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Assessing ecotoxicological effects of a multicomponent anti-icing reagent based on the liquid waste from soda ash production

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ABSTRACT

Severodonetsk-Lysychansk agglomeration (Luhansk Oblast, Ukraine) is an industrially developed region with a large amount of the accumulated industrial liquid waste, which, due to the poor condition of storage facilities, significantly affects the quality of surface and groundwater, i.e., sources of household drinking water supply. To reduce the man-made load, this waste must be processed with subsequent reclamation of storage. The liquid phase of sludge storage of soda produced by OJSC "Lysychansk Soda" is proposed for use as an anti-icing reagent. This work is devoted to assessing the environmental impact of such a multicomponent anti-icing reagent when used on the motor roads of the region. The liquid waste contains inorganic salts, mainly chlorides, sulfates, and carbonates of calcium, magnesium, sodium, and ammonium, as well as heavy metals Mn, Sn, Zn, and As in trace amounts. The environmental impact of such a liquid depends mainly on the local landscape features (type of soil, vegetation cover) and meteorological conditions (quantity of seasonal precipitation, the required application rate of reagents). We conducted an analysis of the dilution of the anti-icing reagent by winter precipitation and determined the expected concentrations of chloride ions as the main factor of danger on the roadside and in groundwater of sandy soil of the region with the recommended application rate in the studied region. To assess the biological toxicity of the multicomponent mixture, test systems widely used for rapid screening were chosen. During short-term testing of *Daphnia magna S.*, the semi-lethal and the lowest ineffective dilution factors of the liquid were determined, and the phytotoxicity of the liquid was assessed as the dilution factor resulting in a 10% inhibition of the growth of the root system of *Allium cepa L.* We found that the dilution factor of distillery wastewater for safe use should be within 260 ÷ 130, and the maximum permissible application rate of the reagent is from 5 to 9 times, which is usually quite sufficient in the climatic conditions of Luhansk Oblast. Thus, the anti-icing agent can be offered for use on the motor roads of the region in compliance with the recommended application rate.

Keywords: distillery wastewater, anti-icing reagent, dilution factor, biotesting, phytotoxicity, application rate.

INTRODUCTION

Once such powerful enterprises of state importance as OJSC "Lysychansk Soda", LLC "Rubizhne Krasytel", PJSC "Severodonetsk Azot Association" that had been operating on the territory of Rubizhne-Lysychansk industrial complex for several decades, left behind sludge storage, tailings ponds, the industrial liquid waste clarifiers (in total up to 10 in the agglomeration) of different area and extremely unsatisfactory technical condition. Some are located at distances from 30 to 800 m to residential buildings. To enhance the environmental security of the region and for effective post-war recovery and reconstruction of Luhansk Oblast, taking into account the principles of circular economy and sustainable development, methods and technologies for processing large-tonnage waste from chemical and mining industries should already be proposed to obtain quality products.

Sludge storage of OJSC "Lysychansk Soda" (Fig. 1) is located in Luhansk Oblast in the east of Ukraine. The soda plant had been producing soda ash in the amount of 450,000 tons/year and other chemicals for 120 years, but it was liquidated in 2011. The main production waste pumped into the storage (about 20 million m^3) was distillery wastewater, brine sludge waste, low-mineralized wastewater, as well as excess mother liquor, which filled 4 storage reservoirs with a total area of 177.6 hectares.

Gravitational differentiation and pollution of fresh water by man-made solutions resulted in the formation of two zones within the spread in depth: a zone of partial pollution with the dry residue of 0.2–1.0 g/dm^3 to a depth of 35–40 m, and below is a zone of complete pollution with the spread of groundwater with the dry residue of up to 10–40 g/dm^3. The total depth of penetration of man-made solutions is 80–90 m. The groundwater temperature of the upper aquifer in the reservoir is 1.1–1.6 °C higher than the background values of 8–9 °C. The long-term exploitation of the fissure-karst aquifer by five water inlets located around the sludge storage has significantly changed the hydrodynamic conditions of the fissure-karst aquifer and intensified the leak of man-made solutions into the aquifer. The pollution of karst groundwater and changes in its hydrodynamic and geotemperature regime have led to a more than tenfold increase in the dissolution rate of chalk-marl rocks [Korchuganova et al., 2022].

Therefore, this facility with millions of tons of sludge and liquid is a source of air, soil, surface, and the groundwater pollution with chemicals. The environmental condition of Severodonetsk-Lysychansk agglomeration was assessed as from tense to crisis [Kravchenko, 2021], where the presence of solid industrial and household waste landfills, as well as facilities for storing various substances in a liquid state, play a crucial role.

But at the same time, taking into account the principles of the circular economy, such waste storage is a source of material resources for obtaining a range of targeted products. In addition, the development and reclamation of this sludge storage area will enhance the environmental safety of the region by improving the quality of ground and surface water of the Siverskyi Donets river basin, which is the source of the agglomeration's economic and drinking water supply. It will also contribute to the growth of technogenic safety by minimizing the risk of the storage dam collapsing and shifting millions of tons of waste into the river and ultimately will reduce the volume of extraction of new georesources for the production of marketable products. This is also included in the well-known 'secondary mining' concept to achieve a win-win situation of resource sustainability and environmental protection, as well as creating a healthy society based on waste recycling [Li, 2015].

ANALYSIS OF LITERATURE AND PROBLEM STATEMENT

Soda ash is produced by the ammonia-alkaline method with the formation of a large amount of industrial waste, namely liquid and sludge. Thus, in China, more than 10 million tons of soda residue is accumulated annually, which has such characteristics as high alkalinity and reactivity, and well-developed pore structure, which makes it a valuable raw material for the production of environmentally functional materials, but at the same time, it causes serious environmental pollution in storage areas [Zong et al., 2023].

Depending on the location of the production plant and raw material deposits, the post-distillation suspension (waste) is subjected to full dispersion by discharging into the sea or a river with a strong current and/or separated by sedimentation into sludge and liquid dispersion. Sludge is stored in clarifiers, and the liquid phase is discharged into the local watercourse with or without pH adjustment. Complete dispersion ensures the assimilation of solid material with natural deposits of a similar composition. Thus, chlorides and other

Figure 1. Photo of the alkaline lake of sludge storage No. 4

soluble salts from the liquid fraction are distributed in the sea salt water or in rivers with a high flow, which are able to ensure water quality for further use. With a careful study of environmental aspects and the correct choice of the discharging site, it is possible to guarantee that such a disposal system will have an acceptable impact, being fully assimilated by the environment [Integrated Pollution, 2007]. Thus, observations of the chloride content in Lake Traunsee (Austria), where up to 40.000 tons (equivalent to dry residue) of solids from the soda plant in the city of Ebensee were discharged annually for 120 years, show that the ability to recover from soluble chloride waste is very high even for such inland bodies of water as Lake Traunsee. A year after ceasing soda ash production in 2006, the concentration of chlorides decreased by approximately 75%, and their residual content was mostly associated with the activity of salt works in Ebenze and the drainage of mother liquor in the amount of ~70 t/day into this water [Steinhauser, 2008].

