ANALYSIS OF GASEOUS POLLUTANTS IN THE ATMOSPHERE OF BOTOSANI TOWN

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Key words: pollutants, immissions, carbon monoxide, nitrogen oxides, sulphur dioxide, air quality.

Abstract. Immissions of carbon monoxide (CO), sulphur dioxide (SO_2) and nitrogen oxides (NO_x) were measured in the central area of Botosani municipality, since January 2008 until December 2009 (Environmental Protection Agency, Mihai Eminescu Avenue, at the altitude of 160 m). The data represent hourly average of the three pollutants concentrations, the measurements being performed with the automatic station – urban background type, from the agency endowment. The purpose of this work is to present the air quality and the connection between concentrations and tendencies of gaseous pollutants in the climatic conditions and in anthropic activities specific in Botosani town. Yearly averages of carbon monoxide (CO), sulphur dioxide (SO_2) and nitrogen oxides (NO_x) for the years 2008 and 2009 were: 0.250 mg/m^3 and 0.280 mg/m^3; 7.26 µg/m^3 and 8.29 µg/m^3, respectively 37.71 µg/m^3 and 30.53 µg/m^3. Generally, the maximum values of the pollutants immissions are registered in the cold semester of the year, and the minimum values of the immissions, in the warm semester. The medium value of the ratio CO/ NO_x = 5,03 indicates the predominant contribution of the mobile sources in the atmosphere pollution process, and the value of the ratio SO_2/NO_x = 0.14 indicates the fact that the punctiform pollution sources are responsible of the pollution with SO_2 in Botosani town.

Introduction

At the level of Botosani municipality, the observations over the air quality are assured by the Environmental Protection Agency (APM/EPA), by its own monitoring system, with an automatic station urban background, with analyzers of carbon monoxide (CO), sulphur dioxide (SO_2), nitrogen oxides (NO_x), placed on Mihai Eminescu Avenue, n. 44, in a populated area, without the direct influence of the industrial emission sources (situated at a distance longer than 2 km) and a traffic area (at a distance longer than 200 m). The station is placed on an open, grassy area without major obstacles in the representativeness area. The urban area

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is residential and commercial. The height of the sampling point is at 3,7 , from the ground, the sampling time is 24 hours, continuously, and the calibration is automatically.

The pollutants life cycle implies emission, dispersion, transport, chemical transformation and their submission to the surface of the ground. The spread of contaminants emitted and their transformation in immission is dependent on weather conditions and closely related with regional relief where the pollution sources, climatic factors, respectively meteorological, are situated, being able to action on the atmosphere pollutants, directly or indirectly.

Directly, the physical parameters of the atmosphere act by increasing or decreasing speeds of reaction, by oxidations, favoring hydrolysis, determining „the resistance time” in the atmosphere for every noxa. Indirectly, it influences the propagation, dispersion or stagnation of the atmospheric noxae, along with the dynamics, statics and transformations wich occur in the air masses that contain it (Apostol et al, 1995).

2. Results and discussions

Sulphur, carbon and nitrogen oxides in the atmosphere, generally, come both from anthropic activities and from natural processes. Carbon monoxide emissions in the atmosphere contribute to generating the greenhouse effect and the main sources at the level of Botosani town are cars and the thermal energy systems (heating stations, individual households).

The main compounds with sulphur are inorganic pollutants resulted from fuels burned in stationary sources (population heating systems which do not use marsh gas, from industrial processes, from the sewage combustion from rural and urban areas) or on a small scale from mobile sources (emissions come from diesel engines). Natural sources are the bacteria (bacterial fermentation in swampy areas), oxidation of sulphur-containing gas resulted from decomposition of biomass. Immissions of sulphur dioxide in Botosani county, result, in quantitative, from: industrial combustion plants (92,23%), combustion in energy industry and transformation industry (7,57%), combustion in processing industry (0,09%), waste treatment and storage (0,05%), production processes (0,019%) and other mobile sources and equipments (0,041%) according to the report concerning status of environmental factors in 2009, of Botosani Environmental Protection Agency.

The nitrogen oxides (NOx) are very reactive gases, which contain nitrogen and oxygen in variable quantities. From the varieties of nitrogen oxides, N_2O (nitrous oxide), NO (nitrogen monoxide), NO_2 (nitrogen dioxide), N_2O_3 (dinitrogen trioxide), only NO si NO_2 play an important part in the atmospheric pollution problems. Immissions of nitrogen oxides which are registered in the atmosphere of Botosani county come from: waste treatment and storage (59,93%), traffic

(20,03%), non-industrial combustion plants (17,64%), energy industry and transformation industry (2,29%), processing industry (0,08%) and the production processes (0,008%).

