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EFFECT OF ROAD DE-ICING SALTS WITH ANTI CORROSION AGENTS ON SELECTED PLANT SPECIES

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Abstract. The effect of $CaCl_2$ and NaCl with anti-corrosion additives (ammonium phosphate and sodium hypochlorite in amount of 3 to 5% of preparation weight), protected by Polish patent no. 198058, applied in concentrations of 4, 8 and 12 g dm^{-3} on germination and seedling vigour of *Lolium perenne* L. cv. Solen and *Festuca rubra* L. cv. Nimba was evaluated. Other studied parameters were: chlorophyll content, chlophyll *a* fluorescence and biomass accumulation in *Canna* × *generalis*, *Rosa rugosa* L. and *Lolium perenne* L. under the influence of the above mentioned substances. It was found that application of de-icing substances delayed and reduced germination of grass seedlings and declined root growth. Red fescue was less tolerant for increased salinity in soil than perennial ryegrass. Application of de-icing substances on rugosa rose, canna lilly and perennial ryegrass plants led to decrease of chlorophyll content, potential photochemical efficiency, performance index and biomass accumulation. Without anticorrosion agents the least toxic was calcium chloride and the most sodium chloride. Additives to de-icing road salts, in general, decreased NaCl toxicity and increased toxicity of $CaCl_2$.

Key words: NaCl, $CaCl_2$, anticorrosion agents, germination, biomass accumulation, chlorophyll *a* fluorescence

INTRODUCTION

Cultivation of plants in urban areas needs overcoming several problems resulting mainly from anthropopressure (acid rains, accumulation of heavy metals in soil, particulate matter pollution and soil degradation) [Zimny 2004, Gawroński and Gawrońska 2007]. In climatic conditions of the northern hemisphere another problem is increased salinity of roadside soils as an effect of using salts for road de-icing [Wrochna 2007]. Soil salinity decreases seed germination and even more significantly influences development of young seedlings [Zapata et al. 2003]. It causes a number of adverse changes in physiological and biochemical processes in plants what often lead to lower biomass

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accumulation [Morant-Manceau et. al. 2004, Kacperska 2005]. Increased salinity causes the increase of: (i) chlorophyll *a* fluorescence [Maxwell and Johnson 2000, Wrochna et. al. 2007], (ii) accumulation of osmotically active substances [Chen and Murata 2002, Wrochna 2007], (iii) concentration of reactive oxygen species [Bartosz 1995, Foyer and Noctor 2000] followed by or in parallel with changes in (iv) anti-oxidative system which activity is usually higher [Munns 2002, Parida and Das 2005, Wrochna 2007]. NaCl influences adversely also soil increasing its pH and leading to soil colloid peptization at Na^+ saturation above 15% [Zimny 2004]. These unfavourable changes eliminate a number of plant species vulnerable for soil salinity and drought from cultivation in urban areas. Therefore, there is a need to find more tolerant species or less harmful substances for maintaining transportation flow in winter months.

De-icing of roads and other transportation routes is regulated by the Ministry of Environment Act from October 27, 2005 "Regulating types and conditions of use of substances on public routes, streets and squares". This Act allows usage of the following substances to eliminate glazed frost, ice and post-snow slipperiness: non-chemical substances (sand, natural or artificial aggregates), chemical substances (for example: sodium chloride, magnesium chloride, calcium chloride) in solid or moistened form and mixture of both. However, due to costs and handling possibility the most frequently used are NaCl and sand [Bieńka et al. 2006]. The massive spreading of salt on roads and highways has many negative effects. Besides environmental concerns, one of the major criticisms of salt use for deicing is its contribution to corrosion of metal in steel bridges, road vehicles and any other metallic objects in close proximity to roads and highways [Hara et al. 2005].

The aim of this work was to compare the effect of calcium chloride and sodium chloride with or without additives reducing vehicle corrosion and modifying pH (products patented with Polish patent no. 198058).

MATERIAL AND METHODS

Research consisted of two biotest experiments conducted in laboratory and the third experiment conducted in pots under controlled conditions in a greenhouse of the Faculty of Horticulture and Landscape Architecture, WULS-SGGW.