Sedimentation and storage are usually used where there are no suitable conditions for complete dispersion. Underground disposal of solids is carried out in cases where salt deposits are located near the production facilities and when the characteristics of the deposits and the salt extraction system allow it.

The proposed directions for processing soda production waste by the Solvay method are mostly focused on using sludge: producing lumpy and chemically precipitated chalk [Mikhailova et al., 2016]; binders [Kasikowski et al., 2004] and construction materials based on them [Qiang et al., 2022]; asphalt-mineral and bituminous-mineral mixtures [Congbo et al., 2021]; in environmental management for wastewater treatment, water eutrophication control, neutralization of acidic mine water, reclamation of soil and landfills, flue gas desulfurization [Zong et al., 2023; Kasikowski et al., 2007]; producing meliorants; as tamponade material [Kuznetsova et al., 2005; Shestopalov et al., 2007].

Table 1. The composition and main indicators of the liquid phase of the sludge storage of OJSC "Lysychansk Soda" (Ukraine)

Indicator	Indicator value
Appearance	Colourless transparent liquid
Density, g/cm^3	1.135 ± 0.005
Hydrogen pH indicator, units	8.85 ± 0.35
Content of mineral salts in the residue after roasting, %	23.85 ± 0.65
Content of $(Ca+Mg)Cl_2$, % wt.	13.7 ± 0.4
Content of NaCl, % wt.	6.25 ± 0.15
Content of SO_4^{2-}, % wt. (in terms of Na_2SO_4)	3.23 ± 0.02
Content of CO_3^{2-}, % wt. (in terms of Na_2CO_3)	0.595 ± 0.015
Content of NH_4^+, % wt.	0.0515 ± 0.0005

Taking into account the composition of the clarified liquid phase (Table 1), it is proposed to use it as a raw material for the production of anti-icing reagents both in the primary composition and the strengthened up to 20% wt. by $CaCl_2$ at very low temperatures [Suvorin et al., 2022].

When developing new compositions of anti-icing reagents, the effectiveness of combating ice, corrosion activity, environmental and hygienic safety are taken as the guiding indicators. A new anti-icing material will be profitable from an economic point of view if it is able to prevent corrosion of motor vehicles [Kravchenko, 2023], reduce damage to infrastructure and be less aggressive to the environment unlike traditional chemicals, as well as convenient to apply.

The environmental safety of the developed material is understood as the ability of its components to pollute surface water, soil, and groundwater, and have a negative impact on the roadside biocenoses within background values or those that do not exceed sanitary and hygienic (environmental) standards.

Once in the environment, anti-icing reagents in the form of liquid outlet, spray or mist generated by traffic and wind can be carried to surface water bodies or adjacent soil, where they retain and accumulate, or combine with groundwater and even transfer to underground horizons. When the soil solution or groundwater comes into contact with the root system of vegetation, these substances can be absorbed by plants. Chlorides seep into the shallow groundwater system in winter and slowly release into streams throughout the year.

The degree of impact on environmental elements depends on many factors, e.g., local landscape features (side slope, drainage direction, type of the drainage system, type of soil, vegetation cover) and meteorological conditions (presence of snow and ice, amount of seasonal precipitation). Environmental impact can be both biotic (impact on individual organisms, populations, and communities) and abiotic (deterioration of soil structure, stratification of lakes, which disrupts seasonal water mixing and oxygen exchange).

Thus, in [Szklarek et al., 2022], it is noted that due to the long-term winter application of road salt (NaCl), the average annual concentration of Cl^- in rivers and lakes increases due to chlorides getting into groundwater. Chlorides reduce the biodiversity of aquatic animals and plants but promote the growth of phytoplankton, especially cyanobacteria. In addition, Cl^- worsens water self-purification by reducing the accumulation of nutrients in macrophytes, thus reducing the rate of denitrification and decomposition of organic matter.

Recognizing the toxicity of salt, some countries have threshold values or guidelines to protect drinking water for humans. For instance, in North America and Europe, the drinking water quality standard for chloride is 250 mg/L, i.e., the concentration at which water begins to taste salty. In Canada, the current guidelines for the protection of aquatic organisms are 120 mg Cl^- l^{-1} for chronic and 640 mg Cl^- l^{-1} for acute toxicity, while the chronic water quality criterion of 230 mg Cl^- l^{-1} and the US EPA acute exposure criterion of 860 mg Cl^- l^{-1} is higher than in the Canadian guidelines.

Elevated chloride concentration levels can have a strong impact on zooplankton, which are a key element in freshwater food chains. Laboratory tests [Arnott et al., 2022] found that six species of Daphnia experienced reduced reproduction and survival at chloride concentrations from 5 to 40 mg l^{-1}, i.e., much below the Canadian water quality guidelines for chronic exposure (120 mg l^{-1}). The high chloride sensitivity is likely due to the soft water used in the studies, whereas most published chloride toxicity tests were conducted in medium or hard water.

However, there are many studies on the fairly rapid adaptation of zooplankton to the increased salinity of freshwater lakes, for example, the work [Coldsnow et al., 2017] demonstrates the evolution of tolerance to a moderate level of salt ($100 \div 1000$ mg Cl^- l^{-1}) in Daphnia during the period from 2.5 months or from 5 to 10 generations. Given the importance of Daphnia in freshwater food chains, this improved tolerance may allow Daphnia to protect food webs from the effects of freshwater salinization.

Soil salinity is a significant stress factor that reduces plant productivity. The study [Soundararajan et al., 2019] determined the effects of anti-icing agents on three different species of creeping plants that commonly grow on the roadsides, such as *Trachelospermum asiaticum*, *Euonymus fortunei* and *Gelsemium sempervirens*. Two chlorides, calcium chloride and magnesium chloride, were applied to plants as splashes or sprays at different concentrations at different intervals. After 6 days of treatment, the results indicated that the application of both $CaCl_2$ and $MgCl_2$ affected the chlorophyll content and physiological processes in vines in a dose-dependent manner.