Monitoring air quality in Botosani town was performed according to the law provisions concerning the surrounding air quality in Romania (Law n. 104/2011), and the pollutants monitored, measuring methods, limit values and alert thresholds are established according to the requirements stipulated by the European regulations (tab. 1).

Tab. 1 - Evaluation of CO, SO2 and NOx concentrations in the surrounding air in a certain area or urban agglomeration

	Critical level	Daily limit value, 24 hours, for human health protection	Hourly limit value for human health protection	Alert threshold
CO	-	10 mg/m^{3*}	-	-
SO2	20 $\mu g/m^3$	125 $\mu g/m^3$	350 $\mu g/m^3$	500 $\mu g/m^3$**
NOx	30 $\mu g/m^3$***	-	-	400 $\mu g/m^3$**

*daily maximum value of the averages on 8 hours
**measured for 3 consecutive hours, in points representative for the air quality, for a surface of at least 100 km^2 or for an entire area or agglomeration;
***yearly critical level for vegetation protection; Legea 104/2011, extras Anexa 3

The town has a surface of 4.135 ha (from which 1.910 ha within incorporated area), a slightly elongated profile on the north - south direction and a medium altitude above sea level of 163 meters (fig.1).

The climate is temperate – continental, with winds predominant from North-West and South-East ditections, with a yearly medium temperature of 9,2^{o}C, an average of the atmospheric precipitations of 567.9 mm/a year and a town population of about 116.110 inhabitants.

In fig. 2, fig. 3 and fig. 4 are presented the evolutions of the monthly medium concentrations of carbon monoxide (CO), sulphur dioxide (SO_2), nitrogen oxides (NO_x) specific of the years 2008 and 2009, in Botosani town.

Yearly medium concentrations of carbon monoxide in 2008 (0.252 mg/m^3) and 2009 (0.278 mg/m^3), didn't exceed the limit value for human health protection. Instead, this indicator has a positive evolution, in the sense of increasing monthly averages in 2009 in regard to 2008, because of increasing the traffic emissions and the number of apartment heating stations.

Carbon monoxide (CO) is influenced by the nitrogen oxides concentration in the atmosphere through both capacity to react with hydroxyl ions (Weinstock et al, 1980; Parrish et al, 1991). The transformation CO in CO_2 is facilitated by the intervention of hydroxyl radicals (OH), a radicals concentration of only $10^{-9} – 10^{-8}$ being enough to transform CO emitted in CO_2. The CO resistance time in the atmosphere of approximately 1 – 3 months, represents the slow mixing and consumption rhythm through the reaction with OH.

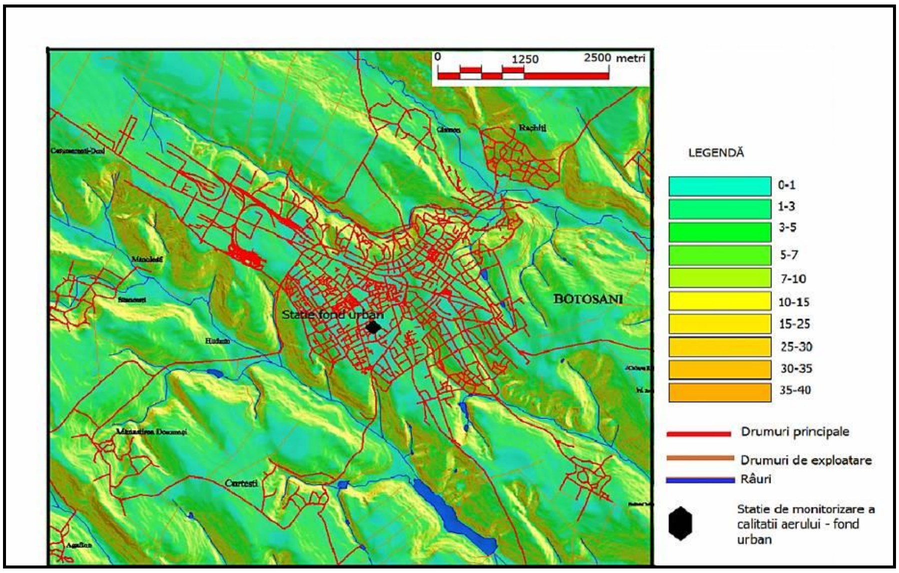

Fig. 1 - Slopes map – Botosani sector

Also, the existence of some soil bacteria which absorb appreciable quantities of CO influence the atmosphere purification process.

