

## SUPPLEMENTARY MATERIAL

### Advances in Polymer Technology

### **Ecotoxicological properties of Tulipalin A-based superabsorbents vs. conventional superabsorbent hydrogels**

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Jaroslav Mosnáček<sup>2</sup>

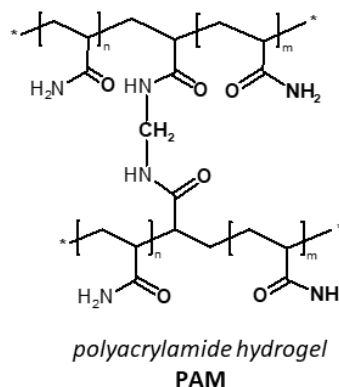
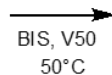
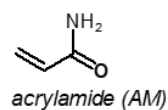
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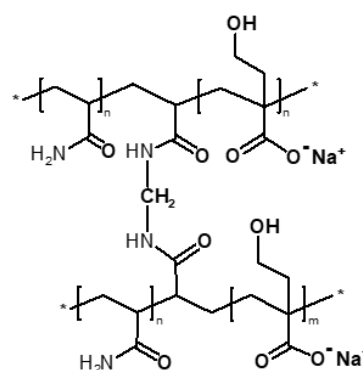
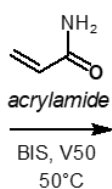
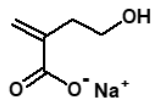
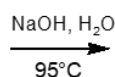
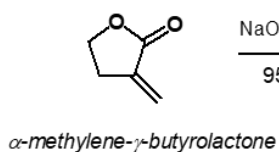
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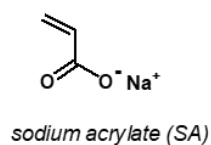
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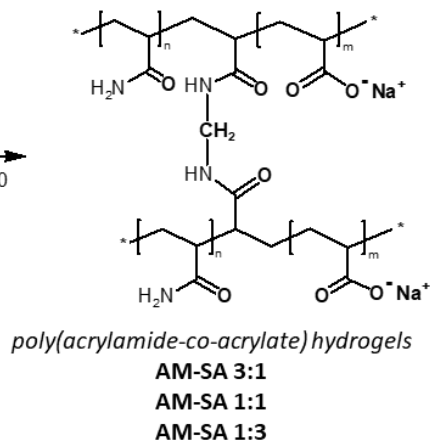
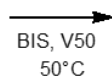
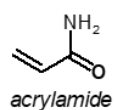
2)



3)



+



Scheme 1: Overall scheme of synthesis of polyacrylamide, poly(acrylamide-co-sodium 4-hydroxy-2-methylenebutanoate) (AM-SHMB) and poly(acrylamide-co-sodium acrylate) (AM-SA) hydrogels with various comonomers ratio.

### ***Synthesis of polyacrylamide hydrogel (PAM)***

Briefly, acrylamide (10 mmol), crosslinker BIS (0.1 mmol) and initiator V-50 (0.02 mmol) were dissolved in water to form 15 wt.% monomer solution. The mixture was injected into a glass tube, purged with argon for 10 min and sealed off. Polymerization was carried out at 50 °C for 4 hours.

### ***Synthesis of poly(acrylamide-co-sodium 4-hydroxy-2-methylenebutanoate) hydrogels (AM-SHMB)***

Briefly, hydrogels AM-SHMB were synthesized using two molar ratios of AM-SHMB (3:1 and 1:1) as follows: SHMB (2.5 mmol for AM-SHMB 3:1 and 5 mmol for AM-SHMB 1:1) was stirred in aqueous solution (2 mL) of NaOH (1.1 equivalent of SHMB) at 95 °C for 2 hours. Solution was neutralized with 1M HCl<sub>aq</sub> to pH = 7 and AM (7.5 mmol for AM-SHMB 3:1 and 5 mmol for AM-SHMB 1:1), crosslinker BIS (0.1 mmol) and initiator V-50 (0.02 mmol) were added and reaction mixture was diluted with water to form 15 wt.% monomer solution. The mixture was injected into a glass tube, purged with argon for 10 min and sealed off. Polymerization was carried out at 50 °C for 4 hours. The conversion was determined from <sup>1</sup>H NMR spectra (Fig. S1). ATR-FTIR spectrum of dry hydrogel is shown in Fig. S2.

### ***Synthesis of poly(acrylamide-co-sodium acrylate) hydrogels (AM-SA).***

Briefly, a solution of acrylic acid (2.5 mmol, 5 mmol and 7.5 mmol for AM-SA 3:1, AM-SA 1:1, AM-SA 1:3 respectively) in 2 mL of water was neutralized with 1M NaOH to pH = 5 and acrylamide (7.5 mmol, 5 mmol and 2.5 mmol for AM-SA 3:1, AM-SA 1:1, AM-SA 1:3 respectively) with crosslinker BIS (0.1 mmol) and initiator V-50 (0.02 mmol) were added to a glass tube. Reaction mixture was diluted with water to form 15 wt.% monomer solution, purged with argon for 10 min and sealed off. Polymerization was carried out at 50 °C for 4 hours. The conversion was determined from <sup>1</sup>H NMR spectra. ATR-FTIR of dry hydrogel is shown in Fig. S3.

### ***Preparation of poly(vinyl alcohol)-tetrahydroxyborate hydrogels PVA-B***

Briefly, borax 2 wt% aqueous solution was prepared by adding 2 g of borax to 98 g of distilled water. Poly(vinyl alcohol), PVA 4 wt% aqueous solution was prepared by dissolving 40 g of the PVA in 960 g of hot distilled water under vigorous stirring to complete solubilisation of the polymer. Solution was prepared in closed vessel to prevent water evaporation. Next, the solution was cooled down to room temperature. The hydrogels were formed applying common procedure, *i.e.* mixing of the solutions in desired ratio:

- 1) PVA-B1: 250 mL of PVA 4 wt% solution/ 15 mL of borax 2 wt% solution;
- 2) PVA-B2: 250 mL of PVA 4 wt% solution/ 30 mL of borax 2 wt% solution;
- 3) PVA-B3: 250 mL of PVA 4 wt% solution/ 45 mL of borax 2 wt% solution.

ATR-FTIR spectrum of dry hydrogels are shown in Figs. S4, S5.

### ***Purification of hydrogels.***

Samples of hydrogel were immersed in excess of ultrapure water. The swollen hydrogel was removed from solution, patted to remove excess water and placed into the fresh ultrapure water. The process was repeated several times to remove all unreacted components. The swollen samples were finally freeze dried to produce a dry hydrogels.

