DOI: 10.21005/AAPZ2016.39.3.03

FOLIA POMERANAE UNIVERSITATIS TECHNOLOGIAE STETINENSIS
Folia Pomer. Univ. Technol. Stetin., Agric., Aliment., Pisc., Zootech. 2016, 328(39)3, 35–52

Robert BICZAK, Barbara PAWŁOWSKA

EFFECT OF THE QUATERNARY AMMONIUM SALTS, TETRAETHYLAMMONIUM HALIDE ON *RUMEX ACETOSA* L., *CHENOPODIUM ALBUM* L. AND *GALINSOGA PARVIFLORA* CAV.: INHIBITION OF GROWTH AND CHANGES IN ASSIMILATION PIGMENTS CONTENT IN PLANTS

WPŁYW CZWARTORZĘDOWYCH SOLI AMONIOWYCH, HALIDKÓW TETRAETYLOAMONIOWYCH NA *RUMEX ACETOSA* L.*, CHENOPODIUM ALBUM* L. I *GALINSOGA PARVIFLORA* CAV.: INHIBICJA WZROSTU ORAZ ZMIANY ZAWARTOŚCI BARWNIKÓW ASYMILACYJNYCH W ROŚLINACH

Department of Biochemistry and Ecotoxicology, Jan Długosz University in Częstochowa, Poland

Streszczenie. Jednym z głównych problemów pojawiających się podczas uprawy roślin jest niszczenie ich przez czynniki szkodliwe, do których zaliczyć możemy m.in. chwasty. Do grupy uciążliwych chwastów, występujących pospolicie na całym obszarze Polski i w wielu rejonach świata, należą *Galinsoga parviflora* Cav., *Chenopodium album* L. i *Rumex acetosa* L. Ze względu na takie rozpowszechnienie rośliny te mogą mieć kontakt z wieloma zanieczyszczeniami, w tym z różnymi związkami chemicznymi, które mogą dostać się do środowiska naturalnego. W prezentowanej pracy przedstawiono wpływ czwartorzędowych soli amoniowych (CSA) – chlorku tetraetyloamoniowego [TEA][Cl], bromku tetraetyloamoniowego [TEA][Br] i jodku tetraetyloamoniowego [TEA][I], wprowadzonych do gleby i zastosowanych w formie oprysku liści roślin, na wzrost i rozwój wybranych gatunków chwastów. Zastosowanie badanych związków w formie doglebowej wykazało, że rośliną najbardziej wrażliwą na badane substancje chemiczne był *Chenopodium album* L., a związkiem o największej fitotoksyczności dla badanych chwastów okazał się jodek tetraetyloamoniowy. Fitotoksyczność badanych soli, zastosowanych w postaci oprysku, uzależniona była natomiast od zastosowanego stężenia QAS oraz od cech gatunkowych roślin użytych w doświadczeniu. Odzwierciedliło się w inhibicji długości roślin i ich korzeni oraz w zmianach zawartości suchej masy i barwników fotosyntetycznych.

Key words: phytotoxicity, dry weight, chlorophyll, inhibition of plant growth and roots, *Galinsoga parviflora, Chenopodium album, Rumex acetosa.*

Słowa kluczowe: fitotoksyczność, sucha masa, chlorofil, inhibicja wzrostu roślin i korzeni, *Galinsoga parviflora, Chenopodium album, Rumex acetosa.*

INTRODUCTION

Galinsoga parviflora – repressentative of *Asteraceae* family, *Chenopodium album* – representative of *Chenopodiaceae* family, and *Rumex acetosa* – representative of *Polygonaceae* family, are the weeds popular inter alia in Poland. All of these weeds are nitrophilous, and their seeds are spread by wind. *Galinsoga parviflora* can make 2–3 generations per year, and the

Corresponding author – Adres do korespondencji: Robert Biczak, Department of Biochemistry and Ecotoxicology, Jan Długosz University in Częstochowa, Armii Krajowej 13/15, 42-200 Częstochowa, Poland, e-mail: r.biczak@ajd.czest.pl

number of fruits produced by it is about 300 000. The seeds can survive in soil even for several years without losing the ability to germinate. This plant grows very quickly, and in favorable conditions blooms already four weeks after germination. *Chenopodium album* is a plant that also produces a lot of seeds that maintain germination capacity for a very long time – even up to 30 years. Except the production of numerous seeds, *Rumex acetosa* has also wintering rhizome. Due to such high ability to survive and easy spreading, these weeds are very difficult to remove from agricultural crops. Concurrently, complete elimination of these plants from the nature is not advisable, since in some parts of the world, including inter alia India, they are used in herbal medicine. *R. acetosa* and *C. album* are also the crops consumed by humans, and *G. parviflora*, due to its high protein content, can be used as green fodder (Matuszkiewicz 2006; Tauzon-Nartea and Savage 2013; Aper et al. 2014; Choundhary and Sharma 2014; De Cauwer et al. 2014; Bazylko et al. 2015; Poonia and Upadhayay 2015).

Despite the advantages resulting from the possibility of some weeds application, their occurrence in the crops leads to many problems for the farmers, since they compete with crop plants for light, water and nutrients, and their rapid development causes that they can choke up the crops. They also cause many other problems such as the delay of harvest or deterioration of crops quality; they hinder mechanical harvesting of the plants and generate the costs associated with harvest cleaning of seeds and weed residues. Chemicals known as herbicides have been used for many years in order to protect the crops from undesirable effects of weeds. Currently, one of substances the most commonly used in weed control are MCPA and 2,4-D. A very interesting and promising group of new herbicides that have appeared in recent years, are so-called herbicidal ionic liquids (HILs), that are such ILs in which one of the ions exhibits herbicidal activity. HILs demonstrate improved biological properties compared to conventionally used herbicides, are characterized by high thermal and chemical stability, and are less soluble in water, which effectively reduces the possibility of surface and groundwater contamination. Besides, the dose of applied active substance can be reduced, for example changing the substituent length, which automatically increases the safety of these compounds use in agricultural practice (Praczyk and Skrzypczak 2004; Niemczak et al. 2015; Pernak et al. 2016).

The big problem in agriculture is observed in the last century immunization of some weed species to herbicides used so far. Although there are some preparations, e.g. MCPA, in respect of which no weeds immunization phenomena is observed, there is still the need for the search for new compounds demonstrating herbicidal properties, with concurrent absence of adverse effects on natural environment. An interesting group of compounds exhibiting potent biological properties are quaternary ammonium salts. Except biological properties, these compounds have a number of other interesting features such as wetting, emulsifying, dispersing, antistatic, preservatives as well as algaecidal, fungicidal and bactericidal properties, that caused they have found a wide range of practical applications. QAS production at the end of the twentieth century was estimated at about million tones/year (Grabińska-Sota 2004). Representatives of quaternary ammonium salts also include tetraethylammonium chloride, bromide and iodide used in the present experiment.

Currently, the studies dealing with QAS effect on terrestrial higher plants, which include weeds, are very sparse. This paper presents an attempt to evaluate and compare the effect of

tetraethylammonium chloride, bromide and iodide on the growth and development of three popular weed species: *G. parviflora*, *C. album* and *R. acetosa*. These substances are characterized by very similar physical and chemical properties and are used in chemical synthesis for the production of many materials, biologically active substances and surfactants. Due to the large range of examined compounds applications and low cost of their production, there is a risk that these salts can get into the natural environment. Therefore, determination of these QAS effect on plants such abundant as weeds seems to be necessary, since it can protect not only them, but also the entire environment from the possible effects of pollution. Concurrently, the study involved the search for entirely new biologically active compounds which would exhibit total or selective herbicidal properties. Such substances could be a potential alternative to currently used pesticides, being at the same time harmless to broadly understood natural environment.

MATERIAL AND METHODS

Chemicals

The quaternary ammonium salts: tetraethylammonium chloride [TEA][Cl] (≥ 98% purity), tetraethylammonium bromide [TEA][Br] (98% purity) and tetraethylammonium iodide [TEA][I] (98% purity) used in the study was purchased from Sigma-Aldrich Chemical Co. The structure of the tested QAS illustrates the general formula: $(C_2H_5)_4N^+ X^-$, where X^- respectively shall mean ion Cl^-, Br^- and I^-.

Examination of tetraethylammonium halides toxicity used on the plants in a form of spraying

A pot experiment for the determination potential phytotoxicity of the [TEA][Cl], [TEA][Br] and [TEA][I] was carried out in the vegetation hall of the Department of Biochemistry and Ecotoxicology at Jan Długosz University in Częstochowa. Equal amount (referred to as wt) of the seeds of examined weeds (*Galinsoga parviflora* Cav., *Chenopodium album* L., *Rumex acetosa* L.) was seeded to plastic pots with a diameter of 90 mm containing 250 g of soil. The soil used in the experiment was light loam with a dissolved matter contain of approx. 10%, an organic carbon of 9.0 g · kg^{-1} and pH equal to 6.0. 3 weeks after germination, the plants were sprayed with solutions of the examined compounds. The compounds for spraying were used in a form of aqueous solutions at concentrations of 0.5%, 1.0% and 2.0%. The controls were prepared in an analogous way, and they were sprayed with distilled water without the addition of compounds.

