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Original Research

# New Micronutrient Fertilizer Biocomponents Based on Seaweed Biomass

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### **Abstract**

In the present paper, the novel environmentally friendly micronutrient fertilizer biocomponents produced via biosorption and based on the biomass of seaweed were introduced. The utilitarian properties of new preparations were examined in germination tests on *Lepidium sativum*. The application of micronutrient biocomponents with zinc resulted in the higher mass of plant and higher content of zinc in comparison with the untreated group and reference materials, leading to the biofortification of plants with this micronutrient (a more than 20-fold increase in zinc level was obtained). It was observed that the dosage of zinc influenced plant mass and element content of plants. Statistically significant correlations between zinc and other microand macronutrients were observed. Also, a strong positive correlation (0.55) between zinc and plant mass was found.

The micronutrient biocomponents produced via the biosorption process can constitute an alternative tool for micronutrient fertilization as preparations characterized by high bioavailability of nutrients and high biodegradability constituting an "eco-friendly" method for micronutrient biofortification of plants.

fertilizers [6].

**Keywords:** waste biomass, biosorption, zinc, micronutrient fertilizers, bioavailability

# Introduction

The role of micronutrients is crucial for living organisms. Their participation in proper functioning of various biochemical pathways was proved. There are some notifications describing micronutrient deficiency in soils and plants, and hence in humans as a problem greater than hunger [1]. Micronutrient malnutrition was indicated as the main reason for serious health problems and developmental disorders [2]. From all micronutrients, zinc deficiency contributes to a higher extent to mortality [3]. Zinc is an essential micronutrient due to its important role in crucial biochemical processes in living organisms [4]. The availability is mainly affected by low content of the micronutrient in soils, high soil pH, high salt concentration, and high

effective strategy for micronutrients delivery [8]. There are two ways of plant biofortification: with the use of genetic engineering or via micronutrient fertilization. Genetic biofortification is a cost-effective solution, although the regulations on genetically modified food are still very restrictive, which can hamper its implementation [9]. Agronomic biofortification is a more accepted tool and its implementa-

bating micronutrient deficiency [7]. It constitutes the most

phosphate content [5]. Zinc deficiency was observed also due to modern agriculture and inappropriate application of

Biofortification of plants with micronutrients is currently presented as the main and most efficient tool for com-

fication is considered the most efficient way to combat micronutrient malnutrition [11]. Despite the very important role of micronutrients and their influence on plant condition

tion readiness is higher [10]. Currently, agronomic bioforti-

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and human health, still relatively low attention is put on innovations in micronutrient fertilization [12]. Due to some disadvantages of the application of traditional micronutrient fertilizers (eutrophication, toxicity), there is a need for new innovative preparations that are cheap, biodegradable, and characterized by high bioavailability of nutrients [13].

Biosorption was described as the ability of the surface of non-living biomass to bind and concentrate metal cations [14]. The biosorption was widely used in wastewater treatment for the purification of water solutions from toxic metals [15]. Different materials were used as biosorbents while macroalgae and microalgae were shown to be characterized by the best sorption properties [16, 17]. Research on the use of the biosorption process in animal feeding currently is underway. The use of biomass of algae enriched with micronutrient ions as an alternative for traditional micronutrient products (inorganic salts and cheaters). It was shown that the application of micronutrient feed additives instead of inorganic salts and chelates - led to the biofortification of animal meat, milk, or eggs with micronutrients [18, 19]. There is also some research describing the application of different types of biomass (peat, compost, berries, seeds) enriched with micronutrients as potential micronutrient biocomponents [20, 21].

The aim of the present work was to examine the possible application of algae biomass enriched with zinc ions in the biofortification of *Lepidium sativum* in comparison with commonly used inorganic salts and chelates.

## **Experimental Procedures**

## Sample Preparation

For the biosorption experiments, three types of algae biomass were used: macroalgae *Fucus* sp. (Fucus), Baltic seaweed (Seaweeds) collected from the Baltic coast during summertime, and postextraction residues (Residues) after supercritical CO<sub>2</sub> extraction conducted on these seaweeds. The biosorption of zinc(II) ions by biological materials was conducted in batch mode in stirred tank reactors (60 L). The concentration of Zn(II) ions (as ZnSO<sub>4</sub>·7H<sub>2</sub>O (Chempur, Poland)) in the solution was 300 mg/L, pH 5 measured in 25°C with the use of a Mettler Toledo SevenMulti pH meter, Switzerland. The concentration of the biomass was 1.0 g of dry mass (DM)/L according to our previous studies [22]. After the experiment, the solution was then filtered and the biomass was air-dried. The content of elements in the enriched biomass was examined by ICP-OES.

