Pol. J. Environ. Stud. Vol. 24, No. 4 (2015), 1621-1631
DOI: *10.15244/pjoes/36985*

Original Research

Impact of Foliar Application of Tytanit on Zn, Li, Ni, Cr, Pb, and Cd Contents in Celery Leaves

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Received: 15 December 2014
Accepted: 18 February 2015

Abstract

A pot experiment was carried out in two one-year series to examine the effect of various concentrations of Tytanit (0.001-3.6%) applied once or twice alongside mineral NPK fertilization, on the content of Zn, Li, Ni, Cr, Pb, and Cd in celery (*Apium graveolens* L. var. *dulce* Mill. Pers.). The total content of select elements was determined in the solution obtained after dry combustion of celery biomass by atomic emission spectrophotometry with the inductively coupled plasma technique (ICP-AES). Foliar application of Tytanit at different concentrations alongside NPK fertilization significantly diversified the content of Zn, Li, Ni, and Pb in the petioles and leaf blades of celery. Together with the incremental concentrations of Tytanit, a reduction in the bio-accumulation of Zn, Li, Pb, and Cr was detected in the aerial parts of the plant, although the accumulation of Ni in the celery biomass increased. A higher content of Ni and Pb was found in the petioles than in the leaf blades. The contents of Zn, Li, and Cr were higher in the leaf blades than in the petioles, while the content of Cd was comparable in the petioles and leaf blades. The double application of Tytanit with an increasing concentration of Ti caused the decreasing Zn uptake by biomass yield of petioles as well as Li with the yield of petioles and leaf blades. The results indicate that celery is susceptible to accumulation of heavy metals. The uptake of Zn, Li, Ni, Cr, Pb, and Cd with the celery yield was unambiguously correlated with the Tytanit application. The quality of yield, and not the volume, should be a determinant used for evaluation in its production.

Keywords: celery leaves, biostimulators, fertilization, trace elements

Introduction

Titanium is one of the most important microelements, which exerts a positive effect on the biochemistry of plants regarding processes leading to earlier and the highest possible crop production. The impact of titanium on the volume and quality of plant yields has been investigated in numerous studies [1-4]. Biostimulators are biologically active substances that may contain, e.g., hormones, protein, and microelements. The application of preparations with titanium results in an increased activity of iron ions, which is positively correlated with the intensity of photosynthesis, chlorophyll synthesis, and the activity of enzymes responsible for free radical sweeping. These processes are very important for the growth and condition of plants exposed to stress caused by low temperature, limited access to light,

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Table 1. The total content of zinc (mg·kg^{-1} D.M.) in petioles and leaf blades of celery leaves.

Fertilization object	I series		II series		Mean for	
	Petioles	Leaf blades	Petioles	Leaf blades	Petioles	Leaf blades
Control object	47.88	67.92	75.78	64.86	61.83	66.39
NPK	54.12	158.1	30.17	91.38	42.15	124.7
I spraying of Tytanit						
0.001%+ NPK	48.58	70.17	54.63	53.72	51.61	61.95
0.01% + NPK	57.59	65.00	122.6	56.32	90.10	60.66
0.1% + NPK	47.69	59.38	54.46	70.40	51.08	64.89
1.0% + NPK	49.88	63.93	60.82	51.03	55.35	57.48
1.2% + NPK	41.41	69.53	29.22	48.33	35.32	58.93
2.4% + NPK	51.17	78.10	70.28	51.65	60.73	64.88
3.6% + NPK	31.63	82.30	67.53	44.87	49.58	63.59
Mean	46.85	69.78	65.65	53.76	56.25	61.77
II spraying of Tytanit						
0.001% + NPK	51.91	68.80	63.90	71.86	57.91	70.33
0.01% + NPK	53.50	63.88	31.82	59.07	42.66	61.48
0.1% + NPK	45.28	72.10	56.89	64.93	51.09	68.51
1.0% + NPK	48.47	140.9	50.52	47.13	49.50	94.02
1.2% + NPK	43.30	67.58	47.10	50.69	45.20	59.14
2.4% + NPK	32.29	69.31	62.20	49.61	47.25	59.46
3.6% + NPK	46.27	86.69	63.99	44.75	55.13	65.74
Mean	45.86	81.32	53.77	55.44	49.82	68.38
$LSD_{0.05}$ for:						
A – number of treatments	n.s.	3.95	7.37	1.41	3.99	7.88
B – concentration of Tytanit	8.77	11.5	21.4	4.07	2.82	12.8
A×B – interaction	8.01	10.5	19.5	3.72	2.58	20.1
B×A – interaction	12.4	16.2	30.2	5.76	7.88	22.3

