Оригинальная статья

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Testing the possibility of using desiccators to study the aerosol effect of liquid deicing material

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***Introduction**. In many countries, there is an additional group of pollutants – deicing materials (DIM) in winter. Salt-containing DIM is one of the factors for increasing the content of $PM_{2.5}$ and PM_{10} in the air. The purpose was to determine the possibility of using desiccators to study the aerosol effect of liquid deicing material, identify the chemical composition in the air at spreading liquid DIM in various ways, and establish the calculated doses for conducting a toxicological experiment to study the DIM aerosol effect on the organism of warm-blooded animals.*

***Materials and methods.** A model experiment was conducted in airtight containers (desiccators) using a liquid DIM that includes NaCl and $CaCl_2$. All chemical compounds were captured in air pumping from the desiccator into a bubbler tank with bidistilled water and then analyzed using ion chromatography.*

***Results.** When comparing the obtained results of main DIM components contained in the air inside desiccators with the maximum permissible concentrations, the excess of Cl^- was detected both for the highest single concentration of 0.1 mg/m³ and for the average daily concentration of 0.03 mg/m³. When applying DIM at a dose exceeding ten times the recommended norms for liquid the DIM, an excess level of the maximum permissible concentration for chlorine (but not for sodium and calcium) is observed.*

***Conclusion**. The method of DIM studying in desiccators is indicative in terms of the choice of concentrations and studying mechanisms of reagent intake for subsequent DIM research conduction using laboratory animals.*

***Keywords:** aerosolization; chlorine; deicing materials; desiccators; particulate matter*

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Отработка возможности использования эксикатора для изучения аэрозольного действия жидкого противогололёдного материала

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***Введение.** Во многих странах в зимнее время года присутствует отдельная группа загрязняющих веществ – противогололёдные материалы (ПГМ). Применение солесодержащих ПГМ является одним из факторов увеличения частиц $PM_{2,5}$ и PM_{10} в атмосферном воздухе. Целью данного исследования была оценка возможности использования эксикатора для изучения аэрозольного действия жидкого ПГМ, идентификация химических соединений в воздухе, образующихся различными способами вследствие распыления жидкого ПГМ, а также определение расчётных доз для проведения токсикологического эксперимента с целью оценки аэрозольного действия на организм теплокровных животных.*

***Материалы и методы.** Модельный эксперимент проводился в герметичных ёмкостях (эксикаторы) при использовании жидких ПГМ, имеющих в составе NaCl и $CaCl_2$. Все химические соединения улавливались в процессе отбора воздуха из эксикатора в барботер с бидистиллированной водой, впоследствии отобранные пробы были проанализированы методом ионной хроматографии.*

***Результаты.** При сравнении полученных данных по основным химическим соединениям, содержащимся в атмосферном воздухе внутри эксикатора, с предельно допустимыми концентрациями установлено превышение по содержанию Cl^- как для максимально разовой концентрации, составляющей 0,1 мг/м³, так и для среднесуточной – 0,03 мг/м³. Превышение предельно допустимой концентрации по хлорид-ионам (за исключением ионов натрия и кальция) отмечалось при использовании концентраций ПГМ, превышающих рекомендованные нормы расхода для жидких ПГМ в 10 раз.*

***Заключение.** Методика исследования аэрозольного действия ПГМ с помощью эксикаторов является показательной для выбора тестируемых доз и изучения механизмов последствий от поступления ПГМ для последующего проведения исследований ПГМ с использованием лабораторных животных.*

***Ключевые слова:** аэрозольное распыление; хлорид-ион; противогололёдный материал; эксикаторы; взвешенные частицы*

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Original article

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Introduction

The problem of the impact on human health of chemical pollutants in the environment of metropolises is more acute than ever. Numerous epidemiological studies worldwide showed the aerosol action of chemicals in the air to pose the most significant risk for stipulated health [1, 2].

In winter, one faces a different group of pollutants (apart from the primary air pollutants near roads) – deicing materials (DIM) used to treat roadways and sidewalks. Many DIMs are compounds of salts. Various groups of DIMs are used in Russian cities: mineral concentrate – halite; a sand-salt mixture consisting of sand, sifting, and technical salt; marble aggregate (calcite) with the addition of sodium chloride and an anti-corrosion inhibitor; crushed granite based on a composition of calcium and sodium chloride, and others [3]. Given that DIMs are significant environmental pollutants in metropolises in winter, it is necessary to conduct researches on the impact of the given contaminants on human health.