## Germination Tests

The aim of experiments was to evaluate the effect of different types of algae biomass enriched with Zn(II) ions in the biosorption process on the germination of seeds and element content of germinated plants, when compared with the control groups of deionized water, cheated, and inorganic salt. Doses of Zn(II) used in the experiment varied from 1.0 to 6.0 mg/Petri dish (four different doses) for each

fertilizer. On this basis, the optimal dose of Zn(II) in the fertilizer was chosen. Five types of fertilizer components were used: macroalgae enriched with Zn(II) ions - Baltic seaweed (Baltic Seaweed-Zn), post-extraction residues (Residues-Zn), Fucus sp. (Fucus-Zn), Zn-EDTA chelate (Symposia Zn, Anwil, Poland), and ZnSO<sub>4</sub>·7H<sub>2</sub>O (Chempur, Poland). To compare the fertilizer properties, germination tests were performed on garden cress Lepidium sativum according to the international norm (the International Seed Testing Association). Plastic Petri dishes covered with cotton (approximately 5.0 g) soaked with deionized water were prepared. On each dish, 50 seeds of garden cress were placed in rows at equal distances from each other. In the next step seeds were subjected to stratification at 1°C for three days. After stratification, appropriate amounts of particular fertilizer were spread evenly on Petri dishes. Each probe was taken in triplicate. Germination tests were performed in a seed germinator (Jacobsen J120/OS) at 25°C for 10 days after stratification. Plants were watered with 5 ml of deionized water during germination test. After the experiment the plant yield from each plate was dried to the constant weight, mineralized, and multielemental analysis by ICP-OES was carried out (three measurements of each probe).

# Analytical Methods

Baltic Seaweeds-Zn, Residues-Zn, and Fucus-Zn (0.5 g), and germinated plant (whole mass from the plate) were purified from organic matter with concentrated nitric acid – 69% m/m (5 ml), spectrally pure (Suprapur, Merck, USA) in teflon bombs in a Milestone Start D microwave oven (USA). The select parameters of the process assured the complete digestion of samples. After mineralization, samples were diluted 10 times with re-demineralized water (Millipore Simplicity) and underwent multielemental analysis. The concentration of elements in digested biomass was determined by ICP-OES Varian-Vista MPX (Australia), equipped with an ultrasonic nebulizer CETAC U5000AT+. The analyses were carried out in a Laboratory Accredited by the Polish Centre of Accreditation (PCA) according to PN-EN ISO/IEC 17025:2005. Quality assurance of the test results was achieved by using Combined Quality Control Standard from Ultra Scientific, USA. The samples were analyzed in three repeats (the reported results of analyses were arithmetic mean, the relative standard deviation was <5%).

# Statistical Analysis

Obtained results were statistically elaborated upon using Statistica software v. 9.0. Normality of the distribution was tested with the use of Shapiro-Wilk Test. Brown-Forsyth test was used for the analysis of homogenity of variance for normal distribution. In the groups that fulfilled the condition of homogenity of variance, an F-test was conducted. Statistical tests for other-than-normal distribution were carried out using Kruskal-Wallis test. It was assumed that the results were statistically significant at p<0.05 and significant at p<0.1.

Material			Γ	The content of	of nutrients in 1	biomass [mg·kg	g-1]		
Wiaterial	Zn	Fe	Mn	Cu	Ca	S	Mg	P	K
Baltic Seaweeds	227±34	3,203±640	366±50	80.7±12.1	17,193±3,439	12,756±2,551	3,836±767	810±121	3,259±652
Baltic Seaweeds-Zn	30,100±6,020	5,070±1,010	94.1±14.1	51.6±7.7	11,900±2,380	23,900±4,790	2,130±426	2,130±425	1,240±242
Residues	98.0±14.7	4,493±899	531±80	16.4±2.5	14,580±2,916	24,420±4,884	6,788±1,358	2,452±490	21,082±42,164
Residues-Zn	29,700±5,940	4,540±907	105±16	28.5±4.3	5,070±1,020	20,800±4,150	1,130±226	1,970±2,390	1,370±273
Fucus	35.9±5.4	311±46.7	57.6±8.6	2.35±0.35	9,756±1,951	17,540±3,508	4,099±820	921±138	2,125±425
Fucus-Zn	59,400±11,880	400±60	14.7±2.2	23.2±3.5	8,750±1,750	23,700±2,730	2,020±403	519±78	1,350±227

Table 1. The content of nutrients in biomass enriched with zinc.