The article [Bykovsky et al., 2018] studied the phytotoxicity of the liquid waste of soda ash production in relation to cress and wheat according to three parameters (seed similarity, length, and dry weight of seedlings) and found that the liquid waste had an acute toxic effect in all parameters. According to the regression equation, the authors calculated safe breeding coefficients, the values of which ranged from 34.4 for cress to 81.8 for wheat. But in the work [Bykovsky et al., 2015] biotesting of distillery wastewater on *Lepidium sativum*, *Scenedesmus quadricauda,* and *Daphnia magna* showed that the harmless dilution factor was 43 for cress, 130 for algae, and 150 for crustaceans.

The water environment contaminated with heavy metals has a negative effect on hydrobionts and can lead to an increase in environmental consequences. The presence of metals significantly affects the quality of the living environment of all groups of aquatic organisms. First of all, it is dangerous when non-essential elements (Hg, Cd, Pb) enter the hydrosphere, since they can accumulate in the cells of hydrobionts, showing cumulative toxicity and genotoxicity. Essential metals are also capable of bioaccumulation, and the excessive accumulation of such elements as Fe, Zn, Cu, and Mn is accompanied with metabolic disturbances in the cells of aquatic biota [Antonyak et al., 2015].

Biotesting of water that contained heavy metals at the level of their MPC (Pb – 0.03 mg/l, Fe – 0.3 mg/l and Mn – 0.1 mg/l) in terms of the survival of hydrobionts demonstrated the toxicity of these metals: *Hydra attenuate* survival in water samples with lead and iron content was 40%, and with manganese content – 50%; 40% of *Ceriodaphnia affinis* survived in water with lead, and 50% survived in water with iron and manganese, respectively; 60% of *Danio rerio* survived in water samples with lead content, 90% with iron content, and 80% with manganese content. Only 100% of the test organisms of *Xenopus* survived in all water samples, but their general physiological condition deteriorated [Vergolyas et al., 2016]. Acute and chronic toxicity experiments were conducted on *Daphnia magna* regarding five heavy metals, namely Hg, Cd, Cu, Pb, and Cr added alone or in a mixture. The order of toxicity of individual metals was defined as follows: Hg>Cd>Cu>Pb>Cr [Meng et al., 2008]. Toxicity from the co-presence of heavy metals was determined to be synergistic, and chronic toxicity tests showed that the reproduction of *Daphnia magna* was significantly inhibited compared to the control group when the concentration of these metals was calculated at the water quality level for fish farming in China.

Other authors [Xin et al., 2015] conducted a comprehensive comparison of the sensitivity of different trophic species to six typical heavy metals (Cu, Hg, Cd, Cr(VI), Pb, Zn) for aquatic organisms. The results demonstrated that invertebrate taxa showed a higher sensitivity to each heavy metal than vertebrates. The greatest adverse effect on vertebrates was from Cu, followed by Hg, Cd, Zn, and Cr. Hazardous concentrations for 5% of species (HC_5) were derived to determine the concentration that protects 95% of species. HC_5 for six heavy metals were arranged in the decreasing order of Zn>Pb>Cr>Cd>Hg>Cu, indicating toxicity in the reverse order.

Salts of heavy metals are toxic and usually lethal to most aquatic organisms even at low concentrations, but when present in some combinations, they can exhibit synergistic or even antagonistic effects, e.g., binary stress from Pb–Zn on roots of *Kandelia obovata* showed an antagonistic effect compared to single stress [Chai et al., 2022], and the As–Hg mixture showed a strong antagonistic effect when exposed to *Proales similis* [Arreguin-Rebolledo et al., 2024]. It is advisable to assess the contribution of heavy metals to the toxicity of distillery wastewater separately.

Chloride (Cl^-) and sodium (Na^+) ions are responsible for many chemical changes and processes in soil leading to increased aggressiveness of water and subsequent leaching of lead and copper. The mobilization of heavy metals from soil into surface and groundwater, including cadmium, chromium, copper, lead, nickel, manganese, and zinc and the mobilization of radionuclides cause an increased risk for the quality of drinking water and human health [Lazur et al., 2020].

Therefore, in order to minimize the harmful effects on the components of the environment, any anti-icing material composition being developed must undergo a comprehensive study (including laboratory and field environmental tests and trials) in order to determine the suitability of use and allowable consumption of this reagent during application on motor roads in compliance with international standards.

RESEARCH AIM AND OBJECTIVES

Environmental impact assessment of anti-icing agents uses screening protocols with a coverage broad enough to consider all potential types of damage and to take into account the specifics of the application area. As a rule, this assessment includes the analysis of the reagent dilution by atmospheric precipitation (with determining the concentration on the roadside and in groundwater), toxicity screening, screening of the potential contribution to eutrophication, and field monitoring.

In 2021, we conducted biotesting of the liquid waste from the sludge storage of OJSC ‘Lysychansk Soda’ (simply called distillery wastewater) in the laboratory of the Department of Chemical Engineering and Ecology of Volodymyr Dahl East Ukrainian National University (Severodonetsk, Luhansk Oblast, Ukraine).

The aim of this work is to assess the ecotoxicological impact of the liquid phase of sludge storage of soda production on environmental elements as an anti-icing reagent under the condition of standardized application on the roads of Severodonetsk-Lysychansk agglomeration.

MATERIALS AND RESEARCH METHODS

The analysis of dilution of anti-icing reagents in the climatic conditions of Luhansk Oblast was carried out in order to determine the concentration of salt solutions formed on the roadside, in particular chloride ions, since the dilution factor that would take place at the distance between the motor road and the aqueous environment (for example, streams, lakes or wetlands) was considered as the first step in assessing potential harm. The dilution factor was determined by the ratio of the recommended amount of the reagent per 1 km of a two-lane motor road to the total amount of seasonal precipitation. To make it more simple (with a margin of safety to compensate for errors), it was assumed that all winter precipitation became runoff and carried anti-icing materials to the roadsides.

$\overline{x}_D$

Screening for toxicity is usually performed based on a complex chemical analysis, which can be used to assess biotic factors in the context of expected dilution and known toxicity thresholds for individual constituents. But in the case of a multicomponent mixture with micro impurities of unknown composition, a purely analytical approach may falsely detect the general toxicity. Instead, biotesting of such liquid will add confidence to the conclusion about whether a particular mixture will cause harm in ecosystems within the limits of expected dilution.