DIM various types of chemical composition assessment in natural conditions in Moscow showed that the level of sodium and chlorine ions in the atmospheric air significantly exceeds the corresponding background indicators of natural origin [4].

Salt-containing DIM usage is one significant factor for increasing the content of the $PM_{2.5}$ and PM_{10} suspended in the air [5, 6]. Airborne fine suspended particles, the source of which is, among others, dried abrasive and salt-containing DIMs remaining on roads, can lead to air quality degradation and negatively impact human health when injected into human lungs [7]. The studies conducted by the US Environmental Protection Agency have shown that aerosol pollutants deposited in the respiratory tract can cause irritation action at first and then inflammation demonstrated in both animal and controlled human studies [8].

The study comparing the impact of abrasive and salt-containing DIMs on air quality near roads revealed the overall and relative contribution of these factors to the content of fine suspended particles in the air [9]. DIM components were determined to make up from 44 to 59% of PM_{10}, at that DIMs used in liquid form contribute less to the formation of PM_{10} than the abrasive DIM. In this regard, and to reduce the negative impact of abrasive DIMs on human health, it is recommended not to use materials with a high content of silt fraction. There is also a tendency in many situations to change from the use of solid salt-containing and abrasive DIMs to liquid DIMs [10]. Thus, an increase in the use of liquid DIM and a decrease in the use of sand in the state of Colorado, USA, in 2002 led to a noticeable reduction in the content of PM_{10} in winter compared to previous years [11].

Currently, desiccators are used along with climate chambers to study the acute or chronic aerosol effects of various chemicals. In Russia, research in desiccators is most widely used to study the toxic properties of disinfectants, including inorganic chlorine compounds and multiple additives [12, 13].

Given that DIM composition includes sodium, calcium, potassium, and magnesium chlorides, the expected values for these compounds can become indicative when assessing the actual content of DIM components in the atmospheric air. The available data on the toxic properties of deicing materials differ [14–17].

Due to methodological and legal differences in the assessment of deicing reagents, there is a need to develop approaches to the evaluation of the hazard/safety of DIM usage and input the necessary data in the regulatory database for environmental, hygienic, and toxicological assessments of deicing reagents as a separate subgroup of chemicals that negatively impact on ecological components and human health [18].

The purpose of the given study was to determine the possibility of using desiccators to study the aerosol effect of liquid deicing material, identify the chemical composition in the air at spreading liquid DIM in various ways, and establish the calculated doses for conducting a toxicological experiment to study DIM aerosol effect on the organism of warm-blooded animals.

Materials and methods

To justify the calculated doses during a toxicological experiment on the study of DIM aerosol effect on the organism of warm-blooded animals and to identify the chemical composition in the air during the spread of liquid DIM, a model experiment was conducted using a deicing reagent that includes: sodium chloride and calcium chloride in mass fractions – 6 and 22 % respectively. The given deicing reagent was used as a model reagent, taking into account the official explanations of the Department of Housing and communal services of Moscow.

Studies were carried out in airtight containers (desiccators) with a volume of 10 liters. The study referred to the main methodological techniques enunciated in the Manual on methods of laboratory researches and tests of disinfectants to assess their effectiveness and safety, used in the territory of the Russian Federation [19].

DIM introduction calculation was made in compliance with the technical regulations, according to which the maximum density of liquid DIM treatment is 70–80 ml/m^2 [20]. Researches were conducted in terms of the study at 6 ml of DIM and at 60 ml of reagent introduction that corresponds to a 10-fold increase in dose introduction to establishing a threshold point of DIM components definition in the air of desiccator, taking into account the sensitivity of the method of ion chromatography using which the elementary analysis of wastewater solutions was carried out.

The liquid DIM introduction was applied in three ways and two concentrations (table 1).

All chemical compounds were captured in the process of air pumping from dessicators into a bubbler tank with bidistilled water for 4 minutes of air aspiration with an absorption rate of 2 dm^3/min on an electric PU-4E aspirator. Chemical analysis of air samples was performed by ion chromatography in accordance with Russian National Standard [21, 22].

Results

The data obtained on the main components of DIM is presented in table 2.

When applying DIM at a dose of 6 ml, there was no excess of the main components of DIM (Na^+, Ca^{2+}, Cl^-).