### Results

The element content of different types of biomass enriched with zinc(II) ions in the biosorption process is presented in Table 1. The highest biosorption capacity for zinc(II) ions was observed for *Fucus* sp. and it was evaluated as 6%. It was twice higher than biosorption capacity of Baltic Seaweeds and Residues. Multielemental analysis showed that macroalgae enriched with zinc(II) ions constituted a source of significant amounts of elements important for plants such as iron, calcium, sulfur, and potassium. After biosorption there is a visible Ca, K, and Mg content decrease (except Residues), in which alkali metals were exchanged with micronutrients (biosorption due to ion exchange).

The influence of different methods of micronutrient fertilization on the mass and content of Zn, Cu, Fe, K, and Ca are presented in Table 2 (elements with normal distribution in statistical result analysis). In Table 3 content of Mn, Mg, Na, S, and Si (elements with other-than-normal distribution in statistical result analysis) is presented. It was shown that increasing doses of zinc led to the increase of plant mass and zinc content. For most cases statistically significant differences were found in zinc, potassium, and calcium content in plants. In Table 2 the antagonism between Zn/Fe, Zn/Mn, and Zn/Ca is visible; with increasing zinc doses, decreases of Fe, MN, and Ca content in plants was

obtained. Zinc was changed with these ions due to biosorption. Analysis of changes in plant mass in relation to different zinc doses enabled us to find optimal doses of zinc for the fertilization of *Lepidium sativum* (4 mg Zn/dish).

The most important correlations between elements in plants are presented in Table 4. The positive correlation between zinc and plant mass was observed (0.55). The existence of negative correlations between zinc and other cationic elements such as Ca (-0.68), K (-0.62), Na (-0.61), Mg (-0.51), and Mn (-0.50) was found. It confirms observations about antagonism between these elements and zinc, and explains the influence of ion exchange during biosorption, which is also related to these ions. Table 5 presents the comparison of element correlations for plants fertilized with traditional fertilizer and with the use of new components with micronutrients. It can be observed that the application of biocomponents with zinc slightly increased some positive correlations between substantial elements, while negative relationships were weakened. Algae components increased the correlation between Mn and Mg and between S and Si. Also, correlation between Fe and Cu was improved. Reduction of antagonistic influence of zinc on Ca, K, Na, and S also was remarkable. The content of Zn(II) in plants fertilized with different zinc components is shown in Fig. 1. Increased doses of Zn(II) result in increased content of this micronutrient in plants.

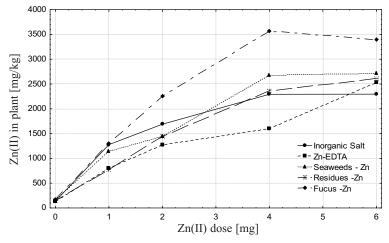


Fig. 1. The content of zinc in plants fertilized with different zinc components.

