Analysis of Nitrogen Oxides Levels Measured in Turceni Area

GHEORGHE LAZAR[1], CAMELIA CAPATINA[2*], CLAUDIA MARIA SIMONESCU[3*]
[1] Environmental Protection Agency, 76 Unirii Str., 210152, Târgu-Jiu, Romania
[2] University „Constantin Brâncuşi" of Târgu-Jiu, Engineering Faculty, 3 Geneva Str., 210152, Târgu-Jiu, Romania
[3] "Politehnica" University of Bucharest, Faculty of Applied Chemistry and Materials Science, Department of Analytical Chemistry and Environmental Engineering, 1 – 7 Polizu Str., 011061, Bucharest, Romania

Nitrogen oxides emitted primarily from the burning of solid, liquid and gases in various industrial plants, residential heating, commercial and from road traffic have many negative effects to the environment and human health. Nitrogen oxides contribute to the aquatic ecosystems eutrophication and to the acidification of environmental components such as soil, and water with consequences to the terrestrial and aquatic ecosystems, buildings and monuments. NO_2 can be transported long distance and has an important role in atmospheric chemistry, including the formation of tropospheric ozone. Exposure to high concentrations of nitrogen dioxide causes inflammation of the lung, increasing risk of respiratory diseases and asthma. Thus, monitoring of NO, NO_2 and NO_x levels are very important for air quality assessment, and to take measures when a pollution episode has been found. Nitrogen oxides (NO, NO_2, and NO_x) have been monitored using an automatic station code GJ – 03 located to the northwest of Turceni Thermal Power Station. Values obtained were compared to the quality standards set by regulations. The hourly concentrations of NO_2 recorded during 2013 were below 200 μg/m³ – value representing the hourly limit value for human health protection. High levels of NO_2 in the area investigated were registered on July and October. The highest NO hourly concentration (190.61 μg/m³) was recorded on October, and the lowest NO hourly concentration (3.56 μg/m³) was recorded in spring and summer months. NO_x highest hourly concentration (396.04 μg/m³) was registered on October. Regarding a possible correlation between the concentrations of NOx and wind direction, it can not be made because the automatic station for monitoring air quality in the area is located to the northwest of Turceni Thermal Power Station, and wind direction from the station (SE to NW) in the months analyzed represented only 4.2 % of the time. Results regarding daily cycles of NO, NO_2 and NOx in the urban atmosphere have shown that their concentrations are strongly affected by traffic emissions, and photochemistry activity.

Keywords: NOx levels, nitrogen oxide in the atmosphere, nitrogen oxide monitoring, air pollution

The atmosphere is a dynamic system, even though at the first analysis it can be considered constant in composition. When we say a dynamic system we refer not only to the changes that occur between the atmosphere components, but also to the interactions with the hydrosphere and biosphere.

Air together with water has the largest contribution to the maintaining of Earth life. Without these two elements, life would not be possible.

Air pollution can be defined as increasing the concentration of one of the components naturally occurring in the atmosphere, or introducing naturally or artificially the new components, with negative effects on the environment, living organisms, but also on the materials. Sources of air pollution include natural phenomena, such as wildfires, volcano eruptions, and land dust are considered natural sources of air pollution. Human activities such as household combustions, transportation, industrial activities, smoking, combustion in power plants are the main anthropogenic air pollution sources.

Air pollution is of increasing global concern due to its negative impacts on the public health, climate and environment [1-7].

Carbon monoxide, ozone, sulfur dioxide, nitrogen oxides, ozone, lead, polyaromatic hydrocarbons, volatile organic compounds, and particulate matter are the major air pollutants.

NOx primarily comprise nitrogen dioxide (NO_2) and nitric oxide (NO) being emitted into the atmosphere by different sources such as industry, vehicles, energy production and distribution, non-road transport, agriculture, biogenic. It is well known that NOx plays the role of catalyst in the chain reactions for ozone production.

Of the total amount of nitrogen oxides emitted into the atmosphere, about 95 % is in the form of nitrogen monoxide (NO), and only 5% is in the form of nitrogen dioxide (NO_2).

Emitted into the atmosphere of nitrogen monoxide, in the presence of atmospheric oxygen and to the action of ultraviolet rays is transformed quite fast into nitrogen dioxide, which is very toxic. Under certain conditions, nitrogen dioxide is transformed in nitric acid with water.