When applying DIM at a dose of 60 ml, the content of Cl^- ions was found at the level of 0.25 mg/m^3 (D1), 1.00 mg/m^3 (D2), 0.25 mg/m^3 (D3). When comparing the obtained results with the hygiene standards – maximum permissible concentrations, the excess of Cl^- ions content was detected for the maximum single concentration of 0.1 mg/m3 and the average daily concentration of 0.03 mg/m^3 [23].

Thus, when applying DIM at a dose exceeding ten times the recommended norms for liquid DIM introduction, the level of

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Table 1 / Таблица 1

Methods of liquid DIM introduction in a model experiment

Методы введения жидкого димера в модельный эксперимент

Desiccator Эксикатор	A method of introduction of the reagent Способ введения реагента	Sampling of air Отбор проб воздуха	The amount of the reagent, ml Количество реагента, мл	
1 (D1)	Exposure of the liquid reagent in the desiccator for 24 hours Выдержка жидкого реагента в эксикаторе в течение 24 ч	24 hours after applying the reagent Через 24 ч после нанесения реагента	6	60
2 (D2)	Aerosol spraying Аэрозольное распыление	Immediately after spraying the reagent Сразу после распыления реагента	6	60
3 (D3)	Application of the liquid reagent by wetting the surface of the desiccator Нанесение жидкого реагента путём смачивания поверхности эксикатора	5 minutes after application Через 5 мин после нанесения	6	60
4 (D4)	Control. Distilled water Контроль. Дистиллированная вода	–	–	–

Table 2 / Таблица 2

Quantity of ions (mg/m³) of the main components of DIM in the air of desiccators

Количество ионов (мг/м³) основных компонентов ПГМ в воздухе эксикаторов

Research Исследование	DIM components found in the air of desiccators Компоненты ПГМ, обнаруженные в воздухе эксикаторов								
	Na^+ (sodium)			Ca^{2+} (calcium)			Cl^- (chlorine)		
	the detection limit of the instrument предел обнаружения прибора								
	0.02			0.005			0.0075		
	M	*SD*	*RSD*, %	*M*	*SD*	*RSD*, %	*M*	*SD*	*RSD*, %
Control	0.19	0.004	1.97	0.05	0.002	4.53	<0.0075	–	–
6 ml of DIM / 6 мл реагента									
D1	0.12	0.002	1.30	0.03	0.0003	1.11	<0.0075	–	–
D2	0.27	0.013	4.85	0.87	0.02	2.27	<0.0075	–	–
D3	0.17	0.003	1.76	0.20	0.002	0.98	<0.0075	–	–
60 ml of DIM / 60 мл реагента									
D1	0.06	0.002	3.99	0.06	0.003	4.41	0.25	0.016	6.25
D2	0.16	0.003	1.73	0.41	0.012	2.93	1.00	0.063	6.25
D3	0.05	0.0005	0.95	0.08	0.0001	0.08	0.25	0.016	6.25

N o t e. *M* is the arithmetic mean; *SD* is the standard deviation; *RSD* is the relative standard deviation.

П р и м е ч а н и е. *M* – среднее арифметическое; *SD* – стандартное отклонение; *RSD* – относительное стандартное отклонение.

chlorine ions excessed the maximum permissible concentration under regulations [20]. This excess was not detected for sodium and calcium ions.

Discussion

DIM's highest indices are observed in air samples taken from aerosol desiccators (D2). This may indicate that the effect on the human organism may be more pronounced at liquid reagent aerosol spraying. It should be noted that the speed and time of settling aerosol particles in the air are important factors determining the surface layer's stability. In addition, particle diameter and micrometeorological factors may affect the actual concentrations of DIM aerosol distribution in the air [24].

The obtained results show the importance of monitoring the concentrations of chloride ions in the atmospheric air since their concentrations may be higher than safe levels regulated by hygiene standards due to deicing materials usage [23]. The main areas of increased attention should include places where there is potentially a significant gathering of people, including bus stops. The study of DIM aerosol-cloud composition will enable preventive measures that exclude the negative impact of DIM on human health.

Conclusion

Thus, taking into account the results of the performed experiment, it can be noted that the method of DIM studying with the help of desiccators is indicative in terms of the choice of concentrations and mechanisms of reagent intake for subsequent DIM researches conduction using laboratory animals. Further study of the DIM effects on the human organism is advisable for inhalation intake, including aerosol spraying.

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(п.п. 1, 2, 4–11, 17 см. References)

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