Assessment of Air Pollution with Benzene and Benzo [A] Pyrene in Regions in North-East Bulgaria

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Abstract – ***An assessment is made of air pollution with benzene and benzo[a]pyrene (BaP) for the period 2007-2014 in three regions of North-East Bulgaria, where automated measurement stations for monitoring air quality are located. An urban station and a traffic oriented station in the city of Varna, as well as an industrially oriented station in the town of Devnya have been included. The seasonal, annual and diurnal variations of the benzene and BaP concentrations in air are studied. The results from the monitoring are processed applying Student-Fisher's t-distribution criterion. The results reveal a descending trend in air pollution with benzene at the urban background station in the city of Varna and the industrially oriented station in the town of Devnya during the period of monitoring, with high statistical significance of the decrease ($0,001 \leq P \leq 0.05$). The average annual concentrations of benzene do not exceed the human health safety norm (5μg/m^3). At the traffic oriented station in the city of Varna the average annual concentrations of benzene and BaP vary, without delineating a specific trend. There are certain seasonal variations in benzene and BaP pollution – higher concentrations during the cold months of the year. The seasonal dynamics are supported by the diurnal variations of the pollutants.***

Measures are proposed for the reduction of carcinogenic pollutant emissions and a decrease in human exposure to them.

Keywords– ***benzene, BaP, air, pollution, seasonal variations***

I. INTRODUCTION

Law on Environment Protection, whose main goal is to protect human health and the living organisms in the environment, stipulates the determining of air quality (AQ) indicators and norms [8]. The basic indicators characterizing AQ in the lower atmosphere are: suspended particles, fine dust particles, SO_2, NO_2/NO_x, CO, O_3, heavy metals, as well as benzene (C_6H_6), and polycyclic aromatic hydrocarbons (PAHs). The requirements for strict control over air pollution with benzene and PAHs come from the proven carcinogenic qualities of benzene and some PAHs like benzo[a]pyrene (BaP). The International Agency for Research on Cancer (IARC) classifies benzene as group 1 (proven to cause cancer in humans), causing benzene leucosis – blood cancer [6]. The criteria for air quality recommended by the WHO for Europe assign no particular threshold limit values for benzene. There is no safe concentration of benzene and the risk analysis must be prepared based on lifelong benzene exposure – throughout the life of a person [3]. BaP is used as an indicator for the carcinogenic qualities of PAHs and is listed in group 1 carcinogens in the IARC classification [6]. In exposed populations, BaP causes cancer all through a person's life: at concentrations in air of 1.2 ng/m^3 – 1 case per 10,000 population; at 0.12 ng/m^3 – 1 case per 100,000 population; at 0.012 ng/m^3 – 1 case per 1,000,000 population [2]. The common effects of benzene and BaP on the exposed population, classifies them together when studying air quality.The aim of this survey is to assess air pollution with benzene and BaP in regions in North-East Bulgaria, trace the annual, monthly and seasonal variations, as well as the keeping of the human health safety norms.

II. MATERIAL AND METHODS

The North-East Planning Region of Bulgaria lies between the Danube to the north, Stara Planina (Old Mountain) to the south and the Black Sea to the east. The region encompasses four administrative regions: Varna, Dobrich, Targovishte and Shumen. The North-East Region is located in the moderate continental climate zone where the Black sea has an expressed softening effect on the climate in the 30-35 km coastal area. The automatic measuring stations are located in North-East Bulgaria which monitor AQ for benzene pollution (a total of 20 for the whole country), and one of them controls BaP as well (a total of 16 for the whole country). The stations are located only in Varna District: two of them are in the city of Varna (Varna Municipality) and on is in the town of Devnya (Devnya Municipality). Varna is the third largest city in Bulgaria and the largest in the North-East Planning Region. It is characterised by a well developed economy, mainly maritime industry (construction and repair of vessels, sea transport) and the tourist sector.

The town of Devnya lies 30 km from Varna and on its territory the following enterprises and plants are located: *Solvey Sodi AD* – a plant producing soda ash, *Agropolychim AD* – manufacturer of nitrogen and phosphorous fertilizers, *Devnya cement AD* – manufacturer of dry mortar and cement; *Deven* Thermal Power Station, the *Martsiana* Quarry, Varna-West Port and a phosphogypsum depot.

The monitoring of AQ in regard to benzene pollution covers the period 2007-2014 at three locations: an urban background station with a range of 100 m to 2 km in the city of Varna; a traffic oriented station in the central part of the city of Varna, classified by the Ministry of the Environment and Water Resources (MEWR) as traffic oriented, with a range of 10 to 15 m and as an urban background station with a range of 100 m to 2 km; a station in the industrial region of Devnya – classified by the MEWR as an industrially-oriented station with a range of 10-100 m and as an urban background station with a range of 100 m to 2 km. The monitoring of BaP covers the period 2012-2014 at a traffic oriented station in Varna.