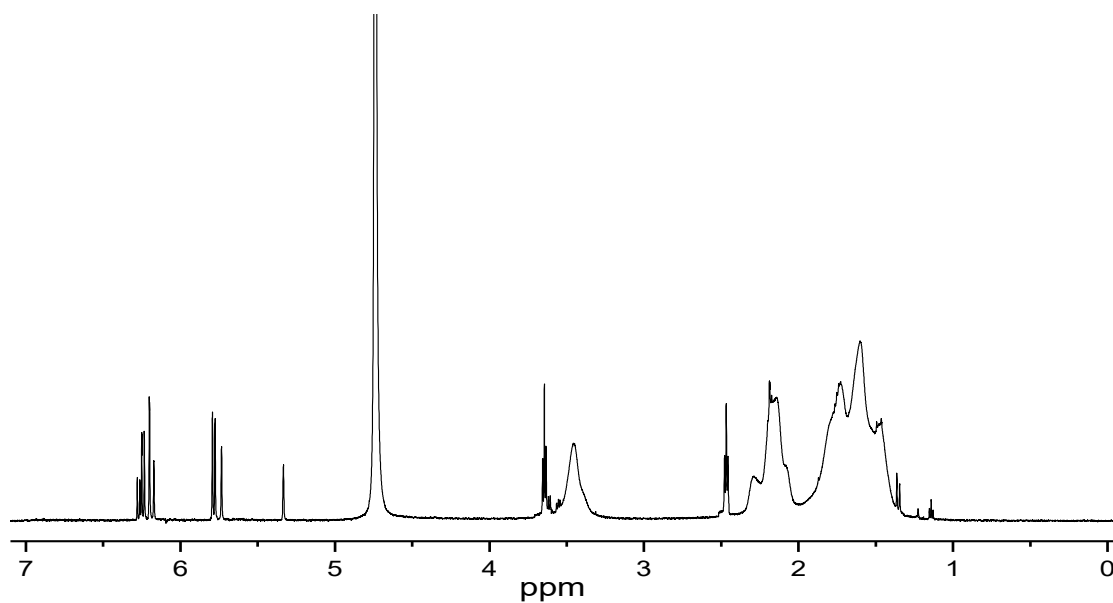


Figure S1:  $^1\text{H}$  NMR spectra of poly(acrylamide-*co*-sodium 4-hydroxy-2-methylenebutanoate) - AM-SHMB 1:1.

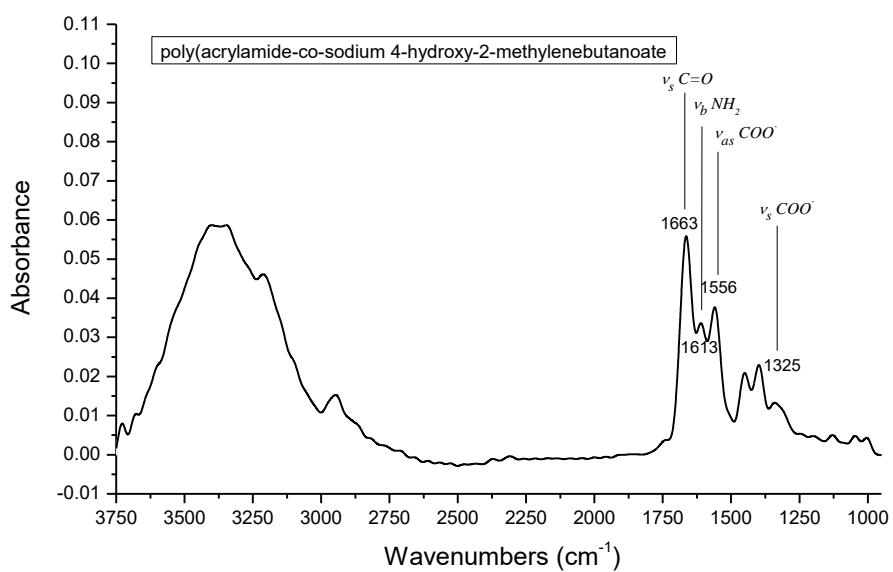


Figure S2: ATR-FTIR spectra of dry poly(acrylamide-*co*-sodium 4-hydroxy-2-methylenebutanoate) hydrogels (AM-SHMB 1:1) in solid state

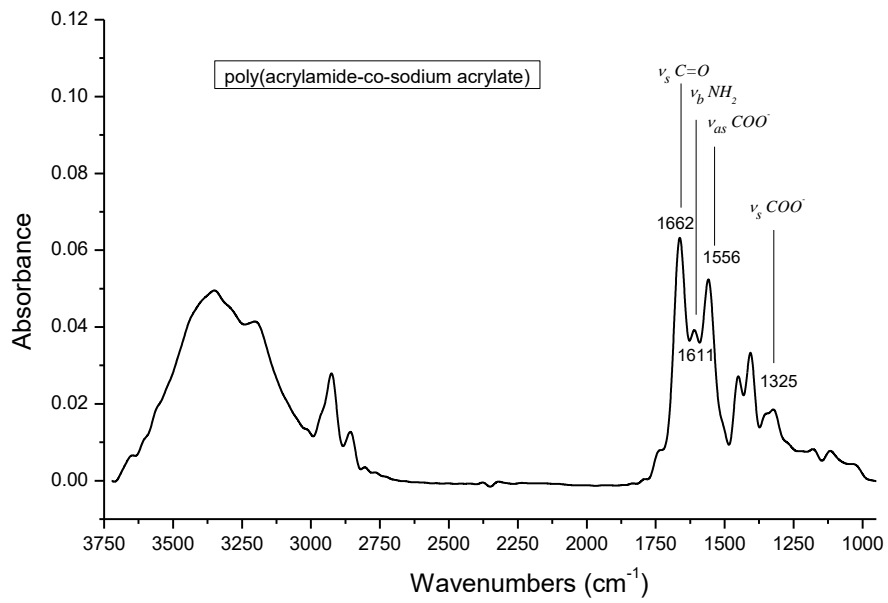
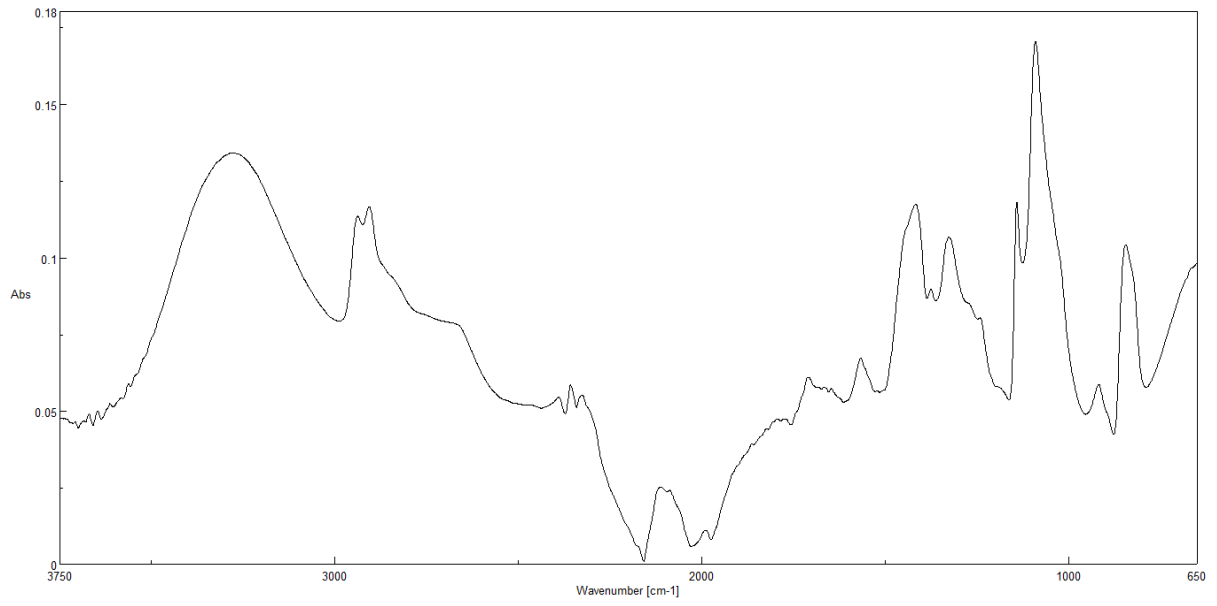
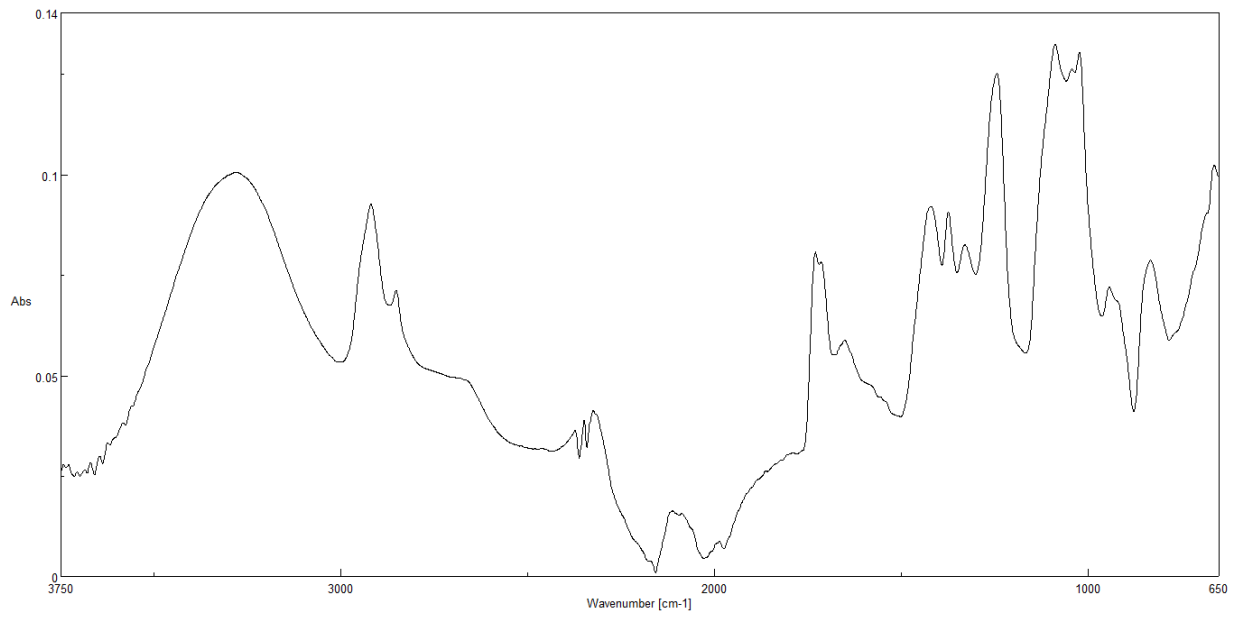


