General Trends in the Environmental State of the Atmosphere of the Industrial Territory of the Nizhny Novgorod Region and the Sanitary Protection Zone of Nizhny Novgorod's City-Forming Enterprise

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Received: 13/06/2020   Accepted: 21/09/2020   Published: 20/12/2020

Abstract
The paper presents the trends in atmospheric pollution of the Balahna agglomeration (Nizhny Novgorod region, Russia), identified based on the ecological and chemical analysis of snow masses accumulated in 2019 and 2020, and also describes some features of the pollution of snow accumulated in 2020 in the protective zone of one of the city-forming enterprises of Nizhny Novgorod. Within Balahna-Pravdinsk, the presence of chlorides, sulfates, and hydrocarbonates in the snow waters was revealed, which may indicate the presence of corresponding ecotoxicants in the gas and dust emissions of the enterprise. Within Nizhny Novgorod, the presence of increased concentrations of ammonia, as well as the presence of nitrogen oxides and dust-like pollution in the atmosphere of an industrial area, was established.

Keywords: Atmospheric pollution level, Ecological analysis of snow, Snow as a deposition medium of ecotoxicants from the atmosphere, Gas and dust emissions, Sanitary protection zone

1 Introduction
In modern urban ecology, there are several environmental problems inherent in almost all urban areas of industrial development type, which most often consists of a spectrum of the same factors of impact on the environment. These include chronic dusting of the local atmosphere over cities and adjacent territories (in the case of agglomeration frameworks), pollution of surface water bodies due to the discharge of both normatively clean and untreated wastewater of industrial, household and storm origin, degradation of the soil cover due to excessive opening and reclamation territories and many other problems [1-6]. Industrial gas and dust emissions containing oxides of carbon, sulfur, and nitrogen, combining with atmospheric moisture, form carbonic, sulfuric, and nitric acids and, thereby, contribute to the acidification of precipitation. This leads to an increase in the general acidification of the atmosphere and its pollution by secondary pollutants. Since the problem of chronic air pollution often takes the form of increasing trends, in modern environmental monitoring, the dynamics of these negative processes are monitored not only by direct laboratory analysis of air masses but also based on the analysis of snow deposits in terms of acidity, the content of priority chemical substances and the presence of solid dusty suspensions [7-11]. Since the snow cover is a temporary depositing medium, for ecotoxicants, it can act as an object for monitoring atmospheric pollution, and its laboratory analysis allows establishing the composition of impurities in the air and tracking possible sources of emissions in the reviewed area [12-15].

The territory of the Balahna-Pravdinsk agglomeration, located in the Nizhny Novgorod region (Russia), is characterized by the presence of pulp and paper (Volga JSC), motor transport (PKF Luidor LLC, RusKomTrans LLC), electrical and electronic (NPO Pravdinskii radiozavod JSC, Uzola LLC), chemical (Biaxplen LLC, Real-Invest Group of Companies), mining and processing (Balkum LLC – INESCO Company Group) and mixed (STP LLC) industries, which can potentially provide a certain impact on the local environment [1, 14, 16].

The industrial territory of Nizhny Novgorod is characterized by the presence of micro-districts that are quite contrasting in
terms of pollution, since in its urban planning it has many industrial centers, including those with various gas and dust emissions as waste. One of such industrial infrastructures of the city is GAZ OJSC, an automobile plant with a long-term successful history and a full-fledged production complex. However, like any city-forming enterprise, the plant in question is characterized by a chronic presence of gas and dust emissions into the atmosphere, which is known to make a certain contribution to the ecological state of the local atmosphere [12, 13, 17]. Our study aimed to assess the ecological state of the local atmosphere within the Balahna-Pravdinsk agglomeration (Nizhny Novgorod region) according to the level of pollution of snow masses accumulated in the zone of the potential impact of industrial territories, as well as to assess the ecological state and the level of pollution of snow cover accumulated at the sanitary protection zone of the city-forming enterprise of Nizhny Novgorod. The study of the snow cover was carried out in compliance with the requirements of regulatory and methodological documents.

2 Materials and methods

Tapping was carried out in mid-March 2019 and at the end of February 2020 in different districts of the cities of Balahna and Pravdinsk, as well as at the end of February 2020 from 7 points tied to the border of the sanitary protection zone of the GAZ OJSC located in the Avtozavodskaya district of Nizhny Novgorod.