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Measuring benzene concentrations is done applying gas chromatography with a flame ionization detector in „on line" mode. BaP is determined in the PM_{10} fraction applying gas chromatography-mass spectrometry. The annual, monthly, seasonal and daily variations in the concentrations of benzene and BaP have been traced in air in the regions of North-East Bulgaria, where the automated measuring stations are located. The results have been statistically processed with the analysis of variance method, and the differences have been assessed with the Student-Fisher's t-distribution criterion.

III.RESULTS AND DISCUSSION

The results from the monitoring show that the concentrations of benzene at the urban background station (city of Varna) are the highest at the beginning of the study (2007) – 2.098µg/m^3 (fig.1). Over the following years a gradual decrease in benzene concentrations is observed, reaching 0.895µg/m^3 (2009), 0.520µg/m^3 (2011) and 0.218µg/m^3 (2013), and these differences hold a high statistical significance ($0.001 \leq P \leq 0.05$). In 2014, once more, higher concentrations of benzene are registered – 0.365µg/m^3, and the increase holds high statistical significance ($P < 0.001$). Over the whole period of study, the concentrations of benzene do not exceed the average annual human health safety norm (5µg/m^3) [12].

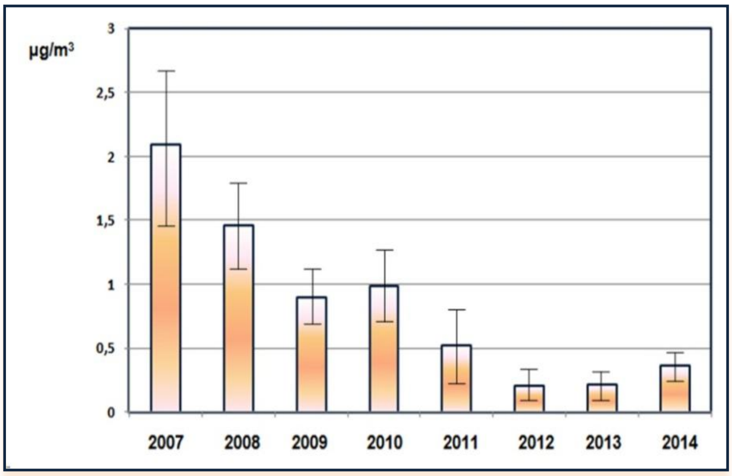


Fig. 1. Average annual concentrations of benzene at an urban background station

At the traffic oriented station in the city of Varna, the situation is very different. The concentrations of benzene vary over the years without great difference. In 2010 the levels of benzene are 0.961µg/m^3; a slight decrease is observed the following year – down to 0.609µg/m^3 ($P < 0.05$), and in 2012 the concentrations of benzene are higher again – up to 1.376µg/m^3 ($P < 0.05$) and 1.035µg/m^3 (2013) (fig.2). At the end of the monitoring period (2014), the values of benzene are already quite low – 0.539µg/m^3 ($P < 0.05$). Over the whole period (2010-2014), the annual average concentrations of benzene do not exceed the human health safety norm (5µg/m^3) [12].

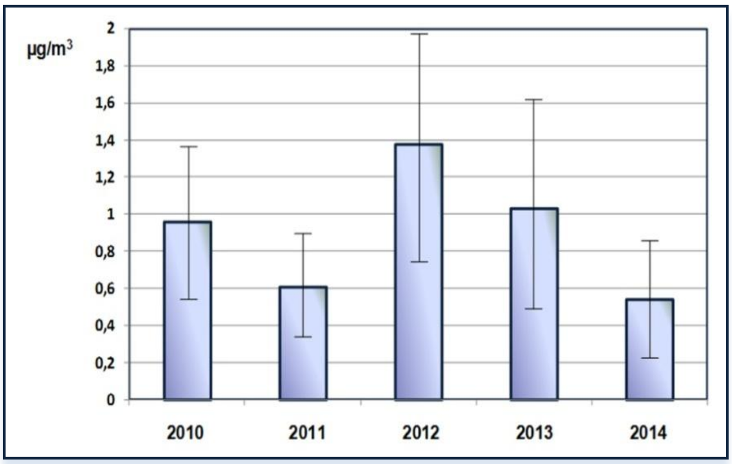


Fig. 2. Average annual concentrations of benzene at a traffic oriented station

At the industrially oriented station in the town of Devnya, a clear descending tendency is observed in the air pollution with benzene. In 2007, the concentrations of benzene are the highest – 1.185µg/m^3, they gradually fall – down to 0.833µg/m^3 in 2009; 0.657µg/m^3 in 2011; 0.603µg/m^3 in 2013 and down to 0.524µg/m^3 in 2014, and the differences hold a high statistical significance ($0.025 \leq P \leq 0.05$) (fig.3). No exceeding of the human health safety norm is observed (5µg/m^3) [12].

