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Research Article

Ecotoxicological Properties of Tulipalin A-Based Superabsorbents versus Conventional Superabsorbent Hydrogels

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The Phytotoxicological Aspects of a Novel Superabsorbent/Hydrogels: poly(acrylamide-*co*-sodium 4-hydroxy-2-methylenebutanoate), prepared from renewable monomer Tulipalin A, on the growth and development of monocotyledonous *Avena sativa* and dicotyledonous *Raphanus sativus*, was investigated and compared with the effect of borate-crosslinked poly(vinyl alcohol), poly(acrylamide), and poly(acrylamide-*co*-sodium acrylate) conventional hydrogels. Tulipalin A-based superabsorbent hydrogels revealed superior properties in terms of the combination of the tested properties. The results confirmed excellent suitability of Tulipalin A-based hydrogels for application as reservoirs of water during plant stress condition. Values of fresh matter (yield) and shoot height of the examined plants growing in soil amended with these hydrogels were ca 10% higher than those of plants growing in soil without hydrogels. Reference borate-crosslinked PVA hydrogels (containing increasing amount of borax crosslinker) revealed harmful effect on plants. The negative effect was observed on most of the investigated properties, increasing with content of the hydrogel in soil and concentration of the borax in it.

1. Introduction

The intensively ongoing climate change leading to heat waves, droughts, or excessive rainfall is one of the most significant environmental, social, and economic problems. From the environmental and horticultural point of view, soil water deficit caused by droughts and subsequently increasing soil salinity is the major limiting factors of plant growth and agricultural productivity [1]. It is therefore crucial to develop new, environmentally friendly materials that can overcome water stress, as the stress affects plants at various levels of their organization, including changes in photosynthesis, respiration, translocation, nutrient metabolism, carbohydrates, ion uptake, and hormones [2].

Currently, hydrogels have become one of the most attractive materials for use in agriculture as a soil conditioner because of their three-dimensional cross-linked hydrophilic polymeric network capable of swelling and holding large amounts of water [3]. They are widely used in agriculture, forestry, and gardening, such as soil water retention agent, seed coating, soil-less cultivation, and artificial turf [4–9]. For agricultural purposes, the application of hydrogels as a soil improvement agent has two important advantages: (1) in drought condition, it is an excellent reservoir of water for plant roots, and (2) it can play the opposite role by protecting plant against waterlogging. In fact, most research on hydrogels focuses on their applicability as a soil conditioner especially in regions with scarce water resources and in places where the opportunity for irrigation is limited. This is due to their ability to retain huge volumes of water in the swollen state, which not only facilitates nutrient utilization by plants during water soil deficiency but also improves soil physical properties such as soil aggregate stability by gluing particles together within aggregates as well as by coating the aggregate surface [10, 11]. Commercial agriculture consumes an increasing amount of water; therefore, from an economical and environmental protection point of view, hydrogels hold water under the surface of soil and thus reduce the frequency of irrigation and water consumption and simultaneously limit the production of excessive amount of wastewater containing undesirable, leached agrochemicals. The usefulness of hydrogels as a reservoir of water available for plants in the root zone has been already described [12–14].

Recently, hydrogels for agricultural purposes have mostly been investigated for their application as carriers of fertilizers in controlled release systems of agrochemicals. The release of active substances is activated by swelling during soil irrigation or rainfall, and the rate of release toward the outside of the hydrogel is related to the swelling rate [15–18]. Some researchers have indicated the use of hydrogels as a medium for seed growth [19, 20].

A large variety of both naturally occurring and synthetic polymers have been already employed for the preparation of hydrogels including cellulose, chitosan, dextran, agarose, collagen, poly(vinyl alcohol), poly(*N*-vinyl pyrrolidone), poly(2-hydroxyethyl methacrylate), poly(acrylic acid), polyacrylamide, poly(*N*-isopropyl acrylamide-*co*-acrylic acid), and poly(ethylene oxide) [21–25]. Because of the low cost, abundance, and ecofriendly properties, polysaccharides are considered as substitutes of petroleum derivatives in the preparation of superabsorbents [26]. In the previous decade, renewable sugar-based monomers received much worldwide attention. γ-Butyrolactone and some of its derivatives represent a suitable source for sustainable polymers. α-Methylene-γ-butyrolactone (MBL), also known as Tulipalin A, belongs to the class of sesquiterpene lactone family. Tulipalin A is derived from 6-tuliposides found in tulips [27] or is synthesized from biomass sugar-based itaconic anhydride [28]. It is considered as a cyclic analog of the most common vinyl monomer—methyl methacrylate [29]. Thus, it can serve as a dual monomer enabling both radical polymerization and ring-opening copolymerization [30, 31]. Kollar et al. (2016) used for the first time the open form of MBL, i.e., sodium 4-hydroxy-2-methylenebutanoate (SHMB) as a comonomer in radical copolymerization [32]. Hydrogels with a superior degree of swelling and comfortable handling were synthesized by copolymerization of SHMB with acrylamide (AM) at various ratios in the presence of *N,N′*-methylenebis(acrylamide) as a cross-linker. The degree of swelling of the synthesized hydrogels was strongly dependent on SHMB content and increased with the increase in the content of SHMB and decrease in the concentration of cross-linker. The authors proved that the obtained SHMB/AM hydrogels possess significantly higher degree of swelling than hydrogels based on copolymers of sodium acrylate with AM.

The aim of the present study was to assess the phytotoxicity of Tulipalin A-based hydrogels and to compare them with conventional and commonly used hydrogels based on poly(vinyl alcohol), polyacrylamide, and poly(acrylamide-*co*-sodium acrylate) in terms of their potential application as a safe reservoir of water in soil stress condition.

2. Materials and Methods

2.1. Materials. Acrylamide (AM, >98 %), α-methylene-γ-butyrolactone (MBL, 97 %), acrylic acid (AA, >99 %), *N,N′*-methylenebisacrylamide (BIS, 99 %), deuterated water (D_2O, 99.9 %), and 2,2′-azobis(2-methylpropionamidine) dihydrochloride (V-50, 97 %) were purchased from Sigma Aldrich, USA, and were used as received. Hydrochloric acid (35 %), analytical grade, was purchased from Centralchem, Slovakia, sodium hydroxide from AFT Bratislava, Slovakia.

Poly(vinyl alcohol), PVA (DP_n = 2000, 86-89 mol% hydrolyzed; Fluka), and borax (sodium tetraborate decahydrate; Pharma Cosmetic, Poland) were used as received.

2.2. Hydrogel Synthesis. The overall scheme of hydrogel synthesis is depicted in Scheme 1 *(Supplementary Material)*.

Poly(acrylamide) (PAM) hydrogel was synthesized according to the method of Calvet et al. (2004) [33]. Poly(acrylamide-co-sodium 4-hydroxy-2-methylenebutanoate) hydrogels (AM-SHMB) with the molar ratios of 3:1 and 1:1 were synthesized according to the method described by Kollar et al. [32]. Poly(acrylamide-*co*-sodium acrylate) hydrogels AM-SA with the molar ratios of 1:1, 1:3, and 3:1 were synthesized according to the method described previously in details by Kollar et al. (2016) [32]. Poly(vinyl alcohol)-tetrahydroxyborate hydrogels (PVA-B1, PVA-B2, and PVA-B3 with molar ratios 33:1, 17:1, and 11:1 w/w, respectively) were prepared according to the commonly used method reported elsewhere with minor modifications [34].