Throughout the testing period (14 days), constant substrate moisture content at the level required for the plants (70% field water capacity), a constant temperature 20 ± 2°C and a light intensity of 160 µmol m^{-2} · s^{-1} were maintained in the system of 16 h/day and 8 h/night.

Visual evaluation of examined weed species growth inhibition, damages or withering was used as an indicator of analyzed compounds toxicity, which was documented in the form of digital images presented in this paper. Also the content of chlorophylls and carotenoids in the examined plants and the inhibition of plants and their roots growth were evaluated. The effective concentrations (EC_{50}) were estimated by the non-linear regression using GraphPad Prism software (GraphPad Software, Inc., La Jolla, CA, USA).

Examination of soil-applied tetraethylammonium halides toxicity

The study concerning the determination of soil-applied salts effect on selected weed species was carried out for 28 days. The test were carried in the vegetation hall, while maintaining the condition of substrate moisture content, temperature and illumination intensity and duration identical to those described in the part of the paper concerning the examination of tetraethylammonium halides toxicity were used in a form of spraying. Examined compounds were added to the soil in a form of aqueous solutions (incorporation), and the weeds were seeded on such prepared substrate. [TEA][Cl], [TEA][Br] and [TEA][I] were used in a concentration of 1000 mg · kg^{-1} of soil dry weight (DW).

Visual evaluation of examined weed species growth inhibition, damages or withering was used as an indicator of analyzed compounds phytotoxicity, which was documented in the form of digital images presented in this paper. Also the content of chlorophylls and carotenoids in the examined plants and the inhibition of plants and their roots growth were evaluated. The effective concentrations (EC50) were estimated by the non-linear regression using GraphPad Prism software (GraphPad Software, Inc., La Jolla, CA, USA).

Determination of pigments content and dry weight

Photosynthetic pigments content was determinate according to the method reported by Oren et al. (1993). Fresh leaves (0.2 g) homogenized in 20 ml 80% acetone using mortar and pestle and were put in centrifuge tube. The extraction was carried out the darkness for 24 h and the extract were centrifuged by 10 min and supernatants were used for pigments content determination. The content of chlorophyll *a*, chlorophyll *b* and carotenoids by measuring the absorbance at 470 nm, 647 nm and 664 nm. The content photosynthetic pigments were expressed as mg · g^{-1} of fresh weight (FW).

The dry weight level was determined using an oven-dry method (Kowalska 2004), drying about 1 g fresh weight of the plant at a temperature of 105°C to a constant weight obtaining. The dry weight content was provided in g · g^{-1} FW.

Statistical analysis

The results were expressed as et mean ± standard deviation. The data from three measurements (n = 3) were analyzed using one-way ANOVA, while the LSD values were calculated using the Tukey test. Differences were considered significant at the $p < 0.05$ level. Moreover, the mean standard deviations were determined, which were plotted as vertical lines in the diagrams presented in the paper.

RESULTS

The results obtained in the discussed experiment concerning an effect of quaternary tetraethylammonium salts with various anions, applied to soil and in foliar form, on weeds growth and development may prove that the examined substances can be considered as the compounds characterized by a selective herbicidal activity. The compound itself to the highest degree affected the observed toxicity to plants. Also applied compound concentration in foliar treatments, genetic characteristics of species and varieties of plants used in the experiment, as well as the form of treatment applied were of a high significance.

The strongest phytotoxic activity in case of soil application with respect to all examined weeds was demonstrated for tetraethylammonium iodide. The strongest activity of that compound was noted in case of *G. parviflora* plants, which seeds in the soil with this compound addition were unable to germinate. Only a few seeds germinated in the case of *C. album*, but the plants practically did not grow and were very limp. Inhibition of *C. album* plants and roots growth was about 80%. *R. acetosa* seeds only germinated, however with a delay, the plants were very small and withered after a few days after germination. Addition of [TEA][Cl] and [TEA][Br] to the soil resulted in over 60% inhibition of *C. album* and *G. parviflora* plant growth, and 30% inhibition in the case of *R. acetosa*, with respect to the control. An inhibition of roots length of the plants growing in soil with an addition of [TEA][Cl] and [TEA][Br] was only observed in the case of *C. album* (Fig. 1, Table 1).

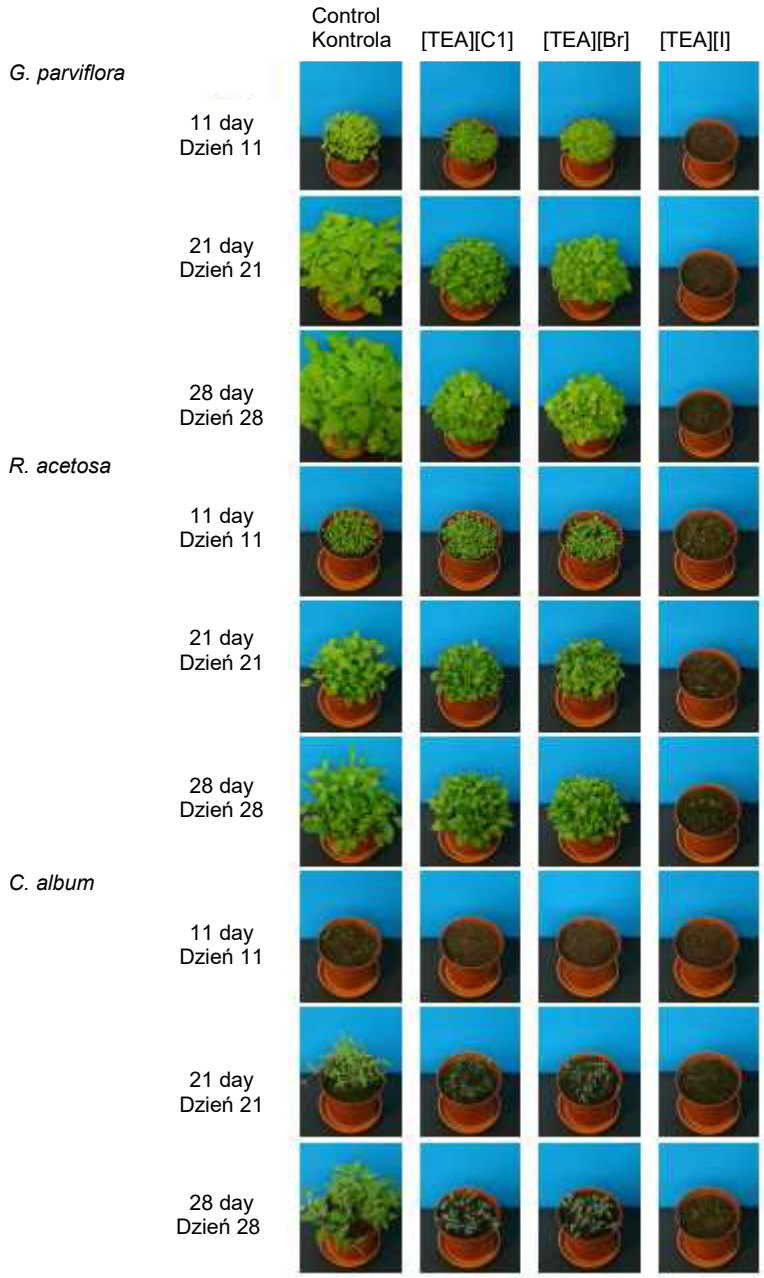

Fig. 1. The reaction weeds in the soil application of [TEA][Cl], [TEA][Br] and [TBA][I]
Ryc. 1. Reakcja chwastów na doglebowe zastosowanie [TEA][Cl], [TEA][Br] i [TBA][I]

Table 1. Inhibition of growth plant and root *G. parviflora*, *R. acetosa* and *C. album* exposed to [TEA][Cl], [TEA][Br] and [TEA][I] in soil (mean ± SD, *n* = 3)
Tabela 1. Inhibicja wzrostu roślin i korzeni *G. parviflora, R. acetosa* i *C. album* narażonych na obecność [TEA][Cl], [TEA][Br] i [TEA][I] w glebie (średnia ± odch. stand., *n* = 3)

	Growth inhibition Inhibicja wzrostu	*G. parviflora*	*R. acetosa*	*C. album*
[TEA][Cl]	plant – roślina	66.93 ± 2.89	33.33 ± 2.45	64.73 ± 6.66
	root – korzeń	–5.67 ± 8.28	0.18 ± 9.61	39.67 ± 3.47
[TEA][Br]	plant – roślina	68.47 ± 3.36	31.97 ± 1.84	62.65 ± 3.93
	root – korzeń	–18.25 ± 9.88	–4.76 ± 4.65	31.62 ± 4.92
[TEA][I]	plant – roślina	–	–	77.79 ± 6.37
	root – korzeń	–	–	79.90 ± 5.74

Moreover, QAS effect on dry weight content in *G. parviflora*, *C. album* and *R. acetosa* plants was determined as a result of the study conducted. The highest influence on the examined weeds dry weight content was demonstrated for [TEA][Cl] addition to the soil. About 18% and 25% increase in dry weight content with respect to the control, was noted after this QAS application for *R. acetosa* and *C. album,* respectively. In the case of dry weight content in plants grown in soil with [TEA][Br] addition, a statistically significant increase in this compound content was only observed for *C. album* and it amounted to about 47%. Dry matter increase for *R. acetosa* was low, and it was only about 9% compared to the control. The examined compounds did not cause any significant changes in *G. parviflora* plants dry weight content (Table 2).

