Interpolyelectrolyte complexes as effective structure-forming agents for Chernozem

I.G. Panova[1*], V.V. Demidov[2], P.S. Shulga[2],
L.O. Ilyasov[1], M.A. Butilkina[2], A.A. Yaroslavov[1, 3]

[1]Department of Chemistry and [2]Department of Soil Science,
M.V. Lomonosov Moscow State University, Leninskie gory 1,
119991 Moscow, Russian Federation
[3]Eurasian Center for Food Security, Lomonosov Moscow State University,
Leninskie Gory 1-12, 119991Moscow, Russian Federation
*Corresponding author: I.G. Panova, e-mail: igpan@mail.ru

Polyelectrolyte complexes as effective building agents for Chernozem

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Abstract

Chernozems or mollisols/black soils are "reference soils" with a high content of organic matter, which ensure a high level of crop yield. In the article, we describe the structural characteristics of a typical medium-thick chernozem taken from Kursk region and their improvement via treatment by a 1 wt% aqueous solution/suspension of interpolyelectrolyte complex (IPEC), a product of electrostatic interaction between anionic potassium humates and cationic poly(diallyldimethylammonium chloride). The native chernozem and polymer-treated chernozem were characterized by laser diffraction, dry and wet sieving methods, transmission electron microscopy, soil washoff in a hydraulic erosion tray, gravimetry, visual control and vegetation miniaturization in Petri dishes with the following main conclusions: (a) Deposition of a positively charged IPEC over the chernozem sample led to an increase in a total amount of agronomically valuable 0.25-1 mm aggregates up to 28% in comparison with a 3% content of aggregates in the native chernozem. (b) An average diameter of the air-dry aggregates, treated by a cationic IPEC, was of 5.5 mm (cf. with 2.5 mm for the untreated). (c) An average diameter of the IPEC-treated water-resistant aggregates was of 2.1 mm (cf. with 0.5 for the untreated). (d) The chernozem pre-treated by the cationic IPEC showed a minimum removal of soil during several cycles of re-watering/drying. (e) All IPEC formulations, stimulated the growth of plants. The results are of interest for preparing low-toxic polymer formulations capable of effective stabilizing fertile chernozem soils.

Keywords: chernozem; interpolyelectrolyte complex; water erosion; soil stabilization; anti-erosion measures; artificial stabilizers.

Introduction

Chernozems (mollisols/black soils) are among the most used soils in agriculture (Liu et al., 2011a; Vysloužilová et al., 2014; Vysloužilová et al., 2016). These “reference soils” with a high content of organic matter and a deep, dark organic-mineral horizon are the most fertile soils in Eurasia and North America (Altermann et al., 2005; Eckmeier et al., 2007; Kabała et al., 2019; Liu et al., 2010; Durán et al., 2011). Chemical and physical characteristics of chernozems are ideal for growing even the most demanding crops (Klimek-Kopyra et al. 2015; Hladky et al., 2018). However, a numerous data shows an intensive reduction of the chernozem areas and a noticeable decrease in the thickness of the fertile layer (Yang et al., 2003; Khmelev & Tanasienko, 2009; Liu et al., 2012; Liu et al., 2010; Khokhlova et al., 2015; Chendev et al., 2015). Additionally, researchers note a decrease in the content of organic components and mineral nutrients, including phosphorus and nitrogen (Ouyang et al., 2013; Spychalski et al., 2018). Physical and chemical degradation of agricultural soils results from erosion processes caused by both climatic changes and imprudent human activities. European Environment Agency reports about 12% of the European land subjected to water erosion (Panagos et al., 2015a) while an average annual loss of arable land in Europe is estimated at 2.46 tons per hectare (Panagos et al., 2015b).

In Russia, the degradation affects more than a third of agricultural lands (Masyutenko et al., 2015), including chernozems which occupy more than 40% of the total arable land of the country. An annual soil runoff from the cultivated land is of 0.56 billion tons (Minprirody of Russia, 2018). Erosion decreased soil fertility by 30-60 % over the past 110 years (Eremin, 2016; Smagin, 2013; Zhilenko, 2010).

For well-structured chernozems, the most destructive is water erosion (Liu et al., 2010; Sarapatka et al., 2018; Tang et al., 2013) when the soil is washed away from the slopes by intense rains, snowmelt water, and spring floods. Natural erosion is aggravated by mechanical disturbance of the soil structure during intensive soil cultivation and ploughing (Bezuglova & Yudina, 2006; Nearing et al., 2017). The surface runoff leads to removal of soil aggregates with water flows and reduce of humus content in soil (Zhang et al., 2012; Demidov & Mushaeva, 2016). When moving in the water stream, soil aggregates are destructed down to smaller particles, which deteriorates the structure of chernozem and increases the amount of washed and unstructured soil in the future (Liu et al., 2016).

In order to increase the resistance of soil to erosion, various approaches have been developed, including fertilizer application (Shein et al., 2011, Liu et al., 2011b; Słowińska-Jurkiewicz et al., 2013; Adesanya et al., 2016), artificial pollution (Gargiulo et al., 2014; Minkina et al., 2017), mulching (Liu et al., 2012; Prosdocimi et al., 2016). The use of artificial structure-forming agents, polymers and copolymers, is considered to be an effective technique for improving the structural state of arable soils (Krauth et al., 2008; Mamedov et al., 2017). However, hydrophilic polymers, commonly used for soil treatment, are quickly washed away from the soil that leads to the loss of the binding effect even with minor natural precipitation (Karol, 2003).

Many years of experience with polymer binders show that an optimum result is achieved when polymer(s) contains both hydrophilic and hydrophobic sites (Zezin et al., 2015; Rodriguez et al., 2018). The former interacts with hydrophilic regions on the surface of soil particles and stick them together; the latter causes the same effect being bound to hydrophobic areas of soil particles. This leads to a sharp increase in the efficacy of polymer binder and its low solubility in water. Such properties are typical for interpolyelectrolyte complexes (IPECs), the products of electrostatic complexation between oppositely charged polyelectrolytes (PEs). IPECs are amphiphilic copolymers with hydrophobic blocks formed by mutually neutralized PE sequences and hydrophilic blocks represented by separated PE units (Kabanov et al., 1991; Kabanov, 2005; Thunemann et al., 2004). This allows IPECs to bind to complementary hydrophobic and ionic regions on the surface of soil particles thus strengthening the polymer-soil crust and minimizing the soil erosion (Panova et al., 2017). At the same time, IPECs do not form impermeable layers on the soil surface but retains its porous structure which ensures air and water exchange and maintain the soil fertility (Panova et al., 2019a; Panova et al., 2020).

Although artificial polymer binders, including IPECs, have already proved their efficacy (Zezin et al., 2015), they are not often used in practice. One possible reason for this is a persistent prejudice of agricultural specialists regarding unusual stabilizers for soil treatment (Cerdà et al., 2018). In addition, green trends in agriculture appear, and more environmentally friendly technologies are introduced to maintain and improve the quality of cultivated soils (Rameshaiah et al., 2015; Crowder & Reganold, 2015; Gouda et al., 2018; Boye & Arcand 2013). All this leads to the need to look for artificial binders for the soil, which will not cause concern in an agricultural society. We offer the use of IPECs consisting of natural anionic macromolecules, potassium humates (PH), and cationic poly(diallyldimethylammonium chloride) (PDADMAC) as potential soil binders. A synthetic large-tonnage PDADMAC is widely used for wastewater treatment; this polymer contains nitrogen, an important plant nutrient. PHs, being extracted on an industrial scale from coal, are natural organic components of the soil itself.

Accepting the crucial importance of chernozem for plant cultivation, in this article we describe the laboratory study on the improvement of structural characteristics of chernozem and its resistance to destruction induced by water erosion. We discuss the effect of the composition and charge of amphiphilic IPECs on the size distribution of chernozem aggregates in air-dry and water-resistant states, the resistance of IPEC-treated chernozem to water runoff, and the biocompatibility of IPECs in experiments with radishes, plants that are very sensitive to toxic compounds. The results are of interest for the preparation of low toxicity polymer compositions capable of effectively stabilizing fertile chernozem soils.

Materials and Methods

PDADMAC with Mw = 400-500 kDa (Sigma-Aldrich, USA) and PH with Mw 9.9 kDa (Humintech GmbH, Germany) were used as received. Both polymers were dissolved in bi-distilled water, prepared by double distillation, which was additionally treated by a Milli-Q Millipore system composed of ion-exchange and adsorption columns as well as a filter to remove large particles. IPECs were obtained via mixing of 1% aqueous solutions of PDADMAC and PH at a desirable molar ratio of PDADMAC cationic groups and PH anionic groups (a desirable charge-to-charge ratio). Three IPECs were prepared: a stoichiometric with Q(0) = (PH)/(PDADMAC) = (PDADMAC)/(PH) = 1, and two non-stoichiometric – an anionic with Q(-) = (PH)/(PDADMAC) = 3 and a cationic with Q(+) = (PDADMAC)/(PH) = 3.

A soil sample was taken on the experimental field near Panino village in the Kursk region (Russia) with section coordinates: 51° 32°'32.2" North and 36 ° 06 °'35.9" 'East. At the sampling site, “grain-grass” cultivation is used with crop rotation: 1) clover, 2) winter wheat, 3) maize, 4) barley + clover. Tillage: plowing for maize 25-28 cm, surface treatment for winter wheat and small tillage for barley. Fertilization: for winter wheat N30P60K60, for maize N80P70K70. Soil sampling was performed on maize crops in the phase of 2-3 leaves. An upper 10 cm layer of the arable horizon was used with the carbon content of 4.96 wt% (determined as described in [Vanchikova et al., 2006; Nikitin, 1983]) and pH 6.4. Based on the field description of the soil horizon, the type of soil was determined as Chernozem of typical medium-sized slightly washed light-loam (Haplic Chernozem (Aric Loamic)) according to the WRB classification (IUSS Working Group WRB, 2015).

Granulometric composition (particle size distribution, PSD) of the chernozem sample was obtained without removal of organic matter and quantified using by the laser diffraction method. The samples were ground in a porcelain mortar with a rubber-tipped pestle for 1 min and sieved through a 1 mm sieve. 0.1 g of the sieved chernozem was put in a glass vessel, then 30 mL of bi-distilled water were added, and the suspension (1/300 ratio) was sonicated for 5 min using a Digital Sonifier S-250D ultrasonic disperser (Branson Ultrasonics, USA). A 450 J/mL power of treatment was shown to be sufficient for dispersing most soil samples down to soil particles with minimum size, known as elementary soil particles or soil building units including minerals and organic particles (Yudina et al., 2018). The PSD was obtained by using the laser diffraction method with a Mastersizer 3000E laser particle sizer (Malvern Instruments, UK).