SO_2 monthly medium concentrations sustain the ascending trend of the yearly medium concentrations beginning with 2000, but they didn't exceed the limit value, daily or hourly for human health protection. But it was exceeded the critical level for vegetation protection 22 times in 2008 and 9 times in 2009. The level of sulphur dioxide immissions depends, on a very small scale, of the traffic, the registered values are due exclusively to the technological processes in the industrial sector and to the town heat power plant which ensures the heating necessary, technological steam and hot water for urban and industrial consumers.

The highest values are registered in May and November. The high values registered in summer are due to the industrial activities, and in winter, to the heating sources and thermal inversions which favour the pollutants stagnation to the ground. The SO_2 immissions evolution is influenced by the temperature and precipitations evolution. The temperature has the role to increase the reactivity, and the water vapours drive to formation of sulfuric acid (H_2SO_4).

In 2008 and 2009, the monthly NOx medium concentrations exceeded the critical level for vegetation protection, especially in cold months, because of combustion processes and of the heating sources which function at maximum capacity. The daily medium concentration exceeded the critical level 116 times in 2008 and 183 times in 2009. The meteorological conditions and photochemical reactions which took place, may be considered factors which influenced the occurrence of pollution processes in Botosani town.

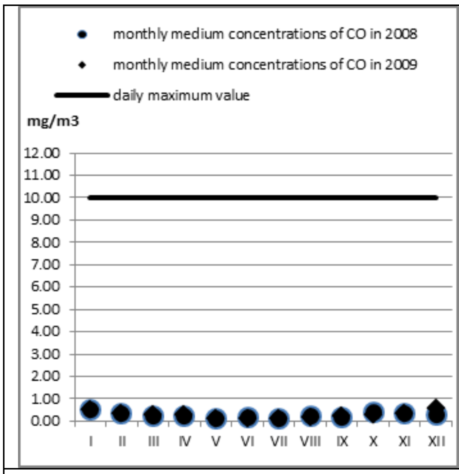

Fig.2 - Monthly medium concentrations of CO (mg/m^3) in 2008 and 2009, in Botosani

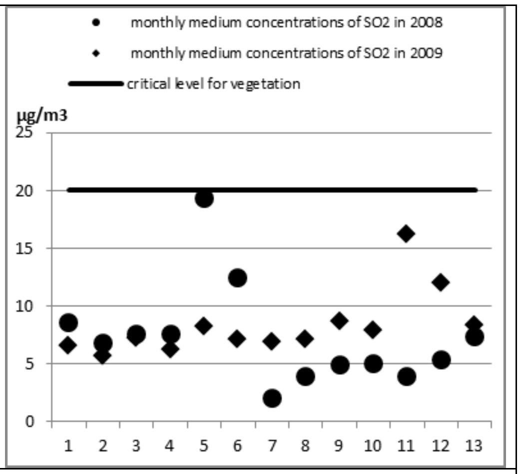

Fig.3 - Monthly medium concentrations of SO_2 (µg/m^3) in 2008 and 2009, in Botosani

The report of the Environmental European Agency, concerning the thematic evaluation of air quality in Europe in 2010, shows that the energetic sector remain a great source of air pollution, responsible for almost 70% of the sulphur oxides (SO_x) in Europe and 21% of the nitrogen oxides (NO_x), despite the significant reduction of these emissions in 1990 until present. There is known the fact that a combustion realised in mobile sources is characterized through a raised level of CO and NOx emissions, ant that realised in punctiform sources is highlighted through a raised level of SO_2 and NOx emissions. Taking into account this thing, it is expected that for the ratio CO/NOx to obtain a raised value at the mobile pollution sources, and for the ratio SO_2/NOx to obtain a low value, a thing valid in reverse, for the punctiform pollution sources.