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	Plant mass [g]	[ø] ss	Zn		Ö		Я		×		Ca	
Dose Mean	. 1	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
	1	0.00329	169abcdefghijklmnopqr	12.9	7.54ª	0.972	111ab	19.3	14,800a.b.c.d.e.f.g.h.i.j.k.l.m.n.o.p	855	2,030ab.c.de.f.g.hi.j	39.0
0.0698	1	0.00160	1,280as.t.u.w.x.y.z.aa.ab.ac.ad.ae.af	312	15.5 <sup>b,c</sup>	7.22	125cd	6.85	21,700a.qr.s.t.u.w.x.y	1,160	3,380a,k,l,m,n,o,p,q	77.9
0.0777ª	1	0.00580	1,690b,ag,ah,ai,aj,ak,al,am,an,ao,ap,aq	9.09	11.0 <sup>d</sup>	1.82	119e,f	6.15	19,600 <sup>2</sup> ,aa,ab,ac,ad,ae,af	474	3,180°5,tu,w,x,y,z	155
0.0823b,c,d	i .	0.00405	2,290c.s.ar.as.at.au.aw.ax.ay.az.ba, bb.bc.bd	268	6.02 <sup>b</sup> ,e,fg,h,i	0.450	96.4 <sup>g,h</sup>	8.90	12,700qaa,ag,ah,ai,ai,ak,al,am, an,ao,ap,aq,ar,as,at,au	654	1,880k.s.aa,ab,ac,ad,ac,af,ag,ah, ai,aj,ak,al,am	9.77
0.0703	i .	0.00708	2,300d,t,be,bf,bg,bh,bi,bj,bk,bl,bm,bn,bo,bp	00.9	11.8	2.13	126 <sup>i,j</sup>	1.86	14,800rawaxay.az.ba.bb.bc.bd, be.bf.bg.bh.bi.bj.bk	424	2,860an,ao,ap,aq	155
0.0625 <sup>b,e,f,A</sup>	1	0.0132	795ag,ar,be,bq,br,bs,bt,bu,bw,bx,by,bz	69.4	15.2°k	2.31	162 <sup>k,1</sup>	34.0	23,700b,ag,aw,bl,bm,bn,bo,bp,bq	1,880	3,490b,aa,ar,as,at,au,aw,ax	552
0.0602 <sup>c,g,h,i</sup>	1	0.0121	1,270e,as,bf,ca,cb,cd,ce,cf,cg,ch,ci,	78.6	21.8a.dfj.l.m,n,o,p.q.r.s. t,u,w,A,B	5.24	144 <sup>տ,ո</sup>	17.8	24,100°, ah, ax, br, bs, bu, bw, bx	999	3,440cabay,az,ba,bb,bc,bd	187
0.0707		0.000557	1,600 fibq.cm,cn,co,cp,cq,cr,cs,ct,cu,	299	6.14c,k,l,ab,ac,ad	098.0	92.3°p	17.5	13,700s.ab.bl.br.by.bz.ca.cb.cc, cd.ce.cf.cg.ch.ci.cj.ck	2,000	1,560l.tan,ar,ay,be,bf,bg,bh,bi,bj,bk,bl,bm,bn,bo,bp,bq	278
0.0662 <sup>j.k</sup>		0.00101	2,530g.u.ah.br.ca.cm.cy.cz.da.db.dc, dd,de,df.dg,dh	119	13.3	3.07	1309-г	9.37	15,300tbm,bs,cl,cm,cn,co,cp,	1,230	2,410 <sup>br,bs,bt</sup>	124
0.0689		0.00343	159 w.ai,at,bg,cb,cn,cy,di,dk,dl,dm, dn,do,dp,dq,dr,ds	15.0	15.2 g,ab	0.854	534a.c.eg.i.k.m.o.q.s.t.u.wx.yz, aa.ab.ac.ad.ae.af	330	25,600 <sup>d,ac,ai,ay,by,cl,cz,da,db</sup> , dc	2830	4,770d.m.u.ac.ao.as.az.be,br.bu, bw.bx,by,bz,ca,cb,cc,cd,ce,cf	1,160
0.0683		0.000153	1,140hau,bh,cz,di,dt,du,dw,dx,dy, dz,ea,eb,ec	117	11.7 <sup>A</sup>	1.22	180%	11.3	24,600e.aj.az bz.cm,dd,de,df,dg	696	3,570adbf.cg.ch,ci,A	93.0
0.0692		0.00309	1,440i.aw,bi,da,dj,ed,ee,ef,eg,eh,ei, ej,ek,el,em	248	12.2 <sup>m</sup>	2.17	183 <sup>t,ah</sup>	18.8	23,800 f.ak,ba, ca,cn,dh,di,dj,dk	1,380	3,490e,ae,bg,bu,cj,ck,cl,cm	346
0.08497e.gi,i,m	l =	0.00153	2,680j.xaj.bs.cd.co.dk.dt.ed.en.eo,	97.2	12.4"	4.08	181 <sup>u,ai</sup>	45.3	13,900u.ad.bn.bt.cz.dd.dh.dl, dm.dn.do.dp.dq.dr.ds.dt.du	1,130	1,860n,wat,ba,bw,eg,ej,en,eo,	215
0.0758n		0.00342	2,720ky,ak,bt,ce,cp,dl,du,ee,et,eu, ew,ex,ey,ez	368	12.8°	1.95	217 <sup>w,aj</sup>	34.4	22,900g,al,bb cb,co,dl,dw,dx,dy	2,130	3,100 <sup>bh,bx,cw,cx,B</sup>	98.6
0.0755°		0.000351	$146^{z,al,ax,bj,cf,cq,db,dw,ef,en,et,fa}, \\$ $^{tb,fc,fd,fe,ff,fg}$	11.5	13.0°	0.983	60 lb,d,fh,jl,n,p,rag,ah,ai,aj,ak, al,am,an,ao,ap,aq,ar,as	201	34,000h.w.ae.am.bc.bo.cc.cpbu.da, de.di.dm.dw.dz.ca.,eb.ec.ed.ef.eg.eh.ei	5,340	5,090 (f.o.x.,af.,ap,au,bb,bi,bs,ck, cn,ew,cy,cz,da,db,dc,dd,de,df,A	211
0.0667 <sup>1,p</sup>		0.000819	552 am,ay,bk,cr,dc,eg,eo,eu,fh,fi,fj,fk, fl,fm,B	404	12.2ª	0.816	159 <sup>x,ak</sup>	3.97	24,400i.an.bd. cd.cq.dn.dz.ej.ek	862	3,350g.ag.bj.by.co.cy.dg.dh	254
0.0693		0.00205	1,440 <sup>laz,b</sup> l,dd,dm,ep,ew,fa,fh,fn,fo, fp,fq,fr,fs	241	12.6 <sup>r</sup>	2.05	161 <sup>y,al</sup>	13.7	23,200jiao,be, ce,cr,do,ea,el,em	1,950	3,500 <sup>h</sup> ,aw,bk,bz,cp,cz,di,dj	160
0.0853 <sup>fh,k,p</sup>		0.00193	2,370m,aa,bu,cg,cs,dn,dx,eh,fb,fi,fn, ft,fu,fw,fx	323	12.5°	1.53	148 <sup>z,am</sup>	17.7	14,800x.bp.bw,db,df,dj,dx,eb,ej,	351	1,910p.y.ba.aw,bc.ca,ch,cl,da,dg ,di,dk,dl,dm,B,C,D	33.2
0.0747		0.00375	2,610n,ab,an,bw,ch,ct,do,dy,ei,fe,fj, fo,fz,ga,gb,gc	266	15.0 <sup>h,ac</sup>	2.90	193адап	11.2	23,900kap,bf, cf.cs,dp.cc,en,et	737	3,150ai,bl,cb,cq,db,dn,C	214
	1											