n.s. – no significant difference

and low activity of the root system [3, 5-8]. Foliar application of growth regulators or fertilizers that contain biostimulators may influence the uptake and accumulation of minerals by plants. They increase plant resistance to adverse stress conditions and support plant protective mechanisms [9-12]. The use of growth promoters in vegetable cultivations may contribute to a reduction of cultivation costs, which is an important economic element. Of the substances that negatively impact the environment, heavy metals attract special attention. Transfer of metals into the edible parts of vegetables depends on cultivation and environmental factors [13-17]. Their harmful impact consists, among other things, in their potential accumulation in organisms and chronic toxicity [18-20]. According to many authors [16, 17, 21-25], vegetables (and leaf varieties in particular), supply the highest amount of toxic heavy metals to the human diet.

The objective of the study was to determine the impact of foliar application of Tytanit at different doses (0.001-3.6%) and at different time points (once and twice), alongisde mineral NPK fertilization, on the total content of Zn, Li, Ni, Cr, Pb, and Cd in the petioles and celery leaf blades.

Material and Methods

A pot experiment was conducted in a greenhouse, in two one-year series with three replications, designed as a totally randomized block. The study was carried out with

Table 2. Total contents of lithium (mg·kg^{-1} D.M.) in petioles and leaf blades of celery leaves.

Fertilization object	I series		II series		Mean for	
	Petioles	Leaf blades	Petioles	Leaf blades	Petioles	Leaf blades
Control object	13.21	7.41	25.76	18.47	19.49	12.94
NPK	11.98	16.42	19.91	43.81	15.95	30.12
I spraying of Tytanit						
0.001%+ NPK	11.34	12.72	21.13	53.38	16.24	33.05
0.01% + NPK	10.48	37.59	20.23	23.38	15.36	30.49
0.1% + NPK	10.78	58.39	22.79	36.33	16.79	47.36
1.0% + NPK	12.21	54.81	37.33	25.44	24.77	40.13
1.2% + NPK	13.97	25.18	24.06	34.70	19.02	29.94
2.4% + NPK	14.90	17.73	17.44	30.91	16.17	24.32
3.6% + NPK	11.07	20.92	27.19	18.77	19.13	19.85
Mean	12.11	32.48	24.31	31.84	18.23	32.16
II spraying of Tytanit						
0.001% + NPK	19.65	16.20	52.60	56.10	36.13	36.15
0.01% + NPK	9.62	49.32	24.98	45.72	17.30	47.52
0.1% + NPK	13.82	32.64	23.69	36.27	18.75	34.46
1.0% + NPK	12.92	19.85	10.28	22.16	11.60	21.01
1.2% + NPK	13.43	22.11	13.10	20.28	13.27	21.20
2.4% + NPK	9.51	34.48	16.25	23.03	12.88	28.76
3.6% + NPK	4.46	18.85	9.11	35.91	6.79	27.38
Mean	11.91	27.64	21.43	34.21	16.67	30.92
$LSD_{0.05}$ for:						
A – number of treatments	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
B – concentration of Tytanit	2.57	14.8	14.9	17.9	6.10	11.8
A×B – interaction	2.35	13.5	13.6	16.3	17.6	10.8
B×A – interaction	3.63	20.9	21.1	25.3	16.1	16.7

n.s. – no significant difference

Tango F1, i.e. a Dutch variety of leaf celery (*Apium graveolens* L. var. *dulce* Mill. Pers.). In both series, four seedlings of celery (at the stage of 3-4 true leaves) were planted into each 10 dm^3 pot in the first decade of June. The pots were filled with organic substrate that contained high peat with loamy sand (according to Polish Soil Science Society) in a 3:1 ratio. The soil material in the pots was limed one month before planting with calcium carbonate according to Hh=1, which generated pH_{H_2O} = 6.60. The total content of select elements in the substrate was (mg·kg^{-1}): Ti – 32.8, Zn – 18.5, Li – 1.80, Ni – 24.2, Cr – 4.62, Pb – 6.80, and Cd – 0.252, as determined in a solution after dry mineralization with the ICP-AES method, using an Optima 3200RL device (Perkin-Elmer). The soil humidity in the pots during vegetation was maintained at 60% (water vapour in grams) of the substrate. The experiment included 16 fertilized objects and one or two applications of Tytanit solution (8.5 g Ti·dm^{-3} in form of complex compound, Intermag Olkusz) at varied concentrations. The experiment was set according to the following scheme: the control object (without fertilization); mineral fertilization at NPK ratio of 1:0.8:1.5 (150 kg N·ha^{-1} – ammonium nitrate, P – triple superphosphate, K – potassium sulphate); and foliar fertilization with Tytanit alongside NPK in the amount of 0.001%, 0.01%, 0.1%, 1.0%, 1.2%, 2.4%, and 3.6%, which corresponded to the range of 0.043 to 150 mg Ti·pot^{-1} (dissolved in 500 cm^3 of water). NPK fertilization was applied a week before planting. The first spraying with Tytanit was done after plant rooting, i.e., in the first decade of July, and for the objects with double application in the first decade of August in