Plant material:

– Seeds and seedlings of perennial ryegrass (*Lolium perenne* L.) cv. Solen and red fescue (*Festuca rubra* L.) cv. Nimba at heterotrophy growth stage,

– Eight week-old plants of perennial ryegrass (*Lolium perenne* L.) cv. Solen, were planted to pots (volume 1 dm^3) filled with horticultural substrate (Universal Kronenerde),

– Eight week-old plants of canna lily (*Canna × generalis*) cv. Herkules were planted to pots (volume 3 dm^3) filled with substrate based on peat moss,

– One year-old plants of rugosa rose (*Rosa rugosa* L.) planted to pots (volume 3 dm^3) filled with substrate based on peat and lessive soil.

Dynamics and germination capacity. Dynamics and capacity of germination of both grass species in the presence of sodium chloride and calcium chloride, both with and without additives (ammonium phosphate and sodium hypochlorite in amount of 3 to

5% of preparation weight), protected by Polish patent no. 198058, were tested in Petri dish biotests. In each Petri dish (Ø 10 cm) lined with double layer of filter paper 50 seeds were placed, poured over with 5 cm^3 of distilled water (control) or tested substances in concentrations of 4, 8, 12 $g \cdot dm^{-3}$, and then incubated for 14 days in temperature 25°C ± 0.5°C in a thermostat chamber with water jacket (TK – 3, Cabrolab, Poland). Germinating seeds were counted and removed every day. Based on obtained results, dynamics of germination using Pipper Index [Pipper 1952] and capacity of germination expressed as percent of germinating seeds were calculated. Pipper Index stands for average number of days needed for one seed to germinate and was calculating according to formula:

$$\text{Pipper Index} = (x_1s_1 + x_2s_2 + \ldots + x_ns_n) / (s_1 + s_2 + \ldots + s_n)$$

where: x – consecutive days of seeds germination, s – number of seeds germinated on a specific day, n – last day of the experiment.

Vigour of seedlings exposed to the tested substances was examined with a stripe biotest. Twenty seeds of each grass species were placed between two stripes of filter paper, which was then rolled and placed in tall beakers (100 ml) and poured over with 10 cm^3 of distilled water (control) or examined substances in concentrations 4, 8, 12 $g \cdot dm^{-3}$. After seven days of incubation in a thermostat root as above and coleoptiles length were measured.

In both biotest number of replications Petri dish biotest and strips per combination was 10 and 4 reflectively with 50 seeds and 20 seedlings in each.

Methodology of the pot experiment. Plants of the examined species were treated with calcium chloride and sodium chloride with or without additives as above in concentrations of 5 $g \cdot dm^{-3}$ for *Rosa rugosa* L., 10 $g \cdot dm^{-3}$ for *Lolium perenne* L. and 15 $g \cdot dm^{-3}$ for *Canna × generalis*. Concentrations of used salts for the studied species were selected on the basis of the results of earlier experiments with sodium chloride conducted in our Laboratory. Experiments were carried out in 5 replications, where replication was single pot with one plant of canna lilly and rugosa rose or 5 plants in case of perenial raygrass.

After treatment, plants were grown for three weeks, during which the following observations and measurements (at weekly intervals) were conducted:

– phenotype observations of plants for the whole duration of the experiment,

– total chlorophyll content (Chlorophyll Content Meter, CCM-200, Opti-Science, USA),

– chlorophyll *a* fluorescence (Handy PEA, Hansatec, UK).

On 22nd day after treatment plants were harvested and fresh weight of the above-ground part was determined.

Results obtained from the experiments were analyzed statistically using the two- and three-factorial analysis of variance (ANOVA) of the Statgraphics 4.1 Plus software. Significance of differences between the combinations was examined with *t*-Student test at $\alpha = 0.05$. Results show the mean values ± SE, n = 4 to 10 (depending on experiment and measured parameter).

RESULTS

Evaluation of the influence of the tested substances on grasses at the germination stage showed that seeds of perennial ryegrass and red fescue germinated best in the presence of distilled water (control) (fig. 1). Usage of the tested substances resulted in decreased germination ability. For perennial ryegrass germination decreased the least in seeds treated with 4 g $CaCl_2 \cdot dm^{-3}$ with additives (96% of control) and the most in seeds treated with 12 g $NaCl \cdot dm^{-3}$ and 12 $NaCl \cdot dm^{-3}$ with additives (89% of control) (fig. 1).

Germination capacity of red fescue was evidently lower than of perennial ryegrass. After application of tested substances decrease of capacity of germination of this species was much stronger with exception of seeds exposed to 4 g $CaCl_2$ with additives $\cdot dm^{-3}$ at which seeds germinated slightly better than in control conditions but not significantly. The lowest germination capacity was noted for seeds treated with 12 g $NaCl \cdot dm^{-3}$ (47% of control) (fig. 1).