Figure S3: ATR-FTIR spectra of dry poly(acrylamide-*co*-sodium acrylate) hydrogel (AM-SA 1:1) in solid state

a)



b)



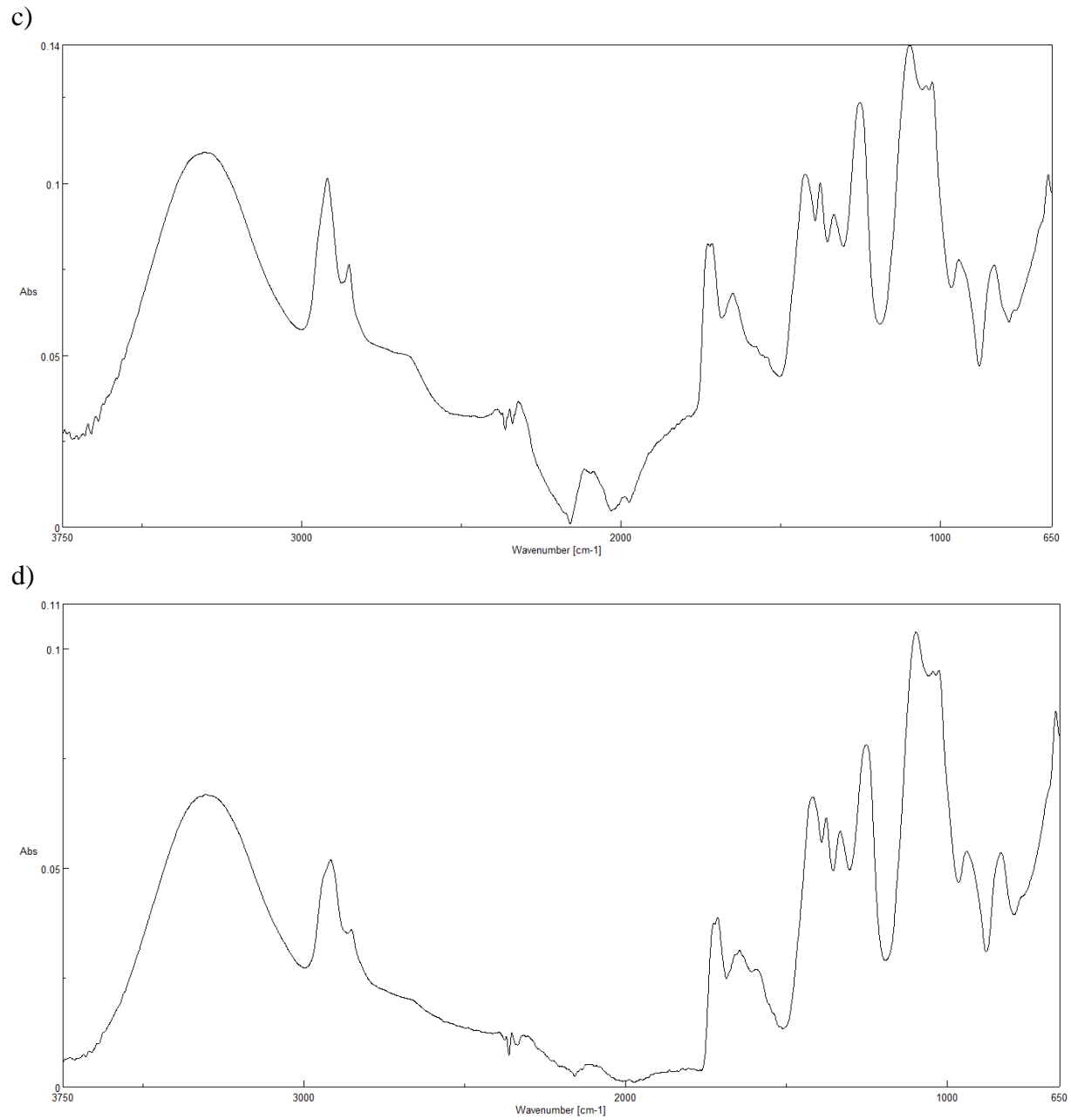


Figure S4: ATR-FTIR spectra of dry a) PVA, b) PVA-B1, c) PVA-B2 and d) PVA-B3, all in solid state