Table 3. Total content of nickel (mg·kg^{-1} D.M.) in petioles and leaf blades of celery leaves.

Fertilization object	I series		II series		Mean for	
	Petioles	Leaf blades	Petioles	Leaf blades	Petioles	Leaf blades
Control object	3.96	0.98	2.47	1.47	3.22	1.22
NPK	1.38	1.24	1.87	1.84	1.63	1.54
I spraying of Tytanit						
0.001%+ NPK	1.54	1.37	1.30	1.59	1.42	1.48
0.01% + NPK	1.61	1.90	1.94	1.86	1.78	1.88
0.1% + NPK	1.16	1.46	2.69	1.28	1.92	1.37
1.0% + NPK	1.74	1.54	1.88	1.18	1.81	1.36
1.2% + NPK	1.36	1.18	3.16	0.96	2.26	1.07
2.4% + NPK	1.35	2.90	1.33	1.45	1.34	2.18
3.6% + NPK	1.89	1.32	2.92	0.99	2.41	1.16
Mean	1.52	1.67	2.18	1.33	1.85	1.50
II spraying of Tytanit						
0.001% + NPK	1.56	1.02	1.65	1.38	1.61	1.20
0.01% + NPK	1.88	2.02	2.40	1.33	2.14	1.68
0.1% + NPK	1.61	1.59	2.11	1.57	1.86	1.58
1.0% + NPK	2.39	1.21	3.13	1.48	2.76	1.35
1.2% + NPK	1.35	1.43	1.41	1.30	1.38	1.37
2.4% + NPK	1.34	1.77	2.07	1.44	1.71	1.61
3.6% + NPK	2.47	1.71	4.61	1.55	3.54	1.63
Mean	1.80	1.54	2.49	1.44	2.14	1.49
$LSD_{0.05}$ for:						
A – number of treatments	0.15	n.s.	0.30	n.s.	0.28	n.s.
B – concentration of Tytanit	0.43	0.58	0.88	0.44	0.80	0.96
A×B – interaction	n.s.	0.53	0.80	0.40	0.73	0.63
B×A – interaction	n.s.	0.82	1.24	0.62	1.14	1.49

n.s. – no significant difference

series I and II of the experiment; celery harvest took place at the beginning of October in both series of the study.

In series I and II, the total content of Zn, Li, Ni, Cr, Pb, and Cd was determined in DM of the petioles and leaf blades. Dry plant material was ground to obtain particles with a diameter of < 0.25 mm and weighed at 1 g into a porcelain vessel; the organic matter was then dry-oxidized at 450ºC in a muffle furnace. The crude ash in the vessel was poured over with 10 cm^3 of diluted HCl (1:1) and then evaporated on a sand bath until dry in order to degrade carbohydrates and extract silica. The content of the vessel, when 5 cm^3 of 10% HCl was added, was filtered through a hard filter into a 100 cm^3 measuring flask and filled with distilled water up to the line. The total content of select elements in the prepared solution was measured with the ICP-AES method. Based on the DM yield of the petioles and leaf blades, the uptake of the select elements with celery yields was determined in series I and II of the experiment [11].

The results were statistically processed with the analysis of variance (Fisher-Snedecor test) for a two-variable experiment. The significance of differences between the means was estimated based on Tukey's test, assuming the significance level at $\alpha = 0.05$. The Pearson's simple correlation coefficients were calculated between the content of Ti in the petioles and leaf blades [11], and the content of Zn, Li, Ni, Cr, Pb, and Cd and the uptake of these elements with celery yields.