Darke	Zn	Plant mass [g]	[g] ss	Zn		Cu		Fe		Ж		Ca	
rione	[mg]	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Control		0.0706	0.00329	169a,b,c,de,f,g,h,ij,k,l,m,n,o,p,q,r	12.9	7.54ª	0.972	111 <sup>a,b</sup>	19.3	14,800a,b,c,d,e,f,g,h,ij,k,l,m,n,o,p	855	2,030a,b,c,d,e,f,g,h,i,j	39.0
	0	0.0576ad.m.n.o.q.r.s.	0.0153	172 ac, ao, ba, bm, ci, cu, de, dz, ej, eq, ex, fp, ft, fz, gd, ge, gf gh	17.5	15.0 <sup>i,ad</sup>	4.29	187ab,ao	23.5	$39,800^{\rm Ly,af,aq,bg,bq,bx,cg,ct,dc},\\ {\rm dg,dk,dq,dy,ed,ek,em,eo,et,eu,ew,ex,ey}$	2,240	$5,620^{i,q,z,aj,aq,ax,bd,bm,bt,ci,}$ $\mathrm{cm,cr,cx,dh,dj,dk,dn,do,dp,dq,dr}$	777
		0.0733	0.00304		407	9.76	0.778	133ac,ap	10.1	22,500m.ar,bh, ch.cu,dr,ef,ep,au	1,700	3,170ak,bn,cc,cs,dc,do,D	318
Fucus-Zn	2	0.0745 <sup>B</sup>	0.00485	2,250pad,bx,cj,dq.ca,ek,fe,fk,fq,ge,gi,gl,gm	102	10.9 <sup>u</sup>	1.26	139 <sup>ad,aq</sup>	13.8	23,100n,as,bi, ci,cw,ds,eg,eq,ew	591	3,450j.al, bo,cd,ct,dd,dl,dp	292
	4	0.0795 <sup>ix,A</sup>	0.00171	0.00171 3,570q.acap.bc.bo.by.ck.cw.dg.dr.cb	109	9.81 <sup>w</sup>	1.23	134ае,аг	15.9	21,800o.atbj. ej.ex.dt.eh.er.ex	1,080	2,940bp.ce,de,dq	582
	9	0.0764 <sup>s</sup>	0.00231	3,400rafaq,bd,bp,bz,cl,cx,dh,ds,ec, em,fg,fm,fs,fx,gc,gh,gk,gm,A	517	13.7 <sup>B</sup>	2.41	139 <sup>af,as</sup>	90.6	9.06 22,900paupkekeydueisesey	2,010	3,260 am, bq.cf.cu,df,dm,dr	229
Statistically	signific	ant differences f	or a given	Statistically significant differences for a given nutrients with normal distribution ab. (p<0.05), AB. (p<0.1), N=54	stribution	1 a,b (p<0.05), A,B	(p<0.1),	N=54.					

