СРАВНИТЕЛЬНАЯ ХАРАКТЕРИСТИКА ВЫБРОСОВ ПРИОРИТЕТНЫХ КАНЦЕРОГЕНОВ СТАЦИОНАРНЫМИ ИСТОЧНИКАМИ В АТМОСФЕРНЫЙ ВОЗДУХ РАЙОНОВ РЯЗАНСКОЙ ОБЛАСТИ

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Цель. Оценка динамики выброса приоритетных канцерогенов от стационарных источников в районах Рязанской области в 2009 и 2016 гг. Материалы и методы. Для анализа использовались официальные статистические данные об объемах загрязняющих веществ, поступающих в атмосферный воздух от стационарных источников. Приоритетность определялась путем расчета приведенного выброса с учетом фактора наклона канцерогенного потенциала при ингаляционном пути поступления. Динамика выбросов канцерогенов оценивалась по темпу прироста. Результаты. Исследование показало, что к приоритетным химическим канцерогенам, поступающим в атмосферный воздух муниципальных образований Рязанской области от стационарных источников, были отнесены: хром (Cr) (VI), углерод (сажа), бензол, бензин (нефтяной) и формальдегид. С 2009 по 2016 гг. регистрировалось сокращение суммарного приведенного выброса канцерогенов на 39,4%, особенно бензола, сажи и формальдегида, что привело к существенному изменению его структуры – значительному увеличению удельного веса Cr (VI) (до 55,7%, в 1,5 раза) и почти двукратном снижении доли бензола (до 23,3%). В указанные годы более 90% суммарного приведенного выброса канцерогенов в Рязанской области формировалось стационарными источниками городов Рязани и Скопина, Рязанского и Скопинского районов. Заключение. Для большинства муниципальных образований Рязанской области было характерно снижение суммарного приведенного выброса канцерогенов, кроме Александро-Невского, Милославского, Пронского, Захаровского и Шиловского районов, в которых, наоборот, отмечалось его увеличение. В г. Рязани на фоне выраженного снижения эмиссии сажи и бензола, соответственно на 81,7 и 69,4%, регистрировалось увеличение выброса в атмосферный воздух формальдегида на 37,4%.

Ключевые слова: атмосферный воздух; выбросы; стационарные источники; канцерогены.

COMPARATIVE CHARACTERISTICS OF EMISSIONS PRIORITY CARCINOGENS BY STATIONARY SOURCES INTO THE AIR ATMOSPHERE OF AREAS OF THE RYAZAN REGION

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Aim. Evaluation of dynamics of emission of priority carcinogens by stationary sources in the regions of the Ryazan region in 2009 and 2016. *Materials and Methods.* For analysis, official statistical data about volumes of pollutants emitted by stationary sources into the atmospheric air, were used. The priority was determined by calculation of equivalent emission with taking into account the slope factor of carcinogenic potential in inhalation entry (SFi). The dynamics of emissions of carcinogens was evaluated by the growth rate. *Results.* The study showed that priority



chemical carcinogens released into the atmospheric air of municipal units by stationary sources included: chromium (Cr) (VI), carbon (soot), benzol, petrol and formaldehyde. From 2009 to 2016 a 39.4% decline in the total equivalent emission of carcinogens was reported, especially of benzol, soot and formaldehyde which considerably changed the structure of emission – a significant increase in the share of Cr (VI) (up to 55.7%, 1.5-fold) and almost twice reduction in the share of benzol (to 23.3%). In the reported years more than 90% of the total equivalent emission of carcinogens in the Ryazan district were formed by stationary sources of Ryazan and Skopin towns, of Ryazan and Skopin districts. *Conclusion*. In most municipal units of the Ryazan district a reduction of the total equivalent emission was noted except in Aleksandro-Nevsky, Miloslavskoye, Pronsk, Zakharovo and Shilovo districts where emission increased. In Ryazan, against the background significant reduction of emission of soot and benzol by 81.7 and 69.4%, respectively, a 37.4% increase in the emission of formaldehyde into the atmosphere was recorded.

Keywords: atmospheric air; emissions; stationary sources; carcinogens.

Atmospheric air is one of the most important environmental factors, the strongest anthropogenic effect on which is produced by industrial enterprises, thermal energy sector and transport [1,3,4]. According to Federal Information Fund of Social-Hygienic Monitoring (FIFSHM), the leading pollutants of the atmospheric air in our country in 2004-2008 were nitrogen dioxide, suspended material, carbon dioxide, sulfur dioxide and also such chemical carcinogens as formaldehyde, lead and its inorganic compounds, benzpyrene, Cr (VI) and phenol compounds of [2]. 50 Million people are exposed to their effect [5], therefore in evaluation of the real danger of carcinogenic pollution of the atmospheric air it is necessary to take into consideration compounds present in it, and also a probability for their combined action. The carcinogenic danger is highest for a part of the population living in the zone affected by emissions of carcinogenic substances from industrial enterprises [6]. Thus, according to Federal Service for Surveillance of Consumer Rights Protection and Human Wellbeing 3.2 million, or more than 2% of population of Russia, are living within the sanitary protection zones of industrial enterprises. There are data about a probable increase in oncological morbidity of the population living in close vicinity of the enterprises that contaminate the atmospheric air with chemical carcinogens [2,5].