The detailed synthesis is described in *Supplementary Material.*

2.3. NMR Spectroscopy. ^{1}H NMR was recorded in D_2O on Varian Gemini 300 instrument at 298 K at working frequency 300 MHz. Chemical shifts are reported in ppm with reference to internal standard, trimethylsilyl propanoic acid (TSP). ^{13}C NMR was recorded in D_2O on Varian MR400 at 298 K. Determination of copolymerization parameters of AM and sodium4-hydroxy-2-methylenebutanoate (SHMB) was perform by *in situ* NMR technique using Varian/Agilent 600 MHz spectrometers equipped with an indirect triple resonance HCN-probe. NMR spectrum of AM-SHMB was described in details by Kollar et al. (2016) [32]. (Figure S1, Supplementary Material)

2.4. ATR-FTIR Spectroscopy. Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) measurements were performed with an FTIR NICOLET 8700 spectrometer (Thermo Scientific, UK) using a single bounce ATR accessory equipped with a Ge crystal. For each measurement, the spectral resolution was 2 cm^{-1} and 64 scans were performed (Figures S2–S5, Supplementary Material)

2.5. Water Holding Capacity, Loss of Soil Moisture, and Plant Growth Test

2.5.1. Measurement of Percentage of Water Holding Capacity (WHC). Soil used for the measurement of WHC has the following characteristics: granulometric composition of soil (sand 77%, dust 4%, and loam 19%) was measured by the sedimentation method. The content of organic carbon was determined to be ca. 2%, pH (KCl) – 6.3, and pH (H_2O) – 6.7, and salinity was 80 mg of KCl/l.

Each hydrogel in the amount of 125, 187.5, and 250 mg, which corresponds to 500, 750, and 1,000 mg of dried hydrogel per kg of soil dry weight, respectively, was well mixed with 250 g of dry soil and kept in a 250-mL capacity plastic pot. When weighted (marked W_d), 200 g of tap water was slowly added into the pot until water seeped out through the holes at the bottom. Next, the pot was three times refilled with seeped water to ensure that the hydrogels absorbed the water to their maximal capacity. After there was no seeping of water from the pot bottom, the pot was weighed again (marked W_s). A control experiment, i.e., without hydrogels, was also carried out. WHC was measured for each hydrogel at every concentration in three replicates.

$$WHC\% = \frac{W_s - W_d}{W_d - W_p} \times 100 \quad (1)$$

W_s is weight of a pot with water saturated soil.

W_d is weight of a pot with dried soil.

W_p is weight of pot without soil.

2.5.2. Measurement of Water Retention. After total water saturation of pots filled with soil containing hydrogels, loss of soil moisture by weighing each pots after the periods of time, 0.5, 1, 1.5, 2, 3, 4, and 5 days, was measured. Percentage water retention (WR%) was calculated as follows:

$$WR\% = \frac{W_T}{W_S} \times 100 \quad (2)$$

W_T is weight of a pot loaded with soil and hydrogels after specified period of time

W_S is weight of a pot loaded with soil and hydrogels totally saturated with water.

2.5.3. Plant Growth Test. Phytotoxicity assessment of all hydrogels was performed in a vegetation hall that met the criteria of the OECD 208 Guideline for Terrestrial Plants Growth Test. Oat (*Avena sativa*) and radish (*Raphanus sativus L. subvar. radicula Pers.*) were selected as the representatives of monocotyledonous and dicotyledonous plants, respectively [35]. Soil used for the phytotoxicity test was the same as that used for WHC measurements. Plant growth assessment was carried out in polypropylene (PP) pots (∅ = 90 mm and volume = 300 cm^3), which were filled with the control soil or with soil mixed with the test hydrogels added at the following concentrations: 250, 500, 750, and 1.000 mg of dry hydrogel per kg of dry weight of soil (s.d.w.). Each concentration was prepared in triplicate (3 pots for each, oat and common radish). Twenty seeds of each plant coming from the same origin were sown under the surface of soil. Seedlings were grown for 14 days under controlled conditions in the vegetation hall. Optimal growth and development of plant was ensured by maintaining proper conditions, including constant humidity at the level required for plant growth (70% field water capacity), temperature (20±2°C), and constant light intensity (ca. 7.000 lux) controlled automatically in a 16 h/day and 8 h/night system.

The phytotoxicity test proposed in this study has been commonly used for the determination of toxicological endpoints such as seedling and root growth, biomass (yield) production, and percent of seed germination or chlorophyll and carotenoid content.

Growth inhibition of root and shoot of oat and radish treated with hydrogels compared to those of untreated plants was measured as described previously [36]. The height of plant seedling was measured from the tip of the longest leaf to the base of culms. Length of root was measured from the tip of the longest root to the root-shoot junction. The growth inhibition ratio of shoots, roots, and fresh matter (yield) was calculated according to

$$\mathrm{GI}\% = \frac{Cp - Tp}{Cp} \times 100\% \quad (3)$$

where Cp is the height/length of shoot/roots (cm) in control plants and Tp is the height/length of shoot/roots (cm) in tested plants. For fresh matter, Cp is the weight of yield (g) in control plants and Tp is the weight of yield (g) in tested plants.

The dry weights (DW) of tested plants were measured after drying at 75°C until the constant weight, according to

$$\mathrm{DW} = \frac{W_D}{W_F} \ \text{(g/g of fresh weight)} \quad (4)$$

where

W_D is weight of plant after drying.

W_F is weight of fresh plant before drying.

The visual evaluation of plants growing in soil treated with the tested hydrogels at the applied concentrations was performed by digital photography. The acquired photos were analyzed to determine any type of damage of tested seedlings, including their growth inhibition, chlorosis, and necrosis.

2.5.4. Measurement of Plant Pigments. Content of photosynthetic pigments including chlorophylls *a* and *b* as well as carotenoids was measured according to the method proposed by Oren et al. (1995) [37]. Briefly, 200 mg of fresh leaves was thoroughly homogenized in a cooled mortar with addition of 20 mL of 80% acetone and then centrifuged. The content of total chlorophyll (chlorophylls *a* and *b*) and carotenoids, expressed as mg/g of dry weight, was calculated according to the absorbance at wavelengths of 470, 647, and 664 nm, respectively.

2.6. Statistical Analysis. The significance of the obtained results was evaluated using the analysis of variance (ANOVA). The least significant difference (LSD) values at a confidence level of 95% were computed using the Tukey test. Moreover, the standard deviation of mean was determined and plotted in diagrams.

Table 1: WHC of the tested hydrogels. Concentrations of lyophilized hydrogels 500, 750, and 1.000 are expressed in mg per kg of soil dry weight.

	Water holding capacity (%)		
Control soil		44.3±0.3	
Sample		Concentration	
	500	750	1000
PAM	46.5±1.0	51.7±0.9	55.3±0.8
AM-SHMB 3:1	46.1±0.8	49.3±1.3	56.9±0.7
AM-SHMB 1:1	47.0±0.6	56.2±0.8	60.4±0.6
AM-SA 3:1	44.5±0.8	49.2±1.0	53.4±0.8
AM-SA 1:1	49.1±0.8	56.4±1.0	61.6±1.1
AM-SA 1:3	46.4±0.8	51.1±1.5	55.6±1.1
PVA-B1	41.3±1.0	46.2±1.1	49.2±1.0
PVA-B2	42.7±1.1	46.7±1.2	50.4±0.9
PVA-B3	43.2±1.0	47.7±1.3	51.6±1.1

3. Results and Discussion

Tulipalin A is a monomer from renewable sources enabling both radical polymerization and ring-opening copolymerization. Herein, it was copolymerized employing its vinyl group and incorporated into polymer network *via* stable C-C bonds. Details of synthesis and characterization including mechanical, thermogravimetric properties, and diffusion coefficient have been already described in details elsewhere [32]. Nevertheless, it should be mentioned that swelling degree of these hydrogels range between 13 000 and 40 000% and it is dependent on both concentrations of crosslinker and content of SHMB. As a comparison, the representative more typical superabsorbent hydrogels comprising AM/sodium acrylate copolymers, prepared under the same conditions, revealed their swelling properties much lower than SHMB-based hydrogels.