The assessment of the toxicity of the studied multicomponent mixture was based on short-term biotesting of test objects (exposure of 48 hours) in an aqueous environment with determining the average semi-lethal factor of dilution $LFD_{50\text{-}48}$ and the lowest ineffective dilution $LID_{10\text{-}48}$ (at least 90% of *Daphnia* alive) for *Daphnia magna S.* [DSTU 4173:2003] and the qualitative changes in the dimensional indicators of the root system of *Allium cepa L.* during 72 hours [Fiskesjö, 1995] with determining inhibitory dilution $ID_{10\text{-}72}$ resulting in a 10%-inhibition of the growth of the root system.

To determine the acute toxicity, the mortality of *Daphnia* in the studied liquid was calculated according to the formula

$$A(\%) = \frac{\overline{x}_c - \overline{x}_r}{\overline{x}_c} \cdot 100 \tag{1}$$

where: $\overline{x}_c$ – the average number of *Daphnia* that survived in the control water, $\overline{x}_r$ – the average number of *Daphnia* that survived in the tested liquid with the corresponding dilution.

The mortality of *D.magna* depending on the dilution factor of the wastewater (log D) was determined using probit analysis, where the probit regression line is described by the equation

$$Prob\left(p_i\right) = \frac{1}{\sigma} logD - \frac{logD_{50}}{\sigma} =$$
$$= a_0 + a_1 \cdot logD =$$
$$= (11.819 \pm 1.498) - (2.398 \pm 0.302) \cdot logD \tag{2}$$

where: σ – the standard deviation of normal distribution, D – the dilution factor of the distillery wastewater; D_{50} – the dilution factor that causes the mortality of 50% of individuals of the studied group.

The inhibition effect (phytotoxic effect) for *Allium cepa L.* was calculated according to the formula

$$EI(\%) = \frac{\overline{x}_c - \overline{x}_D}{\overline{x}_c} \cdot 100 \tag{3}$$

where: $\overline{x}_c$ – the average root length in the control study during 72 hours of observation; $\overline{x}_D$ – the average root length in the distillery wastewater of the corresponding dilution factor during the same observation time.

The chosen dilution range starts at concentrations higher than expected under actual conditions and extends to concentrations lower than expected under actual conditions. Thus, the dilution range of the studied anti-icing reagent was from 50 to 250 times for *Daphnia magna S.* and from 10 to 200 times for *Allium cepa L.*, which corresponds to the approximate range of calculated chloride ion concentrations of 13000 ¸ 520 mg/l, respectively.

RESULTS AND DISCUSSION

Analysis of dilution of the anti-icing reagent by winter precipitation

To estimate the content of chloride ions in groundwater, a model of the mass balance of salt available for dissolution in infiltrating precipitation was used, which allowed determining the equilibrium concentration of chloride ions in shallow groundwater [Johnston et al., 2000], taking into account the recharge rate of this water (depending on the type of soil), road salt loading, and the road network density (Fig. 2). The model did not take into account other sources of chloride ions. In the area of Severodonetsk-Lysychansk agglomeration, groundwater has an average annual precipitation infiltration rate in sandy and loamy soil at the level of 20 cm/year, or 40% of the average multi-year precipitation amount (» 500 mm) according to the model published in [Saprykin et al., 2015].

Chloride levels in freshwater ecosystems naturally range from about < 1 mg/L to nearly 500 mg/L with primary salinization occurring from bedrock weathering, sea spray, precipitation, and saline aquifers, particularly in areas where evaporation exceeds precipitation [Cañedo-Argüelles et al., 2012]. The background concentration of chlorides in the surface water of Severodonetsk-Lysychansk agglomeration varies in the range of 140–300 mg/l and is formed due to natural sources (deposits) of chloride salts, the discharge of saline runoff from mines and wastewater from large industrial enterprises in the region. Thus, in 2021, according to the inventory [Ecological passport, 2022], wastewater with a chloride content of 7.7 thousand tons was discharged into the Siverskyi Donets river and its tributaries.

The groundwater pollution of Lysychansk-Rubizhne industrial complex has been observed since 1976, which is the result of the exploitation of industrial sites, storage ponds of PJSC "Severodonetsk Azot Association" and OJSC "Lysychansk Soda", as well as the concomitant filtration of highly mineralized and polluted wastewater into aquifers [Mikhalkova et al., 2022]. The studied territory has widespread groundwater of the Alluvial and Upper Cretaceous aquifers, which are contaminated with salts, nitrogen, and organic compounds, depending on the production specifics of the enterprises located nearby. The geological and hydrogeological section is represented by bulk soils with a thickness of up to 2–3 m, well-permeable Quaternary sand-clay deposits with a thickness of 0 to 30 m, and chalk-marls with a thickness of 200–250 m. Aquifers of alluvial sand deposits and chalk-marl strata are hydraulically connected to each other by the surface water of the Siverskyi Donets and the Borova rivers. They do not have shielding layers at the top and are not protected from the penetration of pollution from the surface of the earth [Qualitative characteristics, 2019]. The content of chlorides in both aquifers during a ten-year observation varies in a wide range from 0.032 to 159 maximum permissible concentrations. It is local in nature and depends on the area of man-made impact of industrial sites (PJSC "Severodonetsk Azot Association", LLC "RPE "Zorya", OJSC "Lysychansk Soda", LLC "Rubizhne Krasytel", etc.).

Calculations of the concentration of chloride ions in groundwater for soil with a recharge rate of 20 cm/year, typical of sand, for road networks with an average traffic density of motor roads indicate the possibility of exceeding the limit of chronic exposure of 250 mg/l on a regional scale at a chloride loading of 25-35 tons per kilometre of a two-lane road (Fig. 2), which never happens in the studied latitudes since the meteorological conditions for applying such a large amount of salt are not created. Thus, for example, in the city of Severodonetsk and its suburbs, an average of 50 tons of technical salt is used every year during winter, i.e. with a density of 277.6 km per 1 thousand sq. km [Socio-economic analysis, 2019] and the territory of 42.1 km^2, this is equal to 4.33 t/km of coverage. Thus, due to the application of technical salt, the concentration of chlorides in groundwater will be (Fig. 2) approximately 35–45 mg/l, while the concentration of chloride ions from the use of an equivalent amount of distillery wastewater will be almost twice as small, i.e., 17–23 mg/l.