Snow samples were taken manually using a plastic cylinder (ø = 10 cm, h = 20 cm) in opaque plastic bags. For tapping, visually clean and even areas of snow cover were selected; the area of each equaled 10 m². At one site, 5 spot samples were taken, which were subsequently mixed into 1 combined sample. In total, 10 combined samples were taken for each year of research on the territory of the Balahna agglomeration (Figure 1) and 8 combined samples on the territory of the sanitary protection zone of an industrial enterprise in Nizhny Novgorod, including 1 sample from the natural area (field) of the gully-ravine mesorelief near with Druzhba horticultural non-commercial association of citizens (SNT) located 1 km from the highway, taken as a conditional background object (Figure 2). The samples were delivered and analyzed at the Ecological-Analytical Laboratory for Monitoring and Environmental Protection at Minin University.
In the snow meltwater, acidity was determined by a potentiometric method using a MARK-903 pH meter-millivoltmeter according to RD 52.24.495-2005; the content of suspended particles – by a gravimetric method using Vibra HT224RCE analytical balance (Japan) according to GOST 18164-72 (filtration of 1 l of snow water); the content of ammonium and nitrate forms of nitrogen – by ion-selective ionometry using an Expert-001-3 (0.4) ion meter and ELIT-021 and ELIT-051 ion-selective electrodes according to GOST 4192-82; the content of hydrocarbonates – by acid-base titration with 0.1 M HCl solution using a titration device in accordance with GOST R 52407-2005; the content of chlorides – by argentometry with 0.48% solution of AgNO3 in accordance with GOST 4245-72; the content of sulfates – by iodometry with 0.05 M Na2S2O3 solution in accordance with GOST 4389-72 [18].

To determine the conditionally background ecological state of the snow cover in the area under study, the snow meltwater sampled from a field located in a ravine mesorelief near the Druzhba horticultural noncommercial association of citizens (SNT) of the Prioksky district of Nizhny Novgorod at the end of February 2020, was analyzed.

3 Results

The study of the acidification of atmospheric precipitation in the Balahna-Pravdinsky territory, estimated based on the acidity index of local snow masses, showed that, in general, they had a certain acid reaction in the weakly acidic interval. Almost all tapping points showed a downward trend in snow acidity by 2020, except for the sample from point 2 (industrial area).

Air pollution from dust components, estimated based on the particulate matter index, can be considered insignificant. For both years of study, the level of snow dusting turned out to be approximately the same depending on the tapping location: minimal at points 5 and 6, average at points 1, 2, 4, and 8, relatively increased at points 3, 7, 9, and 10, the location of which is confined either to industrial areas or the passage of highways. It should also be noted that in 2020 the dust content in the snow masses was consistently lower than in 2019.

Air pollution by ammonia and nitrogen oxides, estimated based on indicators of the content of ammonium cation and nitrate anion in snow water, turned out to be quite noticeable and especially concerning the ammonium cation. Thus, at points 1, 2, and 10 during the two years of the study, an excess of the level of permissible concentration for ammonia was observed, and in 2020 it was observed additionally at points 5 and 9. It seems that local enterprises are characterized by the presence of ammonia impurities in emissions. The level of ammonium concentration was higher during the snow accumulation period in 2020 almost at all tapping points, and for nitrate anion, it was higher at all tapping points. However, no trend in the territorial distribution of nitrates in the snow waters was revealed.

Regarding the acidity of the snow masses accumulated within the sanitary protection zone of the industrial enterprise in Nizhny Novgorod, it should be noted that they were not characterized by a scattered range of values or an underestimation of indicators. The hydrogen index of meltwater varied in the range of weak reactions and reactions close to neutral.

Table 1: The content of chemicals in the water of snow masses accumulated within the Balahna-Pravdinsky urban agglomeration

<table>
<thead>
<tr>
<th>Tapping point</th>
<th>Acidity (pH, pH units)</th>
<th>Weighted substances, g/l</th>
<th>Nitrate nitrogen (NO3–, mg/l)</th>
<th>Ammonium nitrogen (NH4+, mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.61</td>
<td>6.65</td>
<td>0.019</td>
<td>0.016</td>
</tr>
<tr>
<td>2</td>
<td>6.77</td>
<td>6.60</td>
<td>0.026</td>
<td>0.018</td>
</tr>
<tr>
<td>3</td>
<td>6.48</td>
<td>6.64</td>
<td>0.033</td>
<td>0.024</td>
</tr>
<tr>
<td>4</td>
<td>6.16</td>
<td>6.29</td>
<td>0.018</td>
<td>0.016</td>
</tr>
<tr>
<td>5</td>
<td>6.66</td>
<td>6.98</td>
<td>0.007</td>
<td>0.004</td>
</tr>
<tr>
<td>6</td>
<td>6.29</td>
<td>6.34</td>
<td>0.015</td>
<td>0.012</td>
</tr>
<tr>
<td>7</td>
<td>6.31</td>
<td>6.83</td>
<td>0.029</td>
<td>0.022</td>
</tr>
<tr>
<td>8</td>
<td>6.42</td>
<td>6.47</td>
<td>0.020</td>
<td>0.016</td>
</tr>
<tr>
<td>9</td>
<td>6.06</td>
<td>6.55</td>
<td>0.078</td>
<td>0.064</td>
</tr>
<tr>
<td>10</td>
<td>6.04</td>
<td>6.86</td>
<td>0.047</td>
<td>0.036</td>
</tr>
</tbody>
</table>