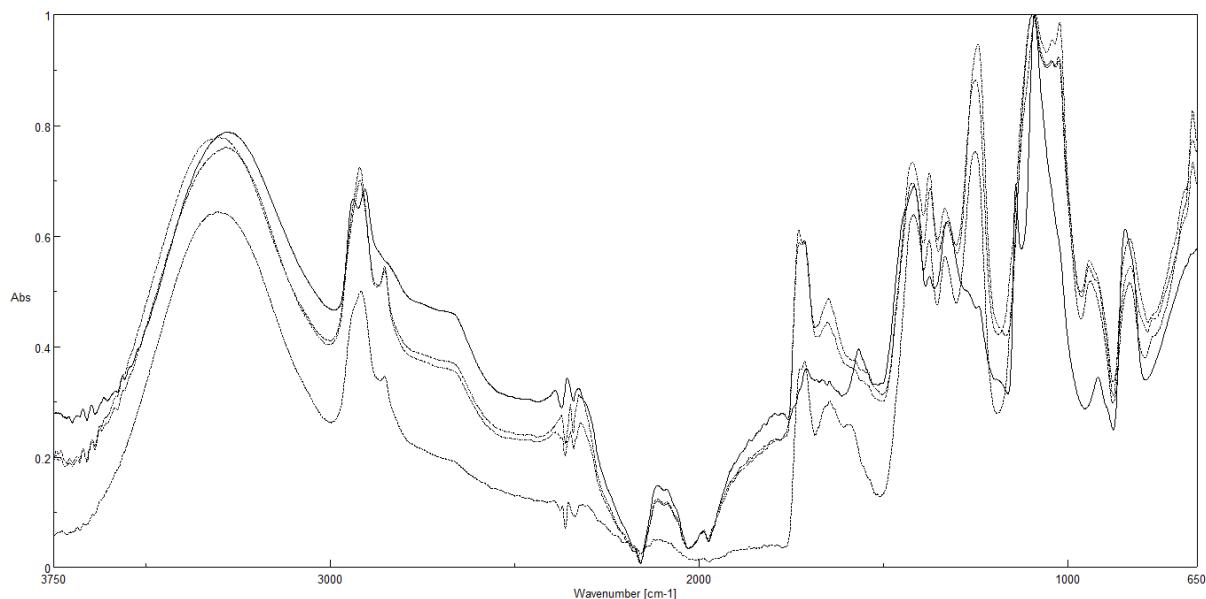


Figure S5: Overlaid ATR-FTIR spectra of dry PVA-B gels and pristine PVA (solid line), all in solid state

The spectra revealed:

Identification	Wavenumber [cm <sup>-1</sup> ]	
1	3550-3200	stretching vibration O-H from the intermolecular and intramolecular hydrogen bonds
2	3000-2849	stretching vibration C-H from alkyl groups
3	1750-1735	stretching vibration of C=O
4	1460-1410	CH <sub>2</sub> bending
5	1150-1085	stretching vibration of C-O (crystals) and C-O-C

Moreover, in comparison to the spectrum of neat PVA, small shift of band attributed to O-H stretching is observed and attributed to cross-linking of the PVA macromolecules. It correlates with appearance of additional band in PVA-B at 1100 cm<sup>-1</sup>.



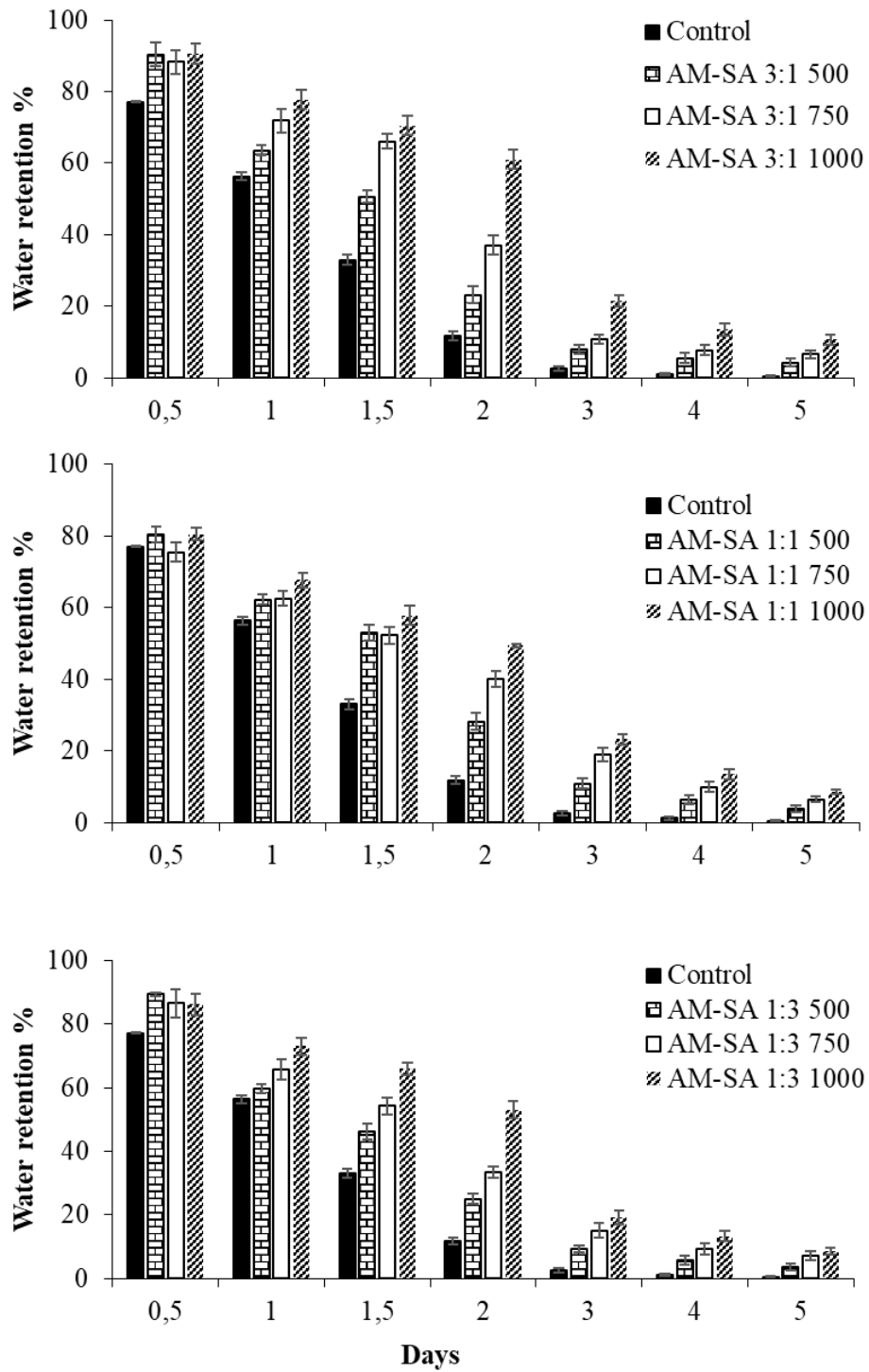


Figure S6: Percentage water retention for pure soil and soil containing various concentrations of polyacrylamide poly(acrylamide-co-sodium acrylate) (AM-SA) hydrogels.