The worst-case scenario could be along the roadside ditches or small wetlands adjacent to major roads. The calculated concentrations of chlorides appearing on the roadside of 1 km of a two-lane road with a width of 6 m when diluted by winter runoff under the condition of

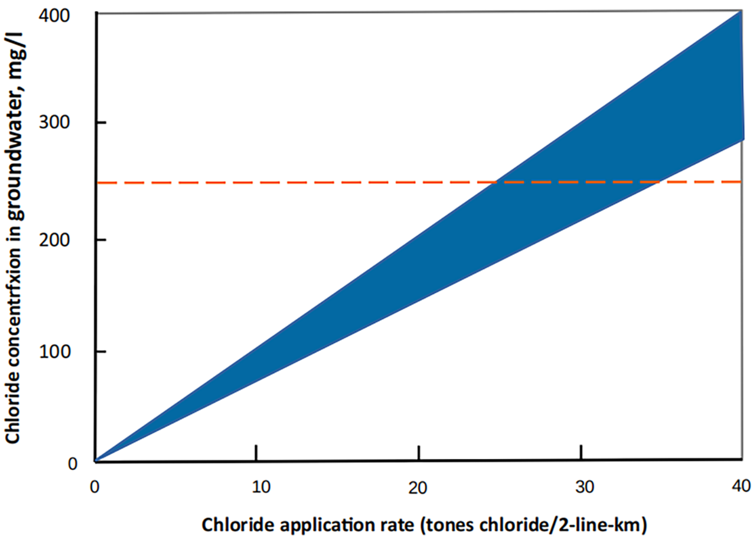

Figure 2. Calculated concentrations of chlorides in groundwater at different chloride application rates and the groundwater recharge rate of 20 cm/year (from [Johnston et al., 2000])

recommended costs are presented in Table 2 and Fig. 3. The long-term average amount of winter precipitation in Luhansk Oblast is 120–150 mm [Krakovska, 2012]. The recent years have been marked by a small amount of precipitation, therefore, a lower value of 120 mm is used for calculations, so, 720 m^3 of seasonal precipitation falls on 1 km of the road surface, which is taken as a basis in calculations of chloride ion concentrations.

Fig. 3 shows the dependence of the expected concentration of Cl^- on the roadside on the application rate during winter. It can be seen that the maximum application rate of distillery wastewater with a consumption of 100 g/m^2 of road surface, which is limited by the acute exposure concentration of 840 mg/l, recommended by the USEPA, is 9 times, i.e., 5.4 tons of wastewater per 1 km. Instead, the equivalent of technical salt, which will have a similar concentration, is only 0.96 t per 1 km of the motor road (four applications).

Regarding eutrophication of surface water, potentially caused by the use of distillery wastewater as an anti-icing reagent, this process is a complex function of all possible influencing factors, namely, nutrient enrichment, water body hydrodynamics, temperature, salinity, carbon dioxide cycle, element balance, etc., as well as microbial and biodiversity.

Ammonium nitrogen in the amount of 0.04% wt. or ~ 460 mg/l can be singled out among the nutrients in distillery wastewater. According to various sources of information, eutrophication is facilitated by a concentration of total nitrogen from 4.2 to 10 mg/L (maximum contaminant level as estimated by the USEPA). That is, when diluted by seasonal precipitation, the concentration of ammonium nitrogen will fall to a safe value, even with several treatments of motor roads.

Assessing the toxicity of the studied liquid in relation to *Daphnia magna* S.

Water flea testing is probably the most common in aquatic toxicity testing practice, as it is

Table 2. Calculating the concentration of chlorides on the roadside when diluted by winter precipitation

Anti-icing reagent	Reagent application standards			Cl^- concentration on the roadside, mg/l
	g/m^2	kg/km	Including Cl^-, kg/km	
Road salt (technical NaCl), 97% wt.	40	240	140.5	201.15
Distillery wastewater	100	600	75.0	90.59

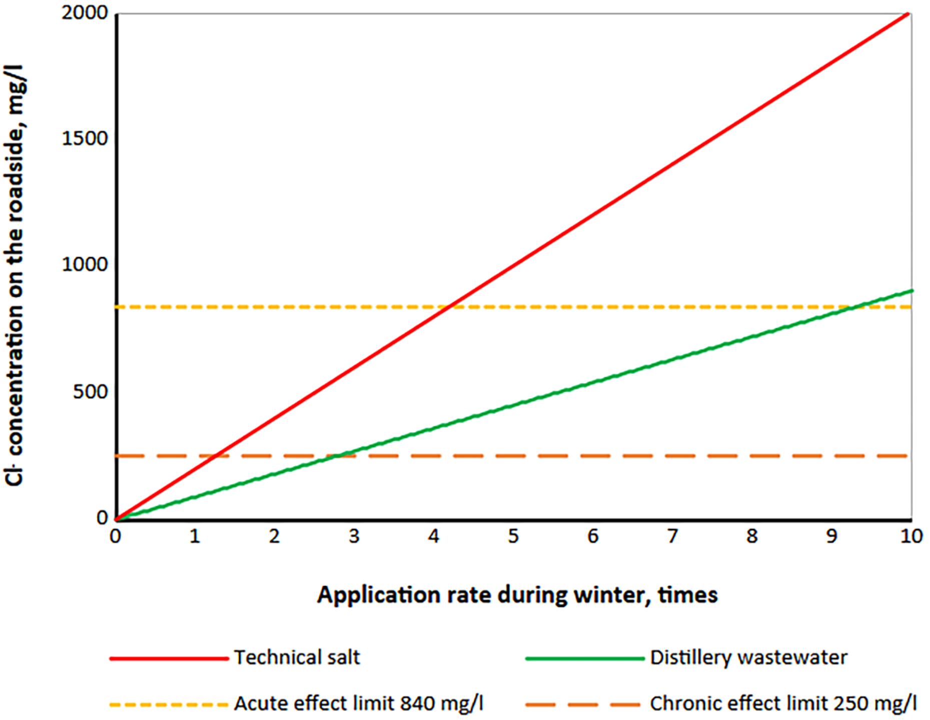

Figure 3. Dependence of the expected concentration of Cl^- on the roadside on the application rate during winter

less complex than testing fish, and provides a good representation of the response of some of the most sensitive species of organisms in the aquatic environment.

