Effect of atmospheric air pollution on local nitrogen cycles in the urban forest ecosystem

O V Bednova¹, V A Kuznetsov²

¹Bauman Moscow State Technical University, 2-nd Baumanskaya street 5, Moscow 105005, Russian Federation
²D.Mendeleev University of Chemical Technology of Russia, 9 Miuusskaya square Moscow 125047, Russian Federation

*Corresponding email: bednova@mgul.ac.ru;

Abstract. In this study, it was shown that in the urban forests bordering highways local disturbances of the nitrogen cycle are observed. In some plots of such forests, zones with a high concentration of nitrogen dioxide may be formed. The mechanisms of this phenomenon were investigated. Using the method of passive dosimetry, nitrogen dioxide absorption rate was estimated at control points in the subcrown space. In the summer period, the light points and the temperature on the soil surface and at a height of 2 m were measured at the control points. It is shown that the formation of internal local zones with a high concentration of nitrogen dioxide in urban forests is regular: surface temperature inversions impede the vertical movement of air, and a decrease in illumination by forest subsurface in comparison with open areas reduces the rate of decomposition of nitrogen dioxide. The influence of these abiotic factors is ambiguous against the background of the transformation of the forest ecosystem during recreational impacts.

1. Introduction

Significant releases of nitrogen compounds into the environment, associated with anthropogenic activities, have become a factor in the disruption of biogeochemical cycles, both locally and globally [1, 2]. One of the main reasons for the change in nitrogen cycles is increasing the technogenic emission of nitrogen oxides into the atmosphere, associated with the burning of fossil fuels, and their subsequent removal from atmospheric air in the processes of dry and wet deposition.

Nitrogen oxides are priority pollutants, first of all, in the conditions of modern large urban agglomerations with their rich transport system. Nitrogen compounds enter the atmosphere of cities mainly in the form of nitric oxide NO, which in the urban air is rapidly oxidized by ozone or free radicals and is converted into nitrogen dioxide – NO₂. This gas is more reactive, more toxic, with greater speed removed from the atmosphere in the processes of wet and dry deposition than NO. The interaction of nitrogen oxides with atmospheric moisture leads to the formation of nitric and nitrous acids. Nitrogen dioxide under the action of visible radiation can decompose, with the formation of nitric oxide again and, causing the formation of toxic ozone in the surface air layer, of atomic oxygen. With a decrease in illumination, the rate of decomposition of nitrogen dioxide decreases, and at night the proportion of nitrogen oxides in the air increases NO₂ [3]. Due to such photochemical features, nitrogen dioxide is often considered as a marker of pollution by nitrogen compounds, and on
the basis of its concentration, conclusions are drawn about the degree of danger of urban air pollution [4].

It is generally accepted that the city’s green infrastructure (and, especially, urban forests) is the main means of improving urban air quality. Derived from the ecological function of green space is their recreational attractiveness. In the case of urban forests, environmental protection is added to the beneficial environmental and recreational functions: forest ecosystems in urban areas are the guardians of regional biodiversity. It is logical that assigning the status of specially protected natural areas to urban forests becomes an increasingly popular measure [5]. Measuring and assessing the success of environmental protection, environmental protection, recreational functions (and, at the same time, the effectiveness of relevant management decisions) of urban forests can be based on indicators of biological communities in combination with results of the monitoring abiotic media, i.e. complex ecological monitoring. This approach allows a better understanding of the relationship between ecosystem processes in the anthropogenic transformation of the nature [6, 7]. In particular, it is necessary to study the "fate" of man-made nitrogen in urban forest ecosystems.

Thus, in recent decades, the phenomenon of eutrophication of forest ecosystems due to man-made nitrogen enrichment has been widely discussed. The changes in forest conditions that are developing at the same time can affect forest biodiversity at all levels of its organization. Forest biocenoses adapt to changes in the nitrogen status of soils by means of species rearrangements. Thus, the positions of plant species that are more demanding (nitrophytes) or eutrophic with respect to soil nitrogen [8-10] gradually begin to grow, corresponding trends are also observed in the species diversity of epiphytic lichens [11, 12], forest invertebrate herbivores [13, 14]. The researchers pay great attention to microbial transformation of nitrogen compounds in the soil [15]. But the question of what happens in the air under the forest canopy due to man-made nitrogen compounds has been little studied.