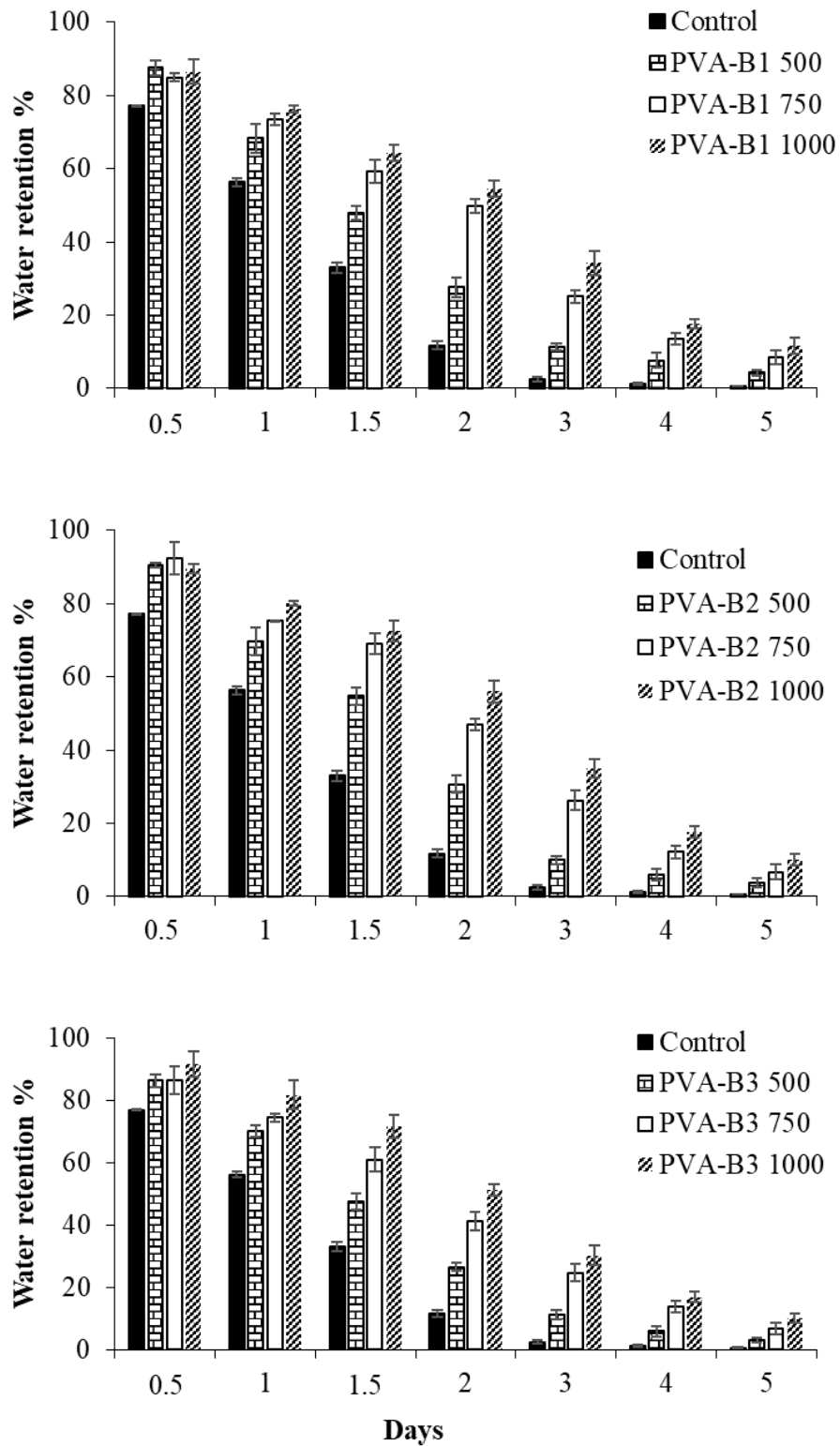


Figure S7: Percentage water retention for pure soil and soil containing various concentrations of poly(vinyl alcohol)-based hydrogels.

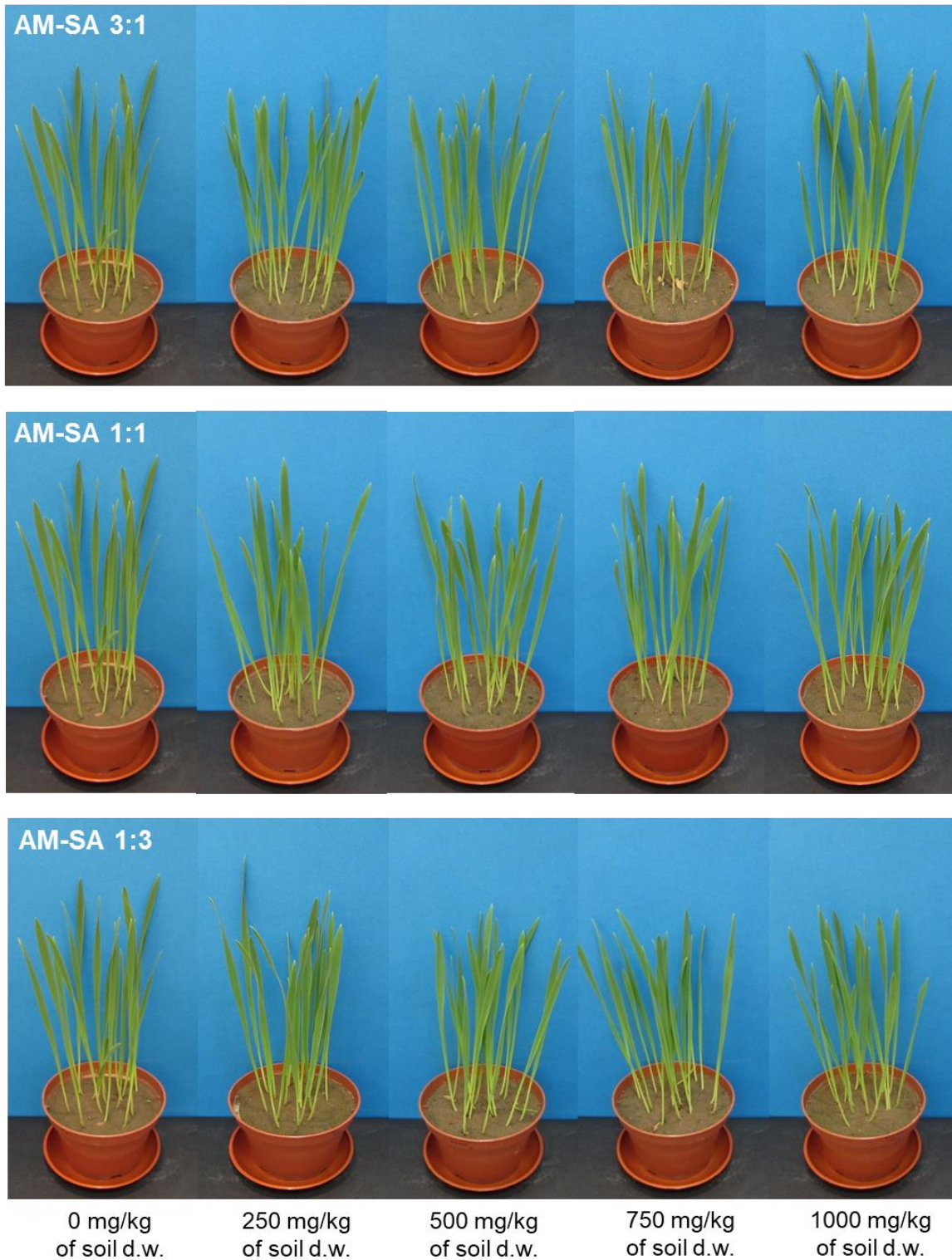


Figure S8: Digital photographs of oat seedlings growing 14 days on soil amended with AM-SA hydrogels.



0 mg/kg  
of soil d.w.

250 mg/kg  
of soil d.w.

500 mg/kg  
of soil d.w.

750 mg/kg  
of soil d.w.

