THE INFLUENCE OF TEMPERATURE ON SULFUR AND NITROGEN OXIDES IN THE ATMOSPHERE OF BOTOSANI MUNICIPALITY

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Abstract: *The pollutants life cycle implies emission, dispersion, transport, chemical transformation and their submission to the earth surface. Spreading of impurities issued and their transformation in immission depends on the weather conditions and closely related with the relief of the region where the pollution sources, the climatic and weather factors are acting directly or indirectly, on the atmosphere pollutants.*

The sulfur dioxide (SO2) immissions and nitrogen oxides (Nox) were measured in the central area of Botosani municipality, since January 2008 until December 2009 (Environmental Protection Agency, Mihai Eminescu Avenue, at 160 m altitude). The data represent monthly averages, calculated after the hourly averages registered both for the temperature and for the two pollutants, by the automatic station urban background type in the agency endowment.

The purpose of this work is to present the evolution of the sulfur and nitrogen oxides concentrations comparing with the air temperature evolution, in Botosani municipality.

Keywords: *temperature, concentrations, sulfur oxides, nitrogen oxides, immission;*

1. Introduction

The climatic and weather factors are implied in chemical reactions which are produced in the Atmosphere between the gaseous emissions, between these ones and natural compounds of the atmospheric air, as with the water in the atmosphere. These factors are also directly implied in the propagation, dispersion or stagnation of polluted air masses. The town has a surface of 4.135 ha (1.910 ha inside land), a slightly elongated profile in the North-South direction and an altitude above sea level of 163 meters. The climate is temperate-continental, with winds prevailing from North-West and South-East, with a yearly average temperature of 9,2oC, a rainfall average of 567.9 mm/year and the town population of about 116.110 inhabitants.

The main compounds with sulfur are inorganic pollutants resulted from fuels burned in stationary sources (heating systems of population not using gas, from the industrial processes, from domestic combustion in rural or urban area) or only slightly from mobile sources (emissions come from diesel). Immissions of nitrogen oxides registered in the atmosphere of Botosani county come after treating and storage of traffic waste, non-industrial combustion plants, energetic industry and transformation industry and processing industry.

2. Results and discussions

The sulfur dioxide (SO2) is very soluble and reactive in the atmosphere. In the absence of the catalysts it doesn't react easily, but, during the day, in the presence of the ultraviolet radiation, the reaction speed increases considerably. It dissolves easily in fog and clouds, producing sulphurous acid, which is rapidly oxidized by the oxygen dissolved in water, resulting sulfuric acid. The direct oxidation with oxygen is difficult. During the night the reactions are favored by the humidity relatively increased, and during the day, by the photochemical reactions. Rains dissolve the sulfur dioxide, purging enough the atmosphere. The average resistance time in the atmosphere of this emission is 4 days.

The most important properties of SO2 are the reducing ones. These properties give birth to environment pollution problems and involve in the transformation the pollutants suffer in the atmosphere.

The sulphate ions (SO42-) exist in the atmosphere which contained sulfur dioxide or hydrogen sulfide, being present in the atmosphere as aerosol. From the sulphate ions present in the atmosphere as aerosol, 50% have the diameter bigger than 0,3 microns. These particles are submitted according to the Stokes law (the speed the particles fall raises with their diameter square). The particle which has half of the other diameter falls four times slower. The small particles fall so slowly, that they are suspended almost undetermined in the air and they settle only after coagulation. This way, fine particles usually remain in the air days or weeks, while the rough ones settle faster. Besides of this sedimentation process, the particles with diameter bigger than 0,5 microns can be removed from the air by their absorbtion in the falling raindrops.

The temperature influences the degree of solubility of SO2 molecules in the water molecules. So, the higher temperature will be the higher degree of solubility will be. Because the SO2 immissions reduction depends on the water quantity in the atmosphere, the temperature role can be referred only by comparing two months with approximately equal precipitation quantities.