Table 2. Effect of [TEA][C], [TEA][Br] and [TEA][I] in soil on dry weight [g · g^{-1} FW] weeds (mean ± SD, *n* = 3)
Tabela 2. Wpływ [TEA][C], [TEA][Br] i [TEA][I] wprowadzonych do gleby na zawartość suchej masy [g · g^{-1} św.m.] chwastów (średnia ± odch. stand., *n* = 3)

		Dry weight ± SD Sucha masa ± odch. stand.	$LSD_{0.05}$ $NIR_{0,05}$
G. parviflora	Control – Kontrola	0.1256 ± 0.0107	0.0195
	[TEA][Cl]	0.1283 ± 0.0054	
	[TEA][Br]	0.1289 ± 0.0138	
	[TEA][I]	–	
R. acetosa	Control – Kontrola	0.0868 ± 0.0015	0.0062
	[TEA][Cl]	0.1020 ± 0.0055	
	[TEA][Br]	0.0945 ± 0.0013	
	[TEA][I]	–	
C. album	Control – Kontrola	0.0952 ± 0.0020	0.0023
	[TEA][Cl]	0.1186 ± 0.0006	
	[TEA][Br]	0.1404 ± 0.0005	
	[TEA][I]	–	

Also the content of assimilation pigments in *G. parviflora*, *C. album* and *R. acetosa* plants growing in soil with an addition of [TEA][Cl] and [TEA][Br] was determined in the present study. Higher changes in assimilation pigments content were observed after tetraethylammonium chloride application. A decrease in the content of chlorophyll *a*, chlorophyll *b*, total chlorophyll and carotenoids was noted in case of all examined weeds. A similar effect on plants was observed in case of [TEA][Br] addition to the soil. A decrease in all assimilation dyes was also observed in the examined weeds. The changes in the ratio of chlorophyll a/b and total chlorophyll to carotenoids were dependent both on QAS type, and plant species (Table 3).

Table 3. Changes in the content of assimilation pigments [mg · g^{-1} FW] in *G. parviflora*, *R. acetosa* and *C. album* leaves exposed to [TEA][Cl], [TEA][Br] and [TEA][I] in soil (mean ± SD, *n* = 3)
Tabela 3. Zmiany zawartości barwników asymilacyjnych [mg · g^{-1} św.m.] w liściach *G. parviflora, R. acetosa* i *C. album* narażonych na obecność [TEA][Cl], [TEA][Br] i [TEA][I] w glebie (średnia ± odch. stand., *n* = 3)

		Control Kontrola	[TEA][Cl]	[TEA][Br]	[TEA][I]	$LSD_{0.05}$ $NIR_{0,05}$
G. parviflora	Chl *a*	1.391 ± 0.001	1.049 ± 0.009	0.994 ± 0.004	–	0.010
	Chl *b*	0.414 ± 0.005	0.330 ± 0,006	0.312 ± 0.006	–	0.010
	Chl*a+b*	1.805 ± 0.004	1.378 ± 0.012	1.306 ± 0.008	–	0.015
	Car	0.338 ± 0.002	0.284 ± 0.001	0.269 ± 0.001	–	0.003
	a/b	3.362 ± 0.039	3.184 ± 0.053	3.186 ± 0.055	–	0.091
	Chl/car	5.33 5± 0.037	4.859 ± 0.024	4.865 ± 0.023	–	0.053
R. acetosa	Chl *a*	1.028 ± 0.011	0.976 ± 0.011	1.029 ± 0.017	–	0.025
	Chl *b*	0.291 ± 0,003	0.278 ± 0.005	0.278 ± 0.007	–	0.010
	Chl*a+b*	1.319 ± 0.014	1.255 ± 0.016	1.308 ± 0.024	–	0.034
	Car	0.259 ± 0.002	0.247 ± 0.003	0.247 ± 0.004	–	0.018
	a/b	3.530 ± 0,022	3.506 ± 0.039	3.701 ± 0.049	–	0.071
	Chl/car	5.098 ± 0.012	5.080 ± 0.007	5.301 ± 0.019	–	0.025
C. album	Chl *a*	1.198 ± 0.019	0.960 ± 0.010	1.020 ± 0.016	–	0.029
	Chl *b*	0.343 ± 0.011	0.285 ± 0.003	0.281 ± 0.016	–	0.021
	Chl*a+b*	1.540 ± 0.010	1.245 ± 0.013	1.301 ± 0.032	–	0.038
	Car	0.285 ± 0.007	0.212 ± 0.003	0.223 ± 0.007	–	0.011
	a/b	3.497 ± 0.159	3.367	3.630 ± 0.166	–	0.245
	Chl/car	5.402 ± 0.103	5.870 ± 0.025	5.846 ± 0.036	–	0.119

Chl *a* – chlorophyll *a* – chlorofil *a*, Chl *b* – chlorophyll *b* – chlorofil *b*, chl *a+b* – chlorophyll *a* + chlorophyll *b* – chlorofil *a* + chlorofil *b*, car – carotenoides – karotenoidy, a/b – chlorphyll *a*/chlorophyll *b* – chlorofil *a*/chlorofil *b,* chl/car – (chlorophyll *a* + chlorophyl *b*)/carotenoids – (chlorofil *a* + chlorofil *b*)/karotenoidy.

Weaker and selective herbicidal properties were exhibited by [TEA][Cl], [TEA][Br] and [TEA][I] used in a form of spraying on *G. parviflora*, *R. acetosa* and *C. album* plants. *G. parviflora* appeared to be the plant the most resistant to applied QAS, regardless of the compound concentration. The only change observed in the appearance of this species plants, after their spraying with examined QAS solutions, were small yellow and brown spots appearing on the individual leaves. However, this did not disturb the plants in their further, normal development. In the case of *R. acetosa*, an effect of salt applied on plants mainly depended on its concentration. An application of spraying with 0.5% [TEA][I] solution did not cause any changes in plants appearance, while spraying with 0.5% solutions of [TEA][Cl] and [TEA][Br] resulted in marked chlorotic and necrotic changes after 1 day of the treatment. *R. acetosa* plants looked like they were burned, a small part of the plants withered in the subsequent days, but its place was quickly occupied by other plants that developed normally. The changes in plants appearance were also observed one day after spraying with 1.0% solutions of [TEA][Cl] and [TEA][Br], and about half of *R. acetosa* plants withered in the subsequent days. However, other plants continued to grow and take the place of those which withered. A little weaker activity was demonstrated for an application of 1.0% [TEA][I] solution, but also in this case the changes in *R. acetosa* plants appearance were observed already in the first day after spraying. Some of the plants turned brown, and these plants withered in subsequent days. Similar changes were observed after an application of all salts in a concentration of 2%, however the extent of examined weed plants damage was larger than that observed at a lower concentration. Remaining *R. acetosa* plants grew more slowly than

those on the control objects. In case of *C. album*, an application of the examined QAS in a form of solutions with a concentration of 0.5% did not lead to the formation of major changes in these plants appearance, while 1.0% solutions of [TEA][Cl], [TEA][Br] and [TEA][I], and 2.0% solutions of [TEA][Cl] and [TEA][Br] caused that part of *C. album* plants withered a few days after spraying, and those that remained grew more slowly than the control plants. An application of [TEA][I] in a concentration of 2.0% in *C. album* lead to visible and large changes on the leaves, and all plants withered 3 weeks after the treatment (Fig. 2–4).