Toxicity tests used 24-hour-old, laboratory-grown, first-generation *Daphnia* from parents adapted to water breeding during 48 hours. 10 individuals were selected in a glass, the experiment was repeated three times for each dilution. *Daphnia* were not fed during testing. Control water and water for dilution was tap water (total hardness 2.6 mmol/dm^3) dechlorinated by settling and aeration for 7 days. The water temperature was maintained at the level of 18–22 °C, and the light regime corresponded to the change of day and night. Solutions for testing were prepared by mixing appropriate volumes of distillery wastewater (clarified liquid phase, taken from sludge storage No. 4 of OJSC "Lysychansk soda" of Luhansk Oblast, Table 1) with water prepared for dilution. The pH value of the obtained solutions ranged from 6.5 to 8.5 units. The concentration of dissolved oxygen during all experiments ranged from 6 ÷ 2 mg/l. The percentage of living organisms was recorded after 24, 48, and 96 hours.

If mortality was at or above 50%, such a solution was considered to have an acute toxic effect. At $A \leq 10\%$, it was considered that the studied solution did not have an acute toxic effect.

Data homogeneity was checked using Fisher's exact test, the χ^2 test, and the Monte Carlo method, which were implemented in the R software environment. The observations turned out to be homogeneous.

The calculation of $LFD_{50\text{-}48}$ values was carried out based on probit analysis. The Chi^2 test was used to assess the degree of correspondence of the probit model to the experimental data. The Monte Carlo method was used to calculate the 95% confidence interval.

The significance criterion was set at $p < 0.05$. Mortality of *D. magna* during 48 hours of observation in Prob(p_i) depending on the dilution factor of distillery wastewater (log D) is shown in Fig. 4. When diluting 1/50 and 1/60, the death of an average of one-third of *Daphnia* was observed after 24 hours, and after 48 hours, the complete death of all test objects was observed. The semi-lethal dilution factor for *D. magna* is $LFD_{50\text{-}48} = 138$ (the upper limit of the 95% confidence interval is 145.1, the lower limit is 131.3), which roughly corresponds to the calculated concentration of chloride ions of 930 mg/l.

Using the method of inverse confidence intervals ("fiducial limits"), estimates of confidence intervals were calculated for the dilution factors causing 10–90% mortality of *D. magna*. The result is presented in Fig. 5.

Thus, the harmless dilution factor of distillery wastewater, when at least 90% of *Daphnia magna S.* remain alive, is $LD_{10\text{-}48} = 235$ (the upper limit of the confidence interval is 257.9, the lower limit is 218.8), which approximately corresponds to the calculated concentration of chloride ions of 555 mg/l.

Studying the adaptation of *Daphnia* in chronic experiments over several generations is our goal in future research.

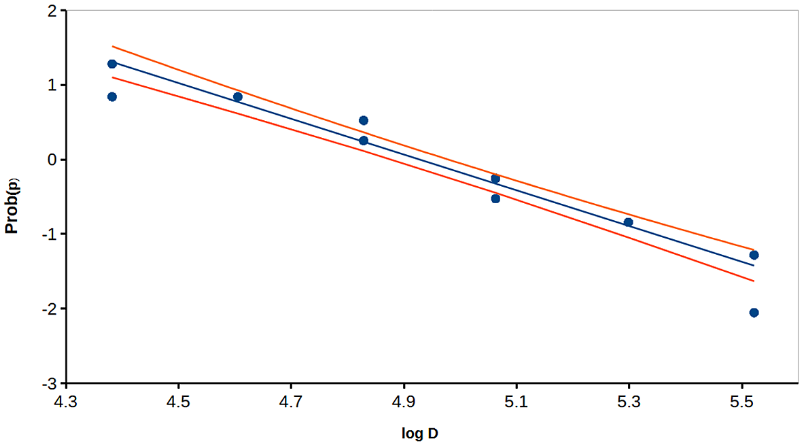

Figure 4. Dependence of mortality (Prob) on the logarithm of the dilution factor of distillery wastewater: ▬ – regression line, ▬ – limit levels of the 95% confidence interval

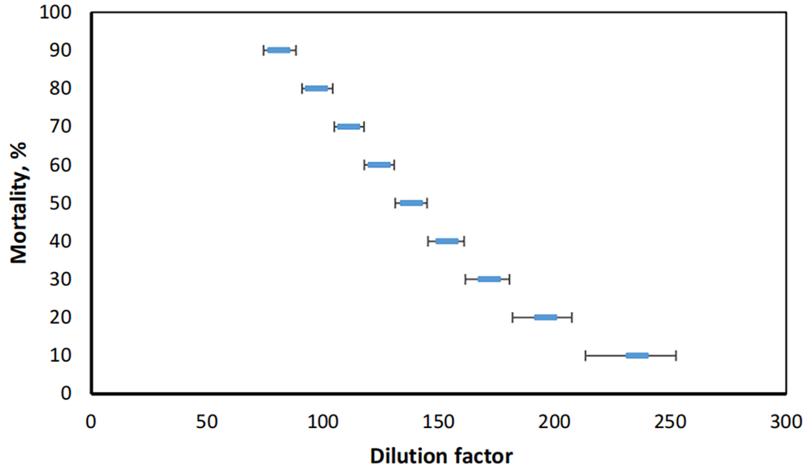

Figure 5. Dependence of the average dilution factor of distillery wastewater on the probability of *Daphnia's* death

Assessing the toxicity of the studied liquid in relation to *Allium cepa* L.

Plants are generally very sensitive to salt stress during germination and early growth. The toxicity of distillery wastewater relative to higher-order plants was assessed using the *Allium* test by determining the macroscopic parameter of the root length, as well as its colour and elasticity.

Observing the inhibition of the growth of the root system under the influence of distillery wastewater was carried out on small bulbs (*Allium cepa*) of the same size weighing about 10–13 g, which were peeled by removing free outer skin so that the root primordia were immersed in the control water (tap water, dechlorinated for 24 hours) or solutions of distillery wastewater of different dilution. New portions of solutions, equal to the evaporated volumes, were added to the test tubes daily. In each series of experiments, the exposure time was 72 hours at a temperature of 21–22 °C using artificial light of medium intensity. After the experiment, the root length was measured. To be statistically assessed, all experiments (10 bulbs each) were organized in three repetitions. The Shapiro-Wilk test was used to test the hypothesis of normal distribution in the samples.

The results of observations of 6 series of tests after three days of exposure to distillery wastewater of various degrees of dilution on the length of the roots are shown in Table 3.