Thus, a comparative evaluation of the structure of emissions of toxicants into the atmospheric air and their dynamics, taking into account carcinogenic potential, is an important step in elaboration of ecological safety measures.

Aim of work was evaluation of the dynamics of emission of the priority carcinogens in the regions of the Ryazan district.

Materials and Methods

To achieve the set aim, the following tasks have been solved:

• lists of priority chemical carcinogens contaminating air in the municipal units of the Ryazan district, were compiled;

• a comparative assessment of alterations in the structure of emissions of priority chemical carcinogens released by stationary sources into the atmospheric air of municipal units of the Ryazan district, was carried out;;

• a comparative assessment and ranking of regions of the Ryazan district for the dynamics of emissions of priority chemical carcinogens into the atmospheric air.

Data about emissions of carcinogens were taken from digests "Protection of the Atmospheric Air, Current Expenditures on Protection of the Environment and Ecological Payments" of Federal State Statistics Service for 2009 and 2016 [7,8]. The priority of carcinogens was determined by calculation of the equivalent emissions (the product of the value of a chemical carcinogen emis-

sion into the atmosphere and SFi – slope factor of a carcinogenic potential with inhalation entry) with their subsequent ranking [9]. The priority list included substances from the ranked list of carcinogens whose total contribution into the overall equivalent emission of carcinogens was 97%. Statistical processing was conducted using χ^2 and methods of correlation statistics.

Results and Discussion

The study showed that in 2016 the priority chemical carcinogens released into the atmospheric air in the Ryazan district by stationary sources included the following pollutants arranged in the order of decrease in their contribution to the overall emission: Cr (VI), carbon (soot), benzol, petrol and formaldehyde (Table 1).

Table 1

Substance	M _i , tons	SFi	M _i × SF _i , conventional tons	Structure of Equivalent Emission, %
Cr (VI)	0.413	42	17.346	58.4
Soot	377.14	0.0155	5.84567	19.7
Benzol	146.993	0.027	3.968811	13.4
Petrol	33.652	0.035	1.17782	4.0
Formaldehyde	10.467	0.046	0.481482	1.6
Total	97.1			

Priority Carcinogens Entering the Atmospheric Air of Municipal Units of Ryazan District with Emissions from Stationary Sources

Note: SFi – slope factor for carcinogenic potential in inhalation entry; Mi – emission (entry of pollutant into the atmosphere); $Mi \times SFi$ – equivalent emission (emission taking into account expressiveness of carcinogenic effect).

In 2009, the leading contributor to the total equivalent emission of carcinogens into the atmospheric air of the Ryazan district was benzol (44.2%) (Figure 1). The second leading pollutant was Cr (VI) with more than one third contribution, followed by soot, petrol and formaldehyde arranged in the order of decreasing contribution.

The 17-year period in the history of Russia was marked by considerable changes of industry, which brought about significant changes in the structure of the equivalent emission of carcinogens into the atmospheric air of the Ryazan district by the stationary sources. Thus, in 2016, contribution of Cr (VI) to the total equivalent emission of the stationary sources increased 1.5-fold as compared with 2009, and reached 55.7% which provided the leading position of this pollutant among other identified carcinogens in the Ryazan district. Besides, in the structure of emissions the share of benzol almost twice decreased, and the share of petrol increased, while the shares of soot and formaldehyde did not show any significant changes.

In Table 2 the dynamics of emissions of priority carcinogens in Ryazan district and in some of its municipal units is presented. The studies showed that within 8 years the total equivalent emission of carcinogens entering the atmospheric air of the Ryazan district, decreased 39.4%, and in 2016 made 16.9 conventional tons (conv. tons). With this, an expressed reduction of the entry of almost all priority carcinogens into the atmosphere was noted, especially of benzol (by 68.8%), soot and formaldehyde (by 47.6 and 43.0%, respectively).



Fig. 1. Structure of the total emission of carcinogens

In 2009 and 2016 the main contributors to the total equivalent emission of carcinogen entering the atmospheric air of the Ryazan district, were stationary sources of Ryazan city, with the share of 74.7 and 61.3% of emissions, respectively, although in this period the emission of carcinogens into the atmospheric air of the district center decreased 50.3% and was 10.4 conv. tons in 2016. Thus, reduction was mostly due to decrease in the emission of soot and benzol (by 81.7 and 69.4%, respectively). With this, entry of formaldehyde into the air decreased 37.4%, and its equivalent emission in 2016 made 0.24 conv. tons.

The studies showed that Skopin region ranks second in the value of consolidated equivalent emission of carcinogens into the atmosphere, although by the end of the considered period its volume decreased 19.9% and made 1.57 conv. tons. The detected reduction of emissions was mainly due to considerable reduction of entry of soot and benzol (by 97.9 and 99.7%, respectively), and to a complete stoppage of entry of formaldehyde into the atmospheric air.