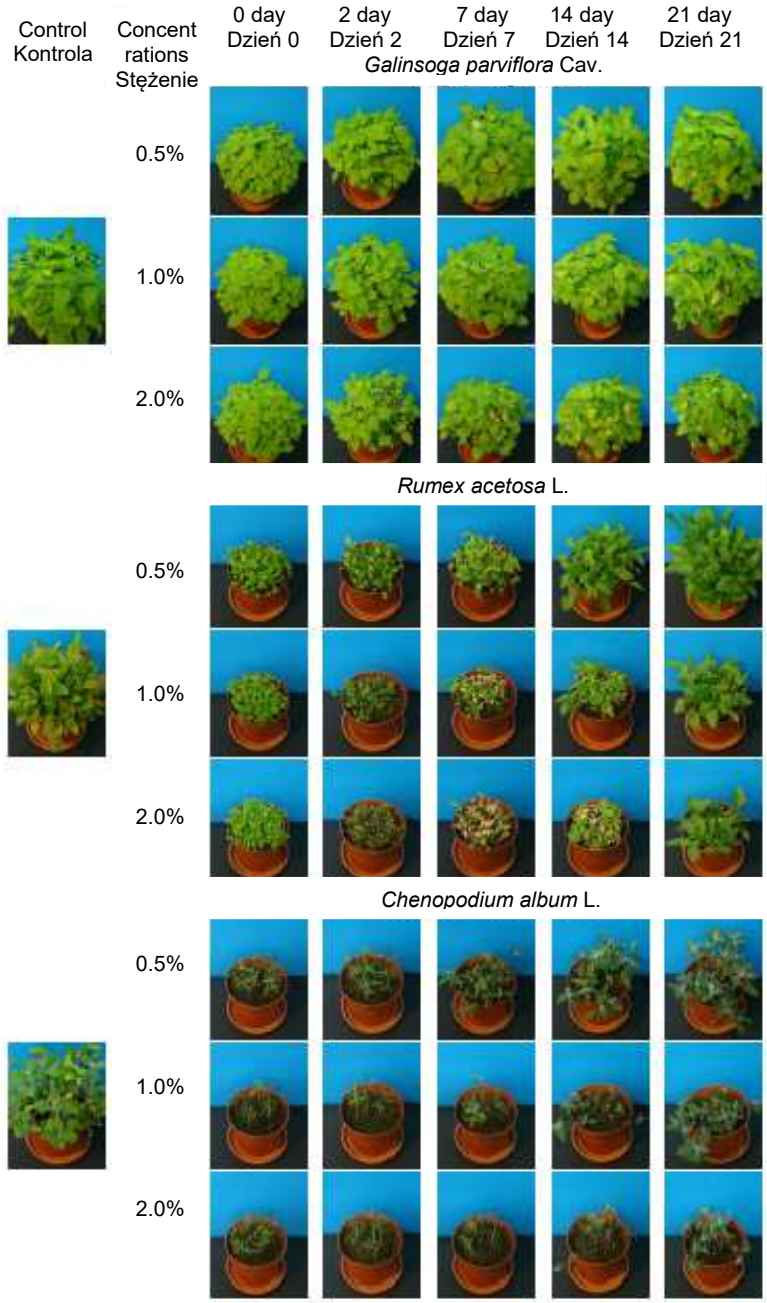

Fig. 2. Reaction of plants on spraying with 0.5%, 1.0% and 2.0% solution of tetraethylammonium chloride [TEA][Cl]
Ryc. 2. Reakcja chwastów na oprysk roztworami chlorku tetraetyloamoniowego [TEA][Cl] o stężeniu 0,5%, 1,0% i 2,0%

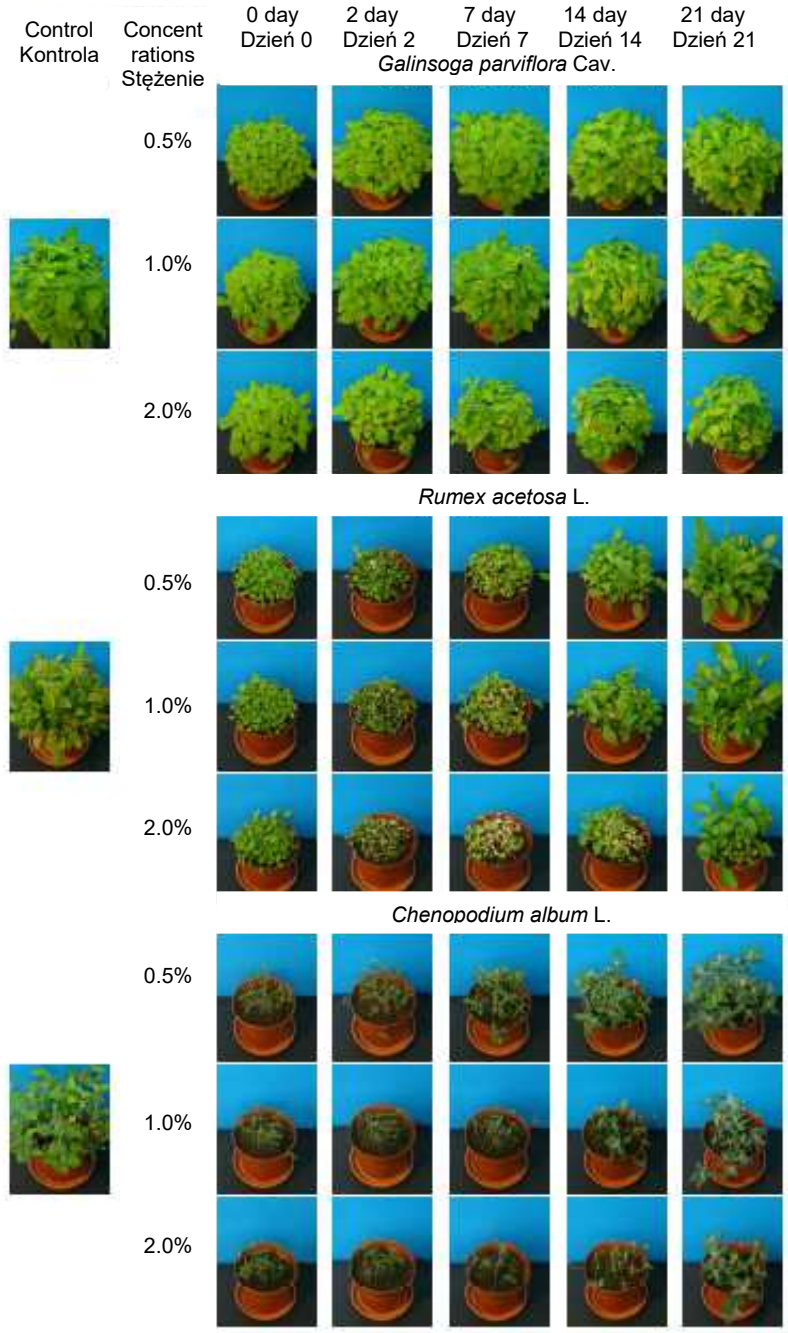

Fig. 3. Reaction of plants on spraying with 0.5%, 1.0% and 2.0% solution of tetraethylammonium bromide [TEA][Br]
Ryc. 3. Reakcja chwastów na oprysk roztworami bromku tetraetyloamoniowego [TEA][Br] o stężeniu 0,5%, 1,0% i 2,0%