The table shows that the root growth rate is different for each dilution factor and control. The growth rate of onion roots in 72 hours in tap water (control) is 131.88%, which is more than the roots of onions germinated in distillery wastewater of different dilution factors, except for 1/200 dilution, where the results were not statistically significant. The absence of a statistically significant difference between the average values of the bioparameter in the control and the studied samples indicates the absence of significant changes in the growth

Table 3. Inhibitory effect of distillery wastewater on the root growth of *Allium cepa*

Degree of dilution	Average root length $\overline{x}$ ± SEM			Change rate in 72 hours (%)	% from control	Inhibition effect, %
	24 hours	48 hours	72 hours			
control	12.61 ± 0.27	20.5 ± 0.76	29.24 ± 0.54	131.88	-	-
1/200	12.5 ± 0.24*	20.35 ± 0.7*	28.75 ± 0.54*	130.00	98.32	1.68
1/150	12.26 ± 0.13*	17.55 ± 0.45	24 ± 0.93	95.76	82.08	17.92
1/100	9.27 ± 0.19	11.66 ± 0.22	15.4 ± 0.64	66.13	52.67	47.33
1/50	8.78 ± 0.12	10.08 ± 0.13	11.78 ± 0.48	34.17	40.29	59.71
1/30	7.81 ± 0.16	8.98 ± 0.18	9.92 ± 0.29	27.02	33.93	66.07
1/10	1.75 ± 0.29	2 ± 0.27	2.17 ± 0.28	24.00	7.42	92.58

Note: *the difference of the result from the control is not statistically significant $p > 0.05$; SEM – standard error of the mean.

processes of the bioindicators. That is, it means that the solution in the studied sample is of almost the same quality as in the control study and has almost no toxic properties.

Fig. 6 shows the inhibition of the onion root growth every 24 hours compared to the control study. There is a clear dose-response in the inhibition of the root length by exposure to different concentrations of distillery wastewater.

To determine the dilution factor that leads to a 10% effect of inhibition of the ID_{10-72} root system growth, a non-parametric method was used, based on simulation by the Monte Carlo method in combination with cubic spline interpolation. Figure 7 shows the dependence of the relative root length on the dilution factor of distillery wastewater and the calculated approximation of the limit of the confidence interval. The average value of the dilution factor at which the root growth inhibitory effect reaches 10% is 164.5 with the upper and lower limits of the 95% confidence interval of 155.5 and 175.5, respectively.

Discussion of some aspects and recommendations for application

The article [Çavuşoğlu, 2023] studied the effect of the solution of only NaCl on *Allium cepa L.,* where the control group was soaked in tap water, and the bulbs of the working group

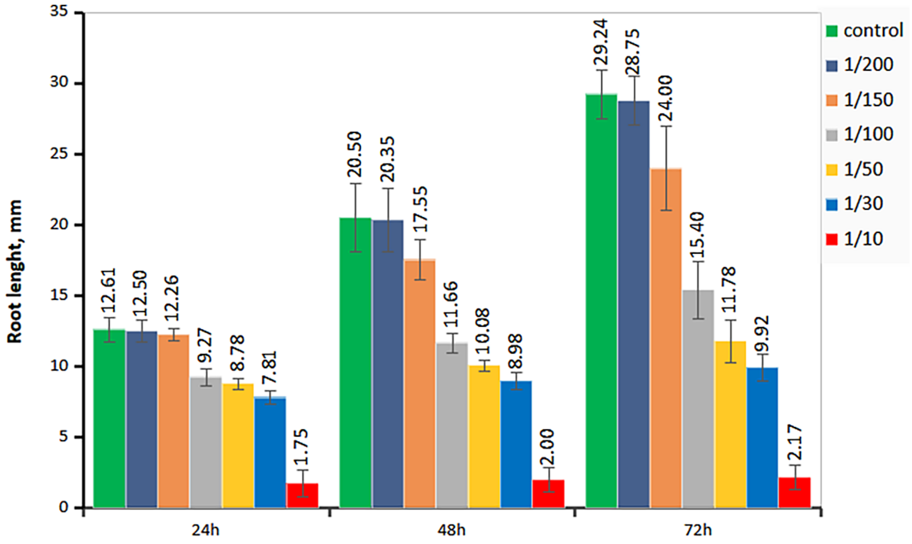

Figure 6. The effect of distillery wastewater of different dilution factors on the inhibition of *Allium cepa L.* root growth compared to the control ($\overline{x}$ ± SD)

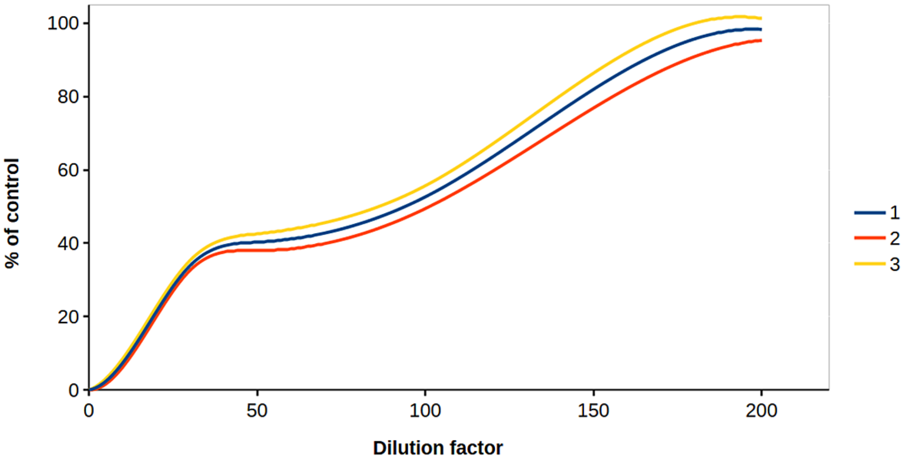

Figure 7. Dependence of the relative root length of *Allium cepa L.* on the dilution factor of distillery wastewater: 1 – middle line; 2 – probability line of 0.025; 3 – probability line of 0.975

were grown in a medium of 0.15 M NaCl (5250 g/l Cl^-) for 7 days. The authors noted that NaCl stress significantly inhibited germination and root length; the average root length of the bulbs of the working group at the end of the experiment was only ~19% of the average root length of the control group. This concentration of chloride ions in the distillery wastewater solution corresponds to the dilution factor of 25, which correlates with the results of our research (Fig. 7).

However, in the works [Bykovsky et al., 2018; Bykovsky et al., 2015] biotesting of the liquid waste of soda ash production was carried out on other plant test objects and the harmless dilution factor was found to be in the range from 34 for cress to 150 for *Daphnia magna*. The difference in the obtained results can be influenced by many factors, but the main one is the different composition of the liquid waste, which is formed due to the use of raw materials from other minerals. Limestone from the Bilohoriv chalk quarry and brine from the Bakhmut rock salt deposit were used in the production of soda ash at OJSC ‘Lysychansk Soda’.