Table 4. Total content of chromium (mg·kg^{-1} D.M.) in petioles and leaf blades of celery leaves.

Fertilization object	I series		II series		Mean for	
	Petioles	Leaf blades	Petioles	Leaf blades	Petioles	Leaf blades
Control object	0.529	0.569	0.719	0.686	0.624	0.628
NPK	0.387	0.472	0.424	0.667	0.406	0.570
I spraying of Tytanit						
0.001%+ NPK	0.367	0.446	0.446	0.680	0.407	0.563
0.01% + NPK	0.456	0.662	0.773	0.895	0.614	0.779
0.1% + NPK	0.322	0.360	0.625	0.652	0.474	0.506
1.0% + NPK	0.400	0.485	0.631	0.590	0.516	0.538
1.2% + NPK	0.268	0.467	0.951	0.692	0.610	0.580
2.4% + NPK	0.351	0.871	0.593	0.790	0.472	0.831
3.6% + NPK	0.270	0.625	0.565	0.643	0.418	0.634
Mean	0.348	0.559	0.655	0.706	0.501	0.633
II spraying of Tytanit						
0.001% + NPK	0.429	0.438	0.598	0.607	0.514	0.523
0.01% + NPK	0.332	0.423	0.800	0.764	0.566	0.594
0.1% + NPK	0.363	0.805	0.713	0.678	0.538	0.742
1.0% + NPK	0.447	0.672	0.973	1.130	0.708	0.921
1.2% + NPK	0.339	0.469	0.632	0.656	0.486	0.563
2.4% + NPK	0.302	0.571	0.739	0.506	0.521	0.540
3.6% + NPK	0.271	0.568	0.428	0.431	0.350	0.500
Mean	0.355	0.564	0.698	0.682	0.526	0.626
$LSD_{0.05}$ for:						
A – number of treatments	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
B – concentration of Tytanit	0.080	n.s.	0.189	0.202	0.140	0.040
A×B – interaction	0.074	0.244	0.172	0.184	0.160	0.085
B×A – interaction	0.115	0.378	0.267	0.285	0.102	0.117

n.s. – no significant difference

Results and Discussion

The results of the pot experiment demonstrated, in the majority of cases, the significant impact of the different Tytanit concentrations applied against the background of constant NPK fertilization, and on the bio-accumulation of the investigated elements in the celery petioles and leaf blades. As reported in the literature, the concentration of metals in plants mostly depends on the species, plant part, and properties of a given element [15, 16, 19, 20, 24, 26, 27].

The content of Zn (Table 1) in the celery petioles in series I of the study ranged from 31.63 to 57.59 mg·kg^{-1}, while in series II the range was from 29.22 to 122.6 mg·kg^{-1}. In the celery petioles, the content of this metal was markedly diversified under the impact of different Tytanit concentrations in both series of the study. An incremental concentration of Tytanit caused a decrease in the content of zinc, especially in series I of the experiment. The average content of zinc in the petioles of celery treated with foliar Tytanit against the background of NPK fertilization in series I was comparable with the control object and was lower than in the object with NPK. In series II, the content of this metal in the petioles was higher in the control than in the treatments with Tytanit and double as as high as in the treatments with NPK. In the leaf blades, the bio-accumulation of zinc was higher than in the petioles except for some doses of Tytanit and the control in series II of the experiment. The highest content of this element in the leaf blades was detected in the treatment fertilized with NPK in both

Table 5. Total content of lead (mg·kg^{-1} D.M.) in petioles and leaf blades of celery leaves.

