AIR POLLUTION LEVEL IN URBAN REGION OF BUCHAREST AND IN RURAL REGION

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Abstract: - Interest in the urban challenges raised by the growing debates on sustainable development and global environmental change has increased very rapidly in recent years. The paper presents the air pollution level in two areas: urban and rural. The monitoring was made in the urban area Bucharest, more exactly a residential area Pipera between 05.05 – 07.05.2008 and in a rural area, Surlari Geomagnetic Observatory between 07.05 – 09.05.2008. We analyzed the results of CO, O₃, SO₂, NO, NO₂ and non-methane hydrocarbons concentrations measured. Wind velocity and air temperature were measured by a small weather station. Naturally we observed that the concentrations in the rural area were very different from those in the urban area, smaller.

Key-Words: - air pollution, air quality, sustainability, urban and rural areas

1 Introduction
We all know that the more a city expands the more pollution it will be. Urbanization brings with it many transformations of nature including pollution. Every city will have a crucial role to play in the minimization of activities contributing to ozone depletion and global warming. The environmental sustainability of cities requires looking both outward and inward in managing the processes of change [5].

The first set of measurements was made in Pipera, a district situated in the north of Bucharest, more exactly in the depot precinct RATB Pipera between 05.05 – 07.05.2008 (fig.1). Until 1995, it was an ordinary village. In this time, more than 1400 houses were built here. The depot stands near a major road and carry a considerable volume of traffic.

The second set of measurements was made at Geomagnetic Observatory Surlari – Căldărășani, situated at 25 km N-E from RATB Pipers into a forest between 07.05 – 09.05.2008. The location is presented in figure 2.

We measured the carbon monoxide, ozone, sulphur dioxide, nitrogen monoxide, nitrogen dioxide, total and non-methane hydrocarbons (THC, NMHC).

Fig. 1 Ratb-Pipera depot

Fig. 2 Surlari geomagnetic observatory
2 Methods

2.1 Carbon monoxide

2.1.1 Horiba APMA 350
Carbon monoxide was analyzed by an Ambient CO Monitor – Horiba APMA 350 based on the principle of light absorption in the infrared region, known as "non-dispersive infrared absorption" (NDIR). The monitor is designed to eliminate routine calibration cycles and to provide long-term stable measurements and unattended continuous operation, and having a newly developed cross-flow modulation (CFM) technique which results in remarkable improved zero drift performance and sensitivity.

The broadband infrared radiation produced by the light source passes through a chamber filled with gas, generally methane or carbon dioxide. The gas absorbs radiation of a known wavelength and this absorption is a measure of the concentration of the gas. There is a narrow bandwidth optical filter at the end of the chamber to remove all other wavelengths before it is measured with a pyro-electric detector.

2.1.2 Siemens Hawk optical device
The IR Hawk from Siemens Environmental Systems is an infrared DOAS (Differential Optical Absorption Spectroscopy) instrument which can be configured to detect any species from CO, CH₄, C₂H₄, NO, HF, total hydrocarbons <C₈.

Open path techniques have an advantage over point source detectors; thus the sampled volume is so much greater that the effect of non-uniformity of mixing in the sample is mitigated and a more representative value of the concentration of the compound to be measured is obtained. The beam path can extend up to 400 m and the limit of detection is typically better than 50 ppb over such paths.

2.2 Ozone
The analyzer APOA 350E can be used for in-situ measurements of ozone.

The measuring principle of UV absorption guarantees a continuous measurement. The measurement is based on a comparison between a reference gas, without O₃, and the sample gas. Both gases are led into the cell alternating by a magnet valve. The cell is irradiated by a low-pressure mercury vapor lamp with 253.7 nm wave length (UV) and the measurement signal is determined by difference in the unequal absorption.

2.3 Sulphur dioxide
The APSA-370 is based on Ultraviolet Fluorescence (UVF) analysis to measure SO₂ concentrations in ambient air. It uses an innovative detector and a new optical system for low background, high sensitivity (0.05 ppm), and greatly improved stability.

The fluorescent chamber design gives measurements with minimum influence from moisture.

2.4 Nitrogen monoxide and nitrogen dioxide
The concentration of nitrogen dioxide and nitric oxide was determined using a Horiba Model APNA-350E Ambient NOₓ Analyzer. This employs a chemiluminescence technique to determine the level of nitrogen dioxide.

Nitric oxide is oxidized by ozone to nitrogen dioxide with a higher electronic state within a reaction chamber. The resulting chemiluminescence as it is ‘de-activated’ is measured through an optical filter by a photodiode.