To obtain water-stable micro-aggregates with a 0.25 mm size and less, chernozem was ground in a mortar within 1 min and sieved through a 1 mm sieve. Then 0.25 g of the sieved chernozem was put in a plastic test tube with 35 ml water and shaken for 1 h using a Multi Bio RS-60 multirotator (Biosan, Latvia) (Yudina & Milanovskiy, 2017). Thus prepared suspension was tested for micro-aggregate particle size distribution (MSD) using the laser diffraction method with a Mastersizer 3000E laser particle sizer (Malvern Instruments, UK). The combination of MSD and PSD data allowed the calculation a micro-aggregation degree (Baver & Rhoades, 1932) as:

$$K = ((a-b)/a) \times 100\%,$$

where a is a volume fraction of undestroyed micro-aggregates with a size of 0.05 mm and more (from the MSD data) and b is a volume fraction of elementary soil particles with a size of 0.05 mm and more (from the PSM data). The higher the K value, the more water-resistant micro-aggregates.

Finally, the chernozem sample was sprayed with water and dried at room temperature for 4 days. After that, the sample was sieved through a set of sieves followed by weighting each fraction; no additional mechanical treatment like ultrasonic or shaking was not applied. The ~1.25 cm top layer from treated air-dry chernozem were analyzed. This allowed a size distribution of air-dry aggregates in the control chernozem sample. After that, the fractions were mixed using the protocol described earlier (Savinov, 1936; Vadyunina & Korchagina, 1986). The total sample ("re-constructed chernozem") was put into a cylindrical container filled with water for 10 min and then fractioned again by sequential passing through the same set of sieves but immersed in the container. Each fraction was dried and weighed that allowed the size distribution of water-resistant chernozem aggregates. The results were used to calculate average diameters of aggregates in air-dry and water-resistant states (D_{ad} and D_{wr}, respectively), taking into account the weight contribution of each fraction.

After the chernozem sample was examined for micro-aggregate distribution, air-dry aggregate distribution and water-resistant aggregate distributions, these characteristics were tested for the chernozem sample treated by individual cationic PDADMAC and anionic PH, and PDADMAC-PH IPECs with varied charge-to-charge ratio. The soil samples were treated by single spraying of a 1 wt% aqueous solution/suspension of individual polymers or IPECs with a consumption rate of 2 L/m^2 and dried for 3-4 days. Bi-distilled water was used in control experiments.

A fraction of the air-dry chernozem aggregates with size from 0.25 up to 1 mm was used to study the resistance of soil to water erosion. 100 g of this chernozem fraction was placed in a Petri dish, and 20 mL of water (control) or 1 wt% aqueous solution of an individual polymer or 1 wt% aqueous IPEC formulation were sprayed over the sample surface. The samples were dried for 3-4 days to constant weight. Irrigation with bi-distilled water was performed for 10 min from a height of 20 cm in a pulsed mode using a sprayer with a pressure of 2 atmospheres and a water feed rate of 100 mm/h. The slope of the dish during irrigation was of 35º. Wastewater (ca. 200 mL in each experiment) along with washed soil was collected in a special tray and centrifuged. The precipitate was dried to constant weight. This approach was used earlier in our work (Panova et al., 2019a, Panova et al., 2020) and followed the conditions of water treatment described in (Sepaskhah & Bazrafshan-Jahromi, 2006).

Additionally, the resistance of chernozem to water erosion was studied using a hydraulic erosion tray equipped by a water source with a controlled water flow rate, a device for measuring an amount of washed soil and a sediment collector. As shown earlier (Kerzhentsev et al., 2006; Demidov et al., 2010) the results of the hydraulic tray experiment adequately describe the washoff of soil induced by natural reasons (rain, melt water, etc.). Taking into account the large soil consumption, the native chernozem sample was used in these experiments. The IPEC formulations and bi-distilled water (control) were deposited over the soil at a consumption rate of 2 L/m^2. The sample was dried for 3 days, after that the flow of tap water run down the tray with a controlled speed for 30 minutes. During this time, the soil and water got into the sediment collector, from where the washed soil was taken and dried in the air to a constant weight. After collecting the washed soil, the sample in the tray was dried for 3-4 days, and the erosion experiment was conducted again with a higher water flow rate. Totally, 6 washing/drying cycles were performed with constantly increasing water flow rate. So, each specific IPEC formulation was deposited over the soil only once, and then 6 washing/drying cycles were done with this once-treated soil. An intensity of soil washout was represented as the mass of soil removed from one square meter of the tray area per one second.

Biocompatibility of polymers was estimated through growing of a test culture, radish, on the polymer-treated chernozem. 20 g of chernozem and 100 radish seeds were placed in a Petri dish, then 20 mL of a 1 wt% aqueous solution of a polymer or IPEC (20 mL of bi-distilled water in a control experiment) was deposited over the sample. The dishes were covered with a transparent film to prevent evaporation of water. 6 days after, the plants were taken out of the dishes, soil was removed with water, and an average length of stems was determined based on 20 plants from each dish. Then, the radish was dried to constant weight at room temperature and weighed, thus allowed the total biomass. The average germination rate was of 80 ± 3%.

All experiments were repeated three times. Statistical processing of data was performed using the Microsoft Excel program: average values and standard deviations were determined, confidence intervals were calculated with a correlation coefficient of 0.95. The average values and confidence intervals are presented in Table 1. The graphs and histograms show the average values of the corresponding parameters and confidence intervals as error bars.

Results and Discussion

1. PDADMAC-PH IPEC formation.

It has been shown previously (Panova et al., 2019; Panova et al., 2020), that, in neutral aqueous solutions, anionic PH electrostatically interact with cationic PDADMAC resulting in the formation of a PDADMAC-PH interpolyelectrolyte complexes stabilized by multiple salt bonds between ionic groups of both polyelectrolytes. At a equimolar ratio between anionic units of PH and cationic units of PDADMAC, Q(0) = (PH -) / (PDADMAC+) = 1, stoichiometric IPECs are formed insoluble in water. An excess of either component gives water-soluble IPEC with Q ≠ 1 (Panova et al., 2020). In our research, three IPECs were prepared and examined: a stoichiometric with Q(0) = 1, and two non-stoichiometric – an anionic with Q(-) = 3 and a cationic with Q(+) = 3. All three types of IPECs contained hydrophobic blocks formed by mutually neutralized PE sequences and hydrophilic blocks represented by separated PE units. Both non-stoichiometric IPEC formulations, dark-brown in colour, remained stable – without phase separation – at least within a month. In the dark-brown stoichiometric IPEC formulation, phase separation occurred during the IPEC preparation with the formation of light-brown sediment against a clear solution background. However, sediment flakes did not stick together with time. Upon intensive shaking, the flakes formed fine coloured suspensions which did not aggregate within several minutes. All formulations – as they are for the non-stoichiometric IPECs and after intensive shaking for stoichiometric IPEC – were deposited over the chernozem surface using a spray gun.

2. Micro-aggregate state of IPEC-treated chernozem.

The granulometric composition of the chernozem sample (PSD) is shown as black columns in Figure 1. A fraction with 0.001-0.005 mm size and a fraction with 0.01-0.05 mm size are predominant (32 and 40 %, respectively), while the total content of a >0.01 mm fraction is of 54 %.

Size distribution of water-resistant micro-aggregates (MSD), obtained via shaking the chernozem sample in a water medium, is shown by grey columns in Figure 1. As follows from the figure, the shaking-in-water procedure resulted in decomposition of 0.25-1.00 mm particles and only microaggregates with a size of 0.25 mm and less was found in the sample. Additionally, the MSD contained a significant amount of 0.05-0.25 mm micro-aggregates which was only slightly represented in the PSD. The Baver micro-aggregation degree K for the MSD is of 86 %.

Treatment of the chernozem sample by polymer formulations led to a qualitative change in the MSD. The results are shown in Figure 2 together with the MSD for the chernozem sample, dried after preliminary treatment with water (control), taken from Figure 1.

In the native chernozem (black columns), the largest amount of micro-aggregates was within a 0.01-0.05 mm size (49%) and a 0.05-0.25 mm (38%). A total amount of agronomically valuable (AV) aggregates from 0.25 up to 1 mm size (Bezuglova & Yudina, 2006; Gajic, Dugalic & Djurovic, 2006) was only 3%. Treatment of the chernozem with anionic (grey columns) and stoichiometric NPECs (stripped columns) led to a negligible increase in the amount of 0.05-0.25 mm micro-aggregates and 0.25-0.5 mm AV aggregates. Contrastingly, the treatment with cationic IPEC (dark grey columns) decreased the amount of 0.05-0.25 mm micro-aggregates by 9% but increased the amount of 0.25-0.5 mm aggregates by 12% and 0.5-1 mm aggregates by 13%, that corresponded to a total increase in the AV aggregates up to 25%. Thus, an impressive increase in the content of agronomically valuable aggregates after treating chernozem with an aqueous solution of a cationic IPEC can be seen. The K value was of 88.4% for the chernozem treated with anionic/stoichiometric IPECs and 90.5% for the chernozem treated with cationic IPEC in comparison with K = 86.3 for the native chernozem.

3. Aggregate state of IPEC-treated chernozem.

The next step was to examine the effect of IPEC formulations on the size distribution of air-dry chernozem aggregates; the latter was prepared via dry sieving the native chernozem sample as described in the Materials and Methods section. The distribution for the native chernozem is shown in Figure 3 (black columns). The maximum aggregate content (27%) fell into a 1.5-5 mm size range; however, there was a significant fraction of micro aggregates with a size lower than 0.25 mm (23%). An average diameter of aggregates in air-dry state is D_{ad} = 2.5 mm. After treatment of the native chernozem with water (see details in Experimental part), the size distribution of aggregates drastically changed (black columns in **Figure 4**). Now the most of thus obtained water-resistant chernozem aggregates (57 wt%) was represented by small particles with a size of 0.25 mm and less with a negligible content of aggregates with size of 1.5 mm and more, while an average diameter of aggregates in a water-resistant state D_{wr} = 0.5 mm.