From the quantities released into the atmosphere every day, about 60 % of nitrogen compounds come from vehicles. Nitrogen dioxide is the most important and most dangerous pollutant. Nitrogen dioxide reacts under the action of ultraviolet radiation and gives nitric oxide and oxygen atoms. A part of it combines with nitric oxide, nitrogen dioxide regenerating process which leads to the maintaining of nitrogen dioxide in the atmosphere. Other atomic oxygen combines with nitrogen dioxide giving peroxiacetilnitrate (PAN) , with particularly strong toxic effects.

Compared with sulfur dioxide, nitrogen oxides are absorbed by plants relatively difficult. Nitrogen dioxide penetrates faster than nitrogen monoxide in the leaves of nitrogen monoxide due to the fact that it is much more soluble. The effective dose of nitrogen oxides that plants receive and their effects are determined by the exposure

* email: camelia_capatina@yahoo.com; claudiamaria_simonescu@yahoo.com

Fig. 1.Setup of the automatic monitoring station GJ - 03 in Turceni area

rate of pollutant. After their penetration through the leaf, nitrogen oxides can act as additional fertilizer plant, but when they are in excess can cause toxicity and injury to the plant.

The one hour exposure of plants to a concentration of nitrogen dioxide about 25 μg/m^3 determines necrosis and leaf fall. The extent of photosynthesis inhibition is 80 % by air pollution by nitrogen dioxide, while perspiration inhibition occurs only in the proportion of 10%. There is a correlation between the degree of inhibition of photosynthesis and the concentration of NO_2, NO and NO_x in the atmosphere. For these two pollutants and mixtures of them, the degree of photosynthesis inhibition is different. Nitrogen monoxide acts much faster than nitrogen dioxide.

From the two constituents of NOx, NO_2 is the more important for air quality since it is more relevant for human health [8]. For animals and humans, the combination of nitrous oxide causes paralysis of the nervous system, and concentrations greater than 100 μg/m^3 cause death. NO_2 is a deep lung irritant causing bronchial neutrophilic infiltration, proinflammatory cytokine production, and responses to inhaled allergens in patients with asthma, both alone, and with sulfur dioxide [9-15]. The literature data revealed an association between NOx and respiratory infections [16, 17].

Strongly oxidizing character of oxides of nitrogen and nitric acid is the main cause of destruction by plastic materials, varnishes, paints used as protective materials of facilities and industrial buildings [18].

As with most industrial areas, Turceni is currently experiencing several episodes of air pollution.

Burning fuels is considered the main cause of emissions of air pollutants in this area as anthropogenic sources. In this respect, the main source of air pollution in the study area is Turceni Thermal Power Station. This is a principal Power Station of the National Power System being one of the largest in the world with a continuous operating mode.

Turceni Thermal Power Plant has 6 power units grouped into 4 large combustion plants (LCPs). The 4 large combustion plants (LCPs) of Turceni Power Station Plant are:

- LCP no. 1 consists of energy blocks no. 1 and 2, each with a heat output of 789MWth and are prompted to operate 20,000 hours during 2008 to 2015;
- LCP no. 2 consists of energy blocks no. 3 and 4, each with a heat input of 789MWth ;
- LCP no. 3 consists of energy blocks no. 5 and 6 (replaced by power unit no. 7 till the modernization of block no. 6) , each with a heat input of 789MWth;
- LCP no. 4 consists of block no. energy 7 with a heat output of 789MWth and notified to work 20.000 h in the period 2008-2015.

The flue gases are discharged into the atmosphere by four reinforced concrete chimneys, each connected to two steam boilers of 1035t/h (energy blocks no. 1 to the chimney no. 1, energy blocks no. 3 and 4 to the chimney no. 2, energy blocks no. 5 and 6 to the chimney no. 3, and the energy block no. 7 to the chimney no. 4).

Deposits of solid fuel (coal) were developed with the building of energy blocks being another important source of air pollution in the Turceni area.

Another important source of air pollution is the transport. Depending on the types of vehicles, in some cities emissions from cars represent between 60-90% of total emissions.

The most important pollutants due to the road traffic are particulate matter, sulfur dioxide, nitrogen oxides, lead, polyaromatic hydrocarbons, volatile organic compounds, asbestos, methane and others.

A special case is the diesel engine, producing significant quantities of sulfur dioxide (from the sulfur in diesel), nitrogen oxides (due to high temperature combustion), particles and unburned hydrocarbons (smoke).

An equally important source, especially in the cold season is the housework. Various fuels like wood, coal, oil and natural gas are burned for different household purposes. From their burning are resulting air pollutants, some of them being very toxic.