Fable 2. Continued

The best effect was achieved for Fucus-Zn while the weakest biofortification was obtained for Zn-EDTA.

As was presented in Fig. 2, Transfer Factor of Zn(II) was inversely correlated with Zn(II) dose. This means that the assimilation of micronutrients by plants decreases with increasing doses. The dependence between zinc dose and mass of plant is presented in Fig. 3. The highest values of plant mass were obtained for dose 4 mg Zn/dish. Further increasing of zinc dose led to a decrease of plant mass. Taking into account the impact of different zinc doses on the mass of plant and micronutrient content, it can be deduced that 4 mg Zn per dish is the best dose for micronutrient biofortification of *Lepidium sativum*.

### **Discussion**

In the present study, it was observed that zinc fertilization with the use of different fertilizer biocomponents led to biofortification of plants. Six experimental groups (Baltic Seaweed, Residues, Fucus and the control groups: Znchelate, inorganic salt, and untreated) were tested in triplicate as fertilizer materials. The biomass from each plate was collected separately, and multielemental composition was analyzed (also in triplicate; N=54).

The biosorption of the three different types of algae biomass led to the enrichment of biological material with zinc. The biomass of Fucus sp. was shown to be the most efficient biosorbent. Zn(II) content in Baltic Seaweed and Residues was two times lower (30,100 and 29,700 mg/kg respectively). The comparable biosorption capacity of Baltic Seaweed and Residues suggests that extraction procedures did not significantly affect the sorption capacity of biological material. It also confirms that the surface of the biomass (cell wall) mainly participates in the biosorption process. All tested materials were shown to be a rich source of other micro- and macronutrients, especially Fe, Ca, S, Mg, and K (Table 1). It was proved that increasing zinc doses led to increased plant mass and zinc content in plants (Table 2, Fig. 1). The differences in plant yield between groups in the experiment were also observed (Table 2). The mass of plants fertilized with zinc was higher than in the control group (0.0706 g) in all groups fertilized with 4 and 6 mg per dish besides Zn-EDTA and Inorganic salt at 6 mg dose (0.0662 g and 0.0703 g). The conducted experiments showed that zinc fertilization with the use of Fucus-Zn was the most efficient, while Zn-EDTA was characterized by the lowest transfer of Zn(II) ions. Fig. 2 shows that the transfer factor of Zn(II) decreased with increasing zinc doses. It showed that overfertilization leads to lower assimilation of nutrients by plants.

Conducted experiments showed that there is a positive correlation between plant mass (0.55) and Zn dose (Table 4). Zinc is one of the most important micronutrients and plays an important role as catalyst, structural, and regulatory ion, being necessary for various biochemical reactions and physiological functions such as photosynthesis, respiration, and chlorophyll biosynthesis [23], and as it was shown has influence on plant mass. The strong correlation was inde-

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Table 3. Content of nutrients in plants (mg·kg<sup>-1</sup>). Elements with other than normal distribution in statistical result analysis.