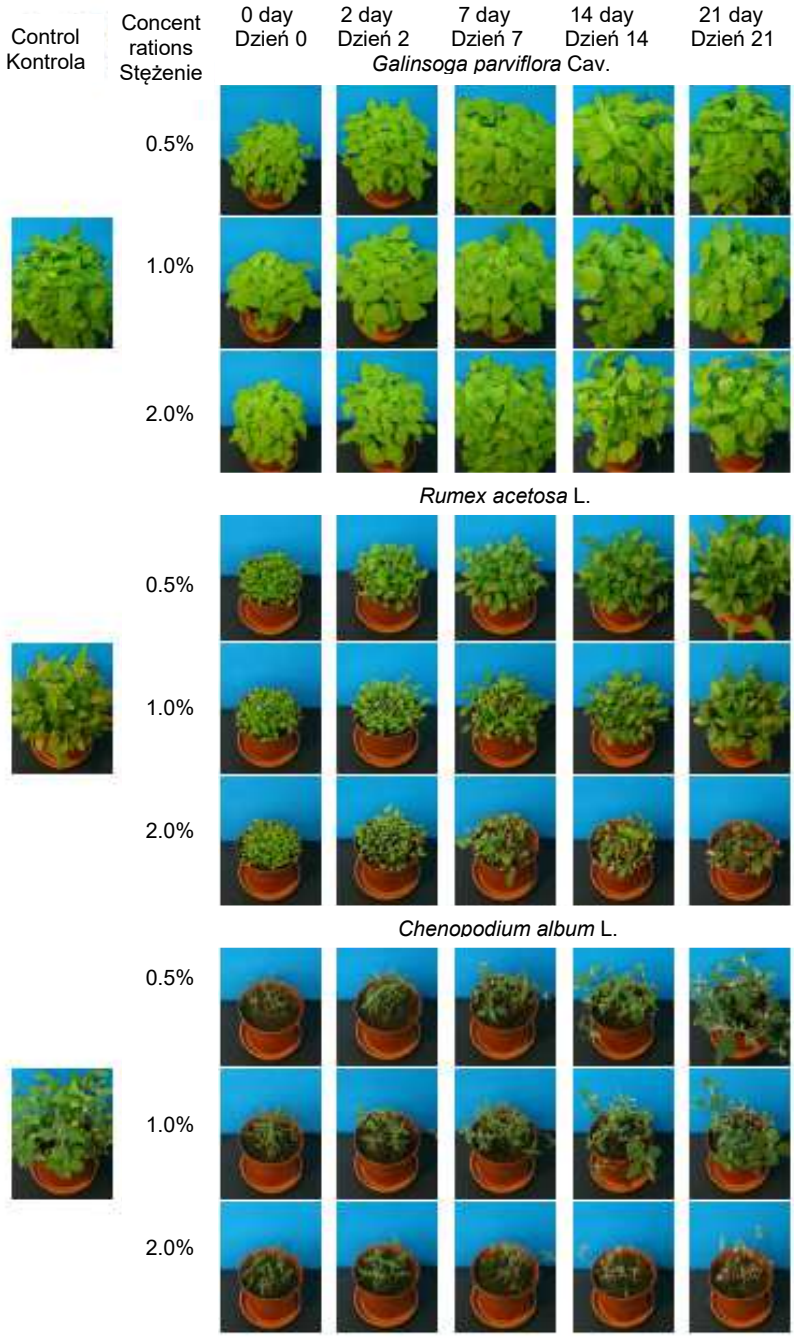

Fig. 4. Reaction of plants on spraying with 0.5%, 1.0% and 2.0% solution of tetraethylammonium iodide [TEA][I]
Ryc. 4. Reakcja chwastów na oprysk roztworami jodku tetraetyloamoniowego [TEA][I] o stężeniu 0,5%, 1,0% i 2,0%

The observations made on the basis of plants appearance are reflected in the length of plants and their roots, as well as in calculated EC_{50} values. Spraying of weeds leaves with all QAS usually caused an inhibition in these plants growth, which was more pronounced with higher concentration of the applied compound. Only an application of spraying with [TEA][I] solutions to *G. parviflora* did not result in plants growth inhibition, irrespective of the concentration used (Table 4).

Table 4. EC_{50} and inhibition of growth plant *G. parviflora, R. acetosa* and *C. album* exposed to [TEA][Cl], [TEA][Br] and [TEA][I] (mean ± SD, *n* = 3)
Tabela 4. EC_{50} i inhibicja wzrostu roślin *G. parviflora, R. acetosa* i *C. album* narażonych na [TEA][Cl], [TEA][Br] i [TEA][I] (średnia ± odch. stand., *n* = 3)

	Concentration of compounds Stężenie substancji [%]	*G. parviflora*		*R. acetosa*		*C. album*	
		Inhibition Inhibicja	EC_{50} [%]	Inhibition Inhibicja	EC_{50} [%]	Inhibition Inhibicja	EC_{50} [%]
[TEA][Cl]	0.5	14.99 ± 5.81	3.49 ± 0.04	7.02 ± 2.67	1.76 ± 0.64	28.31 ± 5.76	3.82 ± 0.07
	1.0	23.92 ± 9.58		37.96 ± 9.53		33.97 ± 2.07	
	2.0	37.83 ± 5.85		51.40 ± 6.07		44.31 ± 5.11	
[TEA][Br]	0.5	20.33 ± 6.41	292.90 ± 0.10	11.59 ± 2.11	2.10 ± 0.25	26.93 ± 5.07	4.20 ± 0.17
	1.0	20.84 ± 7.17		31.28 ± 6.92		38.03 ± 3.50	
	2.0	25.57 ± 9.50		47.27 ± 4.87		40.70 ± 9.46	
[TEA][I]	0.5	–5.24 ± 9.66	non-toxic nietoksyczny	16.79 ± 8.39	1.55 ± 0.05	18.67 ± 2.37	2.60 ± 0.28
	1.0	–8.18 ± 8.73		35.86 ± 6.31		23.80 ± 4.75	
	2.0	–11.88 ± 3.06		58.38 ± 6.14		44.91 ± 2.93	

Due to the fact that the treatments were made in the form of foliar sprays of the weeds, they had a significantly lower impact on the examined plants roots. Statistically significant inhibition of root growth was only found in the case of *C. album* roots after an application of the treatments with [TEA][Br] and [TEA][I] solutions, and *G. parviflora* roots after plants spraying with [TEA][Br] solution at a concentration of 2.0%. No root growth inhibition was noted in the case of *R. acetosa*, regardless of the applied compound and its concentration (Table 5).

Table 5. EC_{50} and inhibition of growth root *G. parviflora, R. acetosa* and *C. album* exposed to [TEA][Cl], [TEA][Br] and [TEA][I] (mean ± SD, *n* = 3)
Tabela 5. EC_{50} i inhibicja wzrostu korzeni *G. parviflora, R. acetosa* i *C. album* narażonych na [TEA][Cl], [TEA][Br] i [TEA][I] (średnia ± odch. stand., *n* = 3)

	Concentration of compounds Stężenie substancji [%]	*G. parviflora*		*R. acetosa*		*C. album*	
		Inhibition Inhibicja	EC_{50} [%]	Inhibition Inhibicja	EC_{50} [%]	Inhibition Inhibicja	EC_{50} [%]
[TEA][Cl]	0.5	–8.78 ± 7.80	3.57 ± 1.09	–19.40 ± 6.20	non-toxic nietoksyczny	–1.43 ± 2.32	non-toxic nietoksyczny
	1.0	0.57 ± 2.05		–6.13 ± 4.61		–6.25 ± 8.72	
	2.0	4.44 ± 3.59		–0.35 ± 6.69		–5.14 ± 7.26	
[TEA][Br]	0.5	–6.73 ± 7.43	4.22 ± 2.56	–3.97 ± 4.39	non-toxic nietoksyczny	2.56 ± 5.45	11.03 ± 0.78
	1.0	6.15 ± 2.15		–6.88 ± 4.73		17.26 ± 2.59	
	2.0	14.18 ± 5.92		–11.85 ± 2.28		17.46 ± 3.67	
[TEA][I]	0.5	–4.91 ± 3.03	non-toxic nietoksyczny	–8.83 ± 3.32	non-toxic nietoksyczny	15.22 ± 4.27	1.62 ± 0.22
	1.0	–4.96 ± 2.74		–11.81 ± 3.72		16.01 ± 3.69	
	2.0	2.66 ± 1.69		–13.02 ± 2.29		65.63 ± 7.85	

Also the dry weight content was determined in the study conducted for the plants sprayed with examined QAS solutions. No significant changes in dry weight content of the plants subject to the treatments were noted in the case of *G. parviflora*, compared to the control. In turn, a decrease in dry weight content was observed in *R. acetosa* and *C. album* plants, and the decrease was greater with higher concentration of [TEA][Cl] and [TEA][Br] solutions used

for foliar spraying of these weed species. Dry weight content decreased after *R. acetosa* plants spraying with [TEA][I] solutions at a concentration of 0.5 and 1.0%, while an application of spraying with 2.0% solution of that compound resulted in a large increase in dry weight content in that plant leaves. In the case of *C. album*, spraying with [TEA][I] solutions at a concentration of 0.5% and 1.0% resulted in no major changes in dry weight content, while an application of 2.0% solution of this salt caused a very high (about 130%) dry matter increase, compared to the control (Table 6).

Table 6. Effect of [TEA][C], [TEA][Br] and [TEA][I] on dry weight [g · g^{-1} FW] weeds (mean ± SD, *n* = 3)
Tabela 6. Wpływ [TEA][C], [TEA][Br] i [TEA][I] na zawartość suchej masy [g · g^{-1} św.m.] chwastów (średnia ± odch. stand., *n* = 3)

		Control Kontrola	Concentration of compounds Stężenie substancji			$LSD_{0.05}$ $NIR_{0,05}$
			0.5%	1.0%	2.0%	
G.parviflora	[TEA][Cl]	0.1595 ± 0.0021	0.1679 ± 0.0019	0.1575 ± 0.0047	0.1674 ± 0.0098	0.0086
	[TEA][Br]		0.1488 ± 0.0119	0.1635 ± 0.0075	0.1516 ± 0.0043	0.0114
	[TEA][I]		0.1646 ± 0.0296	0.1496 ± 0.0114	0.1603 ± 0.0058	0.0249
R. acetosa	[TEA][Cl]	0.1701 ± 0.0123	0.1029 ± 0.0055	0.1041 ± 0.0004	0.0972 ± 0.0020	0.0105
	[TEA][Br]		0.1237 ± 0.0152	0.1252 ± 0.0044	0.1051 ± 0.0042	0.0158
	[TEA][I]		0.1349 ± 0.0087	0.1387 ± 0.0110	0.1889 ± 0.0005	0.0144
C.album	[TEA][Cl]	0.1696 ± 0.0024	0.1684 ± 0.0092	0.1047 ± 0.0004	0.0999 ± 0.0004	0.0073
	[TEA][Br]		0.1480 ± 0.0043	0.1023 ± 0.0010	0.0980 ± 0.0021	0.0042
	[TEA][I]		0.1602 ± 0.0016	0.1498 ± 0.0114	0.3913 ± 0.0005	0.0092