It was theoretically predicted [16] and it was experimentally shown that under conditions of a forest area bordering or completely surrounded by roads, the accumulation of harmful impurities, and, above all, nitrogen oxides, is possible in separate local areas within the territory. In particular, in 2015 we obtained a picture of the distribution of nitrogen oxides concentrations (in terms of NO2) in the subcrown space of the urban forest in the summer period [9]. In the surveyed area in the depths of the forest, zones were found in which the content of nitrogen dioxide practically corresponded to its content in the air along the roadway: on average, it reached 80.6 ± 8.6 \( \mu \text{g/m}^3 \). These concentrations of nitrogen oxides exceed the sanitary and hygienic standards (40 \( \mu \text{g/m}^3 \) [4]), and, therefore, we can talk about a decrease in the efficiency of recreational functions of the forest, which are extremely important in a large city, especially in summer. Need to mark that it is with respect to nitrogen oxides and other researchers have noted a rather low protective effect of urban forests [17, 18].

As the spatial pattern of the distribution of the NO2 concentration (average over the exposure period) indicates, the zone of localization of pollution is confined to the part of the territory characterized by increased recreational disturbance (Figure 1). Under conditions of weakened wind conditions inside the forest, such zones themselves are capable of becoming sources of pollution. But does the specificity of the planting structure matter in this case?

Thus, in the picture of the migration and transformation of nitrogen compounds in the surface air layer of a typical urban forest, located in the zone of influence of motor vehicle pollution, in addition to the horizontal movement of polluted air, two more processes can be significant. First, under certain conditions, surface temperature inversions are observed under the forest canopy [19]. They prevent the exchange of ground-level air with higher layers of the atmosphere, as a result of which the process of vertical movement of air masses stops. Secondly, a decrease in the illumination under the forest canopy in comparison with the open area can lead to a decrease in the rate of decomposition of nitrogen dioxide, and then its share in the composition of forest air will increase [3].
The purpose of these studies was to continue to study the effect of anthropogenic inputs of nitrogen compounds into the air of a typical urban forest on local nitrogen cycles. In particular, the effect of temperature and illumination on the content of nitrogen dioxide in the air of the sub-area forest space was studied.

2. Materials and Methods

The studies were carried out on the spruce forest of the Kuntsevo Dacha –forest in the western part of Moscow. It is the most closely located to the city center part of the forest, it is almost completely surrounded by highways and streets with heavy traffic. There are many coniferous trees in the composition of forest stands, which are known to be the most sensitive to atmospheric pollution. On the territory of the forest, accessible for recreation, 32 points of temporary and permanent monitoring were organized.

The state of the atmospheric air was investigated by the method of passive dosimetry according to the way developed at the Mendeleev University. This method is based on the spontaneous penetration of the analyte to the surface of the sorbent in the process of molecular diffusion [20]. The flow of impurities deposited on the surface depends on their nature and concentration, meteorological conditions, type of surface. One of the features of the proposed method for determining air pollution is that the absorbing surface on top is protected by a water and airtight material. Therefore, gaseous impurities and fine aerosols subject to Brownian motion reach the absorbing surface only from the lower part of the absorber (Figure 2). After exposure, the samplers are transferred to the laboratory, the absorbed impurities are transferred into the solution, and the mass of the absorbed compounds is determined.

The ratio of the mass of absorbed impurities to the area of the absorbing surface and the exposure time allows us to determine the intensity of the process of dry deposition on a given artificial surface. This value characterizes the average for the exposure time the degree of air pollution at a given point of the surveyed area. The method of passive dosimetry allows to determine the air pollution in units of mass of absorbed impurities per unit surface of the absorber, per unit time:
where \( m_i \) is the arithmetic average value of the mass of impurity (mg) sorbed by scavengers at a given observation point during the exposure period; \( S \) is the surface area of the absorber; \( \tau \) is the exposure time.