Observation site and instrumentation

The network of ambient air quality monitoring in the studied area includes one automatic station with codes GJ – 03 located to the northwest to Turceni power station (fig. 1).

Sulfur dioxide (SO_2), nitrogen oxides (NO, NO_2, and NO_x), carbon monoxide (CO), and particulate matter – PM_{10} fraction are monitored using this automatic station.

The data collected by automatic monitoring station are transmitted at an interval of one hour as an hourly average to the local central server located at the Environmental Protection Agency from Tg. Jiu, where, after the verification and validation, data are transmitted to the national center for certification, preparation of reports and public information.

Results and discussions

Concentrations of NO, NO_2, and NO_x registered at automatic stations during 2013 will be analyzed in order to establish the level of these pollutants in the air in Turceni area.The data mentioned in this study were collected from the Environmental Protection Agency Gorj.

Interpretation of the results obtained was done according to Law no. 104/2011 regarding ambient air quality [19, 20]. Under this law, the limit value for nitrogen dioxide, as an hourly average is 200μg/m^3, specifying that it has not been exceeded more than 18 times in a year. This value is mentioned in the air quality directive (2008/EC/50).

Parameter / Month	Data capture (%)	Hourly average concentration ($\mu g/m^3$) (minimum values)	Hourly average concentration ($\mu g/m^3$) (average values)	Hourly average concentration ($\mu g/m^3$) (maximum values)
January	84.6	8.97	23.17	70.29
February	95.3	5.87	19.05	67.41
March	85.0	6.04	15.61	73.51
April	93.3	5.01	12.82	57.51
May	75.0	9.07	21.13	80.61
June	91.3	6.53	15.42	90.24
July	95.5	5.55	14.33	103.47
August	95.1	7.71	19.93	81.81
September	95.8	7.68	15.66	75.18
October	95.8	8.34	19.58	103.78
November	94.8	7.14	18.43	65.75
December	94.2	7.85	25.54	70.87

Table 1
RESULTS REGARDING NO_2 MONITORING IN 2013 IN TURCENI AREA

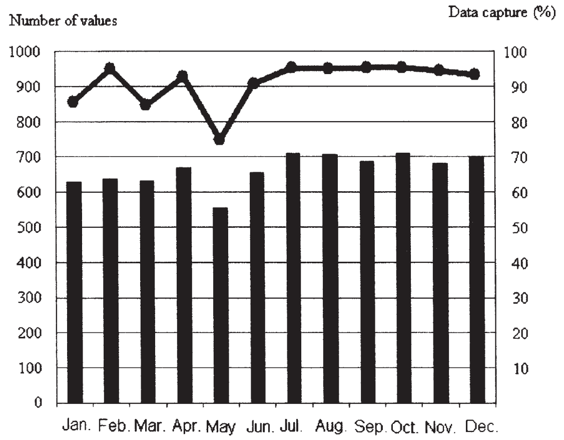

Fig. 2. Number of NO_2 hourly average values and data capture in 2013

Table 1 presents the hourly minimum average concentrations of nitrogen dioxide, average and maximum average concentrations of nitrogen dioxide calculated for each month separately, and the percentage of achieving these measurements related to the number of days corresponding to each month.

A first finding, and the most important from the point of view of environmental protection is that all hourly average values recorded during 2013, are lower than the value of 200$\mu g/m^3$ corresponding to the limit hourly value to protect human health.

In 2013, the number of hourly values for NO_2 levels represented 91.3% of the total hourly values to be achieved in a year.

Number of hourly average values achieved in each month is shown in Figure 2.

Analyzing these data it is seen that, except January, March and May, in the others months, the capture data were above 90%, most of which were registered in September and October, each with 95.8%.

Given the large volume of data (7998 hourly values each year, with an average of 666.5 average values per month) it will be a study based on minimum monthly average NO_2 concentrations, maximum monthly average NO_2 concentrations and monthly average concentrations NO_2. In this regard, the most representative month such as January, April, June, August, October and December will be taken into consideration during the period of study 2013, thus being represented and each season (season) of the year.

Thus, in January was recorded a capture data of 84.6%, and a number of hourly average concentrations of 630.

The lowest hourly average concentration of NO_2 was 8.97 $\mu g/m^3$ being recorded on 26.01.2013 at 3 pm, and the highest hourly average concentration of NO_2 was recorded on 22.01.2013, at 7 pm and was 70.29 $\mu g/m^3$.

