Assessment of the environmental impact of anti-icing materials on plant bioindicators

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Abstract. The article examines the physicochemical effect of anti-icing materials, such as sodium and calcium chlorides, XNKM (Russia) and created on the basis of mineral raw materials of the Astrakhan region (AR), on the state of plant bioindicators. The effect of salts contained in various brands of anti-icing materials on the quantitative content of photosynthetic pigments in test objects - tomato and sunflower - was studied. The choice of test objects is determined by the geographic location of the Astrakhan region and natural and climatic factors. The elemental composition of mineral raw materials was studied by X-ray spectral-fluorescent elemental analysis. Analysis of the elemental composition of AR opoka and AR marl makes it possible to exclude the fact that the main content is made up of oxides of aluminum, silicon and calcium, which makes it possible to predict the effective use of the opoka and marl as components of antidepressants. - ironing materials. The studies carried out and the analysis of the results obtained indicate that when using sodium salts and XNKM, there is a sharp decrease in the content of photosynthetic pigments. It was found that when introducing natural mineral raw materials from the Astrakhan region as an anti-icing material: sand, opoka AR and marl AR, the negative impact on the content of photosynthetic pigments is minimal. During the study, it was shown that the content of calcium ions in the biomass of leaves also varies widely; when calcium salts are added, it naturally increases due to the cumulative effect, but since the mineral raw materials of opoka and marl can exhibit adsorptive activity towards cations, the content of calcium ions decreases. Extensive research shows that the most commonly used anti-icing agents reduce the amount of photosynthetic pigments and calcium in plants.

1. Introduction

Anthropogenic impact leads to disruption of the soil and vegetation cover, soil erosion (erosion), desertification (formation of sand dunes) and, as a consequence, to a decrease in the land fund and its simplification, as well as a decrease in the amount of the ecosystem.

The problem of the influence of deicing reagents on the environment is relevant and relevant in various fields of science [1-2]. In terms of physicochemical properties and anthropogenic indicators, synthetic materials based on sodium, potassium, calcium and magnesium chlorides are most suitable for the fight against winter slipperiness [3], but natural materials are used as an alternative. The advantage of using natural materials is high selectivity, chemical, thermal and mechanical stability, environmental friendliness and economy. Most of the substances that make up the anti-icing materials
negatively affect the vegetation along the cultivated roads [4], since the anti-icing materials spread in winter enter the soil with melt water and further affect the growth and development of plants [5].

The effect of anti-icing materials on plants due to the content of large amounts of salts has a complex negative character. The negative effect of salts on plants is a manifestation of osmotic and toxic effects [6-7]. A change in water-salt metabolism in plant cells leads to an increase in osmotic pressure and a decrease in water absorption. Salinization of soils makes it difficult for water to enter plants, which leads to increased toxicity due to excessive accumulation of ions in the cytoplasm of cells. Visual manifestation of toxicity can be observed by the formation of necrosis on the leaves and stems. A characteristic feature of the effect of anti-icing agents on plants is a change in the content of photosynthetic pigments in their green part [8]. Among them, the most characteristic are the content of chlorophylls Chla, Chlb and β-carotene (β-k).

2. Materials and methods
The influence of widely used materials on the content of Chla, Chlb and β-k was investigated. For the study, anti-icing materials widely used in Russia were selected: sodium chloride, calcium chloride, XNKM (trade mark, Russia, the name of sodium modified magnesium chloride) and created on the basis of mineral raw materials from Astrakhan region (AR): opoka and marl.

In terms of salt composition, formwork AR (marl-opal of the Kamenoyarsk deposit, Chernoyarsk region) and mineral marl AR (Baskunchakskoye deposit) are promising for use as anti-icing agents. Elemental composition (%) obtained by X-ray spectral fluorescence elemental analysis on a Thermo ARL Perform’x Sequential XFR instrument with a 2500 W X-ray tube is shown in Table 1.

| Elemental composition (%) | Marl AR | Opoka AR |
|--------------------------|---------|----------|
| SiO$_2$                  | 52      | 93.2     |
| Al,O$_3$                 | 3.9     | 3.6      |
| MgO                      | 2.7     | 1.4      |
| CaO                      | 39.0    | <1       |
| In total Fe$_2$O$_3$, K$_2$O, Na$_2$O, P$_2$O$_5$,SO$_3$, Cl | < 1     | < 1      |

For this, in the Astrakhan region in early spring, samples of tomato and sunflower leaves were taken. Samples for analyzes were taken from areas treated with the investigated anti-icing materials. Anti-icing materials were used in an amount corresponding to the requirement of 1 g / m$^2$. Plants growing in untreated area were used as controls.