### Figure 2. Airflow structure and impurity concentration profile under absorber

A filter paper impregnated with a sorbent solution is used as an absorber. The use of impregnation on an alkaline basis allows you to determine the intensity of absorption of impurities such as compounds of sulfur, nitrogen, fluorine, chlorine.

In this study, the samples were placed at the control points on the branches of trees located both in the forest edge zone and in the inner space of the forest, and expose for 25-30 days. At the places where absorbers are placed, periodically (from 3 to 5 times during exposure) from 11 to 13 o'clock in the cloudless weather, measurements of illumination and temperature at ground level and at a height of 2 m were carried out. Illuminance was measured for control in open areas.

### 3. Results and Discussion

As shown by our research, the average values of nitrogen dioxide absorption rate, and, consequently, its content in the air varied due to the distance from the outer boundary of the forest (Table 1). In the summer and autumn periods, an increase in the nitrogen dioxide absorption rate in certain internal zones of the territory was observed, which, in our opinion, is primarily due to the seasonal specificity of surface air transfer under the forest canopy and changes in the forest vegetation.

Table 2 shows the results of measuring the values of abiotic parameters – temperature and illumination under the forest canopy during the daytime summer period. It is obvious that in most control points a negative temperature gradient was recorded, indicating the presence of temperature inversion. At the same time, the proportion of control points in which the temperature at a height of 2 m became higher than that on the surface of the earth increased with distance into the forest. At a distance of 10-25 meters from the forest border, it reached 71%. Further, when moving deeper into the forest, the number of control points with temperature inversion remained almost unchanged. This allows us to conclude that the conditions for the accumulation of impurities in the surface air layer are formed in most parts of the territory: temperature inversion prevents the movement of impurities in the vertical direction. It is necessary to pay attention to the decrease in the level of illumination under the canopy of trees, which within the forest has decreased in comparison with the edge of the forest zone (Table 2). Such a decrease in illumination, of course, leads to a decrease in the rate of photochemical transformation of nitrogen dioxide and, as a result, its share in the total content of nitrogen oxides increases. The nitrogen compounds absorption rate by the soil in the processes of wet and dry
precipitation also increases, since, as is known, the velocity of dry deposition of NO$_2$ is approximately ten times higher than that of NO, and it dissolves better in water [21].

**Table 1.** The dependence of nitrogen dioxide absorption rate due to the distance from the outer boundary of the forest.

| Distance from the forest boundary, m | Summer 2017 | Autumn 2017 | Winter 2018 |
|-------------------------------------|-------------|-------------|-------------|
| 0 – 10                              | (1.1±0.7) · 10$^{-2}$ | (9.0±2.0) · 10$^{-3}$ | (3.5±0.8) · 10$^{-2}$ |
| 25 - 50                             | (9.9±4.9) · 10$^{-3}$ | (13.0±3.0) · 10$^{-3}$ | (3.3±0.8) · 10$^{-2}$ |
| More than 50                        | (1.0±0.7) · 10$^{-2}$ | (8.9±2.1) · 10$^{-3}$ | (2.8±0.4) · 10$^{-2}$ |

**Table 2.** Changes in temperature and illumination under the canopy of the urban forest at the control points, the summer period of 2017.

| Distance from the forest boundary, m | Change in temperature | Change in illumination |
|-------------------------------------|-----------------------|-----------------------|
|                                     | The number of control points with temperature inversion, % | Average difference of temperature values at a height of 2 m, $°C$, | Part of control points with dimming, % | Average dimming under the forest canopy, lx |
| 0–10                                | 55                     | +0.12±0.04            | 40                    | 24±10            |
| 25–50                                | 71                     | +0.09±0.03            | 80                    | 46±12            |
| More than 50                        | 70                     | +0.14±0.03            | 73                    | 46±13            |

* Compared to the temperature on the soil surface for control points in which temperature inversion was observed.