Fertilization object	I series		II series		Mean for	
	Petioles	Leaf blades	Petioles	Leaf blades	Petioles	leaf blades
Control object	0.240	0.211	0.122	0.310	0.181	0.261
NPK	0.471	0.340	0.391	0.441	0.431	0.391
I spraying of Tytanit						
0.001%+ NPK	0.799	0.549	0.811	0.311	0.805	0.430
0.01% + NPK	0.331	0.761	0.642	0.312	0.487	0.537
0.1% + NPK	0.492	0.712	0.982	0.223	0.737	0.468
1.0% + NPK	0.654	0.682	0.772	0.395	0.713	0.539
1.2% + NPK	0.515	0.302	0.411	0.374	0.463	0.338
2.4% + NPK	0.221	0.411	0.460	0.772	0.341	0.592
3.6% + NPK	0.250	0.470	0.320	0.480	0.285	0.475
Mean	0.466	0.555	0.628	0.410	0.547	0.482
II spraying of Tytanit						
0.001% + NPK	0.620	0.636	0.511	0.561	0.566	0.599
0.01% + NPK	0.531	0.480	0.594	0.502	0.563	0.491
0.1% + NPK	0.732	0.890	0.355	0.401	0.544	0.646
1.0% + NPK	0.570	0.440	0.411	0.510	0.491	0.475
1.2% + NPK	0.623	0.430	0.369	0.421	0.496	0.426
2.4% + NPK	0.452	0.331	0.357	0.365	0.405	0.348
3.6% + NPK	0.364	0.274	0.202	0.301	0.283	0.288
Mean	0.556	0.497	0.400	0.437	0.478	0.467
$LSD_{0.05}$ for:						
A – number of treatments	0.009	0.004	0.003	0.003	0.005	0.003
B – concentration of Tytanit	0.026	0.010	0.008	0.008	0.016	0.009
A×B – interaction	0.026	0.009	0.007	0.008	0.010	0.008
B×A – interaction	0.036	0.015	0.011	0.012	0.028	0.010

n.s. – no significant difference

series of the study, where it nearly doubled the control, and in the content in the treatments fertilized with Tytanit (the average values). Guo et al. [17] and Chao et al. [24] reported that Zn could be accumulated in celery more easily than Pb and Ni. The high accumulation of zinc results from this element having a physiological function in plants [26].

The content of lithium (Table 2) in the examined celery parts significantly depended on the amount of titanium in both series of the experiment. In the leaf blades of celery from all objects, a substantially higher content of lithium was determined than in the petioles (except for the control object). The single application of Tytanit caused an increase in the content of this element in the petioles parallel to its concentration: up to 2.4% in series I and up to 1% in series II. In the treatment fertilized with the highest concentration of Tytanit (3.6%), the content of lithium was nearly 5-fold lower than with the lowest Tytanit concentration (0.001%). In the leaf blades and in series I of the experiment, the highest content of lithium was detected after a single application of Tytanit at 0.1 and 1%, and after a double application at concentrations of 0.01 and 0.1%. Series II of the study used a single and double application of Tytanit at 0.001%.

The content of nickel (Table 3) was higher in the petioles than in the leaf blades in most of the fertilized treatments. The number of applications and Tytanit concentrations significantly diversified the content of this metal in the petioles in series I and II of the experiment. In series I, the highest content of nickel was recorded in the control object (3.96 mg·kg^{-1}), where it was nearly 3-fold higher than in the object with NPK and with foliar application of

Table 6. Total content of cadmium (mg·kg^{-1} D.M.) in petioles and leaf blades of celery leaves.

Fertilization object	I series		II series		Mean for	
	Petioles	Leaf blades	Petioles	Leaf blades	Petioles	Leaf blades
Control object	0.038	0.025	0.032	0.039	0.035	0.032
NPK	0.034	0.027	0.033	0.031	0.034	0.029
I spraying of Tytanit						
0.001%+ NPK	0.039	0.027	0.053	0.052	0.046	0.039
0.01% + NPK	0.041	0.033	0.051	0.050	0.046	0.042
0.1% + NPK	0.040	0.035	0.055	0.058	0.048	0.047
1.0% + NPK	0.047	0.042	0.058	0.050	0.053	0.046
1.2% + NPK	0.041	0.047	0.060	0.067	0.051	0.057
2.4% + NPK	0.052	0.053	0.056	0.064	0.054	0.058
3.6% + NPK	0.038	0.040	0.052	0.064	0.045	0.052
Mean	0.043	0.040	0.055	0.058	0.049	0.049
II spraying of Tytanit						
0.001% + NPK	0.038	0.030	0.065	0.051	0.052	0.041
0.01% + NPK	0.042	0.035	0.057	0.053	0.050	0.044
0.1% + NPK	0.040	0.035	0.057	0.065	0.048	0.050
1.0% + NPK	0.046	0.051	0.053	0.065	0.050	0.058
1.2% + NPK	0.040	0.043	0.052	0.053	0.046	0.048
2.4% + NPK	0.045	0.045	0.053	0.051	0.049	0.048
3.6% + NPK	0.041	0.049	0.044	0.050	0.043	0.049
Mean	0.042	0.041	0.054	0.055	0.048	0.048
$LSD_{0.05}$ for:						
A – number of treatments	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
B – concentration of Tytanit	0.008	0.011	n.s.	n.s.	n.s.	n.s.
A×B – interaction	n.s.	n.s.	n.s.	0.012	n.s.	0.011
B×A – interaction	n.s.	n.s.	n.s.	0.019	n.s.	0.020