In Botosani municipality, in September 2008 was registered an average temperature of 15,9oC, and in October 2009, 12.0oC. according to the rule before mentioned, the SO2 solubility will be raised at raised temperatures, which means that immissions will have a lower value in September 2008, than October 2009. the SO2 immissions in November 2009 should be higher than those in November 2008. this thing is confirmed by the SO2 concentrations registered with the automatic station at the EPA office and reproduced in tab. 1 and in fig. 1 and 2.

Tabel 1.

Average temperature, precipitations and carbon dioxide values in Botoşani municipality

Luna/an	T(°C)	Precipitații(mm)	SO_2(μg/m3)
Septembrie 2008	15.9	60.20	4.83
Noiembrie 2008	7.8	12.20	4.87
Octombrie 2009	12.0	60.80	8.14
Noiembrie 2009	8.2	11.40	16.19

There can be observed that lower immissions are registered at the highest temperatures, and the highest values of the immissions at low temperatures, arguing this way that the temperature also influences the SO2 molecules solubility.

An important part in establishing the concentrations play the different emission levels in cold, respectively warm months. The values of the high concentrations are registered at law temperatures during winter.

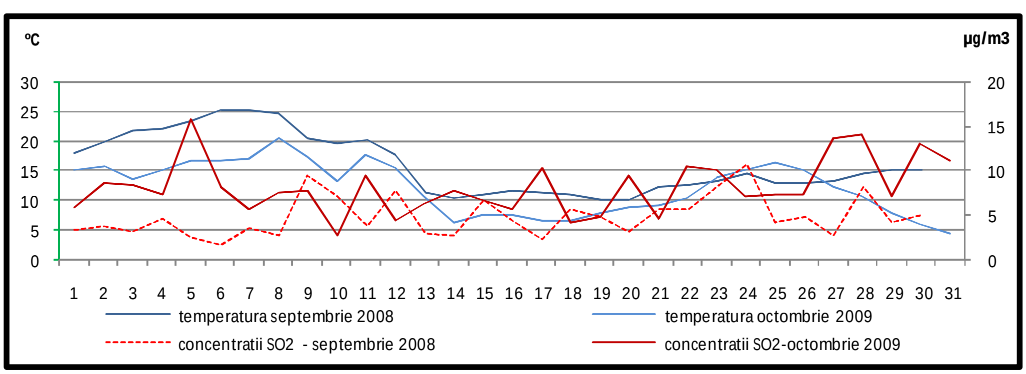

Figure 1. *The evolution of the daily SO2 average concentrations (μg/m^3) and the air monthly average temperature (^{o}C) in September 2008 and October 2009, in Botoşani*

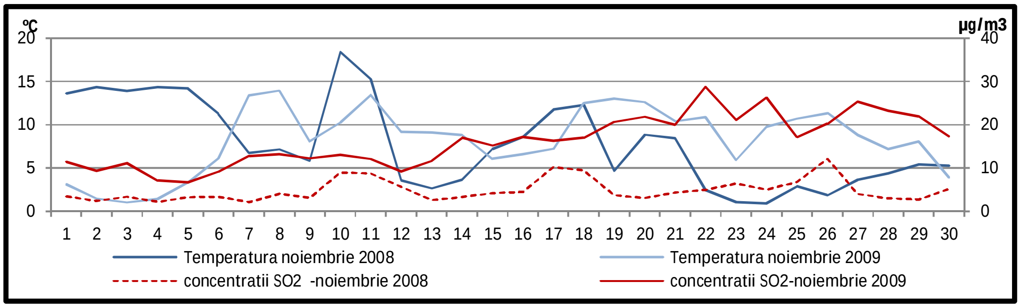

Figure 2. *The evolution of the daily SO2 average concentrations (µg/m^3) and the air monthly average temperature (^oC) in November 2008 and 2009 in Botoşani*

Along with the move to summer the SO2 monthly average concentrations fall and the monthly average temperatures rise, reaching the minimum respectively maximum values in summer. In the autumn, the SO2 concentrations begin to rise, while the temperature falls.