The use of treatments involving plants spraying with QAS solutions, also resulted in the changes in assimilation pigments content in examined weeds plants. *G. parviflora* plants spraying with these substances solutions caused a decrease in the content of chlorophyll *a*, chlorophyll *b*, total chlorophyll, carotenoids, as well as the ratio of chlorophyll *a* to *b*, and the ratio of total chlorophyll to carotenoids in relation to the control sites. Also in *C. album* plants, an application of these substances led to a reduction in the level of all assimilation pigments with respect to their content in the control plants, however there was an increase in the values of chlorophyll *a* and *b*, as well as total chlorophyll and carotenoids ratio. In the case of *R. acetosa*, the changes in assimilation pigments content were dependent on the compound used, and did not demonstrate such clear relationship like these observed in other weeds species. The only pigment, which content increased in *R. acetosa* plants, collected from all experimental sites, were carotenoids. An increase in chlorophyll *a* content as compared to the control was noted in *R. acetosa* plants sprayed with [TEA][Cl] and [TEA][Br] solutions, while the content of this pigment was reduced in the leaves of plants sprayed with solutions of [TEA][I]. The content of chlorophyll *b* and total chlorophyll, as well as the ratio of chlorophyll *a* to *b*, and total chlorophyll to carotenoids in *R. acetosa* plants increased after an application of lower concentrations of the examined compounds, and a slight decrease in the level of these biomarkers was noted in case of the highest concentration used (Table 7).

Table 7. Changes in the content of assimilation pigments [mg · g^{-1} FW] in *G. parviflora, R. acetosa* and *C. album* leaves exposed to [TEA][Cl], [TEA][Br] and [TEA][I] (mean ± SD, *n* = 3)
Tabela 7. Zmiany zawartości barwników asymilacyjnych [mg · g^{-1} św.m.] w liściach *G. parviflora, R. acetosa* i *C. album* narażonych na [TEA][Cl], [TEA][Br] i [TEA][I] (średnia ± odch. stand., *n* = 3)

			Control Kontrola	Concentration of compounds Stężenie substancji			$LSD_{0.05}$ $NIR_{0,05}$
				0.5%	1.0%	2.0%	
[TEA][Cl]	*G. parviflora*	Chl *a*	1.263 ± 0.003	1.191	0.856 ± 0.001	0.898 ± 0.007	0.006
		Chl *b*	0.398 ± 0.012	0.380 ± 0.001	0.286 ± 0.001	0.301± 0.001	0.009
		Chl*a+b*	1.661 ± 0.010	1.571 ± 0.001	1.242 ± 0.002	1.199 ± 0.008	0.010
		Car	0.331 ± 0.007	0.312	0.255 ± 0.001	0.259 ± 0.003	0.006
		a/b	3.176 ± 0.010	3.134 ± 0.012	3.347 ± 0.009	2.987 ± 0.010	0.077
		Chl/car	5.018 ± 0.129	5.030 ± 0.005	4.868 ± 0.021	4.626 ± 0.025	0.103
	R. acetosa	Chl *a*	0.889 ± 0.003	1.161 ± 0.006	1.109 ± 0.008	1.042 ± 0.008	0.010
		Chl *b*	0.319 ± 0.001	0.353	0.305 ± 0.002	0.298 ± 0.002	0.003
		Chl*a+b*	1.208 ± 0.002	1.514 ± 0.006	1.414 ± 0.010	1.340 ± 0.008	0.011
		Car	0.224 ± 0.002	0.264 ± 0.001	0.247 ± 0.001	0.242 ± 0.003	0.003
		a/b	2.786 ± 0.022	3.286 ± 0.020	3.636 ± 0.028	3.504 ± 0.043	0.046
		Chl/car	5.390 ± 0.033	5.739 ± 0.018	5.720 ± 0.030	5.528 ± 0.049	0.053
	C. album	Chl *a*	1.404 ± 0.008	1.286 ± 0.009	1.184 ± 0.005	0.974 ± 0.002	0.010
		Chl *b*	0.407 ± 0.012	0.384 ± 0.012	0.357 ± 0.015	0.267 ± 0.008	0.019
		Chl*a+b*	1.811 ± 0.018	1.670 ± 0.011	1.541 ± 0.014	1.241 ± 0.010	0.021
		Car	0.348 ± 0.007	0.308 ± 0.003	0.274 ± 0.008	0.224 ± 0.002	0.009
		a/b	3.449 ± 0.091	3.350 ± 0.117	3.317 ± 0.144	3.649 ± 0.103	0.178
		Chl/car	5.208 ± 0.062	5.415 ± 0.089	5.630 ± 0.222	5.550 ± 0.101	0.206
[TEA][Br]	*G. parviflora*	Chl *a*	1.263 ± 0.003	0.900 ± 0.006	0.839 ± 0.014	0.701 ± 0.012	0.015
		Chl *b*	0.398 ± 0.012	0.299 ± 0.003	0.272 ± 0.004	0.244 ± 0.004	0.010
		Chl*a+b*	1.661 ± 0.010	1.199 ± 0.007	1.111 ± 0.018	0.945 ± 0.016	0.021
		Car	0.331 ± 0.007	0.331 ± 0.007	0.271 ± 0.001	0.218 ± 0.005	0.007
		a/b	3.176 ± 0.010	3.010 ± 0.029	3.089 ± 0.019	2.871 ± 0.022	0.082
		Chl/car	5.018 ± 0.129	4.423 ± 0.013	4.661 ± 0.034	4.330 ± 0.040	0.108
	R. acetosa	Chl *a*	0.889 ± 0.003	1.140 ± 0.006	0.982 ± 0.007	0.923 ± 0.026	0.021
		Chl *b*	0.319 ± 0.001	0.339 ± 0.001	0.294 ± 0.003	0.280 ± 0.010	0.008
		Chl*a+b*	1.208 ± 0.002	1.479 ± 0.007	1.276 ± 0.009	1.203 ± 0.035	0.029
		Car	0.224 ± 0.002	0.264 ± 0.002	0.243 ± 0.004	0.227 ± 0.007	0.006
		a/b	2.786 ± 0.022	3.366 ± 0.010	3.343 ± 0.020	3.301 ± 0.035	0.036
		Chl/car	5.390 ± 0.033	5.601 ± 0.049	5.248 ± 0.055	5.304 ± 0.024	0.065
	C. album	Chl *a*	1.404 ± 0.008	1.280	1.127 ± 0.018	1.003 ± 0.005	0.015
		Chl *b*	0.407 ± 0.012	0.363 ± 0.003	0.313 ± 0.003	0.300 ± 0.004	0.010
		Chl*a+b*	1.811 ± 0.018	1.643 ± 0.003	1.440 ± 0.020	1.303 ± 0.008	0.022
		Car	0.348 ± 0.007	0.289 ± 0.002	0.250 ± 0.004	0.218 ± 0.001	0.006
		a/b	3.449 ± 0.091	3.525 ± 0.029	3.596 ± 0.028	3.351 ± 0.406	0.083
		Chl/car	5.208 ± 0.062	5.683 ± 0.021	5.758 ± 0.027	5.973 ± 0.060	0.072
[TEA][I]	*G. parviflora*	Chl *a*	1.263 ± 0.003	1.101 ± 0.004	0.947 ± 0.008	0.953 ± 0.017	0.015
		Chl *b*	0.398 ± 0.012	0.350 ± 0.002	0.293 ± 0.003	0.309 ± 0.006	0.010
		Chl*a+b*	1.661 ± 0.010	1.451 ± 0.007	1.240 ± 0.010	1.262 ± 0.022	0.021
		Car	0.331 ± 0.007	0.287	0.259 ± 0.002	0.255 ± 0.003	0.006
		a/b	3.176 ± 0.010	3.147 ± 0.007	3.227 ± 0.017	3.081 ± 0.017	0.079
		Chl/car	5.018 ± 0.129	5.050 ± 0.026	4.789 ± 0.004	4.940 ± 0.037	0.105
	R. acetosa	Chl *a*	0.889 ± 0.003	1.110 ± 0.005	1.113 ± 0.004	0.929 ± 0.005	0.007
		Chl *b*	0.319 ± 0.001	0.321	0.341 ± 0.002	0.335 ± 0.002	0.002
		Chl*a+b*	1.208 ± 0.002	1.431 ± 0.005	1.454 ± 0.005	1.264 ± 0.007	0.008
		Car	0.224 ± 0.002	0.269	0.269 ± 0.010	0.24 3	0.002
		a/b	2.786 ± 0.022	3.454 ± 0.011	3.265 ± 0.015	2.773 ± 0.010	0.024
		Chl/car	5.390 ± 0.033	5.310 ± 0.035	5.400 ± 0.008	5.194 ± 0.035	0.046
	C. album	Chl *a*	1.404 ± 0.008	1.632 ± 0.009	1.341 ± 0.005	–	0.014
		Chl *b*	0.407 ± 0.012	0.447 ± 0.004	0.397 ± 0.003	–	0.014
		Chl*a+b*	1.811 ± 0.018	2.079 ± 0.005	1.738 ± 0.008	–	0.022
		Car	0.348 ± 0.007	0.328 ± 0.001	0.322 ± 0.001	–	0.007
		a/b	3.449 ± 0.091	3.651 ± 0.054	3.377 ± 0.012	–	0.114
		Chl/car	5.208 ± 0.062	6.331 ± 0.023	5.397 ± 0.031	–	0.078

Chl *a* – chlorophyll *a* – chlorofil *a*, Chl *b* – chlorophyll *b* – chlorofil *b*, chl *a+b* – chlorophyll *a* + chlorophyll *b* – chlorofil *a* + chlorofil *b*, car – carotenoids – karotenoidy, a/b – chlorphyll *a*/chlorophyll *b* – chlorofil *a*/chlorofil *b,* chl/car – (chlorophyll *a* + chlorophyl *b*)/carotenoids – (chlorofil *a* + chlorofil *b*)/karotenoidy.