n.s. – no significant difference

Tytanit. In series II, an increase in the content of nickel was found in the petioles of celery fertilized with Tytanit, whereas a reduction was detected in the control treatment in comparison with series I of the study. The highest bio-accumulation of nickel in series II (4.61 mg·kg^{-1}) was detected after a double application of Tytanit at the highest concentration of 3.6%. In the leaf blades, the content of Ni was significantly diversified by the concentration of Tytanit. The content was markedly lower in the control and in the treatment fertilized with NPK than in the treatments with foliar application of Tytanit alongside NPK in series I, being comparable or higher in series II of the experiment.

The content of chromium (Table 4) was considerably diversified by Tytanit concentrations in the petioles and leaf blades of celery in series II of the study. A higher amount of chromium was recorded in the control treatment than with NPK fertilization. In series I of the study, lower bio-accumulation of chromium was found in the petioles than in the leaf blades, yet it was comparable in series II. The addition of Tytanit at a lower concentration resulted in a higher content of chromium in the petioles and leaf blades.

The content of lead (Table 5) in the examined celery parts was significantly diversified by the experimental factors. With a single Tytanit application, parallel to its incremental concentration, there was a reduction in the bio-accumulation of lead in series II of the study, except in the leaf blades. The lowest content of lead was measured in the control objects. On average for the two years of the experiment, a higher content of lead was detected in the petioles than in the leaf blades.

Table 7. Uptake of zinc, lithium, nickel, chromium, lead, and cadmium in the yield of petioles and leaf blades of celery leaves (mg·pot^{-1}), mean from the results of two series.

Fertilization object	Zn		Li		Ni		Cr		Pb		Cd	
	Petioles	Leaf blades	Petioles	Leaf blades	Petioles	Leaf blades	Petioles	Leaf blades	Petioles	Leaf blades	Petioles	Leaf blades
Control object	0.39	0.548	0.124	0.107	0.020	0.010	0.004	0.005	0.001	0.002	0.0002	0.0003
NPK	0.97	3.21	0.368	0.774	0.038	0.040	0.009	0.015	0.009	0.010	0.0008	0.0003
I spraying of Tytanit												
0.001% + NPK	1.63	1.37	0.513	0.730	0.045	0.033	0.013	0.012	0.025	0.010	0.0015	0.0009
0.01% + NPK	3.69	1.66	0.630	0.835	0.073	0.052	0.025	0.021	0.020	0.015	0.0019	0.0012
0.1% + NPK	1.95	1.66	0.640	1.210	0.073	0.035	0.018	0.013	0.028	0.012	0.0018	0.0012
1.0% + NPK	2.35	1.61	1.050	1.120	0.077	0.038	0.022	0.015	0.030	0.015	0.0020	0.0013
1.2% + NPK	1.33	1.38	0.715	0.704	0.085	0.025	0.023	0.014	0.017	0.008	0.0019	0.0013
2.4% + NPK	2.18	1.65	0.581	0.620	0.048	0.056	0.017	0.022	0.012	0.015	0.0019	0.0015
3.6% + NPK	2.09	1.97	0.805	0.615	0.101	0.036	0.018	0.020	0.012	0.015	0.0019	0.0016
Mean	2.17	1.61	0.705	0.833	0.072	0.039	0.019	0.017	0.021	0.013	0.0018	0.0013
II spraying of Tytanit												
0.001% + NPK	2.57	1.54	1.600	0.792	0.071	0.026	0.023	0.011	0.025	0.013	0.0023	0.0009
0.01% + NPK	1.68	1.49	0.680	1.150	0.084	0.041	0.022	0.014	0.022	0.012	0.0020	0.0011
0.1% + NPK	2.02	1.72	0.741	0.865	0.073	0.040	0.021	0.019	0.021	0.016	0.0019	0.0013
1.0% + NPK	1.53	2.29	0.360	0.513	0.086	0.033	0.022	0.022	0.015	0.012	0.0016	0.0014
1.2% + NPK	1.76	1.38	0.516	0.496	0.054	0.032	0.019	0.013	0.019	0.009	0.0021	0.0011
2.4% + NPK	1.65	1.47	0.451	0.713	0.060	0.040	0.018	0.013	0.014	0.008	0.0017	0.0012
3.6% + NPK	2.22	1.97	0.274	0.819	0.143	0.049	0.014	0.015	0.011	0.008	0.0017	0.0015
Mean	1.92	1.69	0.660	0.764	0.083	0.037	0.020	0.015	0.018	0.011	0.0020	0.0014