Monthly average concentration of NO_2 in this period was 23.17 $\mu g/m^3$.

The lowest hourly average concentration of NO was 4.66 $\mu g/m^3$ being recorded on 26.01.2013 at 10 pm, and the highest hourly average concentration of NO was recorded on 23.01.2013, at 9 am being value of 54.81 $\mu g/m^3$.

Regarding NO_x level in January, it was observed that the highest hourly average concentration (145.88 $\mu g/m^3$) was registered on 22 January at 7 pm, and the lowest hourly average concentration (16.14 $\mu g/m^3$) was registered on 26 January at 7 am.

The highest wind speed was recorded at this time of the year. The average speed was 2.64 m/s, and the predominant direction was N-NW to S-SE (68% of the time), and in the rest of the time the predominant direction was from N -NE to S-SW.

In April, data capture was 93.3%, and the number of hourly values was 672 for NO_2 level. The lowest NO_2 hourly average concentration was 5.01 $\mu g/m^3$ being recorded on 29.04., at 14 pm, and the highest value was 57.51 $\mu g/m^3$ being measured on 10.04 at 6 pm.

During this month there was a monthly average of 12.82 $\mu g/m^3$ NO_2 concentration.

The highest hourly average concentration (26.57 $\mu g/m^3$) was registered on 22 April at 1 pm, and the lowest hourly average concentration (3.70 $\mu g/m^3$) was registered on 9 April at 4 am.

The lowest hourly average concentration of NO_x was 11.42 $\mu g/m^3$ being recorded on 14 April at 12 am, and the highest hourly average concentration of NO was recorded on 10 April, at 6 pm being value of 89.43 $\mu g/m^3$.

Average wind speed during this period was 2 m/s, with speeds in the first decade that exceeded the value of 3 m/s. In 53% of the time the wind has blown from the N-NE to S-SW, and the rest time from the N-NW to S-SE.

In June, data capture was 91.3%, and the number of hourly averages was 658 for NO_2 concentration. NO_2 monthly average concentration recorded was 15.42 $\mu g/m^3$.

During this period of the year, the lowest value of NO_2 hourly average concentration was 6.53 $\mu g/m^3$, and it was registered on 25.06, at 9 pm, and the maximum value of the average hourly concentration was 90.24 $\mu g/m^3$ being recorded on 23.06 at 2 pm.

The lowest value of NO hourly average concentration (4.26 $\mu g/m^3$) was registered on 29 June at 4 pm, and the highest value of NO hourly average concentration (43.31 $\mu g/m^3$) was recorded on 18 June at 8 am.

Regarding NO_x level, the measurements indicate that the highest value of NO_x hourly average concentration was 145.91 $\mu g/m^3$ being recorded on 23 June at 2 pm, and the lowest value of NO_x hourly average concentration was 13.61 μg/m^3 being recorded on 25 June at 9 pm.

The average wind speed was 1.56 m/s in June. In 60% of the time the wind direction was from NE to SW, and 40% from NW to SE.

For July, there was a 95.5% data capture, and a number of NO_2 hourly average concentration values of 711.

NO_2 hourly average concentration with the lowest value was recorded on 13.07, at 5 pm, and the value registered was 5.55 μg/m^3, and the highest value (103.47 μg/m^3) was recorded on 26.07., at 1 pm. This value was one of the biggest of the year.

NO_2 monthly average concentration for July was 14.33 μg/m^3.

The lowest value for NO hourly average concentration was registered on 13 July at 5 pm having a value of 4.09 μg/m^3, and the highest value (59.49 μg/m^3) was recorded on 28 July at 12 am.

In this month, it was registered the highest value for NO_x hourly average concentration (185.77 μg/m^3) on 28 July at 12 am, and the lowest value for NO_x hourly average concentration (11.83 μg/m^3) on 13 July at 5 pm.

The average wind speed was from N-NE to S-SW (61.3%), and in the rest of the time from the N-NW to S-SE.

In August, there was a 95.1% data capture, and a 708 number of NO_2 hourly average concentration.

The minimum value for NO_2 hourly average concentration was recorded on 31.08, at noon, and the value was 7.71μg/m^3. The maximum value for NO_2 hourly average concentration was 81.81 μg/m^3 being recorded on 19.08, at noon.

NO_2 monthly average concentration was 19.93 μg/m^3.

The measurements performed in August indicate that the lowest value for NO hourly average concentration (3.56 μg/m^3) was registered on 18 August at 6 pm, and the highest value for NO hourly average concentration (52.58 μg/m^3) was registered on 6 August at 11 am.

The highest value of NO_x hourly average concentration (148.78 μg/m^3) was recorded on 19 August at 12 am, and the lowest value of NO_x hourly average concentration (16.43 μg/m^3) was recorded on 3 August at 6 pm.

During this period the prevailing wind direction was from the N-NW to S-SE for 67.7% of the time, and for the remaining time from the N-NW to S-SE.

October was a month with the largest data capture (95.8%), and with the largest number of NO_2 hourly average concentration values of the year (713).

Also, in this period for NO_2 was registered the highest hourly average concentration in year (103.78 μg/m^3), on 20.10, at 1 pm. NO_2 minimum hourly average concentration of this period was recorded on 04.10, at 3 am, and the value of it was 8.34 μg/m^3.

NO_2 monthly average hourly concentrations of this period was 19.58 μg/m^3.

October was the month with the highest value for nitrogen oxide. Thus, for NO_x was recorded a value of 396.04 μg/m^3 on 20 October at 1 pm, and for NO was recorded a value of 190.61 μg/m^3 on 20 October at 1 pm. The lowest value registered for NO_x was 19.36 μg/m^3 on 18 October at 5 pm, and 5.33 μg/m^3 for NO registered on 19 October at 3 pm.

In this period the wind has blown from the N-NW to S-SV for 61.3% of the time, and for the rest from the N-NE to S-SW. Average wind speed was 1.96 m/s.

December was the time of the year when there were recorded the highest concentrations of NO_2. The value for the monthly average concentration recorded was 25.54 μg/m^3.

This month has been registered a high percent of data capture (94.2%), and a high number of NO_2 hourly average concentrations (701).

The lowest concentration of NO_2 in this period had a value of 7.85 μg/m^3, and it was registered on 10 December, at 1 pm, and the highest value was 70.87 μg/m^3, this value being recorded on of 13 December, at 6 pm.

The lowest hourly concentration of NO (5.49 μg/m^3) was registered on 8 December at 7 am, and the lowest hourly concentration of NO_x (16.87 μg/m^3) was registered on 8 December at 6 am. The highest hourly concentration of NO (99.83 μg/m^3) was registered on 22 December at 7 pm, and the lowest hourly concentration of NOx (206.99 μg/m^3) was registered on 13 December at 7 pm.

Average wind speed at this time of year recorded the lowest, 1.42 m/s, and for some days was less than 1 m/s.

Regarding the wind direction, it can not be specified the predominant direction because 30% of the time was from the SE and NW, 33.3% from NE to SW, 33.3% from NW to SE and 6.7% from SW to NE.

Another conclusion is that the highest concentrations of NO_2 were recorded during the cold season (January, February and December), the amount of monthly concentrations of this period accounting for almost one third of the annual average concentrations (fig. 3).

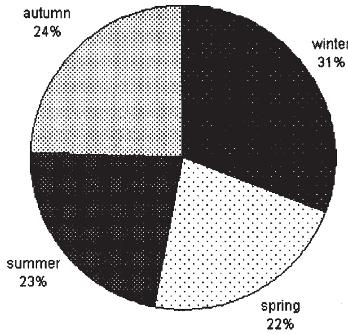

Fig. 3. Distribution of NO_2 monthly average concentrations by seasons

The autumn season was the second after the cold season regarding the value of NO_2 concentration. The lowest concentrations of NO_2 were recorded in the spring season.

Higher concentrations of NO_2 in winter can be attributed to the fact that, during this period, an important contribution to the nitrogen oxides emissions have the fuel consumption for heat production and road traffic. It is acknowledged that, in urban areas, the greatest contribution to the production of nitrogen oxides has cars and vehicle traffic.

It can not be made a correlation between hourly average concentrations and some meteorological parameters such as wind direction and speed due to the fact that the air quality monitoring station is located in the northwest of Turceni Thermal Power Station, and the predominant wind direction (over 70 %) was almost the reverse, from N-NW to S-SE and N-NE to S-SW.

In figure 4 it can be observed that in most of the time (over 70 %) wind direction was from the N-NW to S-SE, and N-NE to S-SW, and NE to SW.

In this respect, the time of year with several changes of wind direction was December.

The highest concentrations of nitrogen dioxide were recorded in December when the wind speed was lower. However, in December were recorded the most frequent wind direction changes, and we can not speak about a predominant direction.

During an ordinary day in the city, the ambient nitrogen oxides follow a regular pattern related to the sunlight intensity and traffic. The daily mean of NO, NO_2, and NO_x of four days characteristics for all seasons were chosen to determine the pattern of nitrogen oxide variation in a

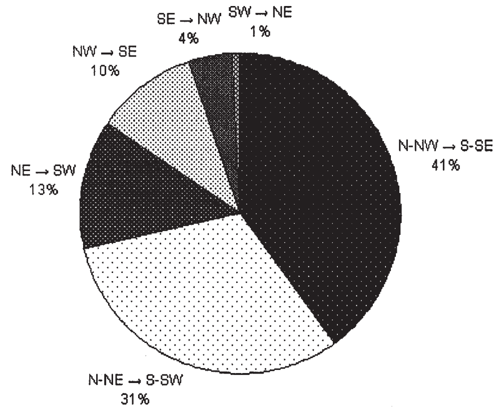

Fig. 4. Distribution of wind direction in Turceni area

day.The variation of the daily mean NO, NO_2, and NO_x is presented in the following figures.

From the figures 5-8 it can be seen that before brightening the day, concentrations of nitrogen monoxide and nitrogen dioxide are stable. With increasing the human activities, between 6-9 am nitrogen dioxide concentrations increase due to traffic. As sunlight intensifies providing UV radiation, nitrogen dioxide concentration increases due to the conversion of nitrogen monoxide into nitrogen dioxide. As a result, the concentration of nitrogen monoxide reduces and begins to accumulate the ozone in the air layer. This trend can be observed more strongly in the time period 11 am – 4 pm for summer and autumn days (figs. 6, 7). Towards evening, when the sunlight intensity begins to decrease and automobile traffic increases, the concentration of nitrogen monoxide begins to increase again (figs. 5-8). The solar energy can not convert nitric oxide to nitrogen dioxide.

Regarding the maximum hourly average concentrations, it appears that they were made between certain time intervals, which vary depending on the season.

The maximum hourly average concentrations in winter were recorded in the time interval 8 to 10 am, in the spring season between 4 to 7 pm, in the summer season between 11 am and 3 pm, and in the autumn season between 12 to 4 pm.

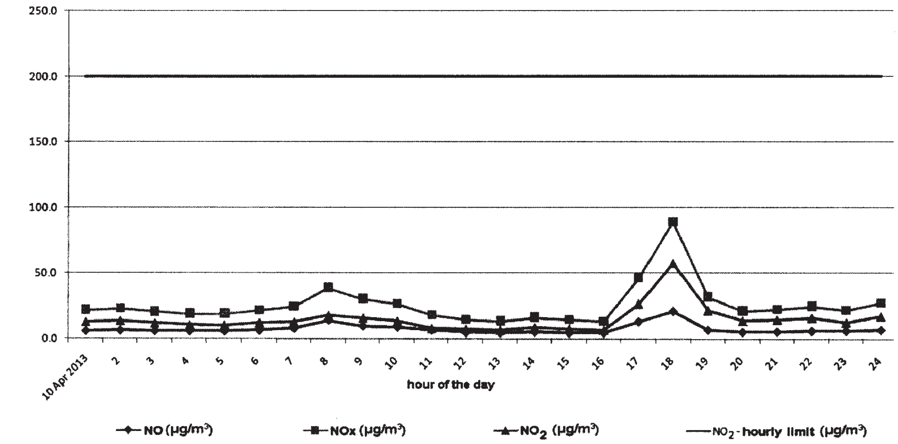

Fig. 5. Daily evolution of NO, NO_2, NOx at GJ-03 Station recorded on 10 April

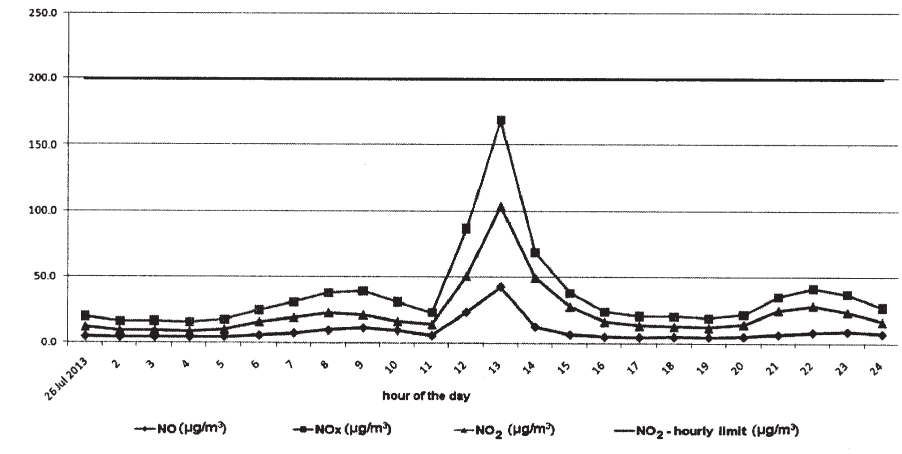

Fig. 6. Daily evolution of NO, NO_2, NOx at GJ-03 Station recorded on 26 July

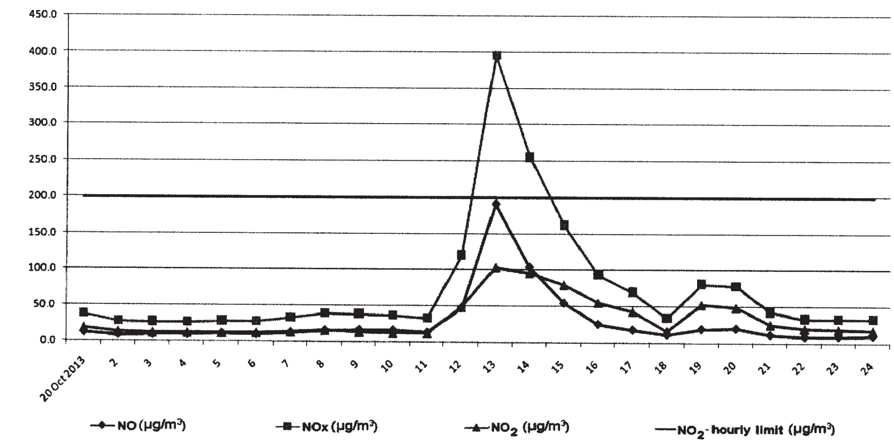

Fig. 7. Daily evolution of NO, NO_2, NOx at GJ-03 Station recorded on 20 October

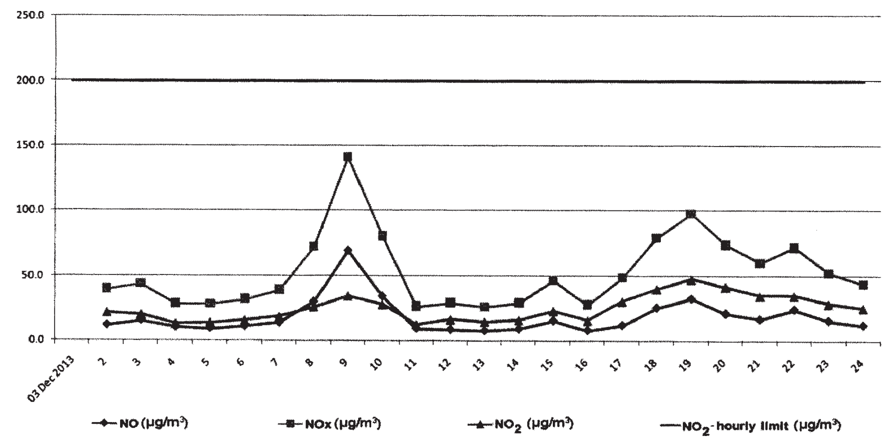

Fig. 8. Daily evolution of NO, NO_2, NOx at GJ-03 Station recorded on 3 December

Conclusions

On the basis of ambient air pollution on Turceni area with nitrogen oxides, the following conclusions can be drawn.

Nitrogen monoxide and nitrogen dioxide are the main pollutants in the lower layers of the atmosphere.

The main sources of air pollution are burning fossil fuels for power generation, road transport and residential heating. In urban areas road transport is the main source of nitrogen oxide.

Nitrogen oxide content was determined based on data provided by an automatic air quality monitoring for assessing the current situation of air quality in Turceni.

Percentage of achieving NOx measurements (data capture) in the year 2013 was 91.3%.

All the hourly concentrations of NO_2 recorded during 2013 were below the level of 200 μg/m^3, corresponding hourly limit value for human health protection.

Highest NO_2 hourly average concentrations were recorded in July (103.47 μg/m^3) and October (103.78μg/m^3) . Their values were less than half the – limit. The lowest hourly average concentrations were recorded in April and July. Their values were approximately 2.5% of limit value.

The results indicate that the increasing NO_2 level can be mainly attributable to increased secondary formation of NO_2 through photochemical reactions in the atmosphere.

NO concentration depends on the human activity. The highest concentrations of nitrogen monoxide in the air of the Turceni were recorded in October (190 μg/m^3), and December (99.83 μg/m^3). This can be due to the burning of fossil fuels for domestic heating.

NOx levels are high in autumn and winter months. The highest value of NO_x level was registered on October (396.04 μg/m^3), and the lowest level was registered on April (89.43 μg/m^3).

Daily cycles of NO, NO_2 and NO_x in the urban atmosphere are strongly affected by traffic emissions, and photochemistry activity.

Thus, in the early morning, the NO concentration is low, and it rises and reaches a peak during the rush hours, when the human activities and traffic emissions are also elevated.

Percentage of hourly average concentrations of nitrogen dioxide related to the season was the highest in the winter season, when the monthly average accounted for almost one third of the annual monthly average.

Control of emissions of nitrogen oxides discharged from thermal coal stations can be performed by modifying the combustion process and residual gas cleaning.

References

1.NISULESCU, Ghe. C., IONEL, I., MALAN, B., DOBRIN, M., Rev. Chim. (Bucharest), **63**, no. 9, 2012, p. 940

2.PERJU, D., PÎRLEA, G.-A., BRUSTUREAN, G.-A., SILAGHI-PERJU, D., MARINESCU, S., Rev. Chim. (Bucharest), **59**, no. 10, 2008, p. 1112

3.VUJIC, B., PAVLOVIC, A., VUJIC, G., JEVTIC, D., Rev. Chim. (Bucharest), **61**, no. 10, 2010, p. 991

4.BUTU, I.M., BUTU, M., CONSTANTINESCU, I., MACOVEI, S., Rev. Chim. (Bucharest), **63**, no. 3, 2012, p. 330

5.STROE, C.-C., PANAITESCU, V.N., RAGAZZI, M., RADA, E.C., Rev. Chim. (Bucharest), **65**, no. 2, 2014, p. 152

6.CĂPĂŢÎNĂ, C., SIMONESCU, C.M., Rev. Chim. (Bucharest) **64**, no. 12, 2013, p. 1471

7.CĂPĂŢÎNĂ, C., SIMONESCU, C.M., Rev. Chim. (Bucharest) **63** no. 12, 2012, p. 1289

8.MAVROIDIS, I., CHALOULAKOU, A., Atmospheric Environment **45**, 2011, p. 6872

9.SOLOMON, C., CHRISTIAN, D., CHEN, L., WELCH, B., KLEINMAN, M., DUNHAM, E., et al., Eur Respir J **15**, 2000, p. 922

10.GHOSH, R., JOAD, J., BENES, I., DOSTAL, M., SRAM, R.J., HERTZ-PICCIOTTO, I., Environment International **39**, 2012, p. 96

11.DELFINO, R.J., STAIMER, N., GILLEN, D., TJOA, T., SIOUTAS, C., FUNG, K., et al., Environ Health Perspect **114**, 2006, p. 1736

12.EVERARD, M.L., Curr Opin Allergy Clin Immunol. **6,** 2006, p. 56

13.KIM, K.-H., JAHAN, S.A., ., Environment International **59**, 2013, p. 41

14.AKAIKE, T., MAEDA, H., Immunology **101**, 2000, p. 300

15.KIM, K-H., JAHAN, S.A., KABIR, E., Environment International **59**, 2013, p. 41

16.GHOSH, R., JESSE JOAD, J., BENES, I., DOSTAL, M., SRAM, R.J., HERTZ-PICCIOTTO, I., Environment International **39**, 2012, p. 96

17.LIU, C., FLEXEDERA, C., FUERTES, E., CYRYSD, J., BAUER,C.-P., KOLETZKO, S., HOFFMANN, B., VON BERGH, A., HEINRICHA, J., International Journal of Hygiene and Environmental Health **217**, 2014, p. 483

18.CRACIUNESCU, O., TARDEI, C., MOLDOVAN, L., ZARNESCU, O., Cent. Eur. J. Biol. **6**(3), 2011, p. 301

19.*** HG nr. 440/2010 privind stabilirea unor măsuri pentru limitarea emisiilor în aer ale anumitor poluanţi proveniţi de la instalaţiile mari de ardere

20.*** Legea nr. 104/20111 privind calitatea aerului înconjurător

Manuscript received: 25.04.2014