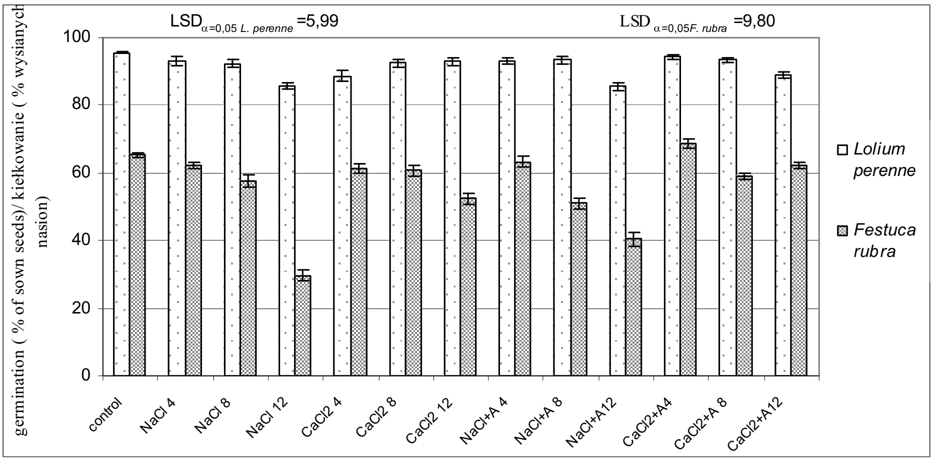

Fig. 1. Germination capacity of perennial ryegrass (*Lolium perenne* L.) cv. Solen and red fescue (*Festuca rubra* L.) cv. Nimba treated with road de-icing substances (4, 8, 12; concentrations of salt in $g \cdot dm^{-3}$, A; additives). Data are mean ± SE, n = 10, with 50 seeds in each

Ryc. 1. Zdolność kiełkowania rajgrasu angielskiego (*Lolium perenne* L.) odm. Solen oraz kostrzewy czerwonej (*Festuca rubra* L.) odm. Nimba traktowanych preparatami do odladzania ulic (4, 8, 12; stężenie soli w $g \cdot dm^{-3}$, A; dodatki). Dane przedstawiają średnie ± SE, n = 10, po 50 nasion w powtórzeniu

Application of de-icing substances delay germination (fig. 2). For perennial ryegrass length of this period increased with increasing salt concentration. Only for concentration 4 g $CaCl_2$ with additives $\cdot dm^{-3}$ this period was shorter than in control. The longest time needed for germination was observed in case of seeds treated with 12 g $NaCl \cdot dm^{-3}$ with additives (fig. 2). For red fescue significantly shorter than in control was the germination time of seeds exposed to the lower concentrations of $CaCl_2$ with additives (4 and

8 g·dm^{-3}) and slightly shorter for seeds exposed to 4 g NaCl with additives ·dm^{-3} and 8 g $CaCl_2$·dm^{-3} (fig. 2). In case of other combinations delay germination period was observed, the longest (by 2.5 days) for seeds exposed to 12 g NaCl·dm^{-3} (fig. 2).

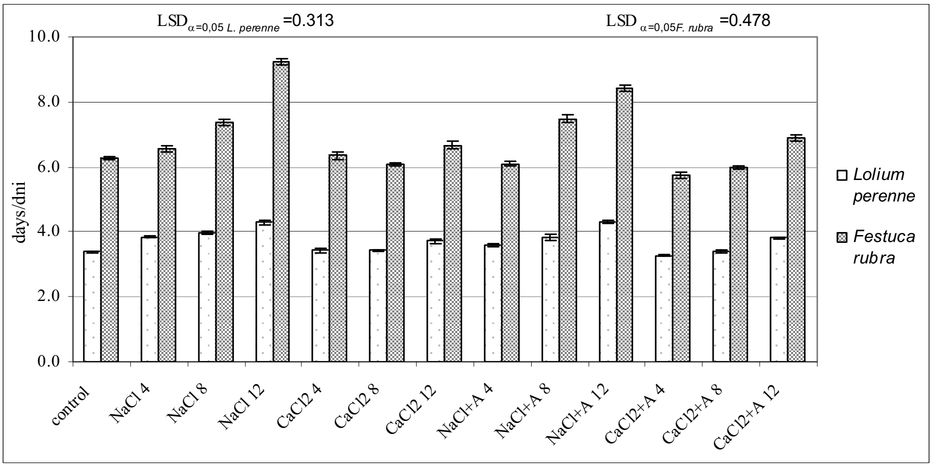

Fig. 2. Pipper Index of perennial ryegrass (*Lolium perenne* L.) cv. Solen and red fescue (*Festuca rubra* L.) cv. Nimba treated with road de-icing substances (4, 8, 12; concentrations of salt in g·dm^{-3}, A; additives). Data are mean ± SE, n = 10, with 50 seeds in each