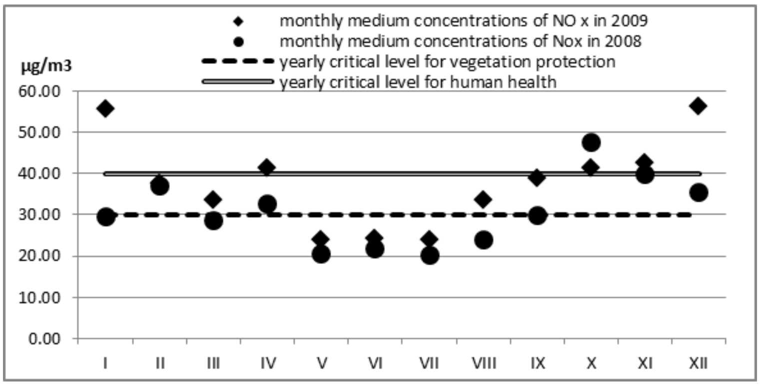

Fig.4 - Monthly medium concentrations of NOx (µg/m^3) in 2008 and 2009, in Botosani

The results of daily measurements performed in 2009, at automatic stations – urban background type, by the environmental protection local agencies, in the main towns in the North-East part of the country, we present as ratio CO/NOx and SO_2/NOx, in tab.2.

Analyzing comparatively the ratio CO/NOx and SO_2/NOx, is highlighted the fact that the mobile sources contribute most to air contamination with CO and NOx in Piatra Neamt, Vaslui, Bacau town in relation to Botosani town, and the punctiform sources, in the same towns are due to SO_2 pollution. In Botosani town, in 2009, the yearly CO medium concentration represents 42,3% of the one of Iasi town, and the SO_2 concentration had the highest value in the six towns in the NE part of the country.

Tab. 2. CO, SO_2 and NOx yearly medium concentrations in 2009

Town	CO(mg/m^3)	SO2(µg/m^3)	NOx(µg/m^3)	CO/NOx	SO2/NOx
Bacău	0.21	5.84	18.36	11.43	0.31
Botoşani	**0.26**	**8.27**	**37.73**	**6.89**	**0.21**
Iaşi	0.45	4.90	40.50	11.11	0.12
Piatra Neamţ	0.21	4.67	13.07	16.06	0.35
Suceava	0.16	4.08	20.31	7.87	0.20
Vaslui	0.28	6.24	24.00	11.66	0.26

Source: ARPM Bacau, Yearly report concerning the environmental factors condition (2010)

From the analysis of the daily and monthly CO and NOx medium concentrations evolution, it is observed how these ones increase and decrease simultaneously (fig.5).

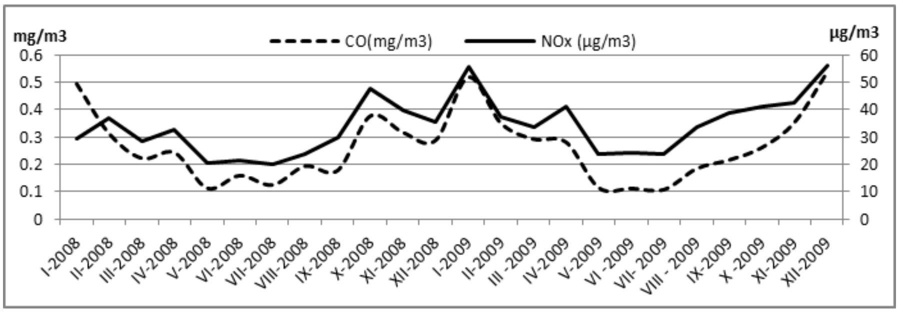

Fig. 5 - NO_x (µg/m³) and CO (mg/m³) monthly medium concentrations during the years 2008 and 2009, in Botosani

If there exists a relation between the CO and NOx concentrations and how tight is the relation between them, there can be demonstrated drawing the straight line of regression, which is the result of the way in which the two data sets co-vary and calculating the Pearson (1) correlation coefficient.

$$r_{xy} = \frac{\frac{1}{n} \cdot \sum_i (x_i - \bar{x}) \cdot (y_i - \bar{y})}{s_x \cdot s_y} \quad (1)$$

Where:

- n is the size of the sample formed of pair measurements (*xy*);
- x_i represents the individual measurements of x variable (NO_x – independent values set)
- y_i represents the individual measurements of y variable (CO –dependent values set)
- x represents the arithmetic average of x variables;
- y represents the arithmetic average of y variables;
- s_x represents the standard deviation for x values;
- s_y represents the standard deviation for y values;

Standard deviations corresponding to the two variables is calculated with the help of the relation:

$$s_x = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n}} \; ; \; s_y = \sqrt{\frac{\sum_{i=1}^{n}(y_i - \bar{y})^2}{n}} \quad (2)$$

The regression straight line equation establishes the following static correlation:

2008, $[CO] = 19.331[NOx] + 18.213$, R^2=0.257

$$2009,\ [CO] = 75.429[NOx] + 17.419,\ R^2=0.6873,$$

and the value of Pearson correlation coefficient, $r_{NOx,CO}$ = 0,50 in 2008 and $r_{NOx,CO}$ = 0,82 in 2009, indicates a positive correlation between the two variables (fig.6 and fig.7).

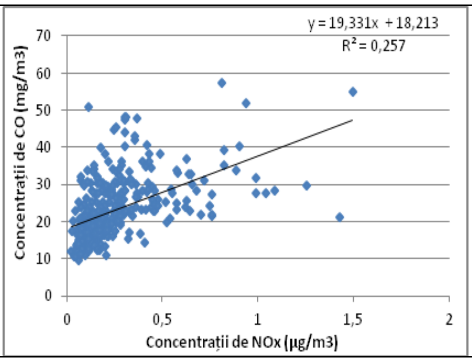

Fig. 6 - Daily CO medium concentrations (mg/m^3) comparative with NOx ones (μg/m^3) in 2008

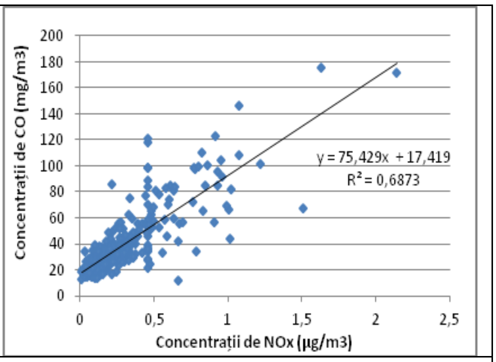

Fig. 7 - Daily CO medium concentrations (mg/m^3) comparative with NOx ones (μg/m^3) in 2009

Similar to all statistic tests, *r*, can't control deformations or effects of other variables, but in case of a sample of over 300 cases, the rejection of the null hypothesis is possible with a weak correlation coefficient (0.118 at the level 0.05 and 0.148 at the level 0.01), that indicates the presence of a positive statistically semnificative correlation between the two variables. So, in 2008, 25% of CO concentration variation was due to the linear relation with NOx, and in 2009, 68%.

Conclusions

The continuous measurements of the carbon monoxide immissions (CO), sulphur dioxide (SO_2), nitrogen oxides (NO_x) were performed in the central area of Botosani town. Excesses of monthly and yearly limit values weren't registered during the period analyzed, except of nitrogen oxides (NO_x). NOx and SO_2 monthly medium concentrations exceeded the critical level for vegetation protection, according to the European rules, especially in the cold months of the year. NOx daily medium concentration exceeded the critical level in 116 cases in 2008 and in 183 cases in 2009, and SO_2 concentration in 22 cases in 2008, respectivelly 9 cases in 2009.

In 2009, CO yearly medium concentration in Botosani town represented 42,3% of the one of Iasi town, and SO_2 concentration had the highest value of the six towns in the NE part of the country. Analyzing comparativelly the ratio CO/NOx and SO_2/NOx, it is highlighted the fact that the mobile sources contribute the most at the air contamination with CO and NOx in Piatra Neamt, Vaslui, Bacau towns in relation to Botosani town, and the punctiform sources, in the same towns, are due to pollution with SO_2.

Comparing the yearly medium concentrations of the three pollutants with the immissions of the other towns in the North-East of the country (Iasi, Bacau, Piatra Neamt, Suceava and Vaslui), at the level of the year 2009, Botosani town occupies the Ist place at the immissions of sulphur dioxide (8.24 μg/m^3), the IInd place at the immissions of nitrogen oxides (24.81 μg/m^3), and respectively the IIIrd place at the immissions of carbon monoxide (0.26 mg/m^3).

68% of CO concentration variation, in 2009 and 25% of the year 2008 variation, were due to linear relation which was established between the CO and NOx concentrations. This analysis was based on hourly measurements performed at a single urban location.

We admit that there is necessary a global study, with a bigger spacial and temporary coverage, in order to realise an objective analysis of correlations which can exist between pollutants and to evaluate air quality in a town.

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