Both above chernozem samples – with air dry aggregates and water-resistant aggregates – were once treated by wt% solution/suspension of three IPECs: with Q(-), Q(0) and Q(+). During the treatment, the polymers penetrated the soil to a 1.25±0.25 cm depth, thus forming a protective polymer-soil composition. The ~1.25 cm top layer from treated air-dry chernozem were analyzed for the size distribution by the sieving method; the results are shown in **Figure 3** as light grey columns for Q(-), striped columns for Q(0) and dark grey columns for Q(+). In all cases, the treatment led to a sharp reduction in micro-aggregates (<0.25 mm (Tisdall and Oades, 1982; Shein, 2005)) a slight increase in the optimum size fraction ratio (1.5-5 mm) and an elevation of the lumpy fraction ratio (8 mm and larger). An average diameter of the IPEC-treated aggregates in the air-dry state D_{ad} was of 4.7 mm for Q(-), 5.6 mm for Q(0) and 5.5 mm for Q(+). These values were twice as much and even higher in comparison with the average size of the chernozem sample before the IPEC treatment (D_{ad} = 2.5 mm). Thus, the treatment with PDADMAC-PH IPECs was accompanied by stabilization of large air dry aggregates.

After that, the size distribution was analyzed for the top layer of water-resistant chernozem treated by IPECs: Q(-) as light grey columns, Q(0) as striped columns and Q(+) as dark grey columns (**Figure 4**). Again, the treatment results in a decrease in micro-aggregates (<0.25 mm) with a simultaneous increase in large aggregates with size of 1.5-5 mm and larger. The average size of water-resistant aggregates increased from 0.5 mm for the native chernozem up to 0.7 mm for Q(-) IPEC, 1.9 mm for Q(s) IPEC and 2.1 mm for Q(+) IPEC. So, the electroneutral IPEC with Q(0) and cationic IPEC with Q(+) showed the best aggregate-stabilizing results.

Thus, the use of polycomplexes improved the structural state of the chernozem. The cationic IPEC markedly increased the mechanical stability of the soil in the air dry and water-resistant states.

4. Resistance of IPEC-treated chernozem to water erosion.

The resistance of the chernozem to water erosion was tested in two versions. First, small-scale experiments were carried out with the chernozem samples prepared in Petri dishes. Briefly, a 0.25-1 mm fraction of the chernozem was put in a Petri dish, and 20 mL a 1 wt% solution/suspension of an individual polymer (PDADMAC or PH) or IPEC were deposited over the soil. In a control experiment, 20 mL of water was deposited over the soil. After drying, the treated chernozem was sprayed by water followed by the collection of wastewater, separation of the precipitate by centrifugation, its drying and weighing. The results are presented in **Table 1**.

A maximum amount of washed soil (10.5%) was found in a control experiment with the native chernozem. The same was found for the PH-treated soil thus showing no protective properties of the individual anionic PH. Better results were obtained for the soil samples treated by the individual cationic PDADMAC and two IPECs, the negative and the stoichiometric: from 2.1 up to 4.2%. Finally, the sample, treated by the positive IPEC, demonstrated the best result with an amount of washed soil of 0.36% or 30 times less than in the control.

The morphology of polymer-soil crusts is presented in the photos in **Figure 5**. The chernozem sample, before treatment of water/polymer formulations (**Figure 5A**), is a homogeneous sample consisting of individual small granules of soil. After re-watering and removal of 10.5 wt% of chernozem granules, the sample was dried that resulted in the formation of a structureless cracked soil (**B**). Similar or very close pictures were obtained for chernozem pre-treated with negative PH (**C**), negative IPEC (**E**) and stoichiometric IPEC (**F**). Against this background, two positive formulations stood out: PDADMAC (**D**) and Q(+) IPEC(**G**). Both led to pronounced preservation of the native chernozem granules and the formation of a minimum number of cracks (**D**, **G**), while the letter showed a minimum amount of washed water, 0.36% (see above).

A deeper insight into the morphology of chernozem samples was achieved with the use of electron microscopy. The granular structure of the 0.25-1.5 mm fraction of chernozem is well displayed in **Figure 6A**. The photo shows well-structured aggregates of irregular shape. At higher magnification, a composite, hierarchically constructed structure of the sample is clearly visible (**B**) in which larger aggregates are an assembly of smaller ones. An intensive water treatment led to drastic changes: dissolution of the larger aggregates down to smaller ones and formation of cracks in the polymer-soil crust (**C** and **D**).

Contrastingly, treatment of the chernozem with the positive IPEC stabilized the structure of the granules. In the experiment, the sample was examined which was treated by the positive IPEC formulation and dried, then sprayed by water and dried again. The IPEC-treated chernozem granules retained their compact structure when affected by water (**Figure 7A**) and IPEC did not close the pores in the soil aggregates (**B**). The latter means that air-and water-exchange in the IPEC-treated soil persisted, an important requirement for fertile soil.

Upon completing the erosion tests with Petri dishes, we conducted large-scale laboratory experiments using the erosion tray. The IPEC formulations were once deposited over the native chernozem. After preliminary drying, the treated soil samples were subjected to 6 washing / drying cycles with a permanently increasing water flow rate (see Experimental section). The results are shown in **Figure 8** where "normalized soil removal", S, is plotted against "water flow rate". First, a control experiment was done with the native chernozem dried after pretreatment only with bi-distilled water. As follows from the figure, at a water flow rate (V_w) of 0.05 m/s no soil removal was detected. An increase in V_w was accompanied by a nearly linear rise of the removed chernozem (curve 1 in **Figure 8**). A total soil removal (S) is a sum of soil removals for 1st cycle, 2nd cycle and so up to 6th cycle. For the native chernozem S = 3.25 g/m^{2}s. Then, the experiment was carried out again but with a soil stabilized by three IPEC formulations: with Q(-) (2), or Q(0) (3), or Q(-) (4). For all IPEC formulations, a progressive decrease in the amount of the washed soil was detected. The Q(-)-treated soil showed a modest result with $S_{Q(-)}$ = 2.1 g/m^{2}s; the better was shown with the Q(0)-treated soil: $S_{Q(0)}$ = 1.21 g/m^{2}s. The most impressive result was obtained with the Q(+)-treated soil. In the latter case, a negligible washing of soil was detected up to the water flow rate of 0.3 m/s with the total removal $S_{Q(+)}$ = 0.16 g/m^{2}s. So, the soil only one-treated by the positive IPEC, successfully resisted to the water erosion. The protective polymer-soil crust retained on the soil surface even after 6 washing/drying cycles, each for 30 min. This model experiment demonstrated the stability of the IPEC-treated soils when affected by several intensive rainfalls.

In **Figure 9A** is shown the photo of the native chernozem with individual small granules of soil without cracking. **Figure 9B** and **Figure 9C** are the photos of chernozem treated by Q(-) IPEC and Q(0) IPEC, respectively, then subjected to 6 washing/drying cycles and finally dried for 2 days. In both photos, we see the structureless surfaces (with no granules on the surfaces) and deep cracks. The use of Q(+) IPEC for pre-treatment of chernozem gave **Figure 9D** which demonstrates the ability of Q(+) IPEC to protect soil aggregates from blurring and to prevent cracking. These results are similar to those described above for a 0.25-1.5 mm fraction of chernozem tested in the small-scale experiments in Petri dishes (see **Figure 5**).

We see therefore that positive IPEC shows the most effective stabilizing properties towards chernozem; such IPEC largely suppressed water erosion of chernozem and the destruction of soil aggregates. The stabilizing effect is likely due to the predominance of finely dispersed clay particles and organic matter in chernozem composition (Minkina et al., 2017), which, being negative at neutral pH [Beckett & Le, 1990; Schoonheydt & Johnston, 2006], are capable of interacting with positive polymers thus forming a network composed of polymers and mineral-organic soil particles **(**Shaikh et al., 2017; Bolto et al., 2001) and modifying the surface of soil aggregates (Kurochkina, 2019). This results in fixing the soil aggregate structure, improving the adhesion of individual soil particles, and increasing in the resistance of soil aggregates to erosion. Even more effective binder is positive IPEC which adsorbs on the soil particles both via electrostatic and hydrophobic interactions (the soil surface carries ionic and hydrophobic domains) (Piccolo & Mbagwu, 1999: Dal Ferro et al., 2012). So, hydrophobic blocks in the positive IPEC make an additional contribution to the water resistance of soil bound to this polymer. Anionic IPEC, also carrying hydrophobic blocks, turned to be the least effective binder which prevents water erosion of chernozem only at low water flow rates.

In the previous papers (Panova et al., 2017, Panova et al., 2019a, Panova et al., 2019b, Panova et al., 2020) we described the use of IPECs for stabilization of several types of soils/grounds with different contents of organic matter. It was shown that positively charged IPEC formed the strongest top layers on the soil/ground surface, which resisted wind and water erosion. In the current article, we demonstrate for the first time the stabilizing effect of cationic IPEC towards chernozem soil. From there, we can conclude that organic matter is not critical for the IPEC formulations to show their stabilizing properties.

5. Biocompatibility of IPEC.

Biocompatibility of polymers used in this work was assessed by controlling the growth of radish, a plant very sensitive to toxic compounds (Nikolaeva & Terekhova, 2017; Voronina et al., 2019). The chernozem was put in Petri dishes together with 100 radish seeds for each dish. The dishes were sprayed by water, or an aqueous polymer formulation, then covered with a plastic film and left to stay for 6 days. In this way 6 samples were prepared: the chernozem treated by water (control, A) and aqueous formulations of PH (B), PDADMAC (C), Q(-) IPEC (D), Q(0) IPEC (E) and Q(+) IPEC (F). Photos of the samples, taken 6 days after planting, are shown in **Figure 10**.

In all cases, seed germination averaged 80±3 %; atypical plants were not observed. Visually, plants in all dishes showed approximately the same development, although seeds in the dish treated by Q(+) PDADMAC germinated a day later than seeds in other dishes. On the sixth day, the plants were taken out of the dishes, soil was removed with water, and an average length of stems was determined (**Figure 11A**). Then, the radish was dried to constant weight at room temperature and weighed, thus allowed the total biomass (**Figure 11B**).

The results of biological tests, in which radish was grown on the chernozem treated by polymers and on a control sample with chernozem, were compared. PDADMAC alone reduced a root length by 20% and the total plant biomass by 12% that was additional evidence of noticeable toxicity of cationic polymers (Strassburg et al., 2015). The other formulations had a stimulating effect on the plant growth, increasing the length of plant stems and the total biomass; the stoichiometric IPEC demonstrated the most pronounced results, an increase in the stem length by 35% and an increase in the biomass by 45%. Interestingly, the positive Q(+) IPEC with 66 mole% of free cationic PDADMAC groups also showed the stimulating effect on both the stem length and biomass, 11-12% in both cases.

We see therefore that IPEC formulations, even positively charged, are non-toxic to sensitive plants and do not suppress their growth when applied as soil binders. Moreover, all IPEC used in the research stimulate the growth of plants.