Probe	Zn Dose	N	ſn	N	Ig	N	la	5	S	S	i
FIODE	[mg]	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Control	-	29.1	0.0411	3,760	127	5,630	936	11,300	1,090	169	12.9
	1	35.9	1.11	5,960	77.8	7,290	194	22,100	192	1,280	312
Inorganic	2	33.5	1.57	5,770	143	6,720	1,210	21,000	608	1,690	60.6
Salt-Zn	4	28.1ª,A	1.43	3,800	92.4	2,680 <sup>a,b</sup>	303	12,300	729	2,290 <sup>a,b</sup>	268
	6	34.0	1.51	5,790	296	4,540	575	19,700	698	2,300	6.00
	1	34.6	0.395	5,690	190	7,390	1,280	23,200	734	795	69.4
Zn-EDTA	2	35.9	2.84	5,330	289	7,280	1,960	22,500	1,220	1,270	78.6
ZII-EDIA	4	24.6 <sup>b,c,B</sup>	4.22	3,190 <sup>A,B</sup>	615	2,710 <sup>c,A</sup>	687	12,600	2,550	1,600 <sup>c,d,A</sup>	299
	6	31.9	1.95	4,760	85.0	4,520	896	20,100	497	2,530	119
	0	72.4 <sup>b,A</sup>	15.6	6,040	417	10,700	1,340	19,400	1,650	159 <sup>a,c</sup>	15.0
Baltic	1	43.3	0.0252	6,410	113	10,000	972	22,320	838	1,140	117
Seaweeds	2	42.7	1.49	6,640	291	8,220	940	22,300	654	1,440	248
-Zn	4	30.1	2.23	3,590	247	4,730	1,560	11,700	722	2,680	97.2
	6	44.1	0.574	6,330	164	8,700	1,300	23,100	952	2,720	368
	0	125 <sup>a,b</sup>	24.3	6,370	88.6	13,100 <sup>a,A</sup>	1,500	21,000	1,020	146 <sup>b,d</sup>	11.5
Residues- Zn	1	43.9	0.463	6,710 <sup>A</sup>	191	8,770	220	23,100	937	552	404
	2	42.4	2.63	6,650	313	8,180	206	22,000	457	1,440	241
	4	31.0	0.321	3,530 <sup>c</sup>	209	3,850	246	11,700	108	2,370	323
	6	43.6	0.945	6,280	206	7,650	1,080	22,800	328	2,610	266
	0	52.9 <sup>B</sup>	8.17	7,210 <sup>B,C</sup>	661	19,400 <sup>b,c</sup>	2,180	23,200	3,090	172 <sup>A</sup>	17.5
	1	36.4	1.48	5,790	229	8,670	414	20,400	256	1,290	407
Fucus-Zn	2	34.8	1.02	5,580	198	8,500	626	20,200	397	2,250	102
	4	31.8	1.46	5,200	385	7,620	497	19,700	864	3,570	109
	6	35.4	2.51	5,710	162	8,310	1,000	21,400	599	3,400	517

Statistically significant differences for a given nutrients without normal distribution  $^{a,b...}$  (p<0.05),  $^{A,B...}$  (p<0.1), N=54.

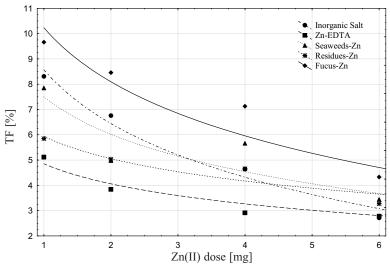


Fig. 2. The change in zinc transfer factor for different zinc doses and different components.

	Plant mass	Al	Ca	Cr	Cu	Fe	K	Mg	Mn	Na	P	S	Si
Al	0.084												
Ca	-0.47	0.52											
Cr	-0.26	0.076	0.27										
Cu	-0.46	0.25	0.28	0.059									
Fe	-0.03	0.86	0.61	0.13	0.12								
K	-0.43	0.33	0.88	0.34	0.23	0.40							
Mg	-0.33	0.17	0.62	0.27	0.06	0.26	0.68						
Mn	-0.076	0.76	0.67	0.31	0.10	0.87	0.57	0.40					
Na	-0.42	0.35	0.85	0.35	0.14	0.38	0.94	0.65	0.53				
P	-0.40	-0.23	0.11	0.22	0.18	-0.13	0.19	0.60	-0.12	0.18			
S	-0.43	-0.064	0.27	0.23	0.33	0.00	0.43	0.57	0.09	0.35	0.62		
Si	-0.21	0.82	0.73	0.25	0.22	0.94	0.56	0.38	0.93	0.53	-0.053	0.11	
Zn	0.55	-0.25	-0.68	-0.21	-0.21	-0.37	-0.62	-0.51	-0.50	-0.61	-0.14	-0.31	-0.49

Table 4. Correlation matrix of element content in plants (N=54, p<0.05).