The dilution factor of the anti-icing liquid is inversely proportional to the frequency of use of such material and the amount of winter precipitation. Taking the amount of seasonal precipitation at the level of 120 mm according to the conservative scenario and observing the application rate of the reagent of 100 g/m^2, we obtain an equation (Fig. 8) that describes such a dependence $D = 1440/n$, where n is the application rate of the anti-icing reagent. It is obvious that the conducted studies are not quite enough, as it is desirable to evaluate the chronic effect of liquid waste on taxonomic groups of hydrobionts and plants. However, based on the results of biotesting on the test objects of *D. magna* and *Allium cepa L.*, the harmless dilution factor of distillery wastewater should be between 260 ÷ 130, therefore the maximum safe application rate of the reagent is from 5 to 9 times, which is usually quite sufficient in the climatic conditions of Luhansk Oblast.

A few remarks should be made about heavy metals in the anti-icing reagent. The amount of heavy metals in the wastewater of a typical soda ash plant with an average capacity of 500,000 t/year is approximately 21.5 t/year, with the following approximate content (may vary depending on the composition of carbonate raw materials and saline solutions used), mg/l [Integrated Pollution, 2007]: Zn – 1.69, Pb – 1.04, Cr – 0.59, Ni – 0.43, Cu – 0.38, As – 0.11, Cd – 0.05, Hg – 0.01. Most of the insoluble salts in the composition of the liquid waste during tens of years in sludge storage have passed into the solid phase of the sediment, as evidenced by the elemental analysis we made using the express analyzer EXPERT 4L (detection limit of elements 1–10 ppm): Fe – 0.304 ± 0.021% wt.; Mn – 190 ± 36 ppm; Sn – 121 ± 30 ppm; Zn – 32 ± 6 ppm; As – 26 ± 6 ppm. Therefore, the content of heavy metals in the liquid phase is much lower.

Average annual concentrations of heavy metals in the control water bodies of Severodonetsk-Lysychansk agglomeration vary in the following ranges (mg/l): Fe – 0.035 ± 0.3, Mn – 0.018 ± 0.193, Zn – 0 ± 0.026, Cu – 0.0003 ± 0.013, Ni – 0.024 ± 0.052. In soil, the level of pollution according to the total Z_C indicator is mostly characterized as satisfactory. A moderate-dangerous level

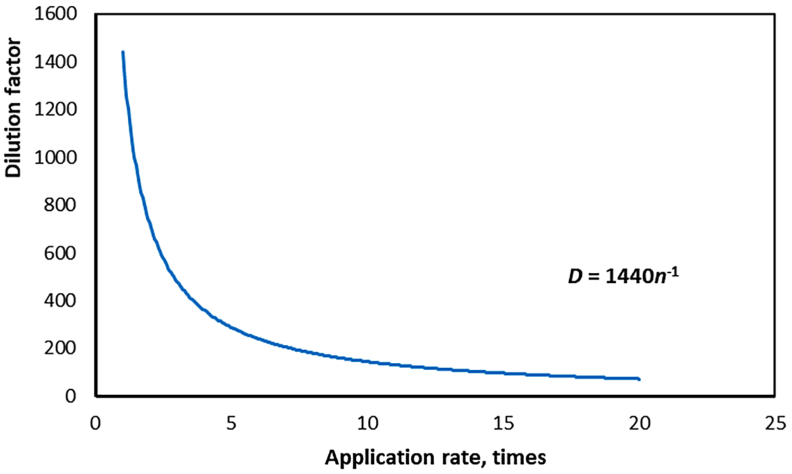

Figure 8. Dependence of the calculated dilution factor of distillery wastewater with seasonal precipitation on the application rate during winter

of pollution is observed mainly in the territory of large industrial enterprises, where the concentrations of such heavy metals as Cr, Zn, Pb, Cu, and Fe may exceed the maximum permissible values.

It should be noted that any chloride road salt contains heavy metals in small amounts, but it is the salt that accelerates the corrosion of vehicles and infrastructure and thus contributes to the increase in heavy metal concentrations in runoff and roadside soil [Bäckström et al., 2003], e.g., the total content of metals in motor road runoff increases in winter by an average of 488.5% Cd, 873.5% Co, 393.5% Cu, 80% Zn, 147.5% Pb. Although the solution of distillery wastewater as an anti-icing reagent, unlike technical salts, reduces the corrosion of cars and infrastructure [Kravchenko et al., 2023], we believe that the impact of heavy metals from the use of such an anti-icing reagent on ecosystems and ecosystem services should be carefully studied, including the last stage of field research. In addition, some types of environmental degradation are difficult to predict using chemical analyses or toxicity tests. More accurate assessments of possible negative consequences require field observations, long-term monitoring, and modelling of the distribution and accumulation of heavy metals included in the reagent in various parts of natural ecosystems in places of intensive use.

To ensure safe use of distillery wastewater on the motor roads of the region, it is advisable to create a combined map of groundwater pollution (located near the liquid waste storage facilities of industrial enterprises of the agglomeration) and the motor roads in order to identify ‘sensitive’ areas, on which it will be prohibited to apply any road reagents, including distillery wastewater due to the potential excessive increase in the concentration of salts in groundwater. To ensure safe conditions for motor vehicles, the road surface in these areas must be treated only with abrasive materials. In order to reduce the load on ecosystems in general, it is desirable to pre-moisten the roads with distillery wastewater before snowfall. With the use of distillery wastewater, it is expected that traditional road salt will be abandoned, so the environmental burden in the areas adjacent to motor roads will decrease. The regulated use of a more advanced composition for preventing icing will contribute to reducing the costs of maintaining the entire transport infrastructure in good condition and will improve the quality of road transport in winter.

CONCLUSIONS

This paper presents the results of studies to assess the potential ecotoxicological effect of the liquid phase of soda production waste when used as an anti-icing reagent by biotesting on the water blouse *Daphnia magna S.* and onion *Allium cepa L.* with the determination of ineffective dilution of the reagent.

Based on the research results, we can state that the proposed multi-component anti-icing reagent based on the liquid phase of soda production waste can be used for winter road maintenance after conducting field observations in the climatic conditions of the Luhansk region of Ukraine. To prevent damage to environmental elements, it is necessary to follow the recommendations for the regulated application of such an anti-icing reagent, namely, no more than 9 times during the winter period.

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