In the period from 2009 to 2016 the total equivalent emission of carcinogens into the atmospheric air of Skopin town decreased 26.6% and made 0.94 conv. tons. or 5.5% of that in the Ryazan district in whole, mainly due to reduction of emissions of Cr (VI), benzol and formaldehyde despite some insignificant increase (by 12.3%) in the emission of petrol. In the territory of Ryazan region the equivalent emission of carcinogens increased 126.1% and amounted 2.42 conv. tons by 2016, and its contribution to the same parameter for Ryazan district rose from 3.8% to 14.2% due to a considerable increase of emissions of Cr (VI) – by 323.1%, petrol – by 96.3%, soot – by 72% and benzol – by 15.4%. To note, stationary sources of the four above mentioned municipal units gave not less than 90% of the total equivalent emission of carcinogens in the Ryazan district. The majority of the rest municipal units of the Ryazan district were characterized by reduction of the total equivalent emission of carcinogens with the most evident reduction rates recorded in Spassk, Rybnovo, Shatsk and Ryazhsk regions where they stayed within 87.9 - 82.3%.

Table 2

Regions and Towns	Total Equivalent Emission, conc. tons*		Structure of Total Equivalent Emission, %		Growth (Reduction)
	2009 year	2016 year	2009 year	2016 year	Rate, %
Ryazan	20.965	10.422	74.7	61.3	-50.3
Skopin region	1.961	1.571	7.0	9.2	-19.9
Skopin	1.275	0.936	4.5	5.5	-26.6
Ryazan region	1.069	2.417	3.8	14.2	126.1
Sasovo	0.831	0.296	3.0	1.7	-64.4
Kasimov	0.390	0.334	1.4	2.0	-14.4
Kasimov region	0.328	0.211	1.2	1.2	-35.5
Klepiki region	0.247	0.224	0.9	1.3	-9.5
Ryazhsk region	0.188	0.033	0.7	0.2	-82.3
Spassk region	0.184	0.022	0.7	0.1	-87.9
Rybnovo region	0.180	0.022	0.6	0.1	-87.7
Shilovo region	0.125	0.165	0.4	1.0	32.4
Mikhailov region	0.091	0.047	0.3	0.3	-48.0
Pronsk region	0.071	0.184	0.3	1.1	160.5
Shatsk region	0.059	0.009	0.2	0.1	-84.9
Chuchkovo region	0.053	0.027	0.2	0.2	-49.5
Korablino region	0.022	0.022	0.1	0.1	-0.4
Yermish region	0.007	0.013	0.02	0.1	91.9
Zakharovo region	0.006	0.013	0.02	0.1	111.1
Miloslavskoye region	0.004	0.014	0.01	0.1	249.4
Aleksandro-Nevsky region	0.002	0.009	0.01	0.1	328.2
Ryazan district, in total	28.057	16.991	100.0	100.0	-39.4
	$\chi^2 = 2.4$ πp	ои $p = 0.9; r_{xy} = 0.0$.982 при р <0.01		

Emissions of Priority Carcinogens in Ryazan District and its Municipal Units in 2009 and 2016

Note: * total equivalent $-\sum_{i=1}^{n} M_i \times SF_i$.

In Aleksandro-Nevsky, Miloslavskoye, Pronsk, Zakharovo and Shilovo regions increase in the total equivalent emission of carcinogens was noted, with the highest growth rate in Aleksandro-Nevsky(328.2%), and the lowest – in Shilovo region (32,4%).

Comparison of distribution of values of the total equivalent emissions of carcinogens in the municipal units of the Ryazan district by χ^2 criterion did not reveal any statistically significant differences (χ^2 =2.4 at p=0.9), which suggests the existence of a common tendency to reduction of emission of carcinogens to the atmospheric air characteristic of the Ryazan district. This suggestion is confirmed by the results of correlation analysis that showed a distinct direct relationship of the total equivalent emissions of carcinogens

Conclusion

Priority chemical carcinogens emitted into the atmospheric air of municipal units of Ryazan district by stationary sources included Cr (VI), carbon (soot), benzol, petrol and formaldehyde. Since 2009 to 2016 a reduction of the total equivalent emission of carcinogens by 39.4%, especially of benzol, soot and formaldehyde which led to a significant change in the emission structure - considerable increase in the share of Cr (VI) (up to 55,7%, 1.5 times) and almost twice reduction of the

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of the total equivalent emission of carcinogens in the Ryazan district was formed by stationary sources of Ryazan and Skopin towns, of Ryazan and Skopin regions.

The majority of municipal units were characterized by reduction of the total equivalent emission of carcinogens, while in Aleksandro-Nevsky, Miloslavskoye, Pronsk, Zakharovo and Shilovo regions its increase was noted. In Ryazan, against a marked reduction of emission of soot and benzol into the atmospheric air, by 81.7 and 69.4%, respectively, an increase in emission of formaldehyde by 37.4% was noted.

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