Strong correlations were bolded.

pendent of zinc fertilization (it was observed for traditional zinc fertilizers and new biocomponents). It can be explained by the participation of zinc in the synthesis of plant growth hormones [24].

The statistical analysis of multielement content of plants showed the presence of some element interdependencies. Zinc was negatively correlated with Ca (-0.68), K (-0.62), Na (-0.61), Mg (-0.51), and Mn (-0.50) (Table 4). It can be explained by the divalent character of these cations and their mutual competition as a result of this feature or removal of these ions during the biosorption process.

Alkali metal ions were exchanged with zinc ions during biodorption (Table 1). In Table 2 antagonism between Zn/Fe, Zn/Mn, Zn/Ca is also visible – with increased zinc doses came decreases in Fe, Mn, and Ca.

Very strong positive relationships were found between: K/Na, Fe/Si (0.94)> Mn/Si (0.93) > Ca/K (0.88) > Fe/Mn (0.87) > Al/Fe (0.86) > Ca/Na (0.85)> Si/Al (0.82) > Mn/Al (0.76) > Si/Ca (0.73). The roles of K, Mg, and Ca in plant metabolism and interdependencies between these macronutrients were also described in the literature [25]. The strong correlation between trivalent ions such as Al³+ and Fe³+

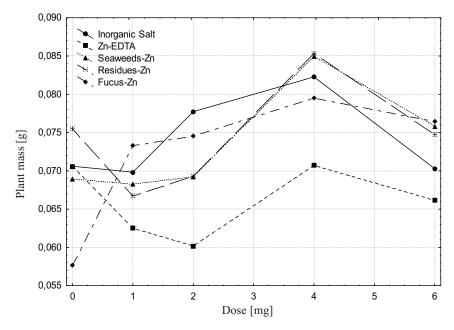


Fig. 3. The differences in mass of plants with different zinc doses and different components.

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Table 5. Comparison of element correlations for plants fertilized with traditional fertilizers and new components with micronutrients.

	Inorganic Salt/Chelate	Algae components
Fe:Cu	0.43	0.46
Mn:Cu	0.50	0.37
Mn:Mg	0.48	0.79
S:Cu	0.43	0.37
S:Fe	0.45	0.41
S:K	0.82	0.48
Mn:S	0.62	0.80
Si:Cu	0.61	0.59
Si:Fe	0.74	0.74
Mn:Si	0.48	0.82
Zn:Ca	-0.82	-0.39
Zn:K	-0.83	-0.43
Zn:Na	-0.79	-0.55
Zn:S	-0.78	-0.34
Zn:MP	0.62	0.65

MP - mass of plant

(r=0.86) were found in our study. This correlation can constitute a result of similar radius of the hydrated ions. Strong correlations also were indicated for K:Mg (0.68)> Mn/Ca (0.67)> Mg/Na (0.65), Mg/Ca, P/S (0.62) > 0.61 Fe/Ca > Mg/P (0.60) > Mn/K, Mg/S (0.57) > K/Si (0.56) > Mn/Na, Na/Si (0.53) > Al/Ca (0.52). A synergistic trend was established for typical antagonistic pairs such as Al/Ca and Mn/Ca (r=0.52 and r=0.67, respectively), while literature describes negative relationships between these elements [25].

## **Conclusions**

Conducted experiments showed that the biomass of seaweeds can be enriched in the biosorption process with zinc ions with good efficiency of the process. Moreover, micronutrient ions bound to the surface of the biomass stayed in bioavailable form. The application of new preparations for micronutrient fertilization of *Lepidium sativum* showed that new micronutrient biopreparations can be used for the biofortification of plants and constitute an alternative tool for commercial micronutrient fertilizers.

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