Ryc. 2. Indeks Pippera dla rajgrasu angielskiego (*Lolium perenne* L.) odm. Solen oraz kostrzewy czerwonej (*Festuca rubra* L.) odm. Nimba traktowanych preparatami do odladzania ulic (4, 8, 12; stężenie soli w g·dm^{-3}, A; dodatki). Dane przedstawiają średnie ± SE, n = 10, z 50 nasionami w każdym

Evaluation of the influence of the tested substances on vigour of perennial ryegrass and red fescue seedlings demonstrated specific species reaction (fig. 3), red fescue seedlings were smaller and had shorter roots and coleoptiles. Seedlings of both species had the longest roots in control and shortest after exposure to 12 g NaCl with additives ·dm^{-3}. Roots growth was limited to the lowest level by calcium chloride in concentration 8 g·dm^{-3} (fig. 3).

The tested substances limited coleoptile growth in red fescue seedlings the least (by 7%) when treated with 8 g $CaCl_2$·dm^{-3} and the most (by 80%) in seedlings treated with 8 g NaCl·dm^{-3} (fig. 4). Perennial ryegrass seedlings had shorter coleoptiles after exposure to NaCl in all concentrations and without anti corrosion agents, similarly as to 8 g $CaCl_2$ with additives ·dm^{-3} and 12 g NaCl with additives ·dm^{-3}. In other combinations coleoptiles were longer than in control; the longest in seedlings exposed to 4 g NaCl with additives ·dm^{-3} (144% of control); (fig. 4).

In the second part of the study the influence of tested substances on: chlorophyll content, fluorescence of chlorophyll *a* and biomass accumulation of *Canna* × *generalis*, *Rosa rugosa* L. and *Lolium perenne* L. plants was examined.

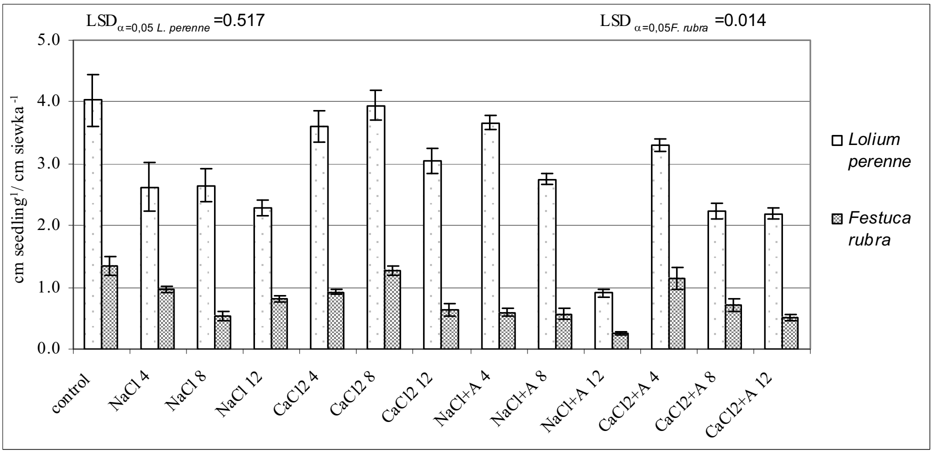

Fig. 3. Root length of seedlings of perennial ryegrass (*Lolium perenne* L.) cv. Solen and red fescue (*Festuca rubra* L.) cv. Nimba treated with road de-icing substances (4, 8, 12; concentrations of salt in g·dm^{-3}, A; additives). Data are mean ± SE, n = 4, with 20 seedlings in each

Ryc. 3. Długość korzenia siewek rajgrasu angielskiego (*Lolium perenne* L.) odm. Solen oraz kostrzewy czerwonej (*Festuca rubra* L.) odm. Nimba traktowanych preparatami do odladzania ulic (4, 8, 12; stężenie soli w g·dm^{-3}, A; dodatki). Dane przedstawiają średnie ± SE, n = 4, z 20 siewkami w każdym