Conclusions

In the laboratory experiments, it was shown that structure and anti-erosion stability of typical chernozem from the Russian Plain was enhanced by the use of three polymeric stabilizers, that were obtained from the same pair of water-soluble polyelectrolytes, but differ in composition and charge. The adhesion of soil colloids as a result of polymer treatment led to an increase in the aggregation of the soil and an increase in the strength of inter-aggregate contacts. The amphiphilic positively charged polyelectrolyte complex enhanced mechanical stability and water-stability of base units/aggregates of chernozem complex grain-lumpy structure most effectively. It was shown that the cationic IPEC shifted the distribution of air-dry aggregates and the distribution of water-stable microaggregates and aggregates towards larger particle diameter in the most pronounced way. At the same time, this complex almost entirely prevents the soil runoff and the destruction of soil aggregates in the course of 6 cycles of water treatment, including cycles with high water stream speeds. It is expected that the strength of forming contacts is significantly higher in the case of use of positively charged IPEC due to its effective binding to negatively charged mineral and organic particles, constituting chernozem. The presence of hydrophobic fragments in the polymer additionally contributes to stabilizing the structure of soil aggregates, enhancing their water-resistance and anti-erosion stability. It was shown that the used polyelectrolyte substances are non-phytotoxic, which means, they do not pose a threat to seed germination and plant growth when used as builders/amendments of agricultural soils.

Conflict of interest

The authors declare no conflict of interest.

Data availability statement

Research data are not shared.

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Figure 1. Granulometric (PSD, black columns) and micro-aggregate (MSD, gray columns) composition of the chernozem sample.

Figure 2. MSD for the chernozem sample before (black columns) and after IPEC treatment.

Q(-) IPEC = (PH)/(PDADMAC) = 3, light grey columns; Q(0) IPEC = (PH)/(PDADMAC) = 1, striped columns; Q(+) IPEC = (PDADMAC)/(PH) = 3, dark grey columns.

Figure 3. Size distribution of air-dry chernozem aggregates before (black columns) and after IPEC treatment. Q(-), light grey columns; Q(0), striped columns; Q(+), dark grey columns.

Figure 4. Size distribution of water-resistant chernozem aggregates before (black columns) and after IPEC treatment. Q(-), light grey columns; Q(0), striped columns; Q(+), dark grey columns.

Figure 5. Photos of a 0.25-1.5 mm fraction of chernozem before (A) and after re-watering / drying. Pre-treatment was carried out with water (B), PH (C), PDADMAC (D), Q(-) IPEC (E), Q(0) IPEC (F), Q(+) IPEC.

Figure 6. Microphotographs of chernozem granules before (A, B) and after treatment with water (C, D). A 0.25-1.5 mm fraction of chernozem was used.

Figure 7. Microphotographs of the chernozem granules pre-treated by Q(+) IPEC, then dried and treated by water. A 0.25-1.5 mm fraction of chernozem was used.

Figure 8. Dependence of soil washout intensity vs. water flow rate for the chernozem (curve 1) and chernozem treated with IPEC: Q (-) (curve 2), Q (0) (curve 3) and Q (+) (curve 4). The initial (unfractionated) chernozem was used.

Figure 9. Photos of unfractionated chernozem in erosion tray (A) and chernozem after treatment by IPEC formulations and 6 washing/drying cycles (B-D). IPEC: Q(-) (B), Q(0) (C) and Q(+) (D). See details in the text.

Figure 10. Radish 5 days after radish seed planting in 0.25-1.5 mm fraction of chernozem was used. chernozem. After seed planting chernozem was treated with water (A), PH (B), PDADMAC (C), Q(-) IPEC (D), Q(0) IPEC (E) and Q(+) IPEC (F).

Figure 11. Average length (A) and total biomass of radish (B) grown in the presence of individual polymers and IPECs (6 days after planting).

Table 1. The percentage of washed chernozem, pre-treated by water and polymers and dried within 3 days. A 0.25-1 mm fraction of chernozem was used.

Polymer composition	**Washed chernozem, %**
Water (control)	10.5±1,2
PH[1]	9.8±1,1
PDADMAC[2]	3.1±0,7
Q(-) IPEC[3]	4.2±0,5
Q(0) IPEC[4]	2.1±0,3
Q(+) IPEC[5]	0.36±0,21

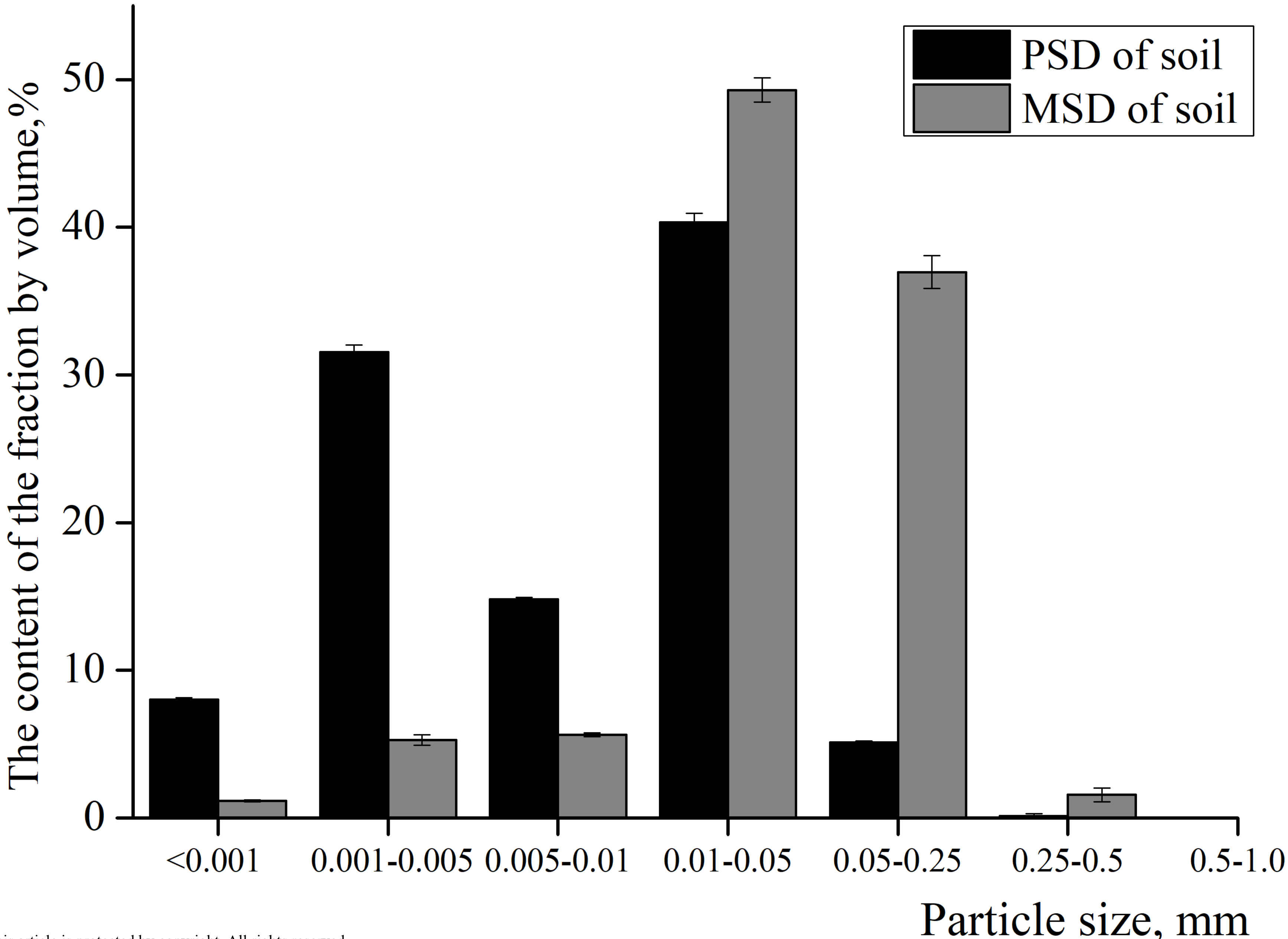
1)PH - potassium humates;

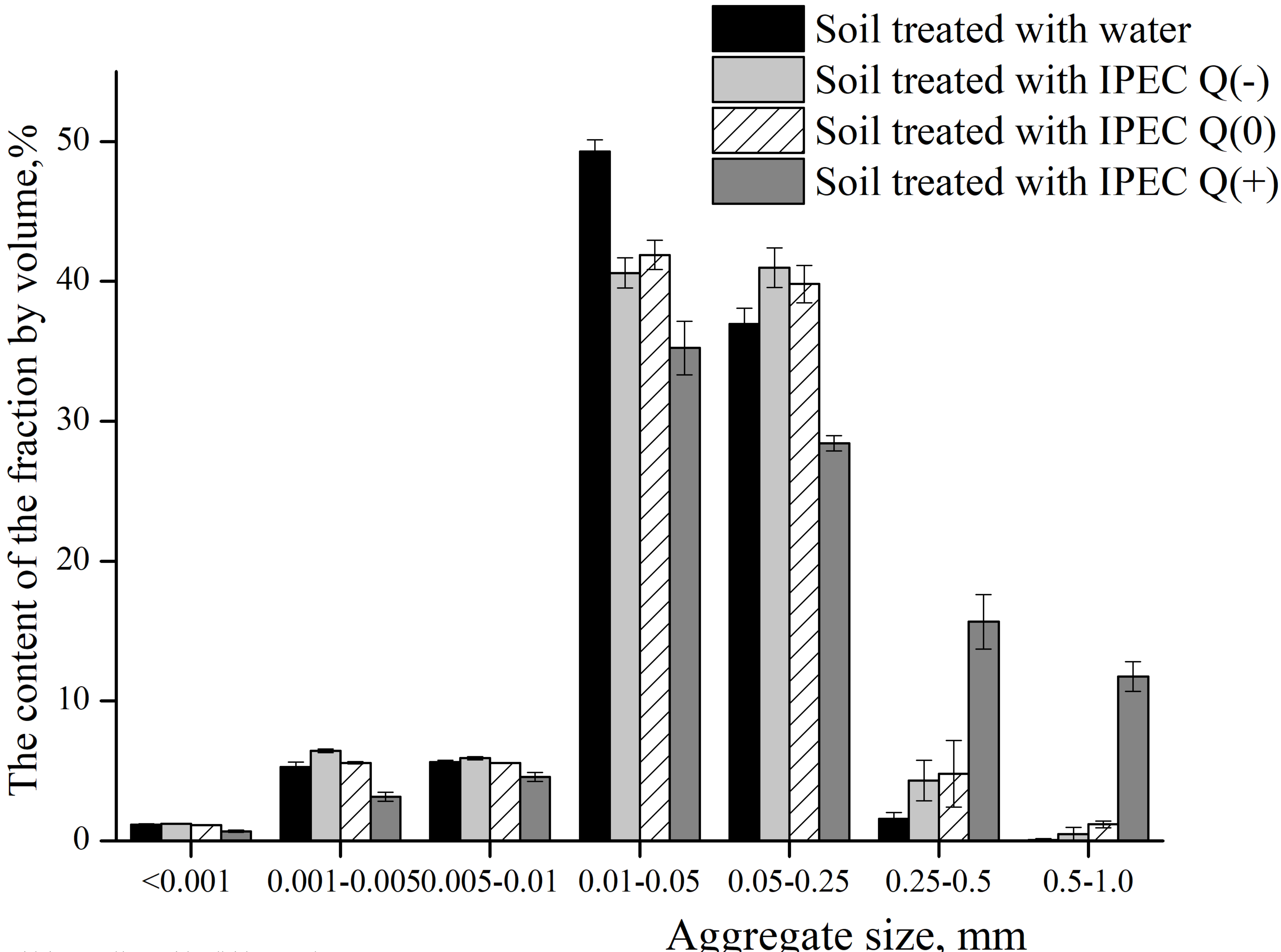
2) PDADMAC - poly(diallyldimethylammonium chloride);