The content of cadmium (Table 6) in the aerial parts of celery was markedly lower in the control and the treatments objects fertilized with NPK than with foliar application of Tytanit. In the majority of cases, the investigated factors did not exert any significant impact on the content of cadmium. The concentration of Tytanit significantly diversified the content of this metal in the petioles and leaf blades only in series I of the experiment. The content of cadmium was comparable in the petioles and leaf blades, being higher in series II than in series I. Guo et al. [17] reported that Cd was transferred easily to the vegetable leaves than Zn and Pb.

Recapitulating the results of the study, it is concluded that titanium in the Tytanit preparation had a varied and ambiguous impact on the accumulation of the investigated elements in the aerial parts of celery (petioles and leaf blades). Reddy and Bhatt [28] detected similar relations in studies on spinach. In the present experiment (on average for the two series), lithium and chromium accumulated more intensively in the leaf blades while nickel and lead accumulated more intensively in the petioles. A similar content of cadimum was determined in the petioles and leaf blades. This suggests a different mechanism of transport and binding of these elements in celery as well as a strategy for this plant to accumulate them in the non-photosynthesizing part of the plant. Smoleń et al. [10] found that in spinach receiving foliar fertilization with Pentakeep V, a substantially higher content of Cd, Cr, and Pb, a comparable content of Ni, and a lower concentration of Li were detected in comparison with celery. According to Biczak et al. [13], mineral NPK fertilization significantly affected the mineral composition and the dry matter yield of celery leaves. Bosiacki and Roszyk [15] and Grembecka et al. [25] determined the most of Cr and Ni in the group of vegetables whose edible part is leaves. Osma et al. [20] reported that an overall metal concentration pattern in vegetables was Pb>Cr>Ni>Zn>Cd.

The uptake of Zn, Li, Ni, Cr, Pb, and Cd with the celery yield was unambiguously correlated with Tytanit application (Table 7). Obviously, the amount of uptaken elements depended mainly on the yield of celery, as has been reported previously [11]. Double spraying caused, on average, a

Table 8. Simple correlation coefficients between the Ti total contents and content of Zn, Li, Ni, Cr, and Pb, and the uptake of these elements with the yield of petioles and leaf blades of celery leaves (mean from the results of two series).

Elements	Ti	Zn^1	Zn^2	Li^1	Li^2	Ni^1	Ni^2	Cr^1	Cr^2	Pb^1	Pb^2	Cd^1	Cd^2
Petioles													
Zn^1	-0.225	1.00											
Zn^2	-0.281	0.940	1.00										
Li^1	-0.614	0.042	0.234	1.00									
Li^2	-0.562	0.090	0.315	0.988	1.00								
Ni^1	0.566	-0.151	-0.112	-0.425	-0.352	1.00							
Ni^2	0.459	-0.063	0.070	-0.257	-0.152	0.946	1.00						
Cr^1	-0.107	0.054	-0.012	0.088	0.050	-0.041	-0.182	1.00					
Cr^2	-0.329	0.221	0.340	0.454	0.477	-0.105	-0.049	0.813	1.00				
Pb^1	-0.635	-0.038	-0.078	0.349	0.269	-0.448	-0.474	0.096	0.063	1.00			
Pb^2	-0.701	0.063	0.138	0.559	0.523	-0.443	-0.362	0.081	0.262	0.926	1.00		
Cd^1	0.483	-0.342	-0.404	-0.331	-0.347	0.323	0.183	0.282	0.034	-0.562	-0.628	1.00	
Cd^2	-0.316	0.064	0.334	0.698	0.763	-0.327	-0.087	0.080	0.559	-0.052	0.270	-0.165	1.00
Leaf blades													
Zn^1	-0.003	1.00											
Zn^2	0.225	0.770	1.00										
Li^1	0.596	-0.272	-0.378	1.00									
Li^2	-0.488	-0.333	-0.235	0.950	1.00								
Ni^1	0.129	-0.103	-0.013	-0.003	0.050	1.00							
Ni^2	-0.024	-0.240	-0.330	-0.064	-0.123	-0.294	1.00						
Cr^1	-0.093	0.607	0.509	-0.430	-0.438	0.423	-0.071	1.00					
Cr^2	-0.078	0.292	0.187	-0.300	-0.359	-0.593	-0.176	-0.091	1.00				
Pb^1	-0.648	0.173	0.017	0.226	0.165	0.256	-0.395	0.442	0.028	1.00			
Pb^2	-0.541	0.115	0.243	0.141	0.210	0.261	-0.389	0.479	-0.021	0.893	1.00		
Cd^1	0.413	0.386	0.374	-0.562	-0.551	-0.003	0.434	0.511	0.122	-0.190	-0.114	1.00	
Cd^2	-0.039	-0.248	-0.072	0.277	0.404	-0.131	-0.091	-0.208	-0.227	0.168	0.284	-0.166	1.00

