sometimes enhanced in the presence of certain organic substances. Anabaena sp., for example, is inhibited by copper to a larger extent in the presence of nitrilotriacetic acid [10]. On the other hand, soil and/or waste-water microorganisms able to grow in media with NTA as the only carbon source have been reported [3], among them some strains recognised as *Pseudomonads* [11].

While polymeric carboxylic acids (PCAs) are poorly biodegradable [5] decomposition of NTA takes place in freshwater. In sea water, however, such degradation of NTA is rather limited [6, 18]. More than 90% of NTA is generally removed during sewage treatment processes and may cause problems in the sewage sludge [6, 18]. In the literature, the eutrophication aspects of complexing agents from P-free washing powders seem to be treated as one problem while remobilisation of heavy metals in the environment is investigated separately.

NTA might affect bacterial, cyanobacterial and algal growth by one of the three mechanisms: supplementing nitrogen; increasing or decreasing the availability of limiting trace elements due to chelation; stimulating the growth of species to a varying degree. These mechanisms may occur simultaneously.

Therefore, the introduction of synthetic polymers capable of forming complexes of similar nature, such as polycarboxylates into marine ecosystems may have substantial ecological consequences. Metal-organic complexses may affect biological processes in phytoplankton populations, especially in the coastal zone characterized by a high degree of pollution and eutrofication.

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Syntetyczne związki kompleksujące w środowisku wodnym: wpływ na organizmy fitoplanktonowe

Streszczenie

Wraz z rozwojem cywilizacji w środowisku morskim pojawiło się szereg substancji (płyny czyszczące, farmaceutyki, kosmetyki i farby) będących efektem działalności gospodarczej prowadzonej przez człowieka.

Wśród związków organicznych istotną pozycję zajmują detergenty. Ograniczenie stosowania fosforanów w środkach piorących i detergentach wiązało się z poszukiwaniem i wprowadzaniem na ich miejsce nowych substancji. Wśród proponowanych budulców detergentów, szczególną uwagę zwracają kwasy aminokarboksylowe, a wśród nich kwas nitrylotrioctowy oraz PCA w formie polimerów. Związki te wykazują silne powinowactwo do jonów metali ciężkich.

Zjawisko to jest bardzo ważnym, ale zwykle niedostrzeganym elementem antropopresji. Jego waga rodzi potrzebę badań nad skutkami obecności tych substancji w naturalnych zbiornikach wodnych, do których wraz ze ściekami komunalnymi i przemysłowymi są wprowadzane.

W niniejszej pracy przedstawiono wyniki badań nad wpływem związków z grupy kwasów polikarboksylowych na wzrost organizmów fitoplanktonowych występujących w strefie przybrzeżnej Bałtyku Południowego.

Wykazano stymulację produkcji chlorofilu a w populacjach dwóch szczepów zielenic (*Scenedesmus microspina*, *Chlorella kessleri*,) oraz dwóch szczepów cyjanobakterii (*Synechocystis aquatilis*, *Gleocapsa minor*) inkubowanych w warunkach stresu żelazowego w obecności PCA. Uzyskane wyniki wskazują, że kwasy amino- i polikarboksylowe mogą ułatwiać pobieranie żelaza w warunkach jego niedoboru i w ten sposób zwiększać produkcję fitoplanktonu. Wykazano większą wrażliwość cyjanobakterii na działanie PCA w porównaniu do glonów z grupy zielenic. Tak więc, obecność kwasów polikarboksylowych w środowisku wodnym prowadzić może do zmian dostępności biologicznej jonów metali.