DISCUSSION

The results of this experiment clearly show that the compound demonstrating the highest phytotoxicity with respect to examined weed plants was tetraethylammonium iodide, introduced directly into the soil in which the seeds were sown. Clearly toxic effect of iodides introduced into the soil in relation to terrestrial higher plants was also reported in the study of Biczak et al. (2013, 2014). Toxic effect of QAS added to the soil may be related to the fact that the soil is an environment of seeds functioning, and the root is an organ responsible for water and nutrients uptake and their transport, so that the plant can live and grow properly (Chapman *et al.* 2012).

When toxic substances are present in the soil environment, they will also be taken up by plant roots and then distributed throughout the whole organism, disrupting thus plants growth and development. The presence of chemical compounds, such as QAS or ILs, in the environment can lead to seeds germination inhibition, or even complete prevention of their germination ability (Peric et al. 2014; Biczak 2016; Pawłowska and Biczak 2016).

The observed QAS effect on the plants can also be related to the salinity of the soil by these compounds. The plants demonstrated different degrees of substrate salinity resistance, and hence differentiated reaction of the examined weeds on tetraethylammonium chloride, bromide and iodide addition to the soil. The salinity can cause disturbances in physiological processes of the plants, physiological drought, and affect morphological and anatomical changes. An effect of the changes observed in plants grown under salinity can include reduced growth rate, chlorotic and necrotic changes on the leaves, changes in chloroplasts and therefore disturbances in photosynthesis process, and even drying of shoots and death of the whole plants. All described effects of salinity of the substrate on which the plants carry out their vegetation are related to oxidative stress occurrence in these organisms (Małuszyńska and Małuszyński 2009; Yao et al. 2010). An effect of [TEA][Cl] and [TEA][Br] on the growth and development of the examined weed species was lower than that found for iodides. It should be concurrently emphasized that QAS interactions with chloride and bromide anions were very similar in nature, as previously reported by Matzke et al. (2009).

An application of examined compounds in the form of spraying also clearly affected the examined weeds. It seems that these compounds may be taken up by the plants, as foliar applied herbicides, through leaf blade surface or stomata (Praczyk and Skrzypczak 2004). *G. parviflora* was the plant the most resistant to applied treatments. A similar effect of ILs used in a form of spraying on *R. acetosa* was also reported by Biczak et al. (2015). In the study presented by these authors, also *G. parviflora* appeared to be the plant most resistant to alkylimidazolium tetrafluoroborates with different lengths of the substituent. In our study, a strong phytotoxic effect of all QAS was observed in the case of *R. acetosa*. High sensitivity of *R. acetosa* to chemical compounds used in a form of foliar spraying was also observed in our previous studies concerning an effect of 2,2'-thioacetic acid on terrestrial higher plants (Pawłowska et al. 2013).

Visible changes in dry weight content affected by the examined compounds were noted in the present study evaluating this factor content as an indicator of phytotoxicity caused by the presence of chemical compounds in the environment. The differences in dry weight level between the control sites, and the sites on which QAS were used, were generally higher with

higher concentration of these salts applied. An increase in dry weight content for *G. parviflora* was noted in the case of examined substances soil-application. An increase in dry weight content in plants, which are in contact with chemical compounds present in the substrate, was also reported by Biczak et al. (2013) and Matusiak et al. (2013). An application of examined compounds in a form of a spraying did not cause so significant changes in dry weight content in *G. parviflora*, while in the case of *R. acetosa* and *C. album* even a decrease in this parameter value was noted. This is consistent with the results of the study conducted by Liu et al. (2015a), who examined broad bean reaction on 1-butyl-3-methylimidazolium chloride introduction in the soil, and noted a significant decrease in dry weight content in that plant leaves. The study conducted within this experiment for different weed species demonstrated that the changes in dry weight content are associated with species differences of the examined plants. Moreover, the study conclusively demonstrated that part of the plants respond to stress induced by exposure to chemical compounds with dry weight decrease, and some on the contrary, with its content increase under such conditions.

The best biomarker of the changes observed in cells caused by the presence of various chemical compounds in the environment is the content of assimilation pigments, which are responsible for photosynthesis process in plants. Some authors reported even a linear decrease in assimilation pigments content with an increase in chemical substances level, including QAS or ILs, in the substrate. Such results were also obtained in the studies on algae, duckweed, broad bean leaves, leek and wheat seedlings (Herman et al. 1998; Wang et al. 2009; Ma et al. 2010; Zhang et al. 2013; Liu et al. 2015b). The authors of cited papers demonstrated that the oxidative stress induced in plants by chemical compounds presence in the substrate leads to an overproduction of reactive oxygen species which damage chloroplasts membranes. This causes disorders in chlorophylls synthesis, in particular chlorophyll *a*, and may lead to premature aging of the plants. This in turn causes a disturbances in chlorophyll *a* to *b* ratio, since under stress conditions just chlorophyll *a* is the main substrate in chlorophyll *b* synthesis (Wang et al. 2009). In our study, we also found some disturbances in the content of chlorophyll *a*, *b*, total chlorophyll, carotenoids, as well as the ratio of chlorophyll *a*/*b* and total chlorophyll to carotenoids, which prove disturbances of photosynthesis process and various capacity of antioxidant systems in the examined species of weeds. As in the case of the studies presented by other researchers, almost linear correlations between assimilation dyes content in the leaves of *C. album* and *G. parviflora* and QAS concentration in the soil were obtained in the present experiment. Similar changes in chlorophylls content in *C. album* affected by NaCl and KCl were observed by Yao et. al. (2010) and Stupnicka-Rodzynkiewicz et al. (2006), who examined chlorophylls content in *Echinochloa* and *Galinsoga* exposed to an activity of eight phenolic acids. Klem et al. (2002) also observed a decrease in chlorophylls fluorescence in *Matricaria* and *Sinapis* under the influence of isoproturon aqueous solutions. Only in the case of *R. acetosa*, there was no decrease in assimilation pigments content in the leaves of this plant, after spraying with examined QAS solutions. No such correlations in *R. acetosa* between chlorophylls content and these substances concentration in the soil can also be caused by an increase in carotenoids content in this plant. Carotenoids are in fact the primary line of defense of PSI and PSII photosystems against ROS, as ascorbate, reduced glutathione or tocopherol (Sun et al. 2007, Arias-Baldrich et al. 2015; Gengmao et al. 2015).

CONCLUSIONS

The study conducted to determine an effect of tetrabutylammonium chloride, bromide and iodide on the growth and development of three different weed species (*C. album, G. parviflora* and *R. acetosa*) conclusively demonstrated that the applied QAS exhibit potential phytotoxic properties. The observed phytotoxicity effect was dependent on the type of treatment (foliar, soil), plant species, and concentration of compound used in the case of foliar spraying. The strongest and total herbicidal properties were demonstrated for tetraethylammonium iodide used in the form of soil-application. [TEA][Cl] and [TEA][Br] showed in turn selective and similar phytotoxic activity with respect to the examined weeds. *R. acetosa* and *C. album* were the plants most sensitive to the applied QAS, while *G. parviflora* was the most resistant to the examined QAS. The observations made on the basis of plants appearance found the confirmation in the changes in dry weight and assimilation pigments content in the examined weeds leaves.

REFERENCES

Aper J., De Cauwer B., De Roo S., Lourenço M., Fievez V., Bulcke R., Reheul D. 2014. Seed germination and viability of herbicide resistant and susceptible *Chenopodium album* populations after ensiling, digestion by cattle and manure storage. Weed Res. 54, 169–177.

Arias-Baldrich C., Bosch N., Begines D., Feria A.B., Monreal J.A., García-Mauriño S. 2015. Proline synthesis in barley under iron deficiency and salinity. J. Plant Physiol. 183, 121–129.

Bazylko A., Boruc K., Borzym J., Kiss A.K. 2015. Aqueous and ethanolic extracts of *Galinsoga parviflora* and *Galinsoga ciliata*. Investigations of caffeic acid derivatives and flavonoids by HPTLC and HPLC-DAD-MS methods. Phytochem. Lett. 11, 394–398.