Another part of the temperature is the creation of vertical transport conditions. The higher temperature will be, the easier will be the air, vertical thermal gradient and instability higher, and SO2 emissions will raise faster in the high troposphere. The most favourable vertical transport conditions of the air volumes are created in summer, when the temperatures are raised. The effect on the SO2 immissions is the reducing. In winter, the lower temperatures aggravate vertical flow, and even blocks it in the thermal inversion situations. In the thermal inversion situations, SO2 emissions are blocked in a layer of several meters till a few hundred meters, where they continue to accumulate. In this season the SO2 immissions are higher than in warm season.

After the two processes which action in the same time and sense during the year, the SO2 immissions evolve this way: they raise step by step to winter because decreasing the intensity or the interval in a day in which it acts; they rich the maximum in winter when the two reducing phenomena of the immissions acts with minimum intensity; they decrease in spring because of development and raising the day period when the two reducing phenomena act; they reach the minimum in summer, after the maximum intensity of the two phenomena (fig. 3).

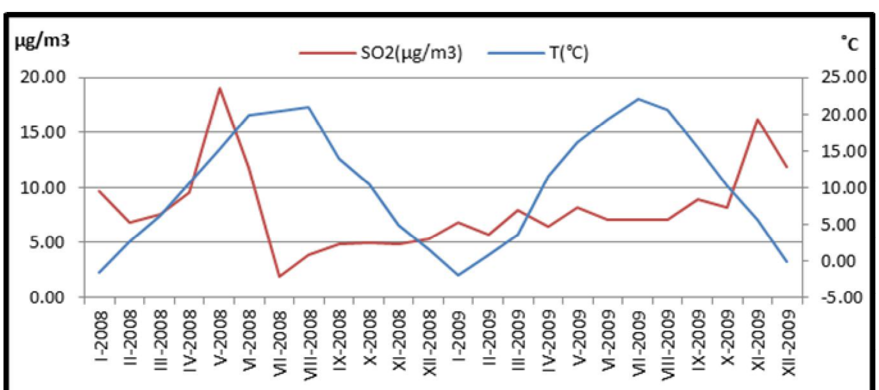

Figure 3. *The evolution of the monthly SO2 average concentrations (µg/m^3) and the air monthly average temperature (^oC) in 2008 – 2009 in Botoşani*

The variation of the SO_2 gaseous immissions show the fact that the higher values belong to the months November – March (cold, winter months), when the activity of the town central heating plant is intensified and also the traditional heating sources.

The nitrogen forms with the oxygen the following oxides: N_2O (diazotisable oxide/nitrous oxide), NO (nitrogen oxide), N_2O_3 (nitrogen trioxide), NO_2 (nitrogen dioxide), N_2O_4 (diazotisabletetraoxide), N_2O_5 (diasotisablepentoxide). There are very frequent pollutants, with raised concentrations and with a high importance at the physico – chemical processes in the atmosphere. A large part of them take part at the natural and biological processes in the environment, being its natural compounds (N_2O, with resistance time of 150 years, take part at biological processes), pollutants themselves being mainly NO and NO_2. These last two emissions take part at the ozone cycle.

Nitrogen dioxide(NO_2) arises by oxidation of the nitrogen oxide, only in the presence of traces of water. The forming speed is inversely proportional to temperature. That's why, in the hot combustion gases the share of nitrogen dioxide is negligible. Always in the urban area the concentrations of nitrogen dioxide vary according to the traffic intensity presenting maximum values in the morning and minimum values in the evening, when the traffic is reduced.

In the presence of the sunlight, the nitrogen oxides may also react with the hydrocarbons forming photochemical oxidants, for forming the photochemical smog being necessary 3 compounds: nitrogen oxides, hydrocarbons and solar energy as ultraviolet.