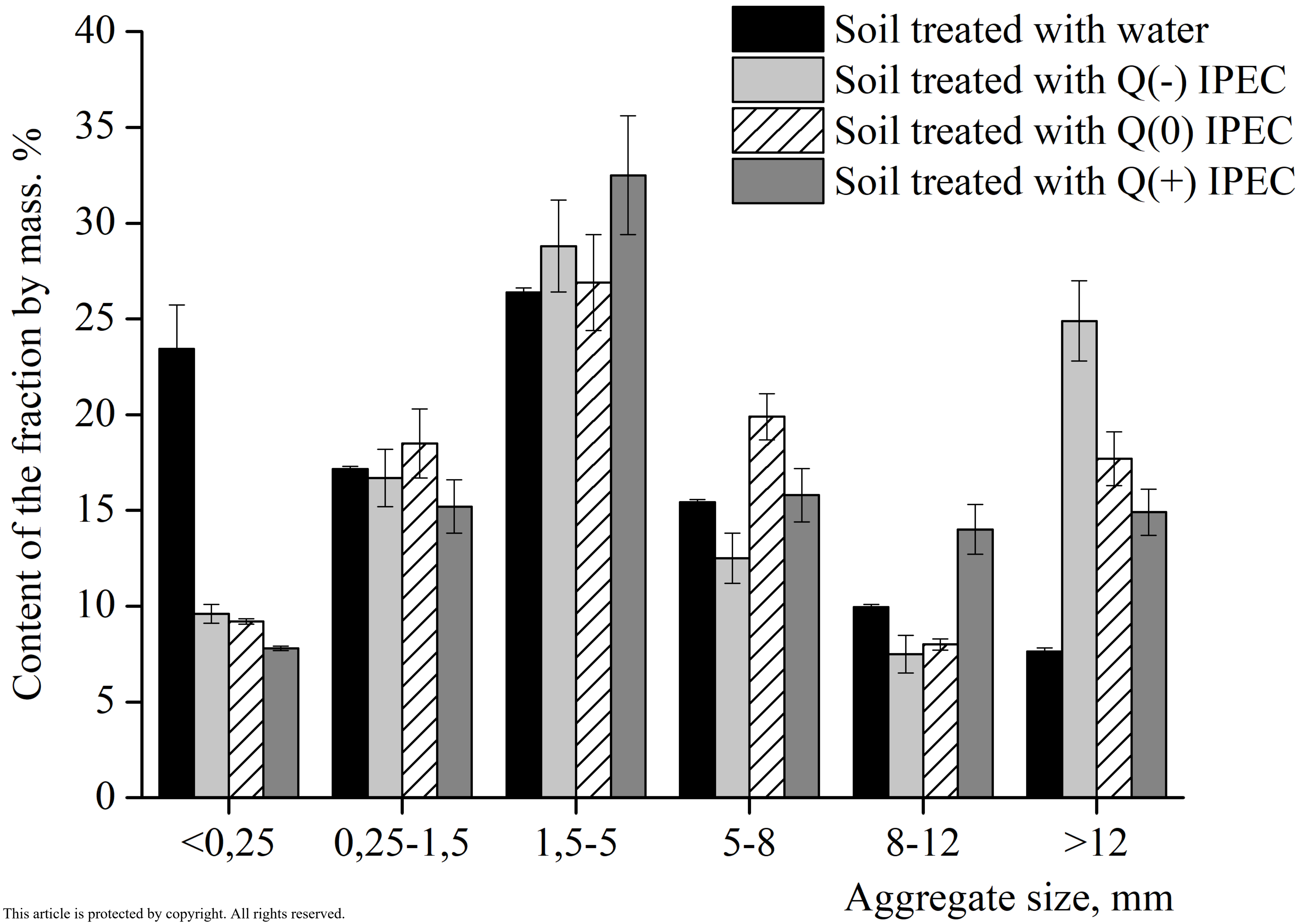
3) Q(-) IPEC = (PH)/(PDADMAC) = 3;

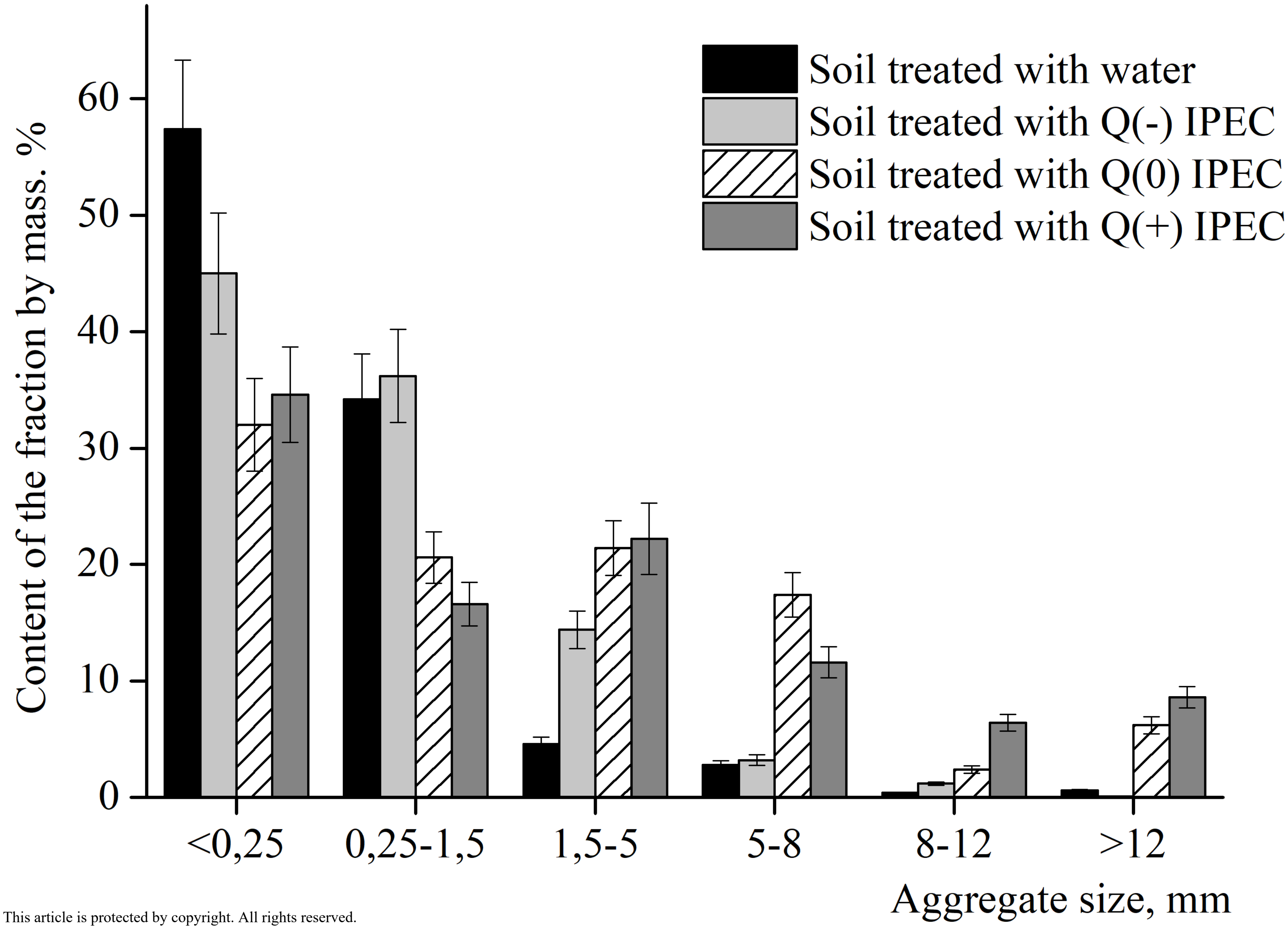
4) Q(0) IPEC = (PH)/(PDADMAC) = (PDADMAC)/(PH) = 1;

