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Original Article

Study on Structure of Nitrogen Oxides Released by Traffic Emissions in Cluj-Napoca Municipality

OROIAN Ioan Gh.*

University of Agricultural Sciences and Veterinary Medicine Cluj - Napoca, Mănăştur St., No. 3 - 5, 400372 Cluj-Napoca, Romania

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Abstract

Urban areas with heavy traffic are subject to many harmful air pollutants, and among them one of the most important are the nitrogen oxides. The study was performed during 18.03.2011 – 27.05.2011 and five recording points were fixed in most circulated areas from Cluj – Napoca municipality: Mănăştur, Gheorgheni (Titulescu Boulevard), Railway Station (Horia Street), Center (Unirii Square) and Mărăşti (Aurel Vlaicu Street). The nitrogen oxides measurements were performed daily, at the same hour for each measurement point, in the afternoon, with mobile monitoring station equipped with Ambient NOx monitor - Horiba. The data were processed with STATISTICA v. 6.0. In the mean time, pressure and relative humidity were quantified. Even some values were higher then admitted limits the averages demonstrate that no serious nitrogen oxides pollution has been identified in the observed areas during studied interval.

Keywords: air pollution, chemiluminiscence, multiple correlation, average nitrogen oxides concentration

1.Introduction

Traffic pollution is serious air quality issue in urban areas, worldwide. Among main traffic pollutants nitrogen oxides occupy an important place, due to their harmful effect on human health (fix haemoglobin from blood, and respiratory tract) [4], and also being ozone precursor as reactant in reactions between them and non – methane hydrocarbons, driven by sunlight [3].

Formation of nitrogen monoxide

In internal combustion engines, the molecular nitrogen from the air captured inside is the main source of the nitrogen that will take part to the reactions leading to nitrogen dioxide.

Gasoline and diesel have small nitrogen levels that will contribute to nitrogen dioxide genesis. These reactions take place in the front of the flame and in gases that leave the flame. The NO quantities increase with the oxygen concentration and temperature [1].

Formation of nitrogen dioxide

In conditions of thermic balance, in burned gases, compared to nitrogen monoxide, the nitrogen dioxide concentration can be neglected. This happens in spark ignition engines. In Diesel engine, major part of NOx is composed of NO_2. The explanation would be that NO formed in front of the flame is converted in NO_2:

$$NO + HO = NO_2 + OH$$

* Corresponding author.
Tel.: 0264596384; Fax: 0264593792
e-mail: neluoroian@gmail.com

In spark ignition engine, prolonged use in idling can increase emissions of NO_2.

The nitrogen protoxide - N_2O is formed from intermediates that react with nitrogen oxide [1].

Formation of nitrogen oxides

In spark ignition engines the fuel - air mixture is characterized by homogeneity, because the process takes place during the intake and compression stroke. Decisive factors influencing NOx emissions are:

- air - fuel ratio;
- the fraction of flue gas, which is located in the unburned mixture in the combustion chamber;
- ignition advance.

In compression ignition engines, excess air is about 10%. Peak concentrations of NOx emissions are placed in the light mixtures.

If the excess air continues to rise due to lower flame temperature, NOx formation rate of molecular nitrogen is reduced [1].

2.Material and Method

Due to heavy traffic, the Cluj – Napoca municipality confronts with important air pollution threats. Recording NOx concentrations in most polluted urban areas at rush hours, is an important step in maintaining these emissions in accepted limits.

The study was performed during 18.03.2011 – 27.05.2011. The recording points were fixed in five most circulated areas from Cluj – Napoca: PP1 – Mănăştur, PP2 - Gheorgheni (Titulescu Boulevard), PP3 - Railway Station (Horia Street), PP4 - Center (Unirii Square) and PP5 - Mărăşti (Aurel Vlaicu Street) (fig. 1).

Figure 1. Prelevation points in Cluj - Napoca

The measurements were performed daily, at the same hour for each measurement point, in the afternoon (table 1). With this aim, a mobile monitoring station equipped with Ambient NOx monitor - Horiba was used [2, 5].