MPC* 6.5-8.5 – 45 1.9

* — normative values are taken for waters related to water bodies used for drinking water and amenities (GN 2.1.5.1315-03 "Maximum permissible concentrations (MPC) of chemicals in the water of water bodies used for drinking water and amenities")

Table 2: The content of chemicals in the water of snow masses accumulated within the sanitary protection zone of the Nizhny Novgorod industrial enterprise

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Snow tapping points</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>C*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspended solids, mg/l</td>
<td>0.0022</td>
<td>0.0138</td>
<td>0.0075</td>
<td>0.0010</td>
<td>0.0054</td>
<td>0.0100</td>
<td>0.0064</td>
<td>0.0060</td>
<td></td>
</tr>
<tr>
<td>HCO3–, mg/l</td>
<td>39.6</td>
<td>35.2</td>
<td>22.0</td>
<td>17.6</td>
<td>26.4</td>
<td>17.6</td>
<td>22.0</td>
<td>13.2</td>
<td></td>
</tr>
<tr>
<td>Cl–, mg/l</td>
<td>6.5</td>
<td>5.5</td>
<td>5.0</td>
<td>5.2</td>
<td>4.3</td>
<td>6.1</td>
<td>5.0</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>SO42–, mg/l</td>
<td>29</td>
<td>28</td>
<td>21</td>
<td>20</td>
<td>23</td>
<td>20</td>
<td>24</td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>

C* — control
The tapping and analysis of the sample at the control point showed a lower pH value in comparison with the samples from the study area (Table 2). The content of dust particles, in general, turned out to be at the minimum level and most tapping points, below the control level. An exception was shown by samples from points 2 and 6, where the detected dust accumulation was higher than the rest.

Atmospheric pollution with carbon oxides, estimated based on the indicator of the content of bicarbonate anion in the water of the snow, had some trends in the distribution: its highest concentrations were found in the snow accumulated in the western and northwestern directions, which could be due to with the wind pattern of the city territory. Air pollution with chlorine-containing substances, estimated based on the chloride anion content in snow samples, did not have clear distributions in the prevalent wind directions. However, as such, it attracts attention, since it is known that the background level of chlorine content in the atmosphere is quite low. A tendency in the accumulation of sulfates in the snow masses, which indicates the content of sulfur oxides in the atmospheric air, was observed in a similar way to the content of hydrocarbontes. There was also a certain tendency for the concentration of sulfate anions in the snow to increase from the northwestern and northern directions.

4 Discussion

Nizhny Novgorod and the adjacent territories of its agglomeration are considered one of the largest industrial centers in the Volga Federal District and Russia as a whole with a wide urbanization infrastructure and a high degree of air pollution from the operation of car engines. Besides, in the Nizhny Novgorod region, automobile production and machine tool engineering, as well as chemical, pharmaceutical, petrochemical, and other types of industry are actively developed. For these reasons, air pollution by many ecotoxicants within the city limits remains one of the main environmental problems of metropolitan cities [2, 13].

Although snow is not an ecologically standardized system as an object for assessing the state of the environment, many researchers point out its high importance in ecological studies of the environment. The reason for this is the many physical and chemical factors of snow formation, air transport of its masses, and pollution processes. Due to the natural processes of concentration of pollutants in snow, the content of pollutants in it is considered one of the significant criteria when assessing the ecological state of the atmosphere [7, 8, 9, 16]. Pollutants and aerosol particles accumulated in snow masses are practically not affected by chemical reactions, preserving their primary state, which is important when assessing pollutants entering the atmosphere. The high ability of the snow cover to adsorb pollutants and suspended matter makes it possible to consider the state of snow as a definite indicator in assessing the spatial distribution of industry-related pollution in the city air environment.

5 Conclusion

Thus, based on the study carried out, the meltwaters of the snow masses accumulated in the industrial zones of the Nizhny Novgorod region were characterized by a significant presence of suspended impurities, sulfates, chlorides, ammonium, and nitrate forms of nitrogen and hydrocarbontes. It should be emphasized that environmental studies of snow deposits from industrial areas, on the one hand, allow us to identify trends in the level of pollution of the local atmosphere. On the other hand, to confirm these findings and acquire a full understanding of the quality and ecological state of atmospheric air, annual long-term research on the indicator dynamics is required.

Ethical issue

Authors are aware of, and comply with, best practice in publication ethics specifically with regard to authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests and compliance with policies on research ethics. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language.

Competing interests

The authors declare that there is no conflict of interest that would prejudice the impartiality of this scientific work.

Authors’ contribution

All authors contributed to data collection, study design, data analysis, interpretation, and writing of this article.

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