Biczak R., Pawłowska B., Bałczewski P., Bachowska B., Herman B. 2013. Phytotoxicity of ionic liquid containing phosphorus atom. Ecol. Chem. Eng. A 20, 621–630.

Biczak R., Bałczewski P., Pawłowska B., Bachowska B., Rychter P. 2014. Comparison of phytotoxicity of selected phosphonium ionic liquid. Ecol. Chem. Eng. S 21, 281–295.

Biczak R., Pawłowska B., Feder-Kubis J. 2015. The phytotoxicity of ionic liquids from natural pool of (−)-menthol with tetrafluoroborate anion. Environ. Sci. Pollut. Res. 22, 11740–11754.

Biczak R. 2016. Quaternary ammonium salts with tetrafluoroborate anion: Phytotoxicity and oxidative stress in terrestrial plants. J. Hazard. Mater. 304, 173–185.

Chapman N., Miller A.J., Lindsey K., Whalley W.R. 2012. Roots, water, and nutrient acquisition: let's get physical. Trends Plant Sci. 17, 701–710.

Choudhary S.P., Sharma D.K. 2014. Bioactive constituents, phytochemical and pharmacological properties of *Chenopodium album*: a miracle weed. Int. J. Pharmacogn. 1, 545–552.

De Cauwer B., Devos R., Claerhout S., Bulcke R., Reheul D. 2014. Seed dormancy, germination, emergence and seed longevity in *Galinsoga parviflora* and *G. quadriradiata*. Weed Res. *54*, 38–47.

Gengmao Z., Yu H., Xing S., Shihui L., Quanmei S., Changhai W. 2015. Salinity stress increases secondary metabolites and enzyme activity in safflower. Ind. Crops Prod. 64*,* 175–181.

Grabińska-Sota E. 2004. Ocena oddziaływania czwartorzędowych soli amoniowych na środowisko wodne [Evaluation of impact of quaternary ammonium salts on water environment]. Zesz. Nauk. PŚl. [in Polish]

Herman B., Biczak R., Gurgul E. 1998. Effect of 1,10-phenanthroline on peroxidase and catalase activity and chlorophyll, sugar, and ascorbic acid contents. Biol. Plant. 41, 607–611.

Klem K., Špundová M., Hrabalová H., Nauš J., Váňoá M., Masojídek J. 2002. Comparison of chlorophyll fluorescence and whole-plant bioassays of isoproturon. Weed Res. 42, 335–341.

Kowalska I. 2004. Zawartość wybranych składników szpinaku (*Spinacia oleraceae* L.) uprawianym przy zróżnicowanej zawartości wapnia [The concentration of selected nutrients in the spinach (*Spinacia oleraceae* L.) grown at different levels of calcium]. Rocz. AR Pozn. 360, 105–110. [in Polish]

Liu H., Zhang S., Zhang X., Chen C. 2015a. Growth inhibition and effect on photosystem by three imidazolium ionic liquids in rice seedlings. J. Hazard. Mater. 286, 440–448.

Liu T., Zhu L., Wang J., Wang J., Xie H. 2015b. The genotoxic and cytotoxic effects of 1-butyl-3-methylimidazolium chloride in soil on *Vicia faba* seedlings. J. Hazard. Mater. 285, 27–36.

Ma J.-M., Cai L.-L., Zhang B.-J., Hu L.-W., Li X.-Y., Wang J.-J. 2010. Acute toxicity and effects of 1-alkyl-3-methylimidazolium bromide ionic liquids on green algae. Ecotoxicol. Environ. Saf. 73, 1465–1469.

Małuszyńska I., Małuszyński M.J. 2009. Badanie wpływu zasolenia gleby na wzrost i rozwój wybranych gatunków roślin [Study of soil salinity on growth and advancement of selected plant species]. Inż. Ekolog. 21, 32–39. [in Polish]

Matusiak A., Lewkowski J., Rychter P., Biczak R. 2013. Phytotoxicity of new furan-derived aminophosphonic acid, N-aryl furaldimines and 5-nitrofuraldimine. J. Agric. Food Chem. 61, 7673–7678.

Matuszkiewicz W. 2006. Przewodnik do oznaczania zbiorowisk roślinnych Polski. Warszawa, Wydaw. Nauk. PWN. [in Polish]

Matzke M., Stolte S., Arning J., Uebers U., Filser J. 2009. Ionic liquids in soil: effects of different anion species of imidazolium based ionic liquids on wheat (*Triticum aestivum*) as affected by different clay minerals and clay concentrations. Ecotoxicology 18, 197–203.

Niemczak M., Giszter R., Czerniak K., Marcinkowska K., Walkiewicz F. 2015. Bis(ammonium) ionic liquids with herbicidal anions. RSC Adv. 5, 15487–15493.

Oren R., Werk K.S., Buchmann N., Zimmermann R. 1993. Chlorophyll-nutrient relationships identify nutritionally caused decline in *Picea abies* stands. Can. J. For. Res. 23, 1187–1195.

Pawłowska B., Biczak R. 2016. Evaluation of the effect of tetraethylammonium bromide and chloride on the growth and development of terrestrial plants. Chemosphere 149, 24–33.

Pawłowska B., Biczak R., Bałczewski P. 2013. Fitotoksyczność kwasu 2,2'-tiodioctowego w stosunku do wybranych roślin wyższych [Phytotoxicity of 2,2'-thiodiacetic acid relative to selected higher plants]. Inż. Ochr. Środ. 16, 487–498. [in Polish]

Peric B., Sierra J., Martí E., Cruañas R., Garau M.A. 2014. A comparative study of the terrestrial ecotoxicity of selected protic and aprotic ionic liquids. Chemosphere 108, 418–425.

Pernak J., Niemczak M., Materna K., Żelechowski K., Marcinkowska K., Praczyk T. 2016. Synthesis, properties and evaluation of biological activity of herbicidal ionic liquids with 4-(4-chloro-2-methylphenoxy)butanoate anion. RSC Adv. 6, 7330–7338.

Poonia A., Upadhayay A. 2015. *Chenopodium album* Linn: review of nutritive value and biological properties. J. Food Sci.Technol. 52, 3977–3985.

Praczyk T., Skrzypczak G. 2004. Herbicydy. Poznań, PWRiL, Poland. [in Polish]

Stupnicka-Rodzynkiewicz E., Dabkowska T., Stoklosa A., Hura T., Dubert F., Lepiarczyk A. 2006. The effect of selected phenolic compounds on the initial growth of four weed species. J. Plant Dis. Prot. (spec. iss.) 20, 479–486.

Sun B., Jing Y., Chen K., Song L., Chen F., Zhang L. 2007. Protective effect of nitric oxide on iron deficiency-induced oxidative stress in maize (*Zea mays*). J. Plant Physiol. 164, 536–543.

Tuazon-Nartea J., Savage G. 2013. Investigation of oxalate levels in sorrel plant parts and sorrel-based products. Food Nutr. Sci. 4, 838–843.

Wang L.-S., Wang L., Wang L., Wang G., Li Z.-H., Wang J.-J. 2009. Effect of 1-butyl-3-methylimidazolium tetrafluoroborate on the wheat (*Triticum aestivum* L.) seedlings. Environ. Toxicol. 24, 296–303.

Yao S., Chen S., Xu D., Lan H. 2010. Plant growth and responses of antioxidants of *Chenopodium album* to long-term NaCl and KCl stress. Plant Growth Regul. 60, 115–125.

Zhang B., Li X., Chen D., Wang J. 2013. Effects of 1-octyl-3-methylimidazolium bromide on the antioxidant system of *Lemna minor*. Protoplasma 250, 103–110.

Abstract. One of the main problems observed during plants cultivation is their destruction caused by harmful factors, which include, inter alia, the weeds. The group of troublesome weeds commonly occurring across Poland and in many regions of the world include *Galinsoga parviflora* Cav., *Chenopodium album* L. and *Rumex acetosa* L. Due to such wide dissemination, these plants may come into contact with a number of contaminants, including various chemical compounds that can get into the natural environment. This paper presents an effect of quaternary ammonium salts (QAS) – tetraethylammonium chloride [TEA][Cl], tetraethylammonium bromide [TEA][Br] and tetraethylammonium iodide [TEA][I], introduced into the soil and applied as foliar spraying, on the growth and development of selected weed species. An application of examined compounds in the soil demonstrated that *Chenopodium album L*. was the plant the most sensitive to examined chemicals, and tetraethylammonium iodide was the compound with the highest phytotoxicity to the examined weeds. Phytotoxicity of the examined salts applied in the form of spraying was in turn dependent on QAS concentration and species of plants used in the experiment. This was reflected in an inhibition of the length of plants and their roots, as well as the changes in dry weight and photosynthetic pigments content.

The work was financed by a statutory activity subsidy from the Polish Ministry of Science and Higher Education for The Faculty of Mathematics and Natural Sciences of Jan Długosz University in Częstochowa.