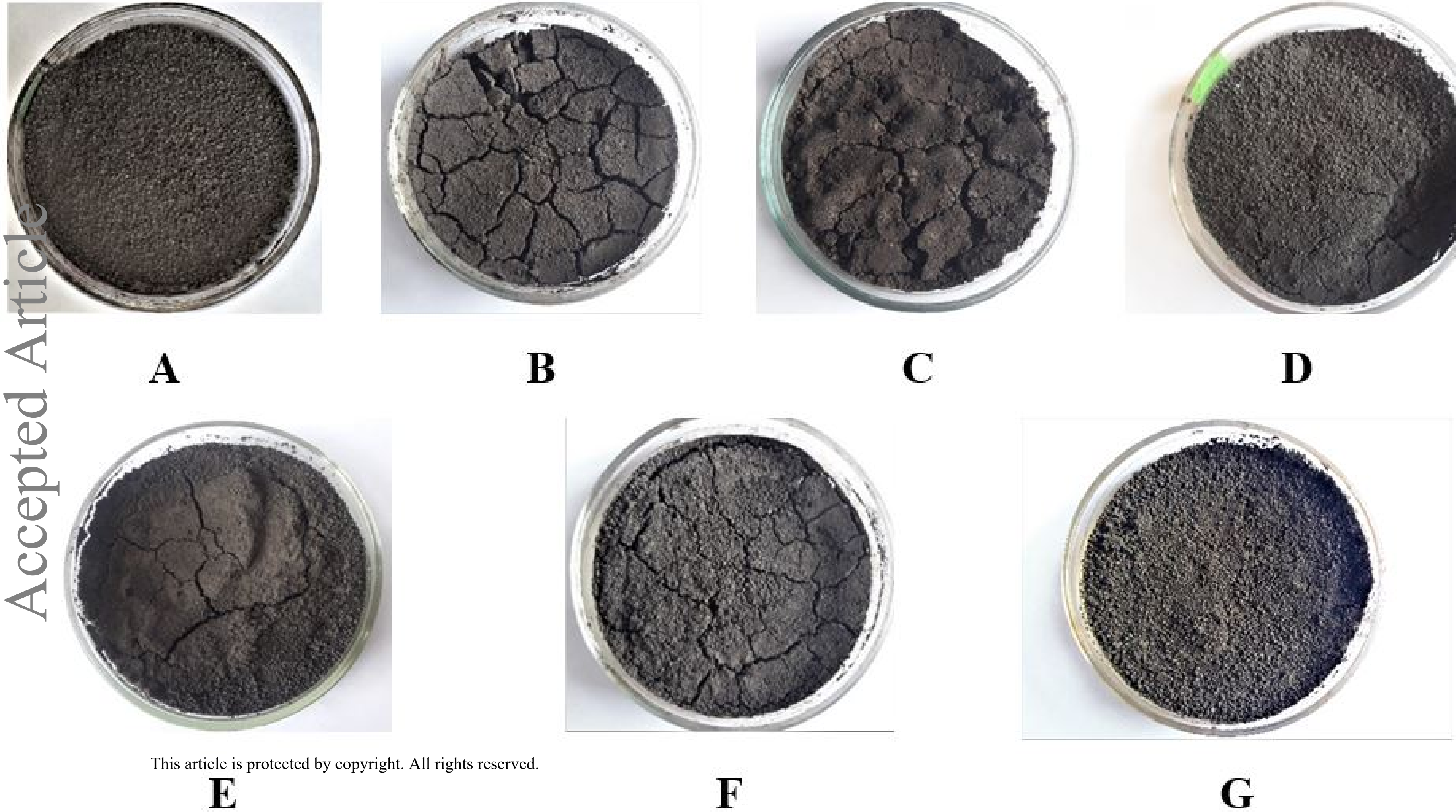
5) Q(+) IPEC = (PDADMAC)/(PH) = 3

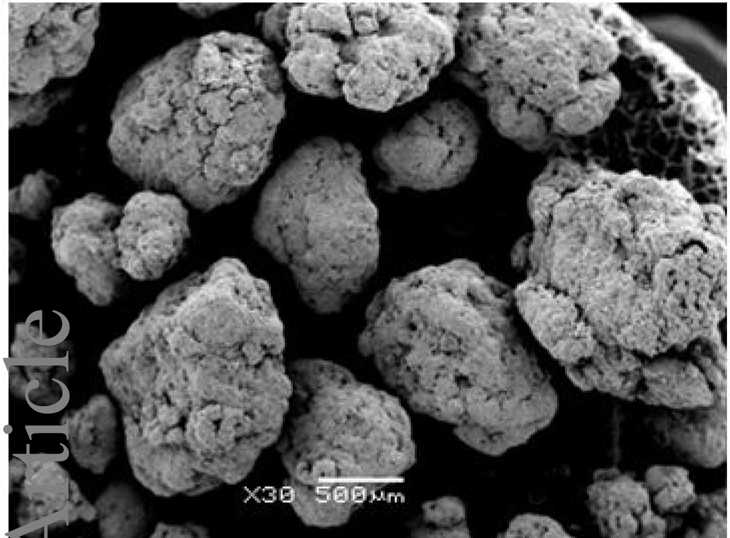

PSD of soil
MSD of soil
The content of the fraction by volume,%
0
10
20
30
40
50
<0.001
0.001-0.005
0.005-0.01
0.01-0.05
0.05-0.25
0.25-0.5
0.5-1.0
Particle size, mm


Soil treated with water
Soil treated with IPEC Q(-)
Soil treated with IPEC Q(0)
Soil treated with IPEC Q(+)
The content of the fraction by volume,%
50
40
30
20
10
0
<0.001
0.001-0.005
0.005-0.01
0.01-0.05
0.05-0.25
0.25-0.5
0.5-1.0
Aggregate size, mm

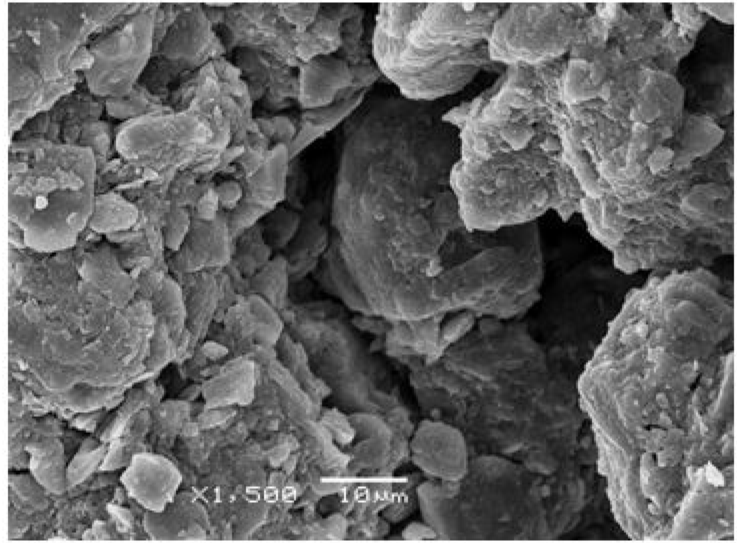

Soil treated with water
Soil treated with Q(-) IPEC
Soil treated with Q(0) IPEC
Soil treated with Q(+) IPEC
Content of the fraction by mass. %
0
5
10
15
20
25
30
35
40
<0,25
0,25-1,5
1,5-5
5-8
8-12
>12
Aggregate size, mm


Soil treated with water
Soil treated with Q(-) IPEC
Soil treated with Q(0) IPEC
Soil treated with Q(+) IPEC
Content of the fraction by mass. %
60
50
40
30
20
10
0
<0,25
0,25-1,5
1,5-5
5-8
8-12
>12
Aggregate size, mm