The analyzer conforms to SR EN 1421 Standard [11] and 89/336/EEC Directive, in accordance with Article 10 (1) of the Directive, amended by 93/68/EEC and 99/5/EEC Directives [7, 8, 9, 10].

The data were processed with STATISTICA v. 6.0.programme.

Table 1. Characteristics of measuring equipment

Parameter	Instrument	Uncertainty	Detection limit
NO NO_2 NO_x	Ambient NOx monitor, APNA - 340	4%	0.50 ppb

The measurement principle is based on chemiluminescence. In this case it is produced by the reaction between the nitrogen monoxides with ozone [6, 11].

In analyzer, the air is prelevated through a filter (to prevent contamination of the air prelevation system, especially optical components of the analyzer) and fed to a constant flow value in the reaction chamber, where it is mixed with an excess of ozone only for determination of nitrogen monoxide. Radiation emitted (chemiluminescence) is proportional to the number of molecules of nitrogen monoxide from detection volume and thus proportional to the concentration of nitrogen monoxide. Radiation emitted by an optical filter is selectively filtered and converted to electrical signal by a photo diode or a photomultiplier tube.

To determine the nitrogen dioxide the sampled air is introduced into a converter where the nitrogen dioxide is converted to nitrogen monoxide and analyzed in the same way as described above. Electrical signal obtained from the photomultiplier tube or photo diode is proportional to the sum concentrations of nitrogen dioxide and nitric oxide. The amount of nitrogen dioxide is calculated from the difference between this concentration and that obtained only for nitric oxide (when the air has been taken by the converter).

Chemiluminescence is emission of light during a chemical reaction. During the gas phase reaction of NO and ozone the light intensity is

proportional to the concentration of NO, which is produced when excited electrons from NO_2 molecules decay to a lower level of energy.

This is based on the reaction:

$$NO + O_3 \rightarrow NO_2^* + O_2$$

$$NO_2^* \rightarrow NO_2 + hv$$

Excited nitrogen dioxide molecules (NO_2*) emit radiations within infrared region (600 nm - 3000 nm) with a peak around 1200 nm. To determine nitrogen dioxide, nitrogen dioxide taken from the air is transformed into nitrogen monoxide in a converter, as a result of the reaction:

$$NO_2 \xrightarrow{\text{Converter}} NO$$

Concentrations of nitrogen monoxide and dioxide are directly measured in units of volume (if the analyzer is calibrated using a standard volume), since radiation emitted by chemiluminescence is proportional to nitric oxide concentration per unit volume. Reporting final results are expressed in $\mu g/m^3$ using conversion factors.

3. Results and Discussions

Individual increased values of nitrogen oxides compared to admitted limits [12] were recorded, in few cases (PP3 and PP4), but average weekly values were into the limits admitted by internal regulations.

The highest average value recorded during studied interval was $6.61 \mu g/m^3$ in prelevation point no. 4 (measurements performed downtown), close to the average value recorded in prelevation point no. 3 (measurements performed at the Railway Station).

The highest variability was recorded in prelevation point no.1 and prelevation point no. 2 (Aurel Vlaicu St., Titulescu Bd.), were values of 22.06% and 26.75%, respectively, were obtained for NO_2 (table 2).

Table 2. Average values of nitrogen oxides recorded in prelevation points during 18.03.2011 – 27.05.2011

Parameter	Prelevation point 1			Prelevation point 2			Prelevation point 3			Prelevation point 4			Prelevation point 5		
	$\overline{X} \pm s_{\overline{X}}$	CV%		$\overline{X} \pm s_{\overline{X}}$	CV%		$\overline{X} \pm s_{\overline{X}}$	CV%		$\overline{X} \pm s_{\overline{X}}$	CV%		$\overline{X} \pm s_{\overline{X}}$	CV%	
NO	0.71 ± 0.01	2.34		0.66 ± 0.02	7.42		0.62 ± 0.01	6.48		0.61 ± 0.02	9.01		0.58 ± 0.01	6.22	
NO_2	4.79 ± 0.33	22.06		4.45 ± 0.38	26.75		5.81 ± 0.18	9.82		6.01 ± 0.29	15.24		5.20 ± 0.14	7.43	
NO_x	5.50 ± 0.34	19.35		5.11 ± 0.39	24.00		6.43 ± 0.19	9.16		6.61 ± 0.30	14.35		5.86 ± 0.17	8.09	

The nitrogen oxides measurements were performed in parallel with pressure and relative humidity conditions (figs. 2 and 3), which were within normal limits.