1000 mg/kg  
of soil d.w.

Figure S9: Digital photographs of oat seedlings growing 14 days on soil amended with PVA-B hydrogels.



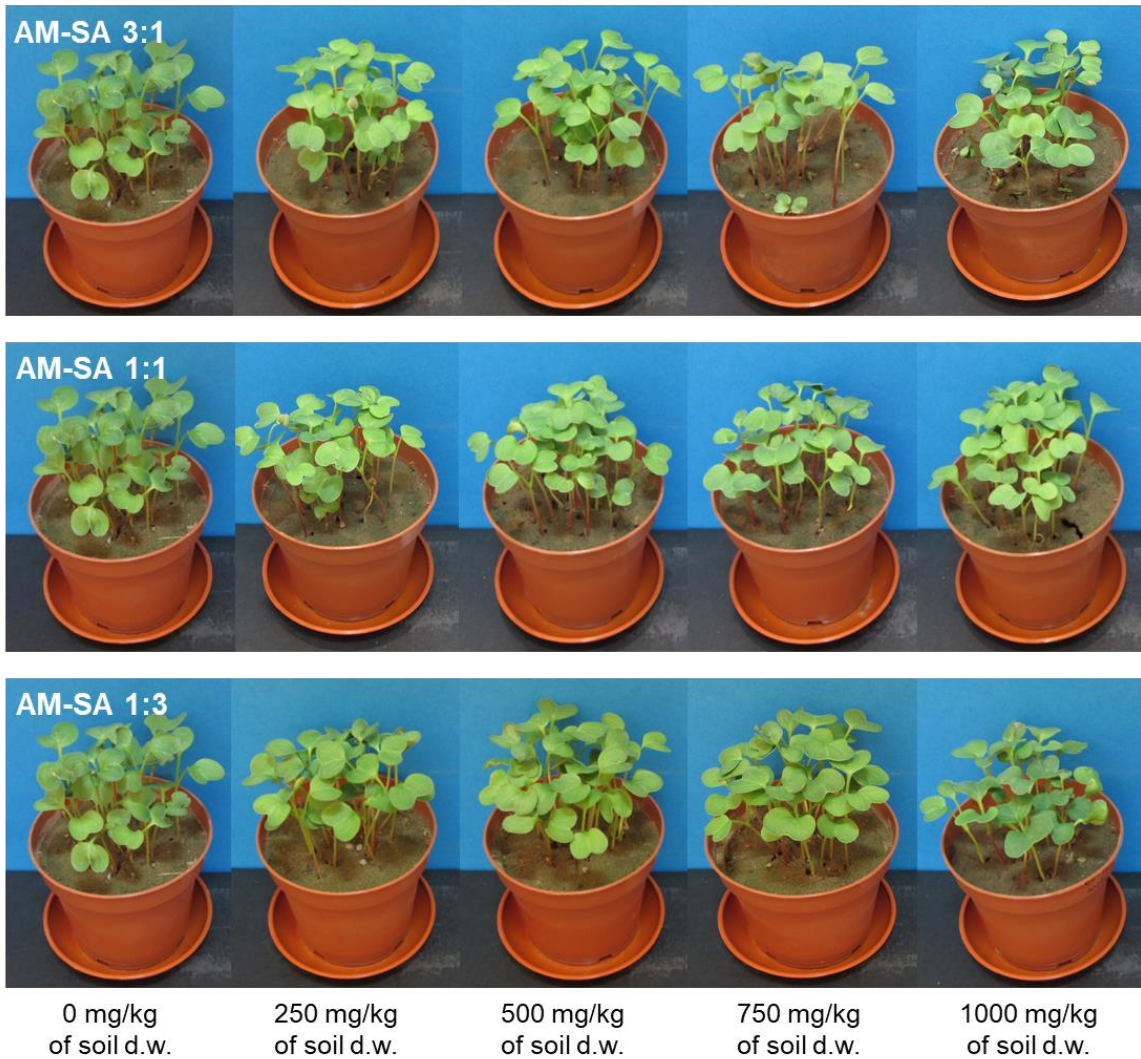


Figure S10: Digital photographs of radish growing 14 days on soil amended with AM-SA hydrogels.



Figure S11: Digital photographs of radish growing 14 days on soil amended with PVA-B hydrogels.



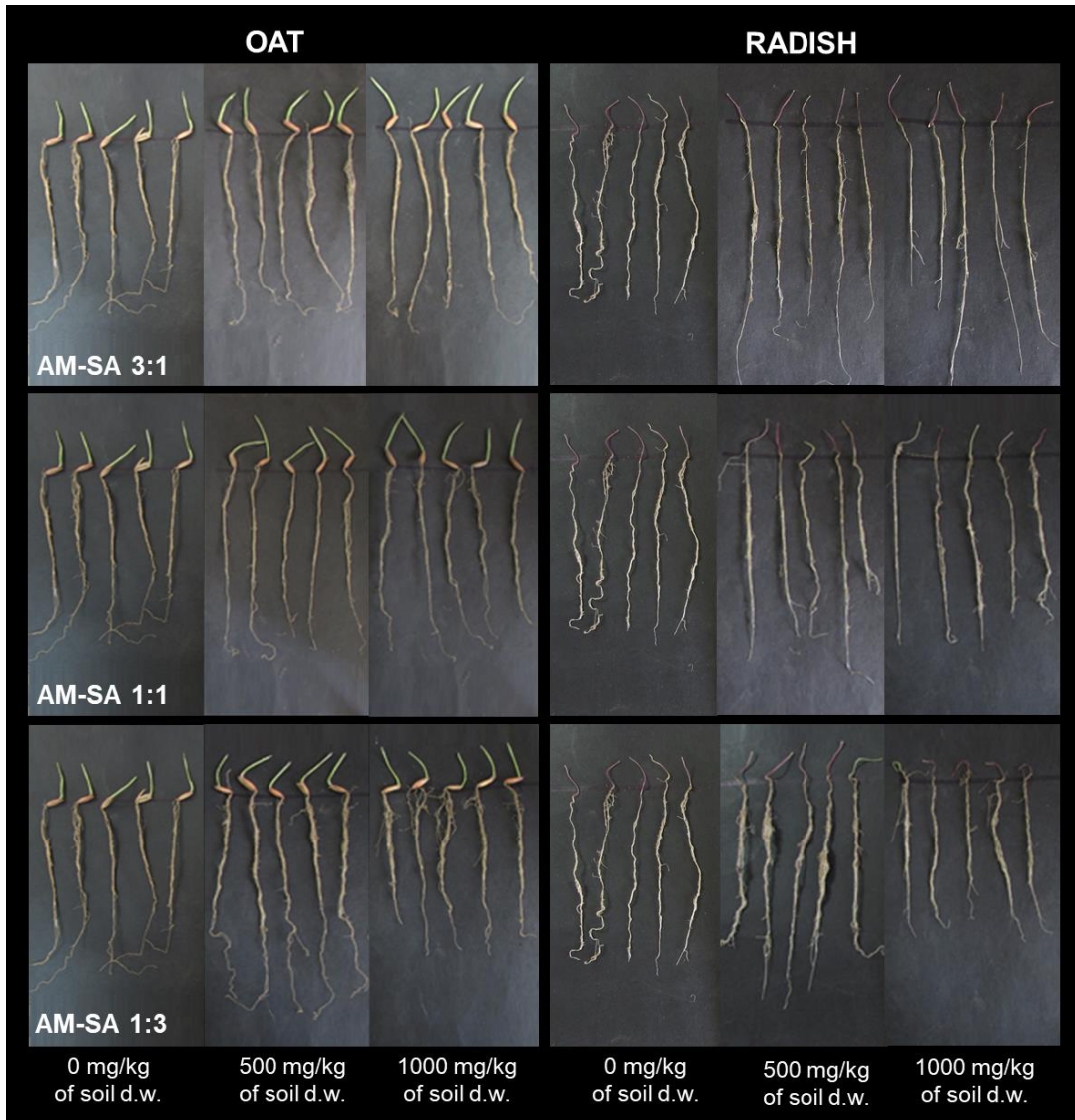


Figure S12: Selected digital photographs of oat and radish roots growing 14 days in soil amended with AM-SA hydrogels.