The Tulipalin-based hydrogel is referenced with poly (acrylamide) and poly(acrylamide-*co*-sodium acrylate) all of them not being expected to undergo biodegradation. Another reference group are poly(vinyl alcohol)-based hydrogels (PVA-B). Borate-crosslinked PVA hydrogels were prepared with increasing amount of crosslinker borax, expecting improving mechanical properties of the gels, as described earlier [38, 39]. ATR-FTIR spectra of dry PVA-B samples revealed crosslinking and semi-crystalline morphology (see Supplementary Material).

3.1. WHC and Loss of Soil Moisture. As expected, WHC increased with the increase in the concentration of hydrogel in soil (Table 1). The influence of hydrogel composition on WHC depends on the water retention properties of the hydrogel under pressure. Samples containing strongly hydrophilic monomers SHMB and SA exhibited the highest values of WHC. Compared to the control sample, WHC increased from 44% to approximately 60%. In contrast, in hydrogels containing borax, there was only a slight tendency of increase in WHC with the increase in the amount of borax in hydrogel.

Moisture retention, which reflects the loss of moisture, was determined considering the WHC as the point at which the soil water holding capacity has reached its maximum for the entire volume of soil in the pot.

Loss of soil moisture of pots with introduced hydrogels was dependent on the concentration of the particular hydrogel samples added to soil (Figures 1, S6, and S7, Supplementary Material).

With the increase in the amount of hydrogel in the soil, the loss of moisture was lower than that for the control sample. Generally, the same tendency was noticed for all samples. Although the moisture retention for the control sample after 2 days was below 15%, for all the samples with the highest tested concentration of hydrogels, it was still in the range of 40–60%, thus showing significant improvement compared to the control sample. In terms of development of crops, an appropriate moisture condition provides higher absorption of water and nutrients by the plants, thus enabling full development of crops. Therefore, the management of soil WHC is a crucial factor that allows for the optimization of crop production. The tested hydrogels met the criteria of materials that can improve physicochemical properties of soil and enable plant growth. Obviously, in the field condition, the application of hydrogels to soil should be strongly correlated with soil texture and organic matter of soil, which are the key components responsible for the WHC. Nevertheless, the obtained results confirmed that the application of hydrogels to soil has to be managed properly, because plant growth and development are dependent on both their composition and their concentration in particular in soil. Recent literature review on the potential application of hydrogels was focused on their usefulness mostly as soil conditioners for agricultural purposes. Agaba et al. (2011) reported the advantages of hydrogels during plantation forest establishment. Moisture retention of commercially available cross-linked sodium polyacrylate hydrogels influenced soil properties, including aeration, temperature, nutrient transport, and water uptake and transformation, resulting in enhanced plant growth [14]. Demitri et al. (2013) examined the applicability of the three formulations of cellulose-based hydrogels, cross-linked by carbodiimide, as a carrier in the controlled release of water and nutrients in arid and desert areas.

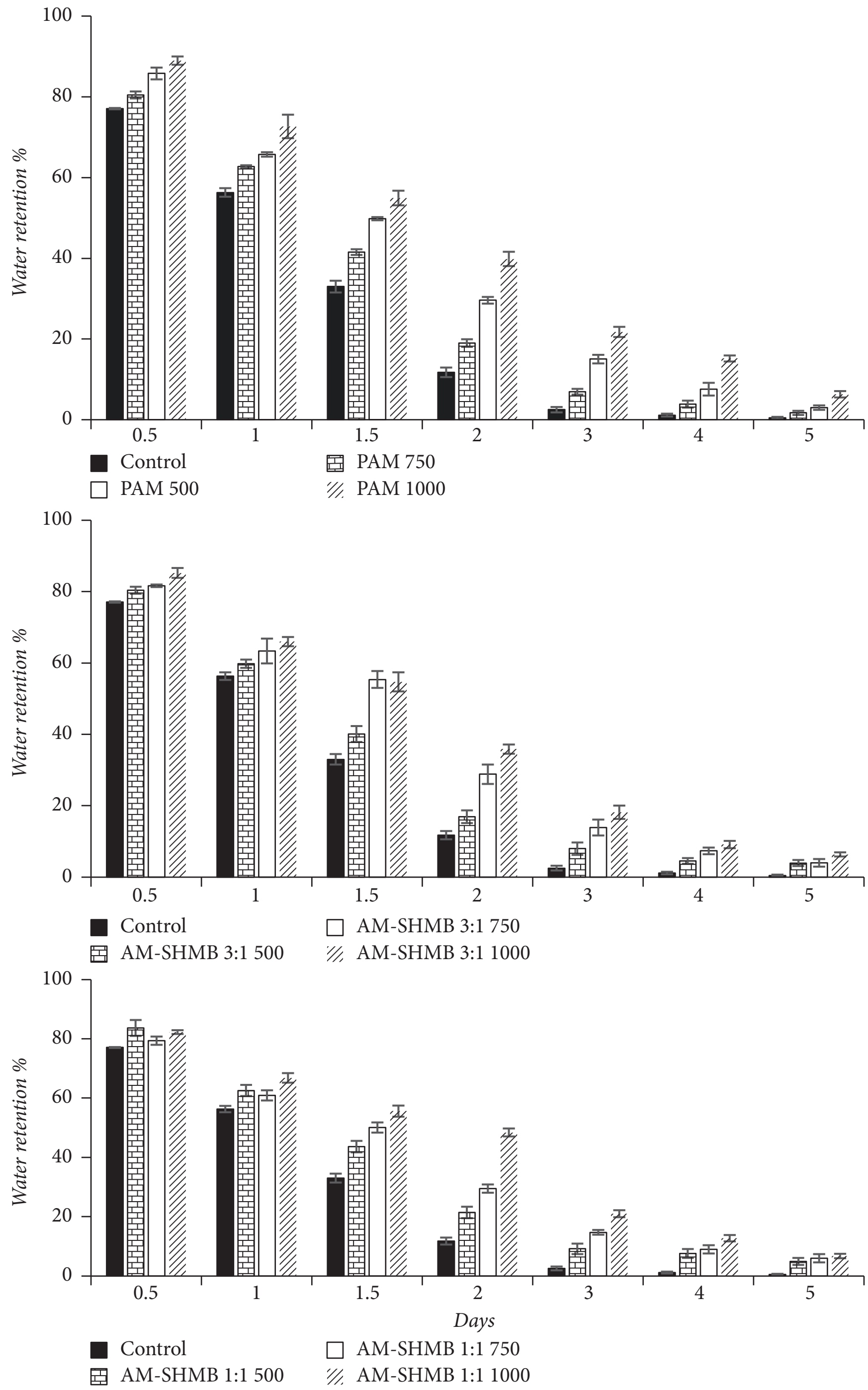

FIGURE 1: Percentage water retention for pure soil and soil containing various concentrations of polyacrylamide (PAM) and poly(acrylamide-*co*-sodium 4-hydroxy-2-methylenebutanoate) (AM-SHMB) hydrogels.

The authors reported that applied hydrogels may control the release of stored water as the soil dries, thus maintaining soil humidity over relatively long time. Moreover, the presence of hydrogel increases soil porosity that provides better oxygenation to plant roots [40].

Parvathy and Jyothi (2014) reported the effect of saponified cassava starch-*g*-poly(acrylamide) hydrogel on the physicochemical and biological properties of soil. The amount of moisture retained in the soil that provided a better control of release of adsorbed water was dependent on the concentration of the used hydrogel [41].

3.2. Plant Growth Test—Germination, Growth Inhibition, and Dry and Fresh Matter. Growth inhibition (GI) of shoot height, root length, and fresh matter of tested plants are presented in Tables 2–4. Average values (mean of three replicates) with calculated least significant differences are presented in Table S1 (Supplementary Material).

Table 2: Effect of PAM, AM-SHMB 3:1, and AM-SHMB 1:1 hydrogels on the shoot height, root length, and fresh matter of oat and radish seedlings (mean ± SD).

Concentration [mg/kg of soil d.w.]	*Inhibition biomarkers [%]*					
			Shoot height			
	Oat			Radish		
	PAM	AM-SHMB 3:1	AM-SHMB 1:1	PAM	AM-SHMB 3:1	AM-SHMB 1:1
250	-0.6±0.3	-1.0±0.2	-0.8±0.2	0.5±0.2	-0.2±0.2	0.8±0.4
500	0.2±0.1	-2.3±0.2	-2.1±0.3	4.8±0.4	-2.2±0.4	-0.5±0.3
750	-0.2±0.8	-5.2±0.6	-5.0±0.6	7.2±1.1	-5.7±0.1	-4.6±0.2
1000	-0.4±0.6	-8.5±0.2	-6.2±0.4	6.9±0.6	-8.3±0.3	-7.9±0.3
			Root length			
	Oat			Radish		
	PAM	AM-SHMB 3:1	AM-SHMB 1:1	PAM	AM-SHMB 3:1	AM-SHMB 1:1
250	-1.1±0.3	0.3±0.1	-0.1±0.1	1.2±0.3	3.5±0.8	1.2±0.2
500	-3.1±0.7	-0.3±0.4	-1.4±0.5	3.8±0.7	2.1±0.6	3.2±0.5
750	-4.2±0.6	-0.7±0.4	-2.0±0.5	5.0±0.3	1.0±0.4	6.8±0.5
1000	-5.9±0.8	-0.8±0.4	-2.8±0.5	6.5±0.7	-0.9±0.7	9.7±0.1
			Fresh matter			
	Oat			Radish		
	PAM	AM-SHMB 3:1	AM-SHMB 1:1	PAM	AM-SHMB 3:1	AM-SHMB 1:1
250	-2.6±0.6	-0.8±0.1	-0.4±0.2	1.2±0.1	-0.8±0.3	1.9±0.2
500	-2.3±0.1	-2.8±0.3	-1.3±0.3	5.6±0.1	-4.1±0.1	0.0±0.1
750	-2.5±0.3	-4.1±0.2	-4.9±0.3	4.8±0.2	-5.4±0.2	-5.8±0.3
1000	-2.2±0.1	-8.5±0.2	-5.9±0.3	5.0±0.3	-7.9±0.1	-8.5±0.0

The results obtained in the experiment revealed that the first group of analyzed hydrogels including PAM- and Tulipalin A-based (AM-SHMB) superabsorbents did not affect the tested parameters of the plants significantly. For radish, pure PAM exhibited stronger influence on all tested parameters than for oat; however, GI did not exceed 8% in both cases compared to the control plants (Table 2). Further, GI of fresh matter and shoots of oat almost did not differ from that of control plants when treated with PAM. It should be noted that this hydrogel caused slightly enhanced growth of oat roots as compared to untreated plants; this finding is important during crop cultivation in soil with moisture deficiency.

Higher content of AM-SHMB 3:1 and AM-SHMB 1:1 hydrogels in soil slightly promoted the growth of shoots and fresh matter of both examined plants (ca. 10% as compared to untreated plants). The ratio of AM and SHMB in the hydrogel sample did not affect the promotion of shoot and green matter growth. The effect of Tulipalin A-based hydrogels on GI of roots of both tested plants was insignificant, except at higher concentration of AM-SHMB 1:1 hydrogel, which slightly inhibited the growth of radish roots; however, the GI did not exceed 10%.

Results of growth inhibition obtained in the group of AM-SA hydrogels revealed various influence on GI% values. Increasing concentration of AM-SA 3:1 hydrogel in soil resulted in slight promotion of growth of green parts and fresh matter of oat seedling (Table 3), while there were almost no changes in GI of roots. However, it should be noted that at low concentration of this hydrogel, slight inhibition particularly of fresh matter was observed. In contrast, increasing concentration of AM-SA 3:1 hydrogel in soil caused increase in shoot and fresh matter GI in radish (10% as compared to untreated plants). However, slightly positive effect was observed on radish root length.

AM-SA hydrogels with higher concentration of sodium acrylate (see AM-SA 1:1 and AM-SA 1:3 in Table 3, Figures S8 and S10 Supplementary Material) produced preferably negative effect on green part and fresh matter growth with mostly positive GI% values for both tested plants, even though the inhibition was still up to 10% as compared to control plants. The roots of both tested plants exhibited quite resistance against AM-SA 1:1 hydrogel, and the GI% values almost did not change when compared to that of control plants even with increasing concentration of AM-SA 1:1 hydrogel in soil, Figure S12, Supplementary Material. The increasing concentration of AM-SA 1:3 hydrogel caused a gradual increase in the percentage growth inhibition of roots from negative GI% values for the lowest applied concentrations of hydrogel in soil, i.e., 250 and 500 mg/kg, to positive GI% with slight inhibition of shoot growth reaching approximately 5–7% as compared to control plants.

GI of shoots, roots, and fresh matter of both examined plants treated with PVA-B hydrogels was dependent on the hydrogel concentration (Table 4). The higher the concentration of PVA-B substances in soil, the more harmful the effect (Figures S9, S11, Supplementary Material). Radish roots were found to be most sensitive against the tested hydrogels, because their GI was dependent not only on the increasing concentration of PVA-B in soil but also on the

Table 3: Effect of AM-SA 3:1, AM-SA 1:1, and AM-SA 1:3 hydrogels on the shoot height, root length, and fresh matter of oat and radish seedlings (mean ± SD).

Concentration [mg/kg of soil d.w.]	*Inhibition biomarkers [%]*					
	Shoot height					
	Oat			Radish		
	AM-SA 3:1	AM-SA 1:1	AM-SA 1:3	AM-SA 3:1	AM-SA 1:1	AM-SA 1:3
250	1.8±0.6	2.8±0.6	3.6±0.8	4.5±0.4	2.1±4.6	2.8±2.7
500	1.6±0.6	3.6±1.1	5.9±0.8	5.1±0.0	3.5±0.3	3.1±0.5
750	-2.6±0.2	7.9±0.5	7.7±0.6	7.5±0.4	3.8±0.6	4.5±0.6
1000	-7.3±0.7	9.5±0.6	8.7±0.7	9.8±0.0	4.1±0.4	4.8±0.3
	Root length					
	Oat			Radish		
	AM-SA 3:1	AM-SA 1:1	AM-SA 1:3	AM-SA 3:1	AM-SA 1:1	AM-SA 1:3
250	1.3±0.4	-0.4±0.2	-10.4±1.1	-9.4±1.2	-2.2±0.9	-6.8±0.3
500	0.3±0.6	-0.9±0.5	-9.3±0.7	-7.3±0.5	-1.5±0.1	-6.1±0.6
750	-0.1±0.1	-1.1±0.2	3.1±0.5	-6.2±0.5	0.6±0.2	1.2±0.7
1000	-0.6±0.6	-1.2±0.7	7.1±0.2	-5.2±0.4	1.2±0.5	5.5±0.5
	Fresh matter					
	Oat			Radish		
	AM-SA 3:1	AM-SA 1:1	AM-SA 1:3	AM-SA 3:1	AM-SA 1:1	AM-SA 1:3
250	4.1±0.3	5.0±0.3	3.9±0.1	4.5±0.1	3.2±0.1	6.2±0.1
500	3.7±0.3	7.1±0.2	6.3±0.3	6.0±0.1	4.2±0.0	4.0±0.2
750	2.6±0.1	7.9±0.0	6.9±0.2	7.2±0.1	5.5±0.1	2.0±0.1
1000	-4.9±0.1	11.4±0.0	7.3±0.2	10.3±0.0	5.8±0.1	-5.8±0.1

Table 4: Effect of PVA-B1, PVA-B2, and PVA-B3 hydrogels on the shoot height, root length, and fresh matter of oat and radish seedlings (mean ± SD).

Concentration [mg/kg of soil d.w.]	*Inhibition biomarkers [%]*					
	Shoot height					
	Oat			Radish		
	PVA-B1	PVA-B2	PVA-B3	PVA-B1	PVA-B2	PVA-B3
250	5.3±0.3	-0.2±0.3	0.4±0.4	3.9±1.0	2.2±0.1	3.5±0.3
500	5.6±0.1	2.0±0.5	3.5±1.2	6.5±0.7	5.5±0.5	8.9±0.7
750	6.9±0.9	5.1±0.7	5.3±0.6	9.2±1.1	9.9±1.1	13.5±1.0
1000	7.5±0.7	8.3±0.7	10.5±1.0	11.2±1.5	14.5±0.9	20.8±0.2
	Root length					
	Oat			Radish		
	PVA-B1	PVA-B2	PVA-B3	PVA-B1	PVA-B2	PVA-B3
250	2.3±0.8	3.3±0.4	9.3±1.0	2.4±0.2	3.3±0.3	4.2±0.2
500	6.8±0.2	5.6±0.3	13.6±0.3	5.8±0.8	7.8±0.4	10.4±0.6
750	7.9±0.8	9.6±0.3	16.0±1.2	10.3±0.4	15.3±1.2	18.3±1.0
1000	9.1±0.4	10.9±0.4	18.0±0.5	15.6±1.0	22.6±0.4	30.9±0.4
	Fresh matter					
	Oat			Radish		
	PVA-B1	PVA-B2	PVA-B3	PVA-B1	PVA-B2	PVA-B3
250	5.4±0.1	-1.2±0.3	1.3±0.2	6.5±0.1	2.1±0.2	2.5±0.2
500	5.0±0.3	2.1±0.2	2.5±0.3	7.5±0.3	5.6±0.3	13.3±0.3
750	6.5±0.0	7.6±0.1	7.8±0.2	16.3±0.1	17.4±0.1	18.2±0.1
1000	8.2±0.0	16.3±0.1	14.5±0.2	18.2±0.2	19.9±0.1	24.4±0.1

Table 5: Average values (mean of three replicates) of percent germination of oat (*Avena sativa*) and common radish (*Raphanus sativus*) treated with tested hydrogels. Least significant differences for samples (LSD_S) and concentration (LSD_C) are given at the bottom of the table. % germination refers to the number of emerged plants (in brackets) expressed as a percent of control plants. Concentration of samples is given in mg/kg of soil dry matter.

Sample	Concentration							
	OAT				RADISH			
	250	500	750	1000	250	500	750	1000
PAM	100 (19)	100 (19)	100 (19)	95 (18)	94 (17)	94 (17)	94 (17)	94 (17)
AM-SHMB 3:1	100 (19)	100 (19)	100 (19)	95 (18)	100 (18)	94 (17)	94 (17)	94 (17)
AM-SHMB 1:1	100 (19)	100 (19)	100 (19)	100 (19)	94 (17)	94 (17)	94 (17)	89 (16)
AM-SA 3:1	100 (19)	100 (19)	100 (19)	100 (19)	94 (17)	94 (17)	94 (17)	94 (17)
AM-SA 1:1	100 (19)	100 (19)	95 (18)	95 (18)	94 (17)	94 (17)	94 (17)	94 (17)
AM-SA 1:3	100 (19)	100 (19)	100 (19)	100 (19)	100 (18)	94 (17)	94 (17)	94 (17)
PVA-B1	100 (19)	100 (19)	95 (18)	95 (18)	94 (17)	94 (17)	89 (16)	89 (16)
PVA-B2	100 (19)	95 (18)	95 (18)	95 (18)	100 (18)	100 (18)	94 (17)	94 (17)
PVA-B3	95 (18)	95 (18)	95 (18)	95 (18)	100 (18)	94 (17)	89 (16)	89 (16)
	LSD_C = 1							
	LSD_S = 1							

amount of borax in hydrogel. The GI of radish roots treated with samples PVA-B1, PVA-B2, and PVA-B3 at their highest concentration in soil was in the following order: 15<23<31%, respectively, while these values for the roots of oat were as follows: 9<11<18% (Table 4, Figure S13, Supplementary Material). It is expected that increasing the amount of borax in hydrogel will cause increased toxic effect on the plant roots, because according to European Chemical Agency and reports from the US National Library of Medicine, borax ($B_4Na_2O_7{\cdot}10H_2O$), may cause serious health and environmental hazard [42, 43]. Comparing the inhibitory effect of hydrogels PVA-B on radish and oat roots, it should be noted that the value of GI% for radish was *ca.* two times higher than that for more resistant oat.

Among all tested hydrogels, those based on PVA showed the most harmful effect on the shoot growth of both plants; this effect, however, was much more noticeable for radish than for oat. In the group of PVA-B hydrogels, it was found that increasing amount of borax in hydrogel played an important role in the inhibition of radish shoot growth; that is, the higher the content of borax in hydrogel, the higher was the inhibition. Shoots of oat were much less sensitive to the increasing concentration of borax in hydrogel. Generally, comparing the changes in tested parameters in both plants treated with all examined hydrogels, dicotyledonous radish was more sensitive specimen than monocotyledonous oat.

The analysis of the obtained results for GI of fresh matter, shoot, and root of oat and radish revealed that PAM, AM-SHMB, and AM-SA hydrogels caused very low harmful effect (ca. 10% as compared to control plants) on the tested parameters even at the highest applied concentration in soil. Among these hydrogels, those consisting of AM-SHMB units, especially with AM-SHMB 3:1 ratio, were found to have the least toxic substance and very low negative effect on radish root growth as compared to that on control plants. Considering the inhibitory effect on shoot and fresh matter of both oat and radish, in contrast to other tested hydrogels, Tulipalin A-based hydrogels as superabsorbents even slightly promoted the growth of green parts of the tested plants, thus resulting in negative value of percentage GI, especially at higher hydrogel concentrations.

Recently, because of growing interest and availability of commercial hydrogels for agricultural purposes, an increasing number of studies are devoted to the effect of hydrogels on plants. Seed germination and seedling development are crucial phases in early growth and development of any plant species. The successful establishment of agricultural crops depends on moisture availability and is often restricted by poor soil moisture level especially in water deficit environments.

Percentage germination of both plants treated with all tested hydrogels was similar and ranged from 89 to 100% as compared to control plants (Table 5). The highest inhibition of germination was caused by PVA-B hydrogels; however, the effect was negligible and more dependent on the concentration of hydrogels in soil than on the type of hydrogel.

Zhang et al. (2017) prepared cellulose anionic hydrogels that exhibited microporous structure and high hydrophilicity, resulting in excellent water absorption property. The seed germination experiments confirmed that the cellulose anionic hydrogels with suitable carboxylate content could act as a plant growth regulator and promote the germination and growth of seeds [20]. Montesano et al. (2015) evaluated the cellulose-based hydrogel that consisted of two cellulose derivatives, sodium carboxymethylcellulose, and hydroxyethylcellulose, using citric acid as a cross-linking agent on the growth of two radish (*Raphanus sativus* L. var. *radicula* Pers.), cucumber (*Cucumis sativus* L.), alyssum (*Alyssum* spp.), and Centaurea (*Centaurea* spp.) [44]. Additionally, the effects of hydrogel on cucumber and basil were examined in cultivation trials carried out in a greenhouse condition. The authors reported that beside the clear influence of the hydrogel in increasing the container capacity (the maximum amount of water present in the substrate after saturation and

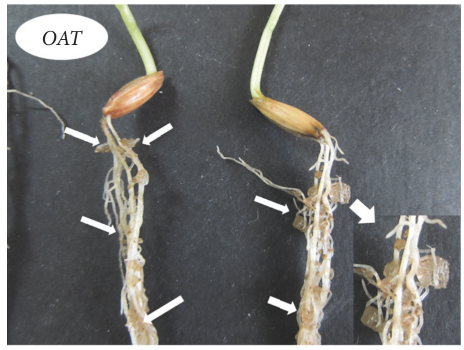

Figure 2: Digital photograph of the oat root zone in the presence of Tulipalin A-based hydrogels.

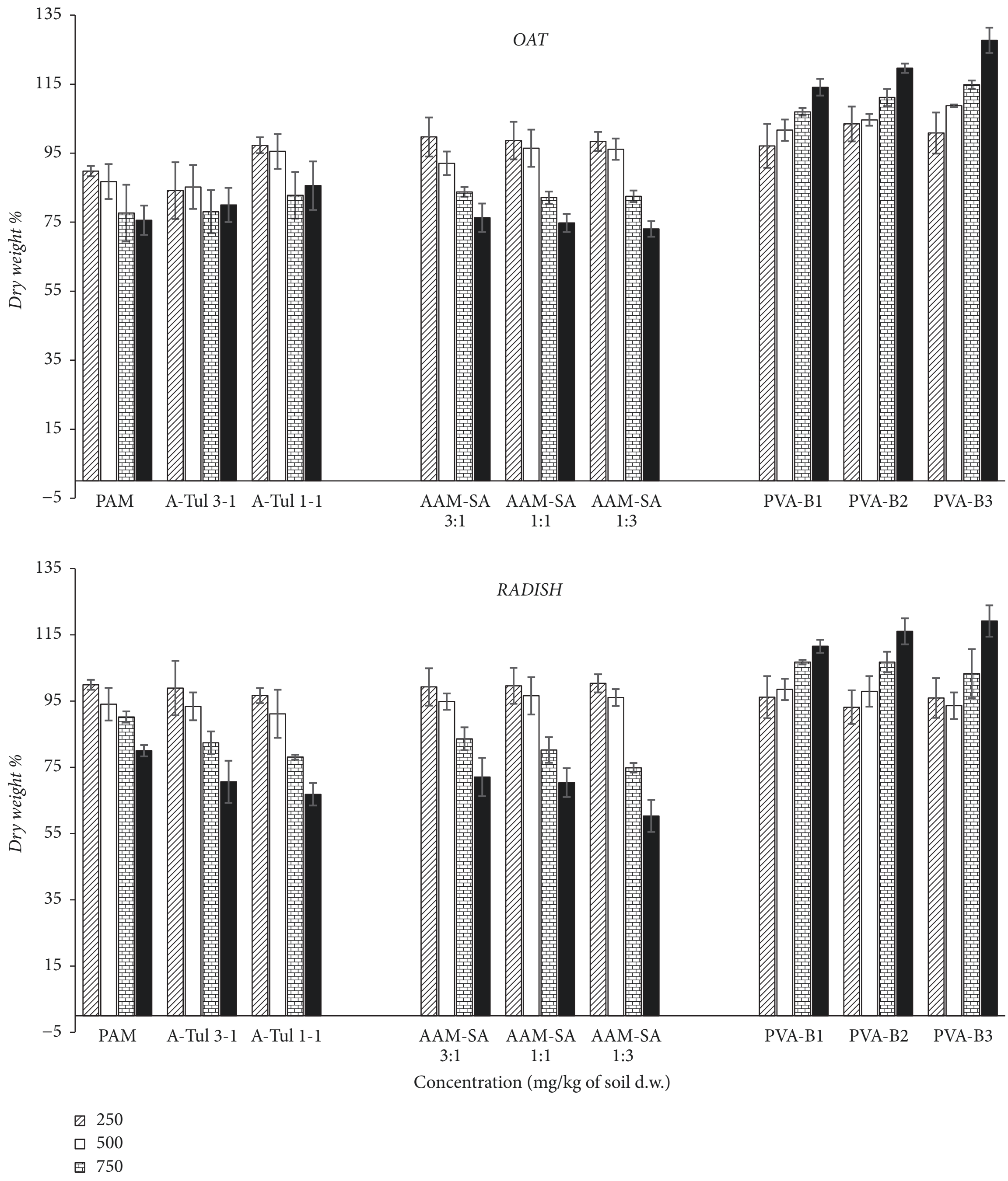

Figure 3: Changes in dry weight of treated plants expressed as percent value of untreated plants.

Figure 4: Digital photographs of roots of oat and radish growing in the presence of PAM and Tulipalin A-based hydrogels.

at the end of the dripping), neither the seeds of vegetable nor the ornamental species showed any symptom of phytotoxicity in the presence of the hydrogel. Moreover, Centaurea showed a very high germination index as the root development and the average number of seeds germinated in the presence of hydrogel was significantly higher than that of the control. The sweet basil plants grown on perlite amended with hydrogel also showed enhanced growth in terms of fresh biomass after 46 days of growth. These results confirmed the positive effects of hydrogels often reported on plant growth promotion and the reduction of the detrimental effects of water stress [45, 46]. Akhter et al. (2004) investigated the influence of hydrogel prepared by polymerization of acrylamide (*N,N*-methylenebisacrylamide) and mixed Na and K salts of acrylic acid on the moisture properties of sandy loam and loam soils as well as on growth response of three plant species, viz. barley (*Hordeum vulgare* L.), wheat (*Triticum aestivum* L.), and chickpea (*Cicer arietinum* L.). Their results revealed that the addition of the tested hydrogel improved the water storage of soils and enhanced seedling growth. Seed germination of wheat and barley was not affected, but seedling growth of both species was improved by hydrogel treatment. The hydrogel treatment caused a delay of few days in wilting of seedlings grown in both soils compared with control conditions. Further, the hydrogel treatment was effective in improving soil moisture availability and thus increased plant establishment. Lee et al. (2013) examined the effect of anionic polyacrylamide and synthesized biopolymer using lignin, corn starch, acrylamide, and acrylic acid on soil erosion, water quality, and growth of Chinese cabbage (*Brassica campestris* L.). The authors did not note any toxic effects in germination tests. The introduction of both tested hydrogels to soil increased cabbage dry weight [47]. Other authors also found that PAM application in soil improved cotton germination in field conditions [48].

As seen from the oat root photo (Figure 2), the direct presence of hydrogels in the root zone can allow for the filling of the empty spaces in soil and facilitate water and nutrient uptake.

Increasing the concentration of Tulipalin A-based hydrogels in soil caused a decrease in dry weight (especially for radish) with a simultaneous increase in fresh matter and shoot height (ca. up to 9%) compared to control plants (Figure 3, Table 2). The reason why green parts of plants grow intensively is that the roots system of plants also strongly develop by branching and as a consequence have larger surface area to supply the plants with nutrients and water (Figure 4).

In contrast, shortened roots of plants due to PVA hydrogel exposure limited both fresh and dry matter of the plant.

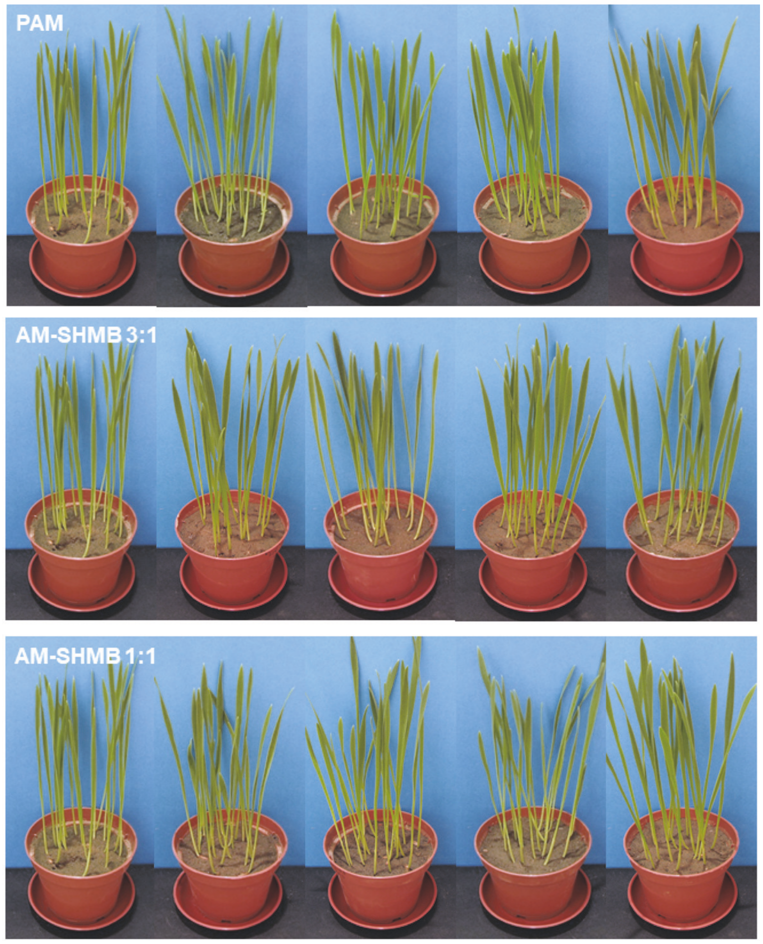

Figure 5: Digital photographs of oat seedlings growing for 14 days in soil treated with PAM and Tulipalin A-based hydrogels.

In contrast to the above mentioned hydrogels, although dry weight inhibition was noted for both plants treated with increasing concentration of AM-SA hydrogels, the changes in fresh matter values varied depending on the composition of hydrogel. Sample AM-SA 3:1 promoted the growth of shoot and fresh matter for oat but inhibited the growth of shoot and fresh matter for radish. In contrast, sample AM-SA 1:3 inhibited fresh matter of oat, but the increasing concentration of the same sample positively influenced the fresh matter level in radish plants.

PVA-B hydrogels inhibited both fresh and dry matter of both plants, and the extent of toxicity was dependent on the increasing concentration of hydrogel and the amount of borax in it. The higher the concentration of hydrogel and borax, the stronger the inhibition of fresh and dry matter and shoot and root growth. This implies that roots exposed to these hydrogels do not facilitate water uptake from soil, thus limiting water uptake and nutrient distributions. The most rational reason is the presence of borax salt that strongly absorbs water in the very close neighborhood of roots. Among all tested hydrogels, Tulipalin A-based ones are the most environmentally friendly because they successfully created a reservoir of water that could be uptaken by plant roots during stress conditions such as drought. Moreover, appropriate moisture level in the root area provides an optimal distribution and uptake of soluble nutrients as well as protects roots against excessive amount of salt or other xenobiotics by their dilution directly near the roots.

Visual evaluation of the tested seedlings of both tested plants growing in the soil treated with tested hydrogels is shown in Figures 5 and 6 and S8-S11 (Supplementary Material). No typical symptoms of necrosis defined as rapid cell death through injury or disease were observed. However, yellowing of leaf edges of radish seedlings growing in the presence of increasing concentration of PVA-B hydrogels indicates the beginning of chlorosis defined as decrease in the chlorophyll amount in the green part of plants (Figure S11, Supplementary Material).

3.3. Changes in Chlorophyll and Carotenoid Content. The effect of addition of hydrogel on the content of total chlorophyll and carotenoids in oat and radish sprouts is shown in Figures 7 and S14, S15 (Suppl. Mat.). Generally, increasing amount of hydrogels in the soil resulted in gradual decrease in chlorophyll content in green parts of both plants. Pigment content in plants treated with the tested groups of hydrogels

FIGURE 6: Digital photographs of radish seedlings growing for 14 days in soil amended with PAM and Tulipalin A-based hydrogels.

was in the following order: PVA-B<AM-SA<AM-SHMB and PAM hydrogels.

The lowest impact on the chlorophyll level of both plants was noted for PAM and AM-SHMB hydrogels, with the decrease in chlorophyll and carotenoid content within only 10% (Figure 7). In contrast, even though only slight effect (within 10%) of AM-SA hydrogels was observed on the amount of chlorophyll in oat and on both chlorophyll and carotenoids in radish, much higher harmful effect of AM-SA hydrogels was noted on the content of chlorophyll in oat (Figure S14, Supplementary Material). The composition of AM-SA hydrogels had a minimal effect on the amount of both substances in the plants.

The strongest negative effect on both chlorophyll and carotenoid content was noted for PVA-B hydrogels (Figure S15, Supplementary Material). In addition to the significant effect of the hydrogel concentration on the decrease of these substances in the plants, the decrease was slightly pronounced because of increasing content of borax in the hydrogels. The highest decrease in chlorophyll and carotenoid content was similar for both plants treated with hydrogel PVA-B3 at its highest concentration in soil (34%) as compared to control plants.

On the basis of the obtained results, it is clear that bio-based hydrogels can be successfully used as an environmental-friendly water reservoir for plant growth and establishment in the arid environment. Popular and commercially available nondegradable hydrogels can also be used for agricultural purposes; however, their concentration should be controlled to avoid their biological, negative effect on soil productivity. The addition of the tested hydrogel improved the water storage of soil and enhanced seedling growth.

4. Conclusions

Hydrolyzed form of renewable monomer Tulipalin A can be copolymerized with acrylamide to provide poly(acrylamide-*co*-sodium 4-hydroxy-2-methylenebutanoate) (AM-SHMB) superabsorbent hydrogels. In the present study, the phytotoxic properties of this new type of hydrogel were investigated and compared with the properties of other types of hydrogels such as polyacrylamide (PAM), poly(acrylamide-*co*-sodium acrylate) (AM-SA), and poly(vinyl alcohol)-borax (PVA-B), which are commonly commercially used superabsorbents. AM-SHMB hydrogel with equimolar content of comonomers (AM-SHMB 1:1) together with AM-SA hydrogel showed the highest WHC among the tested hydrogels with significantly higher moisture retention than pure soil. Tulipalin A-based hydrogels, especially with AM-SHMB 3:1 ratio, were found to be least toxic with only very low negative effect on radish root growth as compared to control plants. In addition, compared to other tested hydrogels, Tulipalin A-based hydrogels as superabsorbents even slightly promoted the growth of green parts of both radish and oat plants, especially at

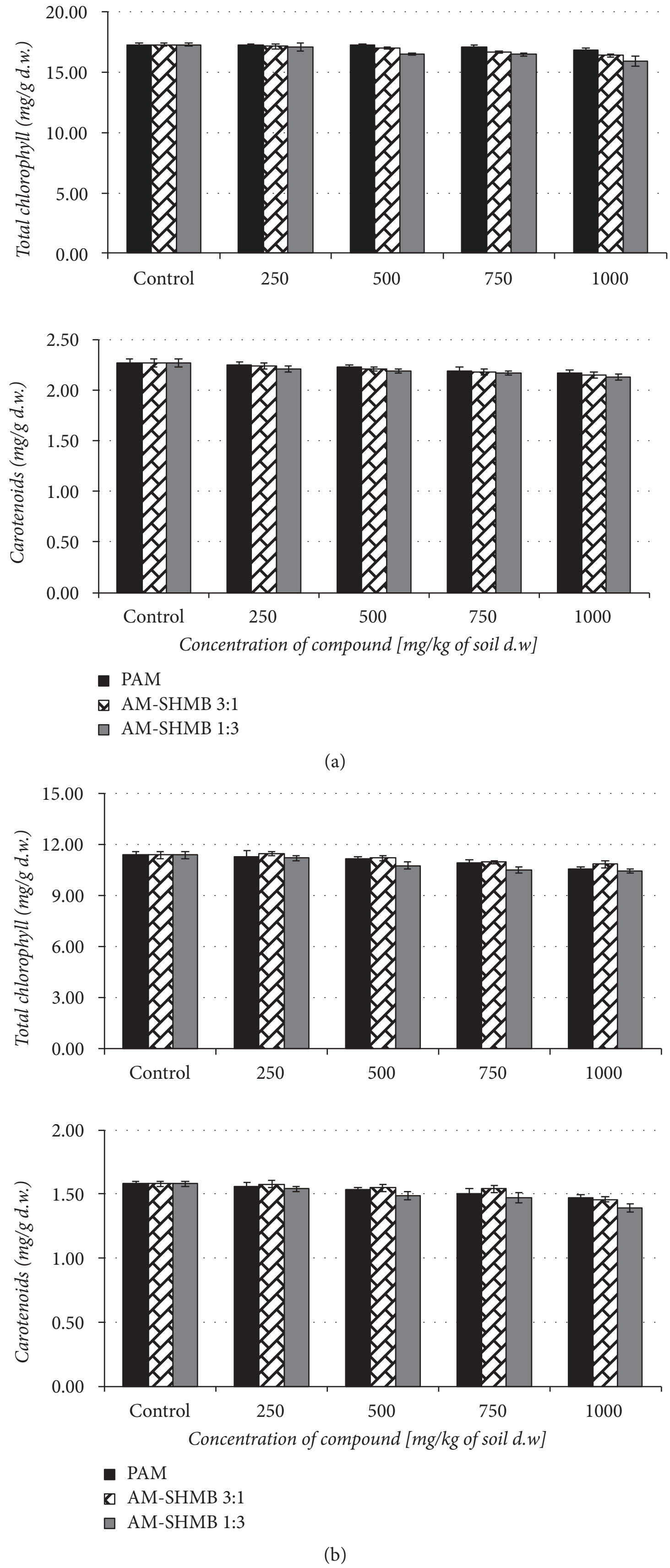

Figure 7: Effect of PAM, AM-SHMB 3:1, and AM-SHMB 1:1 hydrogels on the content of total chlorophyll and carotenoids in oat seedlings (a) and radish leaves (b). Data are expressed as mean ± SD of three replicates for each concentration.

higher hydrogel concentrations. Tulipalin A-based hydrogels, together with PAM hydrogels, also had the lowest impact on the chlorophyll and carotenoid content in both investigated plants, with decrease of these substances within only 10%.

From the obtained results, it can be concluded that Tulipalin A-based hydrogels can be successfully used as an environmentally friendly water reservoir for plant growth and establishment in the arid environment.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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Supplementary Materials

Supplementary Materials available: supporting scheme, figures, and detailed description of hydrogels synthesis. *(Supplementary Materials)*

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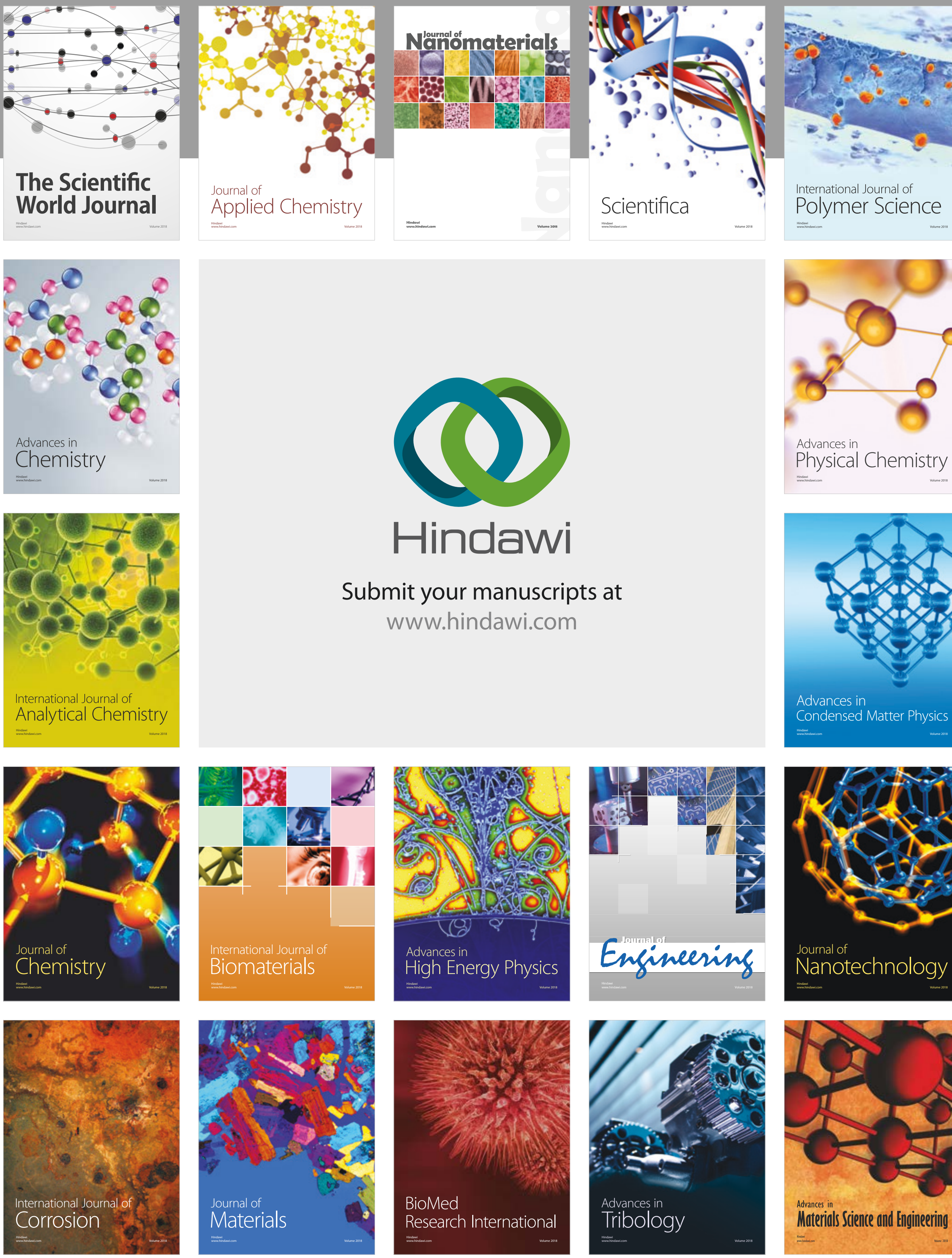
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