The content of photosynthetic pigments in plant leaves was determined photometrically. Samples of plant leaves with washed river sand in a ratio of 1:1 were ground in a porcelain mortar, 5 cm$^3$ of hexane (reagent grade) was poured into the resulting mixture, while β-carotene passed into the organic part. The obtained extract was introduced into a measuring tube with the same solvent, 10 cm$^3$ in volume. The mixture was centrifuged for 10 min at 3000 rpm, then the optical density of the extract was measured at a wavelength of 450 nm in a 1 cm cuvette relative to the solvent used. The supernatant was decanted, and a mixture of solvents hexane (reagent grade) and ethanol (reagent grade) in a ratio from 1:1 to 10 cm$^3$ was added to the precipitate with stirring, the mixture was thoroughly stirred while chlorophylls passed into the organic layer. After 10 min, centrifugation was repeated, then the centrifugate was diluted 10 times with a mixture of solvents of hexane and ethanol in a 1:1 ratio, and the optical density of the solutions was again measured at wavelengths of 645 and 663 nm in a 1 cm cuvette relative to the solvent mixture. The concentrations of Chla, Chlb and β-k were determined according to formulas 1-3 [9-10]:

$$Chl_a = 12.7 \cdot A_{663} - 2.69 \cdot A_{645} \text{ (mg/100 g)}$$ (1)
\[ Chl_b = 22.9 \cdot A_{645} - 4.68 \cdot A_{663} \text{ (mg/100 g)} \]  
\[ m_{\beta-k} = 2.6 \cdot 10^3 \cdot A_{450} \text{ (mg/100 g)} \]

The β-k concentration was determined taking into account the fact that at the maximum of the absorption band (450 nm), the molar absorption coefficient of light of its solution in hexane is 2592.

The content of calcium ions in plant leaves was determined after ashing by direct ionometry.

3. Results

The influence of the components of the anti-icing material on the content of photosynthetic pigments (mg per 100 g of wet weight of leaves) and calcium ions in tomato leaves is shown in the table 2 and in sunflower leaves are given in table 3.

| Indicator | Control | Opoka AR | Mergel AR | Sodium chloride | Calcium chloride | XNKM | Sand |
|-----------|---------|----------|-----------|-----------------|------------------|------|------|
| Chl_a     | 7.56±0.62 | 7.7±0.45 | 6.34±0.45 | 5.03±0.14       | 4.83±0.08        | 4.34±0.08 | 7.43±0.31 |
| Chl_b     | 5.67±0.40 | 6.5±0.09 | 4.76±0.12 | 2.68±0.05       | 2.58±0.11        | 3.16±0.19 | 4.98±0.31 |
| β-k       | 49.8±0.8  | 45.0±1.2 | 48.4±0.7  | 36.8±1          | 36.9±0.5         | 38.4±1.8 | 52.8±1.6 |
| Ionic Ca^{2+} content, g/100g | 0.31±0.01 | 0.18±0.02 | 0.25±0.01 | 0.11±0.01       | 0.11±0.01        | 0.35±0.01 | 0.29±0.01 |

| Indicator | Control | Opoka AR | Mergel AR | Sodium chloride | Calcium chloride | XNKM | Sand |
|-----------|---------|----------|-----------|-----------------|------------------|------|------|
| Chl_a     | 17.6±0.62 | 17.7±0.45 | 17.1±0.82 | 16.8±0.53       | 14.6±0.62        | 15.5±0.75 | 18.3±0.48 |
| Chl_b     | 6.52±0.40 | 6.11±0.50 | 5.94±0.32 | 6.79±0.48       | 5.31±0.40        | 6.52±0.09 | 5.73±0.31 |
| β-k       | 42.1±0.8  | 38.1±1.3 | 40.9±1.9  | 39.8±0.95       | 51.0±1.6         | 45.3±1.3 | 42.4±1.5 |
| Ionic Ca^{2+} content, g/100g | 0.29±0.01 | 0.25±0.02 | 0.12±0.01 | 0.14±0.01       | 0.34±0.03        | 0.35±0.03 | 0.19±0.01 |

4. Discussion

As can be seen from the results presented in tables 2 and 3, the introduction of anti-icing reagents affects the content of photosynthetic pigments in a wide range of values compared to the control. With the addition of sodium salts and XNKM in tomato leaves, a sharp decrease in the content of chlorophylls Chla and Chlb and β-carotene is observed. Natural mineral raw materials: sand, AR opoka and AR marl have a minimal negative effect on the content of photosynthetic pigments. In sunflower leaves, similar patterns are observed. The content of calcium ions in the biomass of leaves also varies widely; when calcium salts are added, it naturally increases due to the cumulative effect, but since the AR mineral of the opoka and the AR marl can exhibit adsorption activity towards cations, the calcium ion content decreases. In addition, studies are being conducted on the possibility of using this mineral raw material in the form of fertilizers [11].

The salts contained in deicing materials act as poisons for plants, negatively affecting root formation by increasing osmotic pressure. As salts accumulate in plants, their viability decreases,
which leads to weakening of plants and a decrease in their fertility. Plants are becoming more susceptible to anthropogenic factors.

5. Conclusion
It is impossible to make an unambiguous conclusion about the effect of anti-icing agents on the content of photosynthetic pigments in plant leaves. The greatest negative effect is exerted by salts containing magnesium compounds (XHKM material).

The following pattern can be traced from the results obtained: most of the widely used anti-icing materials reduce the amount of Chla, Chlb, β-k and calcium. The content of Chla and Chlb changes insignificantly (from 16 to 30%), while β-k and calcium decrease sharply (in some cases, up to 58%).

Anti-icing materials based on sodium, potassium, calcium and magnesium chlorides slightly change the content of photosynthetic pigments in plant leaves. It is impossible to unequivocally state their negative effect - the content of Chla and Chlb varies within insignificant limits.

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