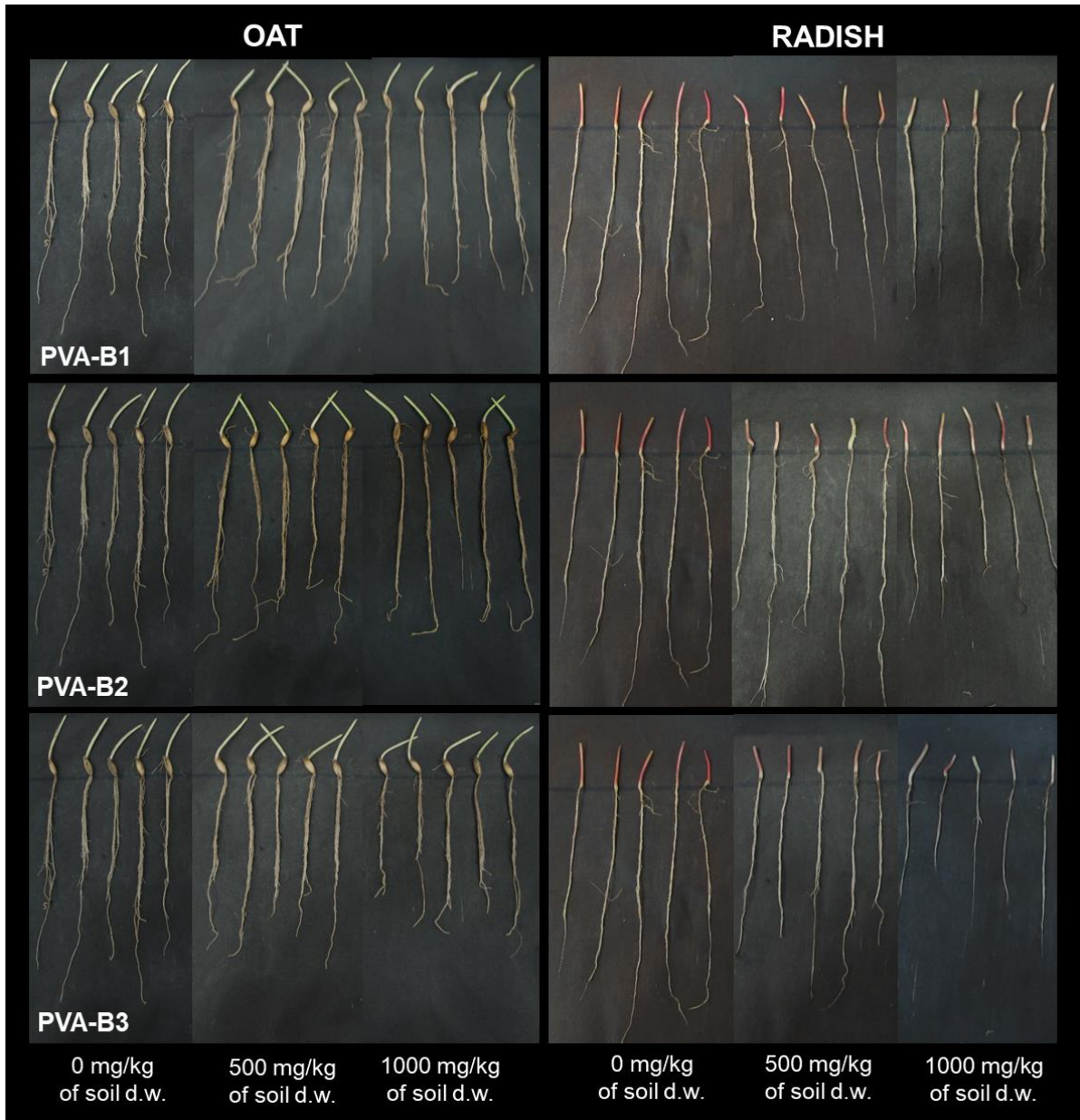


Figure S13: Selected digital photographs of oat and radish roots growing 14 days in soil amended with PVA-B hydrogels.



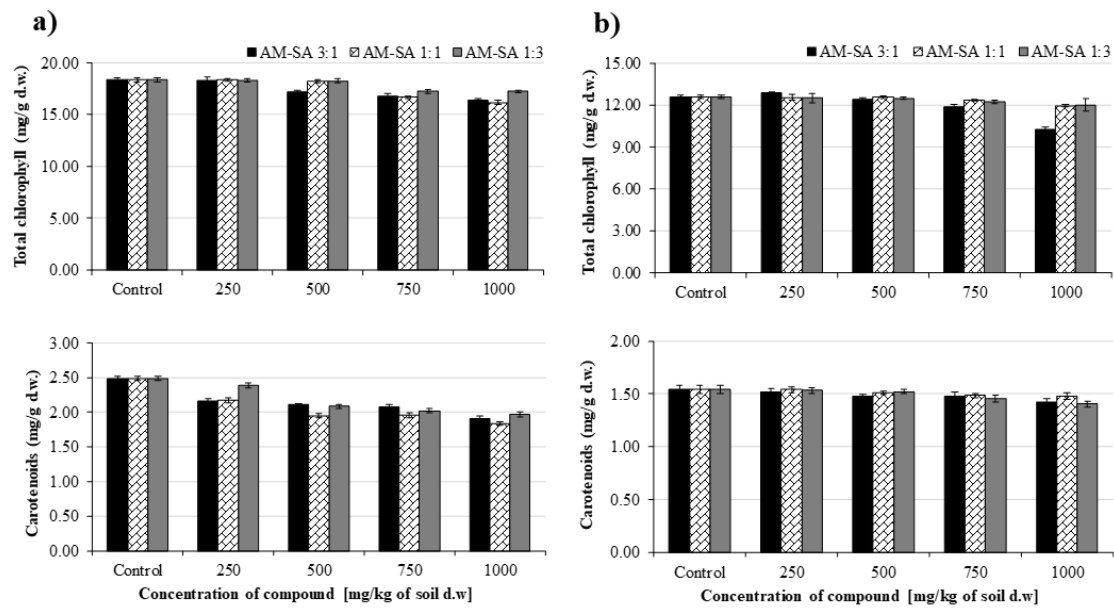


Figure S14: Effect of AM-SA hydrogels on the content of total chlorophyll and carotenoids in oat seedlings (a) and in radish leaves (b). Data are expressed as a mean $\pm$ SD of three replicates for each concentration.