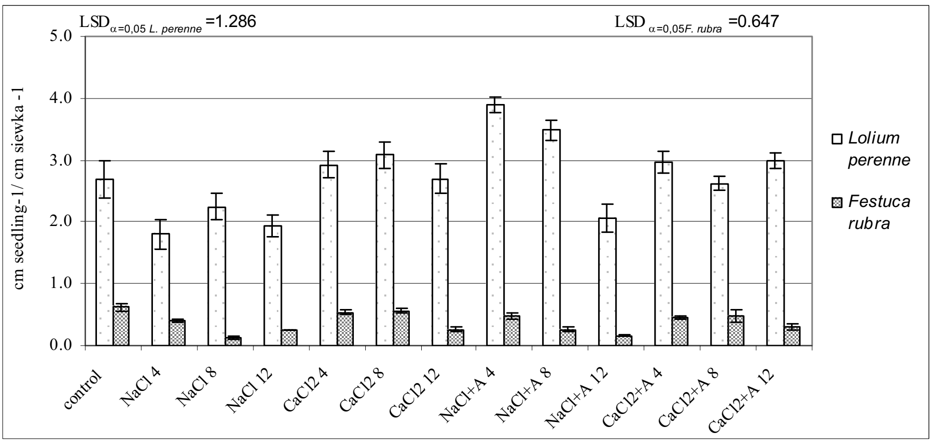

Fig. 4. Coleoptile length of seedlings of perennial ryegrass (*Lolium perenne* L.) cv. Solen and red fescue (*Festuca rubra* L.) cv. Nimba treated with road de-icing substances (4, 8, 12; concentrations of salt in g·dm^{-3}, A; additives). Data are mean ± SE, n = 4, with 20 seedlings in each

Ryc. 4. Długość coleoptyla siewek rajgrasu angielskiego (*Lolium perenne* L.) odm. Solen oraz kostrzewy czerwonej (*Festuca rubra* L.) odm. Nimba traktowanych preparatami do odladzania ulic (4, 8, 12; stężenie soli w g·dm^{-3}, A; dodatki). Dane przedstawiają średnie ± SE, n = 4, z 20 siewkami w każdym

It was found that three weeks exposure of plants to road de-icing substances resulted in lower fresh mass accumulation (fig. 5). Only for canna lily growing at presence of $CaCl_2$ and rugosa rose treated with $CaCl_2$ with additives slight increase of biomass accumulation versus control was noted. Significantly less biomass was produced by plants exposed to sodium chloride alone (19%, 69% and 75% of control for perennial ryegrass, canna lily and rugosa rose respectively). For plants exposed to $CaCl_2$ reduction in biomass accumulation was smaller and damages due to salinity were less visible. Out of the three tested species negative impact of salinity most noticeable was in perennial ryegrass (fig. 5).

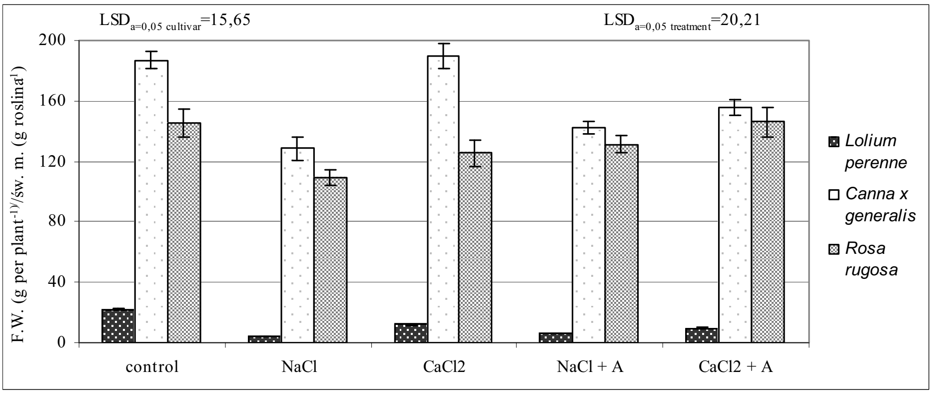

Fig. 5. Fresh biomass of above ground part of *Canna* × *generalis*, *Rosa rugosa* L., *Lolium perenne* L. plants treated with road de-icing substances of 15, 5 and 10 g·dm^{-3} respectively, A: additives. Data are mean ± SE, n = 5

Ryc. 5. Świeża masa części nadziemnych roślin: *Canna* × *generalis*, *Rosa rugosa* L., *Lolium perenne* L. traktowanych preparatami do odladzania ulic w ilości odpowiednio 15, 5 lub 10 g·dm^{-3}, A: dodatki. Dane przedstawiają średnie ± SE, n = 5

Chlorophyll content in leaves of plants treated with tested substances, with few exceptions, was lowered but the response was species-specific and dependent on the time of treatment (fig. 6). Chlorophyll content decreased the most in perennial ryegrass plants and the least in canna lily. In comparison with control for all three species the greatest decrease of chlorophyll content, both for measurements taken 7 and 14 days after treatment, was noted in plants treated with NaCl with additives. Chlorophyll content 21 days after the treatments increased (fig. 6).

The road de-icing substances applied modified the parameters of chlorophyll *a* fluorescence (fig. 7). Potential of photochemical efficiency of photosystem II (Fv/Fm), was the highest in control. In general, each of used substances lowered the Fv/Fm parameter, the least for plants exposed to $CaCl_2$ and significantly the more, for all plants exposed to NaCl. However, for canna lily and rugosa rose plants slight increase of Fv/Fm was noted in the longer time after treatment, while for perennial ryegrass there was a significant decrease of this parameter, especially for plants exposed to NaCl, both alone and with additives (fig. 7).

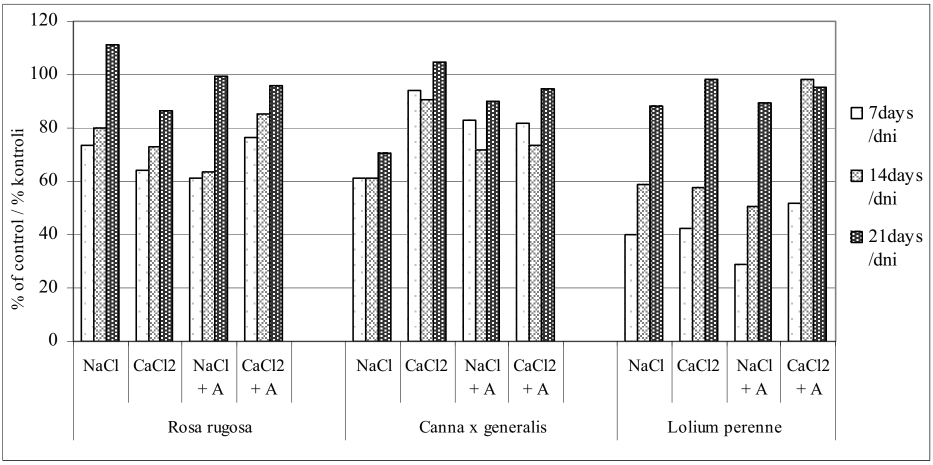

Fig. 6. Chlorophyll content in leaves of *Canna* × *generalis*, *Rosa rugosa* L., *Lolium perenne* L. plants treated with road de-icing substances of 15, 5 and 10 g·dm^{-3} respectively, A: additives

Ryc. 6. Zawartość chlorofilu w liściach roślin: *Canna* × *generalis*, *Rosa rugosa* L., *Lolium perenne* L. traktowanych preparatami do odladzania ulic w ilości odpowiednio 15, 5 lub 10 g·dm^{-3}, A: dodatki