2.5 Methane, non-methane and total hydrocarbons
A Flame ionization analyzer (Horiba Model APHA-350E) is used for continuous and automatic measurement of total hydrocarbons, methane and non-methane hydrocarbons (NMHC) in atmospheric air in the range 0-10 ppm.

The principle used to detect hydrocarbons is flame ionization detection (FID). There are two gas streams. The first stream passes directly into the detector for analysis. The second passes through a burner, which burns heavier hydrocarbons leaving only CH₄. An electrode produces current proportional to the hydrocarbon concentration in both streams and hence provides the THC and CH₄ levels. The difference between the two signals therefore becomes the NMHC level.

3 Results and discussions

3.1 Urban area - Pipera
Figure 4 show the hourly average values of O₃, CO, NO, NO₂, NOₓ and SO₂ for three days in Pipera.

One can observed that the urban ozone concentration increases from its minimum in early morning (low solar radiation) to its maximum in late afternoon and then, at night, decreases till next morning (O₃ is consumed by the reducing chemical such as NOₓ and without any accumulated process) after being generated through a complex series of chemical reactions involving the interaction of sunlight with hydrocarbons and nitrogen oxides from automobile exhaust.
The highest O₃ concentration value during the three days of observation was 0.958 ppm in 06.05.2008 at 13:40, and the lowest value was 0.090 ppm in 07.05.2008 at 03:40. All the ozone peaks coincide with clear sky.

The emissions of nitrogen monoxide and nitrogen dioxide come mainly from traffic and power plants. NO₂ is a clear indicator for road traffic. NO₂ and O₃ are linked through a chemical process. During the night, the reaction (2) shuts off, eliminating the major chemical sources of O (g) and NO (g).

\[
\begin{align*}
\text{NO}(g) + \text{O}_3(g) &\rightarrow \text{NO}_2(g) + \text{O}_2(g) \quad (1) \\
\text{NO}_2(g) + \text{hv} &\rightarrow \text{NO}(g) + \text{O}(g) \quad (2)
\end{align*}
\]

Because O (g) is necessary for the formation of ozone, ozone production also shuts down at night (Fig.3). Thus, at night, neither O (g), NO (g), nor O₃ (g) is produced chemically. If NO (g) is emitted at night, it catalytically destroys ozone (reaction (1)) [3]. So, in the presence of sunlight, the NO₂ that forms from the NO incrementally stimulates the photochemical smog-forming reactions because nitrogen dioxide is very efficient at absorbing sunlight in the ultraviolet portion of its spectrum.

Generally the NO₂ levels are decreasing were the ozone levels are increasing and vice versa. NOₓ is an important precursor of O₃ in the daytime, which constantly consumed by the photochemical reactions and produced lots of O₃, and the reacting intensity changes with the solar radiation. Naturally NOₓ (= NO + NO₂) levels are increasing too. In these 3 days when ozone concentration value was the highest, the nitrogen dioxide concentration value was not necessarily the lowest. The minimum was 0.005 ppm in 06.05.2008 at 06:40.

The observed ratios of [O₃]/ ([NO₂]/ [NO]) are plotted in Fig. 3. The ratio remains at low level (below 5) at night, when there is more fresh NO in air. After sunrise, the ratio rises up, because NO₂ will be formed like in reaction (1). The peak value of the [NO₂]/ [NO] ratio (higher than 120) appear at 00:40 local time.

Sulphur dioxide is a relatively short-lived species (a few days to a few weeks in the atmosphere) and for this reason the concentration of SO₂ is bigger close to the sources. SO₂ is emitted by the combustion of sulfur-containing material; major sources of SO₂ in ambient air include diesel-powered vehicles, coal-fired power plants, petroleum refineries, and metal-processing plants.

The oxidation of SO₂ leads to the formation of sulfate aerosol particles and acidic precipitation [1].
Most studied results showed that SO\textsubscript{2} concentration levels in urban areas do not exceed a 10 ppb (0.01 ppm) range \[2\]. In Pipera area the SO\textsubscript{2} concentration exceeds twice the 0.01 ppm range in 06.05.2008 at 05:40 (0.011ppm) and 06:40 (0.012ppm). The lowest value, 0.001ppm was observed in 05.05.2008 at 10:40.

The primary emission sources of carbon monoxide are associated with combustion processes (transport, heating, industrial activities and biomass burning), along with biogenic sources and oceans. It is also produced from the oxidation of methane and non-methane hydrocarbons. CO is an important trace of atmospheric motions due to its chemical lifetime which varies from weeks in the middle atmosphere to months in the troposphere and mesosphere.