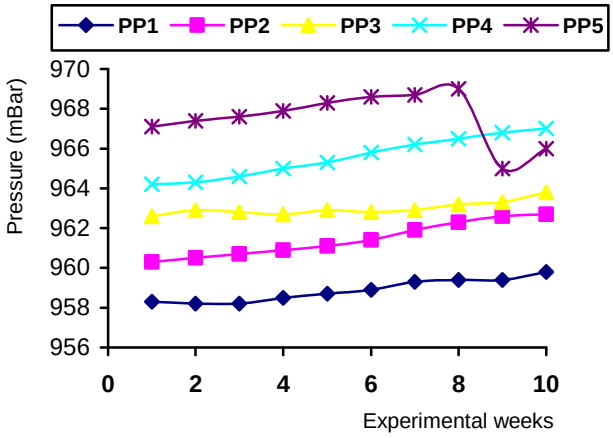

Figure 2. The pressure conditions during the studied interval

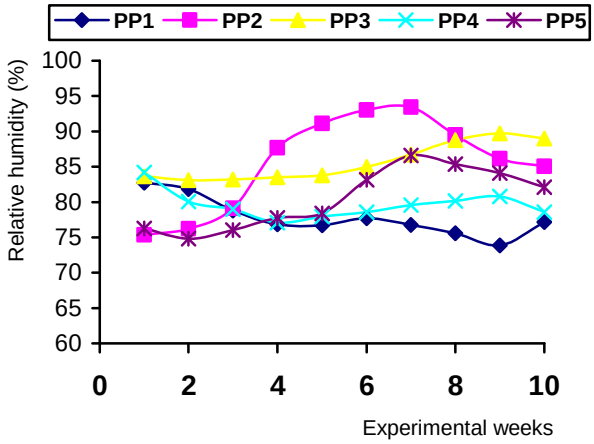

Figure 3. The relative humidity during the studied interval

In PP1, according to regression equation, the highest contribution to average NOx value, by entire experimental interval was brought by nitrogen oxide (fig. 4).

The same was observed in PP2 and PP4 (figs. 5 and 7).

This may be explained by the nitrogen dioxide formation mechanism, which is determined by the engine type, and fuel. The traffic in these areas (PP3 and PP5), is populated by trucks with Diesel heavy – duty engines, where the NO_2 production is higher compared to NO.

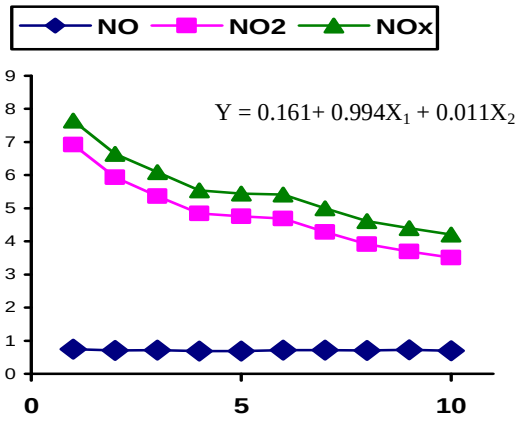

Figure 4. The evolution of NO, NO_2 and NO_x concentrations in PP1 during studied time interval

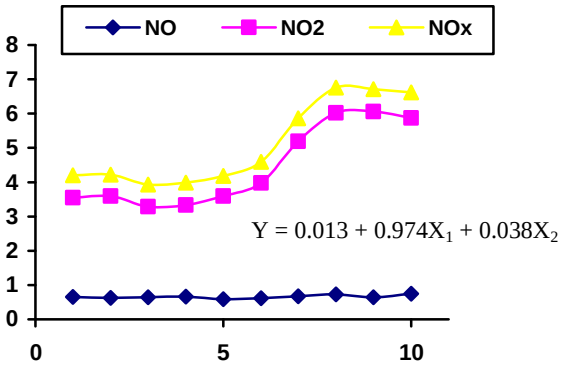

Figure 5. The evolution of NO, NO_2 and NO_x concentrations in PP2 during studied time interval

Major contribution to total nitrogen oxides (NOx) was brought by nitrogen dioxide in PP3 and PP5 (figs. 6 and 8).

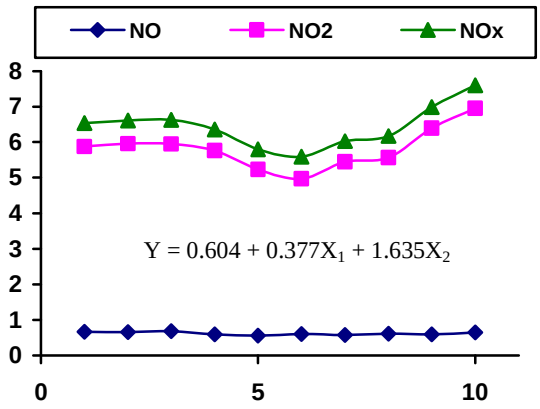

Figure 6. The evolution of NO, NO_2 and NO_x concentrations in PP3 during studied time interval

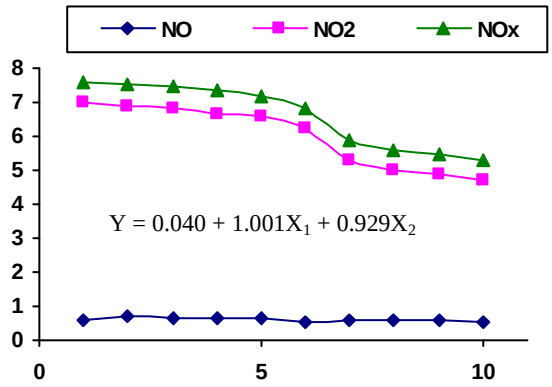

Figure 7. The evolution of NO, NO_2 and NO_x concentrations in PP4 during studied time interval

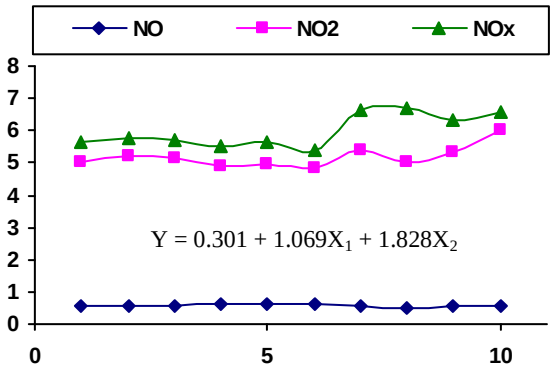

Figure 8. The evolution of NO, NO_2 and NO_x concentrations in PP4 during studied time interval

Strong correlation coefficients were recorded between nitrogen oxides concentrations in PP1 (r = 0.866), while in the other prelevation points they were moderate (r = 0.644 – 0.779), with the lowest determination coefficient in PP3 (r^2 = 0.456) and highest in PP1 (r^2 = 0.866).

Table 3. The multiple correlation coefficients between nitrogen oxides concentrations recorded in prelevation points (PP1 - PP5)

Issue	r	r^2	p
PP1	0.866**	0.751	0.0011
PP2	0.779**	0.607	0.0078
PP3	0.675^{ns}	0.456	0.8529
PP4	0.747*	0.558	0.0129
PP5	0.644^{ns}	0.415	0.8794

4. Conclusions

The initiative of monitoring the Cluj-Napoca municipality areas with the heaviest traffic in rush hours provided a good opportunity to estimate the predominance of NO and/or NO_2 in total nitrogen oxides released in air.

A moderate up to strong correlation was found between nitrogen oxides released by traffic pollution in observed areas, with predominance of nitrogen dioxide in areas where trucks with Diesel heavy – duty engines are allowed.

No serious nitrogen oxides pollution has been identified in the observed areas during studied interval.

Further studies targeting at the exploration of the chemical mechanism of nitrogen oxides production in heavy traffic areas will be useful in creating models of predicting the degree of air pollution potential.

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