$n = 14$, $p<005$, critical value $r=0.514$;
Zn^1, Li^1, Ni^1, Cr^1, Pb^1, Cd^1 – total content
Zn^2, Li^2, Ni^2, Cr^2, Pb^2, Cd^2 – uptake

reduction of the Zn uptake by the petioles and Li uptake with the yield of petioles and leaf blades. The uptake of other elements (Ni, Cr, Pb, and Cd) was comparable (on average) between the single and double application of Tytanit. It was found that the uptake of the examined elements by the petioles was significantly higher than by the leaf blades except for Li. The differences are highest for Ni.

The relationship between the total content of titanium in the petioles and leaf blades of celery (reported by Malinowska and Kalembasa [11]) and the total content of Zn, Li, Ni, Cr, Pb, and Cd as well as their uptake by the petioles and leaf blades are presented as the calculated values of simple correlation coefficients (Table 8). In the two-year experiment, there was a significant positive correlation in the petioles between the total content of Ti and the content of Ni ($r=0.556$) and a negative correlation between the content of Li ($r=-0.614$) and the uptake of this element ($r=-0.562$), as well as between the content of Pb ($r=-0.635$) and the uptake of this element in the yield ($r=-0.701$). The uptake of zinc, lithium, nickel, chromium, and lead in the petioles was significantly and positively correlated with the total content of a given element ($r=0.940$, $r=0.988$, $r=0.946$, and $r=0.813$, respectively). Moreover, it was found that the total content of lithium positively impacted the uptake of Pb (r=0.559) and Cd (r=0.698), while the content of cadmium was negatively correlated with the uptake of lead (r=-0.628) by the petioles of the test plant.

In the leaf blades, there was a significant and positive correlation between the content of Ti and the content of Li (r=0.596), and a negative and significant correlation with the content of Pb (r=-0.648) and its uptake in the yield (r=-0.541). A significant and positive correlation was demonstrated between the total contents of Zn, Li, and Pb and the uptake of these element in the yield of celery petioles (r=0.770, r=0.950, and r=0.893, respectively). The total content of nickel was negatively correlated with the uptake of chromium (r=-0.593), whereas the content of cadmium negatively impacted the uptake of lithium (r=-0.551) by the petioles of the test plant.

Cadmium and lead are elements categorized as major food contaminants due to the highest risk to human health [16, 19, 20, 29, 30]. Excessive amounts of heavy metals (i.e. over the thresholds) are more commonly detected in vegetables, especially leaf varieties, than in fruits [14, 18, 19, 21, 23, 24, 31]. The permissible limits for Cd and Pb in leaf vegetables are, according to the Regulation of The Minister of Health [32] and the Regulation of the European Commission [33], set at 0.20 for Cd and 0.30 for Pb ($mg \cdot kg^{-1}$ fresh mass). The detected contents of these element in celery fertilized with Tytanit did not exceed the limits.

Conclusions

1. Foliar application of Tytanit at different concentrations against the background of NPK fertilization significantly diversified the content of Zn, Li, Ni, and Pb in the petioles and leaf blades of celery leaves. Together with the incremental concentration of Tytanit, a reduction in the bio-accumulation of Zn, Li, Pb, and Cr was detected in the aerial parts of the plant, although the bio-accumulation of Ni increased.
2. A higher content of Ni and Pb was found in the petioles than in the leaf blades. The content of Zn, Li, and Cr was higher in the leaf blades than in the petioles, while the content of Cd was comparable in the petioles and leaf blades.
3. The uptake of the tested elements by the petioles was predominantly higher than by the leaf blades.
4. The results indicate that celery is susceptible to accumulation of heavy metals. The quality of yielding, and not the volume, should be a criterion used for evaluation in its production.

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