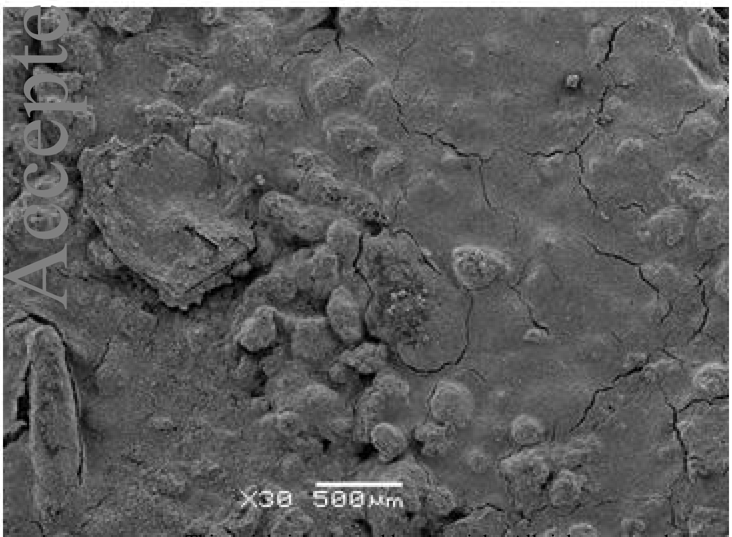

A
B
C
D
E
F
G



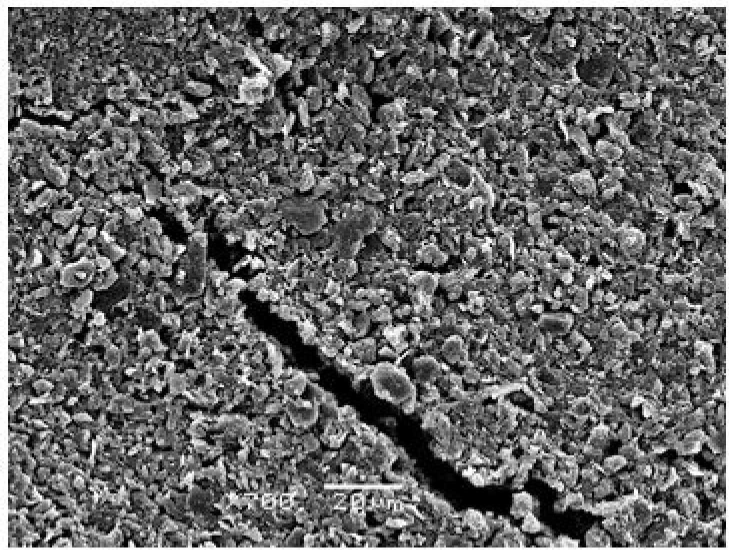
A



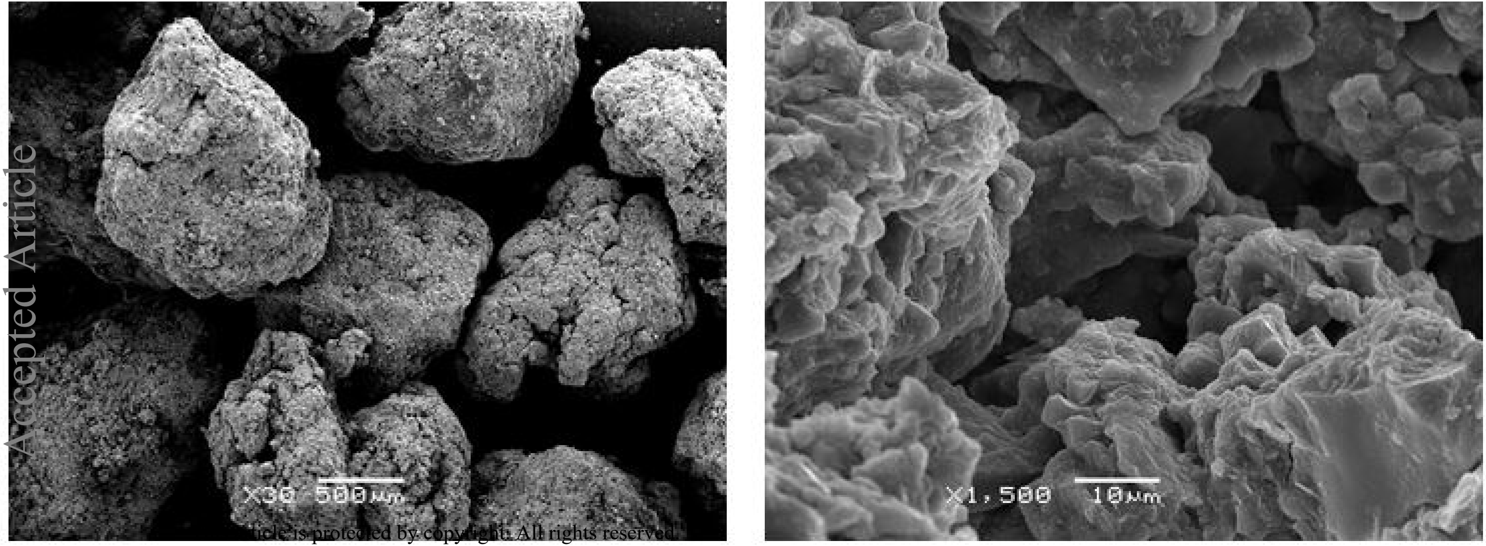
B



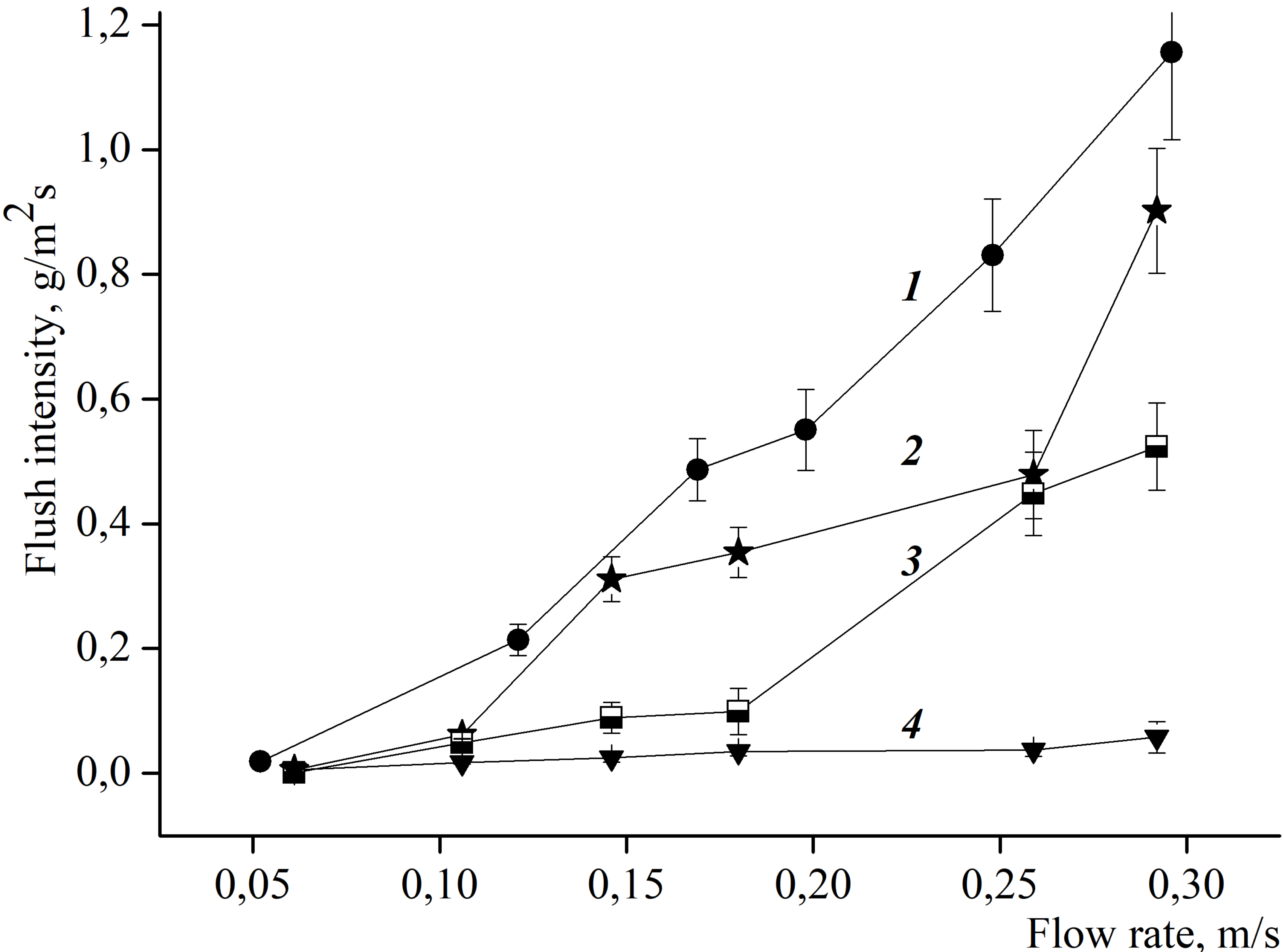
C

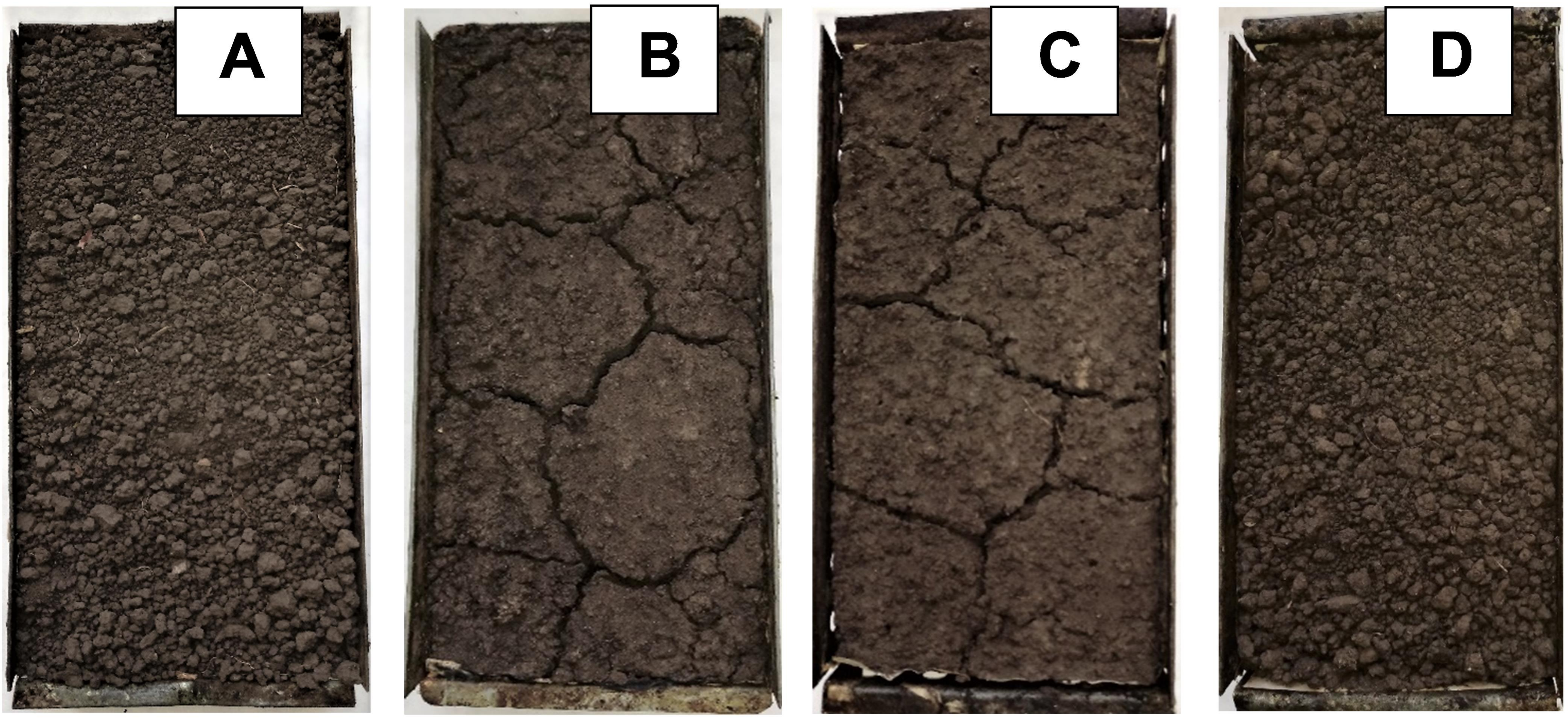


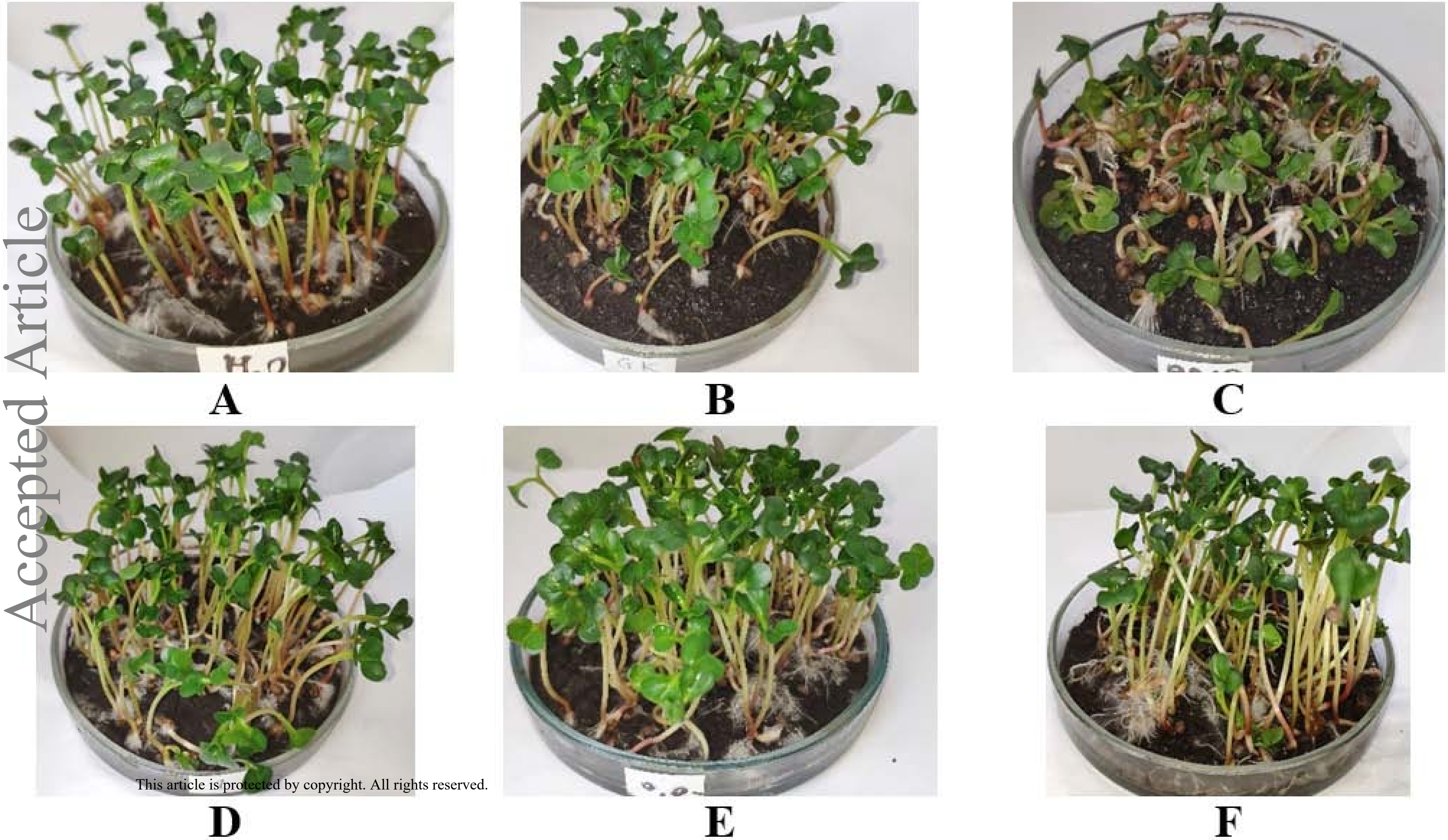
D

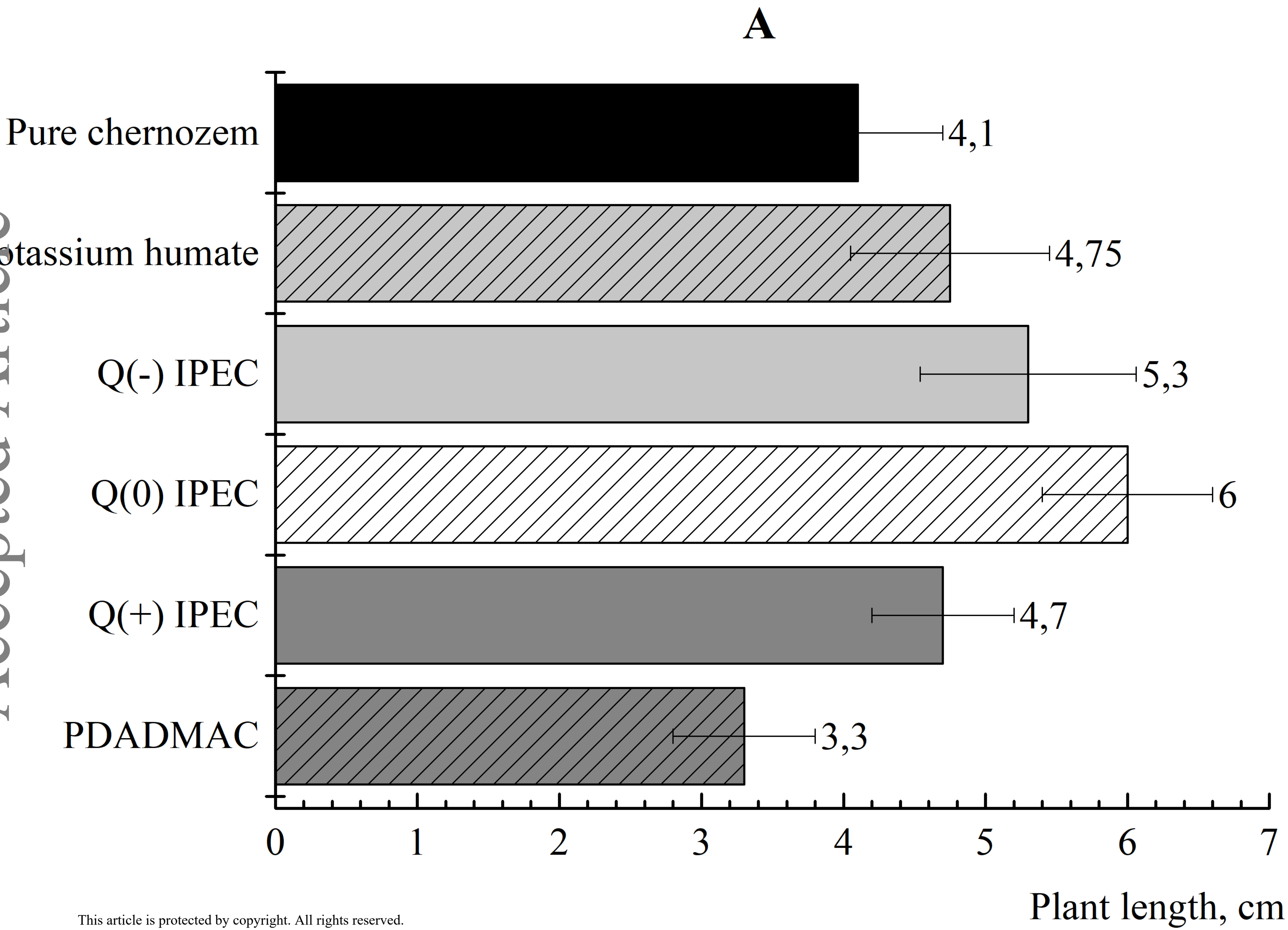


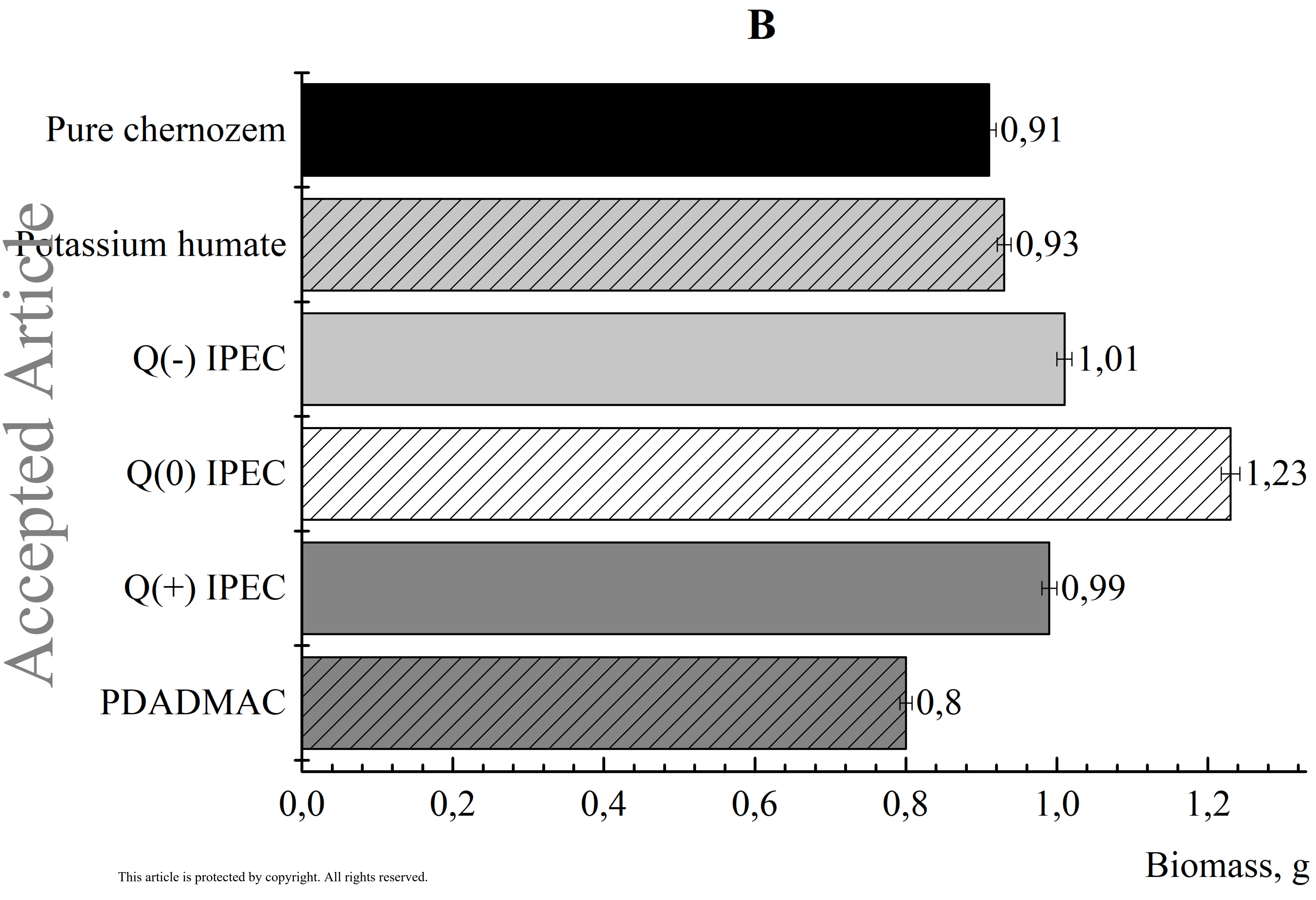
A **B**


1,2
1,0
0,8
0,6
0,4
0,2
0,0
Flush intensity, g/m2s
1
2
3
4
0,05
0,10
0,15
0,20
0,25
0,30
Flow rate, m/s


A
B
C
D


A
B
C
D
E
F


A
Pure chernozem
Potassium humate
Q(-) IPEC
Q(0) IPEC
Q(+) IPEC
PDADMAC
4,1
4,75
5,3
6
4,7
3,3
0
1
2
3
4
5
6
7
Plant length, cm


B
Pure chernozem
Potassium humate
Q(-) IPEC
Q(0) IPEC
Q(+) IPEC
PDADMAC
0,91
0,93
1,01
1,23
0,99
0,8
0,0
0,2
0,4
0,6
0,8
1,0
1,2
Biomass, g