Gasoline burning for starting cars in the morning breaks out the events chain and burning /oxidation atmospheric nitrogen, forming nitric acid, NO (1). This one combines with molecular oxygen and forms in a few hours, nitrogen dioxide (2). The nitrogen dioxide absorbs solar energy and disrupts in nitric oxide and atomic oxygen (3).

In the sunlight, the atomic oxygen combines with gaseous oxygen and forms the ozone (4). If there don't interfere other factors, the ozone and nitric oxygen react forming nitrogen dioxide and gaseous oxygen (5).

$$N_2+O_2 \rightarrow 2NO \quad (1)$$

$$2NO+O_2 \rightarrow 2NO_2 \quad (2)$$

$$NO_2 \rightarrow NO+O^{\circ} \quad (3)$$

$$^{\circ}O+O_2 \rightarrow O_3 \quad (4)$$

$$O_3+ NO \leftrightarrow NO_2+O_2 \quad (5)$$

The last reaction may evolve in both directions, dependent on temperature and quantity of sunlight. If there is a high quantity of sunlight, the equation tends to forming the ozone. Because of the last reaction, the places where the nitrogen monoxide immissions are raised (on streets, in big cities), they will be characterized by lower ozone concentrations, compared with places less polluted with nitrogen monoxide.

There is a close contact between the evolution of the nitrogen oxides concentrations and the temperature for the studied period. The NO, NO_2 and NO_x evolution is inversely proportional to temperature values (fog. 4).

The phenomenon is based the NO_2 oxidation speed raising (present in the determination called generically NO_x) in the same time with temperature raising and intensification of the destruction processesof NO_2 and formation NO and [O], formation and destruction of O_3 with NO participation and NO_2 formation. It is a reversible reaction. In other words, a part of NOx will be kept, in some areas, for a while, as O_3. The ozone formation process is intense at values of the solar radiation wavelength between 290 nm and 320 nm (UV), which also implies raised temperatures (optimal conditions in summer, between 9-12, when the sky is clear and the air is less opaquec

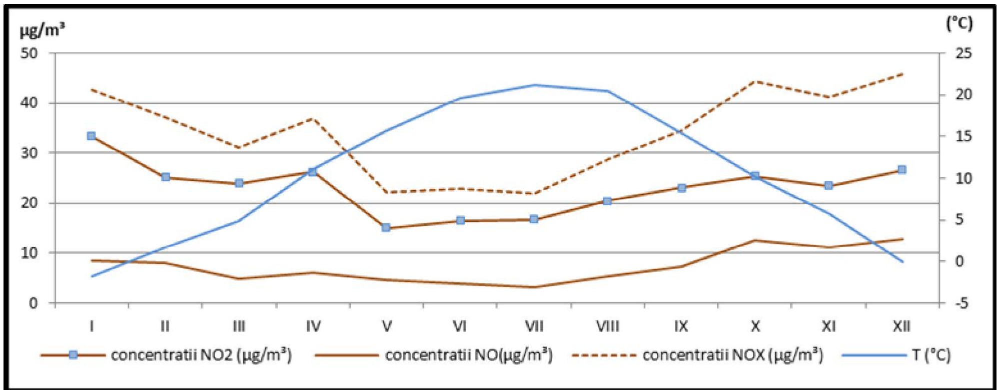

Figure 4. *The evolution of the nitrogen oxides average concentrations (µg/m^3) and the air monthly average temperature (^{o}C) in Botoşani in 2008 – 2009*

The evolution of the nitrogen and ozone oxides concentrations regismen, on July 1, 2009, is detailed in fig. 5. Per 24 hours, the values raise cumulative until 4 p.m., when there is achieved the maximum value of O_3 concentration, and about it, Nox minimum concentration, then O_3 concentration decreases, while NOx concentrations values raise, the maximum being achieved during the night, long time before the sunrise. To the NOx maximum level corresponds the O_3minimum level.

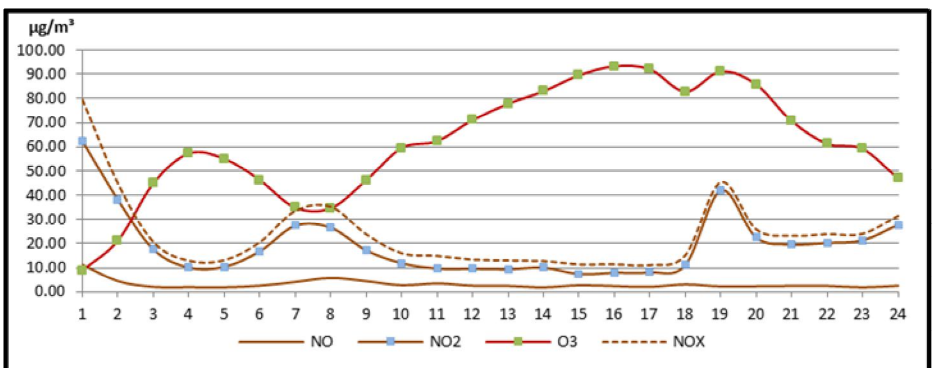

Figure 5. *The evolution of hourly nitrogen oxides average concentrations (µg/m^3) and ozone (µg/m^3) on July 1, 2009, in Botoşani*

Temperature generates the possibility of pollutants vertical transport. The raised it is, the raised will be the air volumes off the ground and they will circulate faster. According to the Van't Hoff law, the chemical reactions speed in any system is raised parallel with temperature raising of the system, with each 10 ° C.

The two phenomena for reducing the nitrogen oxides which act in the same time during the whole year, determine the highest NOx concentrations to be registered in winter, and the lowest, in summer, without ignoring the NOx higher emissions, in winter, because of higher combustions (fog. 6). In spring, the concentrations are decreasing after the intensification of the reducing processes, while in autumn, the situation is reversed.

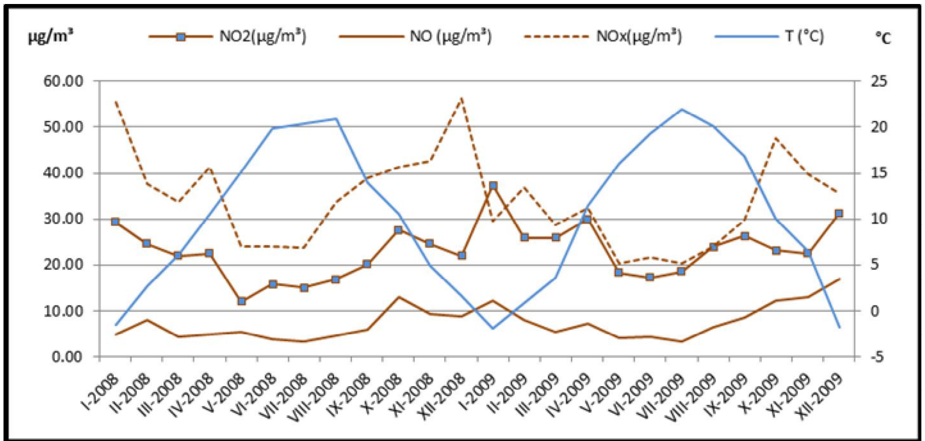

Figure 6. *The evolution of monthly nitrogen oxides average concentrations (µg/m^3) and the air monthly average temperature (^{o}C) in 2008 – 2009 in Botoşani municipality*

3. Conclusions

Air temperature influences the solubility degree of the sulfur dioxide molecules in water molecules and influences the increasing of nitrogen oxides oxidation speed, their evolution being inversely proportional to temperature values. It creates favourable conditions for vertical transport of air volumes which contains pollutants, in high atmosphere, especially in summer, and in winter it creates conditions for their accumulation at ground, because of thermal inversion situations.

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