The entry of additional nitrogen into the soil causes an increase in the migration of its compounds to adjacent environments — vegetation, groundwater, and air [2]. For example, in [22], using the example of the soil of coniferous forests, it was shown that there is a positive correlation between the deposition of technogenic nitrogen and the amount of NO emission from soils.

In the forest ecosystem at the beginning of the growing season, mineral nitrogen is usually “intercepted” by forest biota. In the case of increasing nitrate concentrations in the second half of the growing season, when forest vegetation needs less nitrogen nutrition, the formation of a “free pool” of mineral nitrogen can lead to its loss from the soil as a result of the development of denitrification processes or leaching of nitrates [2]. Of course, in the conditions of uninterrupted supply of technogenic nitrogen under the canopy of urban forests, such trends are intensifying. In addition, it is known that in the recreational forest, the denitrification intensity increases noticeably in areas with compacted soil due to trampling [23]. Thus, the inner zone of the studied urban forest (more than 50 m from the outer borders) is distinguished by a noticeable recreational disturbance (Figure 1). The average value of the nitrogen dioxide absorption rate, associated with its circulation in the surface layer of the air of this part of the territory in the summer-autumn period is comparable with the results obtained for the edge of the forest zone (Table 1). In part, this can be attributed to increased denitrification.

According to the data currently available, denitrification is carried out by a wide range of bacteria belonging to a wide variety of taxa, which along with complete - to molecular nitrogen (N$_2$) can also carry out incomplete reduction of nitrate - to dioxide (NO$_2$), oxide (NO) or nitrous oxide (N$_2$O) [24]. In urban forest conditions, due to the entry of technogenic nitrogen, another mechanism of the denitrification process, chemodenitrification, can occur: the release of gaseous nitrogen compounds from the soil in the form of NO without the participation of microorganisms.

It is important that under natural conditions, the concentration of NO$_2$ in the surface air layer
increases due to nitrogen dioxide emitted from the soil [25]. At the same time, in connection with the temperature inversion observed by the forest subsurface, as noted above, the reverse flow of nitrogen oxides to the soil increases and more nitrate and nitrite compounds are formed, which can accumulate in the soil layer. Additional anthropogenic inputs of nitrogen oxides intensify this process.

High NO exits from the soil are also often correlate with significant re-deposition of NO\textsubscript{2} on the surface of plants and soil, which is considered as a potentially important nutrient migration process [26, 27]. "Returnable" nitrogen, therefore, serves as an additional reason for increasing the nitrogen status of the ecosystem and increasing the abundance of nitrophilous species. And the exchange of NO\textsubscript{x} between the soil and the atmosphere is, therefore, the result of simultaneously occurring processes of production and consumption.

According to the results of phytomonitoring on the sites of continuous observation in the spruce forest of the Kuntsevo Dacha, carried out in 2005 and 2015, nitrophilous species dominate in the species diversity of the grass-shrub layer and there is a tendency to increase their abundance [9]. This is a confirmation of the high and stable nitrogen status of ecosystems and the adaptation of the phytocenosis to the technogenic nitrogen inputs into the soil at given levels of pollution. It should be emphasized that in this planting there are no obvious signs of damage to the stand, specific of the impact zones of large industrial sources of pollution, where the natural mechanism of self-purification and gas absorption by the forest is different [28].

4.Conclusions
Thus, in the conditions of the urban forest that is exposed to recreational effects and the flow of nitrogen oxides from motorways, objective conditions are created for disrupting the local biogeochemical nitrogen cycle. The natural consequences of this process are an increase in the nitrogen status of the forest ecosystem (eutrophication of soils, increased excretion of return nitrogen from the soil, increased participation in the phytocenosis of nitrophilous species) and the formation of zones with elevated concentrations of nitrogen dioxide in the air within the forest. The latter reduces the efficiency of the sanitary-hygienic functions of the forest ecosystem in urbanized conditions.

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