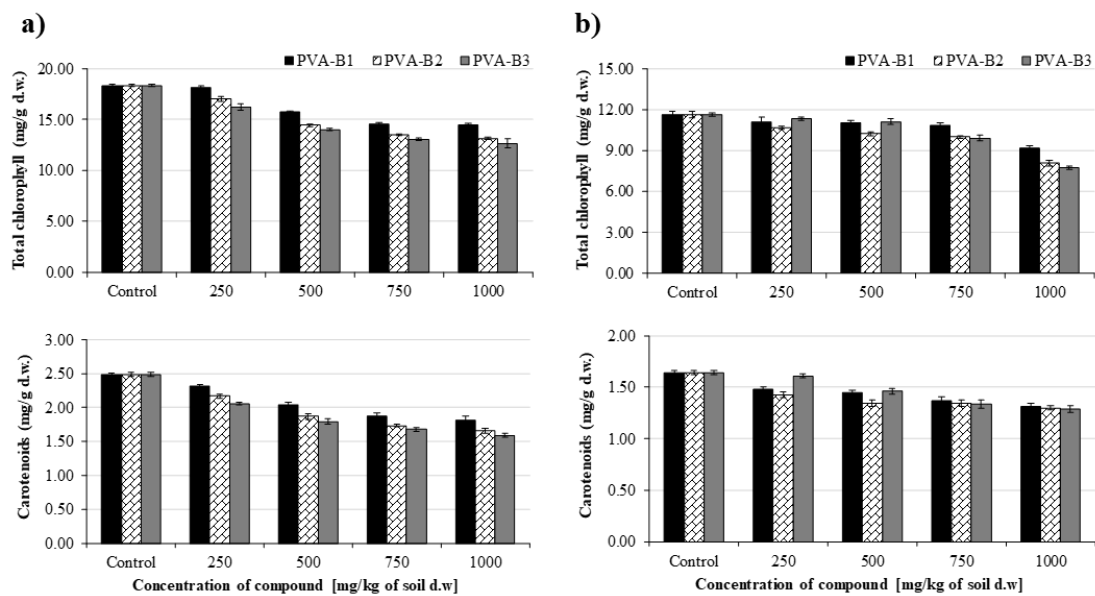


Figure S15: Effect of PVA-B hydrogels on the content of total chlorophyll and carotenoids in oat seedlings (a) and in radish leaves (b). Data are expressed as a mean $\pm$ SD of three replicates for each concentration.

Table S1: Average values of shoot height, root length and fresh matter for *Avena sativa* and *Raphanus sativus*. The least significant difference (LSD) values at a confidence level of 95% for concentrations (LSD<sub>c</sub>) and (samples LSD<sub>s</sub>) are given below the values of each parameter.

<i>Avena sativa</i>																											
Shoot height										Root length							Fresh matter										
Concentration [mg/kg of soil d.w.]	PAM	AM-SHMB 3:1	AM-SHMB 1:1	AM-SA 3:1	AM-SA 1:1	AM-SA 1:3	PVA-B1	PVA-B2	PVA-B3	PAM	AM-SHMB 3:1	AM-SHMB 1:1	AM-SA 3:1	AM-SA 1:1	AM-SA 1:3	PVA-B1	PVA-B2	PVA-B3	PAM	AM-SHMB 3:1	AM-SHMB 1:1	AM-SA 3:1	AM-SA 1:1	AM-SA 1:3	PVA-B1	PVA-B2	PVA-B3
<i>Control</i>	17.3	17.3	17.3	17.2	17.2	17.2	18.3	18.3	18.3	12.0	12.0	12.0	10.8	10.8	10.8	11.2	11.2	11.2	2.124	2.124	2.124	2.202	2.202	2.202	2.135	2.135	2.135
<i>250</i>	17.4	17.5	17.5	16.5	16.4	16.2	17.4	18.4	18.3	12.1	11.9	12.0	10.6	10.8	11.9	11.0	10.9	10.2	2.201	2.141	2.133	2.112	2.092	2.116	2.020	2.161	2.107
<i>500</i>	17.3	17.7	17.7	16.6	16.2	15.8	17.3	18.0	17.7	12.3	12.1	12.1	10.7	10.8	11.8	10.5	10.6	9.7	2.054	2.184	2.151	2.120	2.045	2.064	2.028	2.091	2.082
<i>750</i>	17.4	18.2	18.2	17.3	15.5	15.5	17.1	17.4	17.4	12.5	12.0	12.2	10.8	10.9	10.4	10.4	10.6	9.4	2.136	2.211	2.229	2.144	2.029	2.049	1.996	1.930	2.076
<i>1000</i>	17.4	18.8	18.4	18.1	15.2	15.4	17.0	16.6	17.0	12.7	12.2	12.3	10.8	10.9	10.0	10.2	10.4	9.2	2.171	2.305	2.249	2.309	1.950	2.041	1.961	1.788	1.826
<i>LSD<sub>s</sub> = 0.9</i>										<i>LSD<sub>s</sub> = 0.7</i>							<i>LSD<sub>s</sub> = 0.271</i>										
<i>LSD<sub>c</sub> = 0.7</i>										<i>LSD<sub>c</sub> = 0.6</i>							<i>LSD<sub>c</sub> = 0.210</i>										
<i>Raphanus sativus</i>																											
Shoot height										Root length							Fresh matter										
Concentration [mg/kg of soil d.w.]	PAM	AM-SHMB 3:1	AM-SHMB 1:1	AM-SA 3:1	AM-SA 1:1	AM-SA 1:3	PVA-B1	PVA-B2	PVA-B3	PAM	AM-SHMB 3:1	AM-SHMB 1:1	AM-SA 3:1	AM-SA 1:1	AM-SA 1:3	PVA-B1	PVA-B2	PVA-B3	PAM	AM-SHMB 3:1	AM-SHMB 1:1	AM-SA 3:1	AM-SA 1:1	AM-SA 1:3	PVA-B1	PVA-B2	PVA-B3
<i>Control</i>	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	11.3	11.3	11.3	10.9	10.9	10.9	12.0	12.0	12.0	2.259	2.259	2.259	1.649	1.649	1.649	2.401	2.401	2.401
<i>250</i>	9.9	9.9	9.8	9.5	9.8	9.7	9.6	9.8	9.7	11.1	10.9	11.2	11.9	11.2	11.6	11.6	11.8	11.6	2.231	2.278	2.216	1.551	1.597	1.548	2.246	2.349	2.342
<i>500</i>	9.4	10.1	10.0	9.5	9.6	9.7	9.4	9.5	9.1	10.9	11.1	10.9	11.7	11.1	11.6	11.0	11.6	11.0	2.132	2.351	2.258	1.575	1.580	1.583	2.220	2.266	2.082
<i>750</i>	9.2	10.5	10.4	9.2	9.6	9.5	9.1	9.0	8.7	10.8	11.2	10.6	11.6	10.8	10.8	10.7	10.1	9.8	2.149	2.382	2.390	1.531	1.559	1.616	2.009	2.032	1.963
<i>1000</i>	9.3	10.7	10.7	9.0	9.6	9.5	8.9	8.6	7.9	10.6	11.4	10.2	11.5	10.8	10.3	10.1	9.3	8.3	2.207	2.438	2.450	1.480	1.554	1.744	1.964	1.923	1.815
<i>LSD<sub>s</sub> = 0.9</i>										<i>LSD<sub>s</sub> = 0.8</i>							<i>LSD<sub>s</sub> = 0.201</i>										
<i>LSD<sub>c</sub> = 0.7</i>										<i>LSD<sub>c</sub> = 0.6</i>							<i>LSD<sub>c</sub> = 0.156</i>										