Highest concentrations occur along major traffic arteries during morning and evening rush hours and decrease relatively rapidly with distance from roadways. In fig.4 CO values will achieve high values (rush hours) in 05.05.08 between 09:40÷13:40 (0.97÷1.54ppm); 06.05.08 at 09:40 (0.9ppm) and in 07.05.08 at 09:40 (1.09 ppm).

When methane, a fairly un-reactive hydrocarbon, is excluded from the list of hydrocarbons, the remaining hydrocarbons are called non-methane hydrocarbons (NMHCs). They come from mobile and stationary source fuel usage and combustion; petroleum refining; petrochemical manufacturing; industrial, commercial, and individual solvent use; gas and oil production; and biomass burning.

The equation characteristic for this figure is \[\text{[NMHC]} = 1.3993 \times \text{[NOx]} + 271.2; R^2 = 0.0198\].

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3.2 Rural area - Surlari

Figure 10 show the hourly average values of O\textsubscript{3}, NO, NO\textsubscript{2}, NO\textsubscript{x} and SO\textsubscript{2} for two days at Geomagnetic Observatory Surlari – Caldărişani, situated at 25 km N-E from RATB Pipera, into a forest. During these two days due to technical problems, the Ambient CO Monitor – Horiba APMA 350 did not work, so there were no CO measurements.

During the night, the ratio is small also in rural area, and increases during the day (fig. 8).

The ozone concentration values alter between 0.0804 ÷ 0.2509 ppm. The highest value, 0.2509 ppm was measured in 08.05.2008 at 17:00. The first peak occurs in 07.05.2008 at 23:00, the second at 17:00 in 08.05.2008, the third at 23:00 in
08.05.2008.

Due to the fact that NO can be produced by lightning, the majority of the peaks had appeared in the same time. During 08.05.2008 at 08:00 and 09.05.2008 at 00:00, one can see an increase of NO concentration. The NO₂ value varies between 1.03 ± 1.8 ppb.

Our understanding of O₃ chemistry continues to evolve as we come to comprehend the significant role that NMHCs emitted by trees play in producing elevated O₃ levels on a regional basis [4].

The results show very low SO₂ concentration, below 0.5 ppb.
3.3 Comparison between urban and rural areas

Due to trailer (equipment) transportation between the two areas there is a lack of data.

Although in urban area the SO$_2$ concentrations were higher than in the rural area, they did not exceed neither the hour limit value of 350 µg/m$^3$ nor the 24 hours legal limit value (125 µg/m$^3$) provided by the ORDER no. 592 from June 25; 2002.

In urban and rural areas the NO concentration was very different. Because in the rural area there was not traffic emissions etc. the values were much smaller, even 15 times smaller.

The concentration of all other hydrocarbons in ambient air can range from 100 times less to 10 times greater than the methane concentration for a rural versus an urban location [6].

By analyzing fig.4 and fig.10 one can observed that the [O$_3$]/([NO$_2$]/[NO]) ratio has different values, but the same allure. The values were two times higher in urban area (Pipera) than in rural areas, that means that O$_3$ values are smaller in urban areas and the [NO$_2$]/[NO] ratio has smaller values in rural area.

4 Conclusion

The environmental impact of transport is evident in urban air quality.

As cities continue to grow in size and in their share of the growing global population and economic wealth, their environmental impacts will of necessity continue to be a central theme in the move towards global sustainability. Urbanization brings with it many transformations of nature including pollution. Every city will have a crucial role to play in the minimization of activities contributing to ozone depletion and global warming. The environmental sustainability of cities requires looking both outward and inward in managing the processes of change [5].

The CO, O$_3$, SO$_2$, NO, NO$_2$, CH$_4$, total and non-methane hydrocarbons concentrations concentration data sets were investigated from two types of air quality monitoring stations (urban traffic and rural background) in Bucharest.

All the data obtained will be used to get advanced control systems for continuous, real-time monitoring of the atmosphere in polluted urban regions.

In the absence of other reactions between the gases, the O$_3$, CO, NO, NO$_2$, NO$_x$ concentration should depend of the solar flux and hence upon the season, geographical location and time of day.

By calculating the hourly average value during this 3 day in Pipera area, the O$_3$ concentration had not exceed the alert threshold value of 240 µg/m$^3$ provided by the ORDER no. 592 from June 25; 2002. But, the informing threshold (180 µg/m$^3$) has been exceeded 6 times during the period.

In Surlari area ozone concentrations were very small.

Sometimes the NO, NO$_2$ concentration was higher at night than during the daytime (fig. 4 and fig. 10).

Because of the complexities and expense associated with NMHC sampling and analysis, the atmosphere has not been well characterized, particularly in rural and remote areas. Many NMHC species produced as a result of photochemical reactions are short-lived.

References: