Formaldehyde content in atmospheric air of Saratov

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Abstract. The analysis and estimation of the sources of formaldehyde emissions into the atmospheric air in Saratov are presented. Average monthly, average annual and average long-term concentrations of formaldehyde are calculated. The dynamics of the content of formaldehyde in the atmospheric air of the city is characterized. Seasonal variability of formaldehyde emissions is shown. The spatial distribution of formaldehyde concentrations in the city is given.

1. Introduction
The quality of air is formed as a result of a complex interaction of natural and anthropogenic factors. The state of the air environment is a very important element of urban ecosystem and has a great influence on all aspects of economic and industrial activities of the city's inhabitants. Saratov as a large industrial center which especially needs a system of observations, assessment and forecast in monitoring the state of the environment. In terms of its industrial potential, Saratov belongs to the largest cities of Russia with a diversified industry, among which, first of all, are the oil refining, chemical and construction industries, enterprises for production and distribution of electricity, gas and water, transport and communications. At the enterprises of the electric power industry emissions are discarded into the atmosphere without purification. Enterprises are located mainly in the southern, north-western and north-eastern districts of the city. An important role in the formation of air pollution in the surface layer of the atmosphere is played by the exhaust gases of cars that pollute the atmosphere on the level of medium height of man and pose a greater danger to public health in comparison with emissions from industrial sources [1, 2].

Observations of atmospheric air in the Saratov region are carried out by the Saratov Center of Hydrometeorology and Environmental Monitoring every day (except on public holidays), with a frequency of six days a week, three times a day. The monitoring network for air pollution monitoring in Saratov includes six main posts. Wherein, measurements of formaldehyde concentrations are measured at all monitoring posts (MP’s) of the city. This allows territorially differentiating the results of measurements and conducting a spatiotemporal analysis. Pollution of atmospheric air is determined from the values of impurity concentrations. In this regard, the level of air pollution in Saratov is defined as high. The most common atmospheric pollutants are sulfur dioxide, nitrogen oxides, carbon monoxide, chlorine, formaldehyde, phenol, hydrogen sulphide, ammonia, benz (a) pyrene, dust. Formaldehyde has a significant impact on the pollution of the city atmosphere among other pollutants [3, 4].
2. The problem statement
Formaldehyde refers to small gas impurities; however, it is important in atmospheric chemistry and it is one of the main gas components-air pollutants in cities. It is also considered as priority dangerous compound.

Formaldehyde is classified as a toxic and dangerous substance of the 1st hazard class in accordance with Russian regulatory documents regulating the content of pollutants in the atmospheric air of populated areas, (until 2014 formaldehyde had 2nd class of danger). Formaldehyde hygienic standards in the atmospheric air are: TLV –one time maximum = 0.05 mg·(m$^3$)$^{-1}$, TLV - average daily = 0.01 mg·(m$^3$)$^{-1}$. It should be noted that from July 1, 2014 in Russia, the TLV value of formaldehyde and its hazard class have been changed. TLV -average daily changed from 0.003 mg·(m$^3$)$^{-1}$ to 0.01 mg·(m$^3$)$^{-1}$ (change No. 10 in 2.1.6.1338-03 "TLV of pollutants in the atmospheric air of populated areas", registered in the Russian Ministry of Justice in April 11, 2014 No. 31909 ) [4].

At elevated concentrations, formaldehyde has diverse toxic effect: irritates the mucous membranes of the upper respiratory tract, throat, eyes, causes queasiness and headache [5, 6]. In addition to general toxicity of this compound it can also be a carcinogen [7, 8].

In this regard, valuation of formaldehyde release into the environment is the most important condition for the development of a strategy for reducing air pollution in cities.

Incoming sources of formaldehyde into the atmosphere are varied. They can be divided into groups: industrial and other facilities that use formaldehyde in their activities; stationary burning of fuel and waste; mobile sources; Formaldehyde containing materials; city fires, landfill and industrial waste; natural sources [2, 9, 10].

The source of formaldehyde emissions from vehicles are automobile exhaust gases. The content of formaldehyde in exhaust gases is increased in comparison with stationary fuel combustion systems. This is due to the fact that unlike stationary fuel combustion systems, the combustion duration in internal combustion engine is limited to fractions of a second, and the cold walls of the engine chamber prevent the complete combustion of fuel, which leads to the releasing of products of incomplete combustion [2, 11, 12].

3. Results and discussion
The monitoring network for air pollution monitoring in Saratov includes six main posts. Wherein, measurements of formaldehyde concentrations are measured at all monitoring posts of the city. This allow to differentiate the results of measurements territorially and to conduct a spatiotemporal analysis [13].

The average concentration of formaldehyde in Saratov is 0.019 mg·(m$^3$)$^{-1}$ or 1.9TLV (according to Russian standards).

The change in formaldehyde concentration over the past five years is shown in table 1. Figure 1 it shows the dynamic change in average annual concentrations of formaldehyde.

### Table 1. Average monthly, average annual and Average long-term concentrations of formaldehyde in Saratov for the period 2011-2015.

| Year | Avg-ann | I | II | III | IV | V | VI | VII | VIII | IX | X | XI | XII |
|------|---------|---|----|-----|----|---|----|------|-------|----|---|----|------|
| 2011 | 0.015   | 0.015 | 0.017 | 0.017 | 0.020 | 0.021 | 0.025 | 0.023 | 0.016 | 0.018 | 0.016 | 0.013 | 0.015 |
| 2012 | 0.010   | 0.010 | 0.014 | 0.019 | 0.017 | 0.017 | 0.015 | 0.010 | 0.017 | 0.013 | 0.012 | 0.018 | 0.016 | 0.015 |
| 2013 | 0.015   | 0.015 | 0.018 | 0.020 | 0.021 | 0.021 | 0.023 | 0.024 | 0.028 | 0.024 | 0.021 | 0.019 | 0.019 | 0.021 |
| 2014 | 0.020   | 0.020 | 0.020 | 0.021 | 0.023 | 0.023 | 0.027 | 0.034 | 0.034 | 0.030 | 0.026 | 0.023 | 0.020 | 0.025 |
| 2015 | 0.020   | 0.020 | 0.020 | 0.020 | 0.021 | 0.023 | 0.027 | 0.028 | 0.023 | 0.026 | 0.016 | 0.019 | 0.014 | 0.011 | 0.009 | 0.018 |
| **Average** | **0.015** | **0.015** | **0.017** | **0.017** | **0.020** | **0.021** | **0.025** | **0.023** | **0.020** | **0.019** | **0.017** | **0.015** | **0.019** |
The highest concentrations of formaldehyde were observed in 2014. The average annual value was 2.5TLV (according to Russian standards). The maximum values were recorded in July and amounted to 3.4TLV (according to Russian standards). The minimum was in 2012. The average annual concentration value is 1.5TLV (according to Russian standards).

During annual course (figure 2) it is possible to note an increase in the concentrations of formaldehyde from winter to summer (from July to a maximum of 2.5TLV) and the reduction from summer to winter (with a minimum January, February and December 1.5TLV).

Figure 1. Dynamics of changes in average annual concentrations of formaldehyde.

Figure 2. Dynamics of changes in the average monthly concentration of formaldehyde in Saratov.
According to figure 3, in the seasonal course, there is an obvious increase in formaldehyde concentrations in summer (average 2.3 TLV). The lowest concentration of formaldehyde in the seasonal course is observed in winter. Spring and fall concentrations of formaldehyde range almost on the same level 0.018-0.019 mg·(m\(^3\))\(^{-1}\).

Formaldehyde is a pollutant which concentration values most often exceed daily average threshold limit value.

Analysis of complex air pollution index (API) (table 2) for the last five years has shown that there is a tendency to reduce pollution levels. In 2015 the API decreased almost 2 times in comparison with 2013, but this is largely due not to a decrease in the amount of emissions, but due to law changes in 2014 for threshold limit values for formaldehyde.

![Seasonal dynamics of the concentration of formaldehyde in Saratov.](image)

Figure 3. Seasonal dynamics of the concentration of formaldehyde in Saratov.

| Year | 2011 | 2012 | 2013 | 2014 | 2015 | Avg. annual |
|------|------|------|------|------|------|-------------|
| API  | 11.03| 11.29| 16.39| 13.89| 6.15 | 11.75       |
| Level| high | high | very high | high | increased | high         |

In this way, the analysis of the structure of pollutant emissions has shown that formaldehyde contributes significantly to the formation of high API values. This ratio is maintained for MP’s located near highways, and for MP’s located inside the residential zone (figure 4).

The most polluted by this impurity is atmospheric air near MP-8, which is located near a highway with intensive traffic. The average annual impurity concentration here was 2.1 TLV. Also quite high values are observed at the point MP-6 (2.01 TLV), which is located near the JSC “Saratovstrosteklo” plant, which is the source of formaldehyde emission. The high value of the concentration on MP-6 is determined by the proximity of the highway, so the main source of formaldehyde here, as well as on MP-8 are vehicles.

The table 3 shows some statistical characteristics of the formaldehyde concentration during the study period: mean monthly (\(q\)), standard deviation (\(\sigma\)), standard deviation error (\(\sigma_{e}\)), confidence interval of average concentrations (\(l_{0.95}(q)\)). The calculated statistical characteristics for formaldehyde have a small variability. The error standard deviation is only about 0.001, i.e. 0.1%.
Figure 4 - Concentration of formaldehyde on various MP’s of Saratov.

Table 3. The statistical characteristics of the formaldehyde concentration during the study period.

| Parameter | Season | Year |
|-----------|--------|------|
| $q$, mg·(m$^3$)$^{-1}$ | winter | 0.015 | 0.019 |
| $\sigma$ | spring | 0.004 | 0.005 |
| $\sigma_\sigma$ | summer | 0.008 | 0.006 |
| $I_{0.05}(q)$ | autumn | 0.001 | 0.005 |
|           | Year   | 0.001 | 0.001

4. Conclusions
From the analysis of the formaldehyde content in the atmosphere of Saratov following conclusions can be drawn:
- Formaldehyde makes a significant contribution to the pollution of the atmosphere of the city;
- Sources of formaldehyde are both emissions from industrial facilities and vehicles;
- The amount of formaldehyde is seasonal;
- Formaldehyde concentrations often exceed the TLV;
- A high level of formaldehyde can adversely affect the health of the city's population.
- The calculated statistical characteristics for formaldehyde have a small variability. The error standard deviation is only about 0.001, i.e. 0.1%.

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