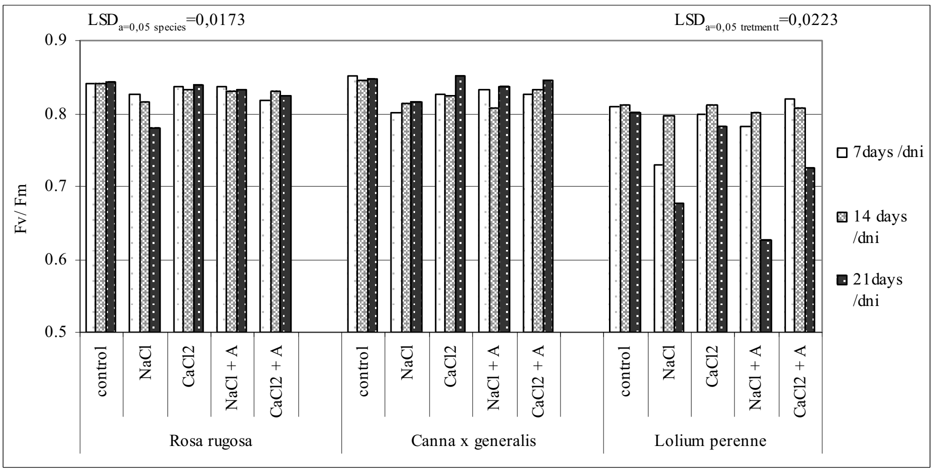

Fig. 7. Maximal photochemical efficiency of photosystem II in leaves of *Canna* × *generalis*, *Rosa rugosa* L., *Lolium perenne* L. treated with road de-icing substances of 15, 5 and 10 g·dm^{-3} respectively, A: additives

Ryc. 7. Maksymalna wydajność fotochemiczna fotosystemu II liści roślin *Canna* × *generalis*, *Rosa rugosa* L., *Lolium perenne* L. traktowanych preparatami do odladzania ulic w ilości odpowiednio 15, 5 lub10 g·dm^{-3}, A: dodatki

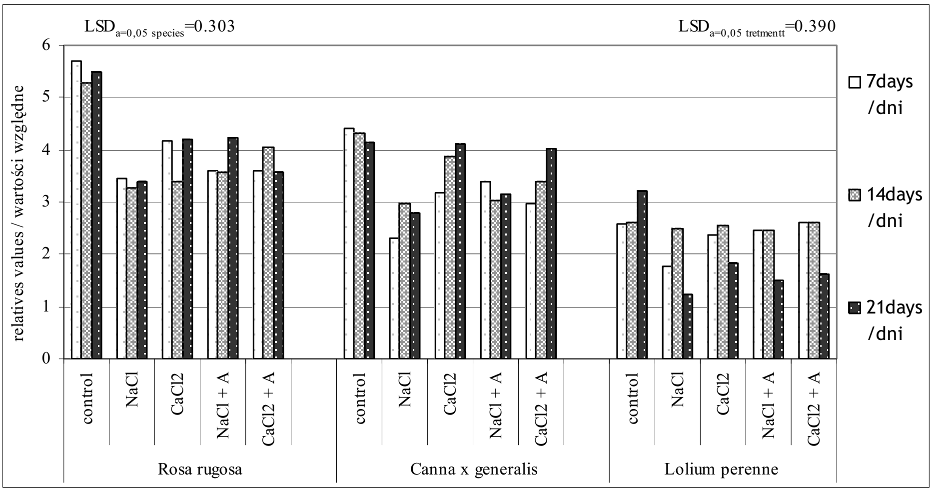

Fig. 8. Performance Index for *Canna × generalis*, *Rosa rugosa* L., *Lolium perenne* L. treated with road de-icing substances of 15, 5 and 10 g·dm^{-3} respectively, A: additives

Ryc. 8. Wskaźnik funkcjonowania PS II roślin *Canna × generalis*, *Rosa rugosa* L., *Lolium perenne* L. traktowanych preparatami do odladzania ulic w ilości odpowiednio 15, 5 lub 10 g·dm^{-3}, A: dodatki

Similar pattern of changes like in Fv/Fm was observed for performance index (P.I.) (fig. 8). P.I. was the highest in control and decreased substantially for plants growing in the presence of road de-icing substances, the most for those exposed to NaCl, and least insignificantly for those exposed to $CaCl_2$. P. I. was increased in rugosa rose plants even after 21 days after treatment, while for perennial ryegrass it was decreased (fig. 8).

DISCUSSION

The road de-icing substances which were the subject of this study were found to be influencing adversely on the treated plants, but this effect varied depending on the examined substance, plant species and time of treatment. From the analysed substances the most toxic for plants proved to be NaCl, which confirms the results known from literature [Tester and Davenport 2004, Zapata et al. 2004, Parida and Das 2005] and from author's earlier studies [Wrochna et al. 2006, 2007]. This substance, especially in higher concentrations, decreased germination capacity, delayed germination, reduced early seedling growth of the analysed grasses, lowered both chlorophyll content and values of examined parameters of fluorescence of chlorophyll *a* and decreased biomass accumulation in all three tested species. The most vulnerable was perennial ryegrass, the least canna lily.

The smallest negative effect of salinity was observed in plants exposed to $CaCl_2$ alone. Reason for this is presence of calcium, which not only is a macroelement necessary for plant growth and development. When salinity stress occurs this element is proved to be involved in commencing protective mechanisms and acts as secondary messenger in signal transduction pathway, which is often described in literature [Bressan and Hasegawa 1998, White and Broadley 2003]. The negative effects of road de-icing agents on plants, recorded in this study, were, at least partially, due to lower water availability to plants as it is bound by ions contained in tested substances after they became a component of soil solution following application [Taiz and Zeiger 2002]. These ions might generate so-called physiological drought in soil [Bandurska 2007]. Besides, higher concentration of Na^+, Cl^- and Ca^{+2} ions in soil often results in their increase in plant tissues [Wrochna et al. 2006, 2008] what in consequence led to ion imbalance in plant tissues as well as to toxic effects of Na^+ and Cl^- if the concentration is to high [Taiz and Zeiger 2002].

From technical point of view, the influence of both NaCl and $CaCl_2$ on corrosives of vehicles, metal constructions and durability of concrete elements is similar, with slight prevalence of $CaCl_2$. However, calcium chloride is very hygroscopic, which makes its storage and use difficult [Bieńka et al. 2006] and, besides that, it may cause alkalization of roadside soils. Results obtained by the authors suggest that the negative impact of NaCl on plants could be reduced by using substances enriched with anticorrosive and pH-reducing additives. According to the patent owners, these substances supposed to provide effective de-icing simultaneously with protecting soil and traffic participants from the consequences of using salt at the same time [Amanowicz – personal communication]. Examination showed less harmful effect of the patented substances on plants, which germinated better and in shorter time, accumulated more biomass, and whose parameters of fluorescence of chlorophyll *a* were generally better than of plants treated with NaCl, however a bit poorer than of those treated with $CaCl_2$.

CONCLUSIONS

1. Calcium chloride and sodium chloride with and without additives (Polish patent no. 198058) delay and reduced germination of perennial ryegrass and red fescue seeds.
2. Growth and development of seedlings was limited by the tested substances to a different degree, the least by calcium chloride, the most by sodium chloride.
3. Fresh weight of rugosa rose, canna lily and perennial ryegrass plants was lowered by tested substances.
4. Performance Index decline significantly in plants exposed to the road de-icing substances.
5. From the analysed road de-icing substances the less harmful for plants was calcium chloride, and the more – sodium chloride.
6. Additives to de-icing road salts, in general decreased toxicity of NaCl, but slightly increased toxicity of $CaCl_2$.

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REAKCJA WYBRANYCH GATUNKÓW ROŚLIN NA ŚRODKI DO ODLADZANIA JEZDNI Z DODATKIEM SUBSTANCJI ANTYKOROZYJNYCH I REGULUJĄCYCH pH

Streszczenie. Celem pracy była ocena wpływu substancji do odladzania jezdni: $CaCl_2$ oraz NaCl w stężeniu 4, 8, 12 $g \cdot dm^{-3}$ z dodatkami antykorozyjnymi (fosforan amonu oraz podchloryn sodu stanowiące 3 do 5 % masy preparatu), objęte polskim patentem Nr 198058, na: dynamikę i zdolność kiełkowania oraz wigor siewek *Lolium perenne* L. odm. Solen i *Festuca rubra* L. odm. Nimba, a także na zawartość chlorofilu, fluorescencję chlorofilu *a* oraz akumulację biomasy u roślin *Canna × generalis*, *Rosa rugosa* L. i *Lolium perenne* L. Badania wykazały, że zastosowanie wymienionych substancji opóźniało kiełkowanie oraz obniżało zdolność kiełkowania u obu gatunków traw, a także redukowało wzrost korzeni siewek. *F. rubra* okazała się bardziej wrażliwą na zasolenie podłoża aniżeli *L. perenne*. Zastosowanie obu związków obniżało zawartość chlorofilu, maksymalną wydajność fotosystemu II oraz wskaźnik witalności, a także akumulację biomasy u roślin każdego z badanych gatunków. Chlorek sodu był bardziej toksyczny aniżeli chlorek wapnia, gdy związki te stosowano bez dodatków antykorozyjnych i regulujących pH, natomiast, gdy stosowano je łącznie z tymi dodatkami, odnotowano zmniejszenie negatywnego wpływu NaCl, a zwiększenie toksyczności $CaCl_2$.

Słowa kluczowe: NaCl, $CaCl_2$, dodatki antykorozyjne, kiełkowanie, akumulacja biomasy, fluorescencja chlorofilu *a*

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