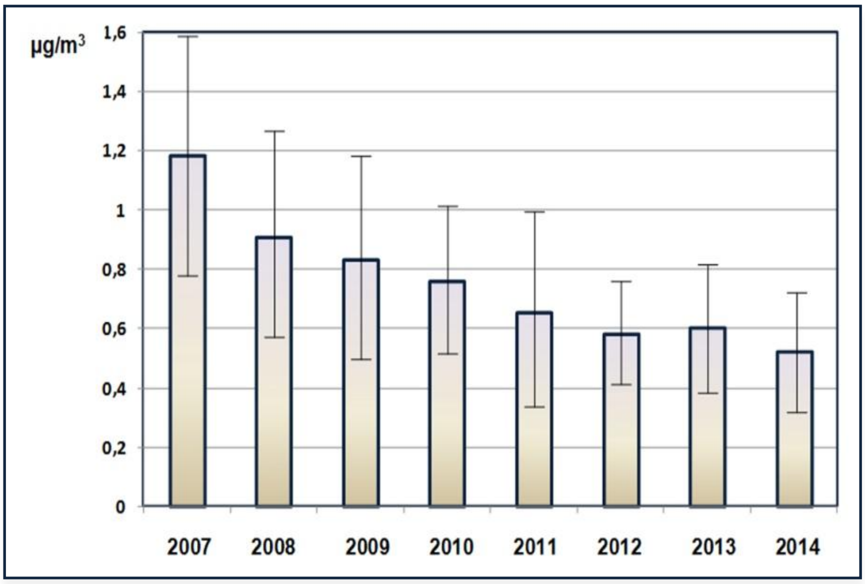


Fig. 3. Average annual concentrations of benzene at an industrially oriented station

The results from the monitoring of BaP at the traffic oriented station in the city of Varna show variations in air pollution. At the beginning of the study (2012), the concentrations of BaP are 0.601 ng/m^3, falling to 0.171 ng/m^3 ($P < 0.05$) and rising again to 0.680 ng/m^3 in 2014 ($P < 0.05$) (fig.4). No exceeding of the target norm of BaP in the PM_{10} fraction for any one calendar year is observed (1 ng/m^3) [11].

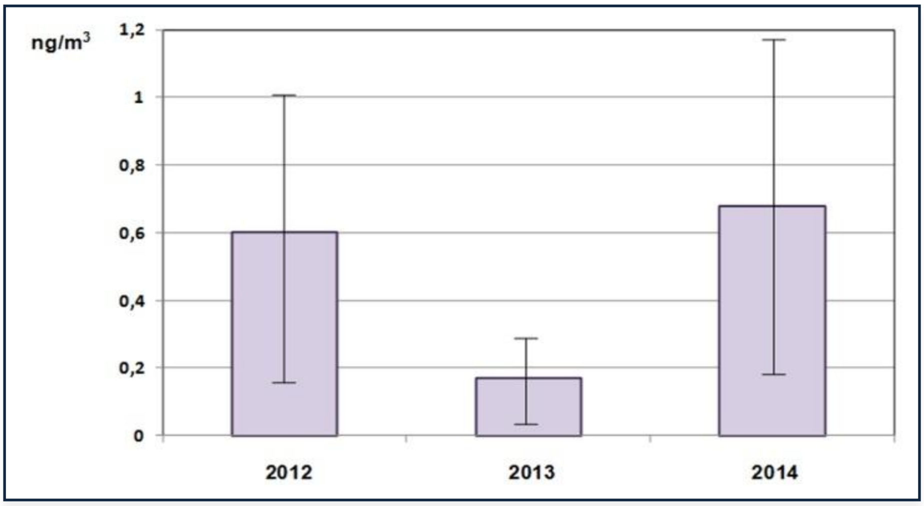


Fig. 4. Average annual concentrations of BaP at a traffic oriented station

Some authors' research shows that for the period 2013-2014, the average concentration of BaP in the $PM_{2.5}$ fraction is 0.30 ng/m^3 with a range of 0.04÷1.08 ng/m^3 [7]. Other authors establish that the average concentration of BaP in the $PM_{2.5}$ fraction, in a one-year study, is 0.27 ng/m^3 and the admissible norm is not exceeded only 7 days out of 149 [16].

The monthly and seasonal variations in air pollution show that the concentrations of benzene at the urban background station are higher during the cold period (CP), as compared to the warm period (WP) of the year. In 2007, the concentrations of benzene during the cold months fall between 1.305 and 4.329µg/m^3, and during the warm months – between 0.865 and 2.716µg/m^3.The variations during the rest of the years is analogous, despite of the fact that the values are lower. During the CP of 2009, the average monthly concentrations of benzene vary between 0.837 and 1.606µg/m^3, and during the WP – between 0.553 and 0.900µg/m^3; in 2010 – between 0.581 and 2.177µg/m^3 (CP) and between 0.653 and 0.839µg/m^3 (WP); in 2012 – between 0.171 and 0.293µg/m^3 (CP) and between 0.132 and 0.183µg/m^3(WP) and in 2014 – between 0.340 and 0.655µg/m^3 (CP) and between 0.123 and 0.374µg/m^3(WP) (fig.5). No exceeding of the average annual human health safety norm is observed (5µg/m^3).

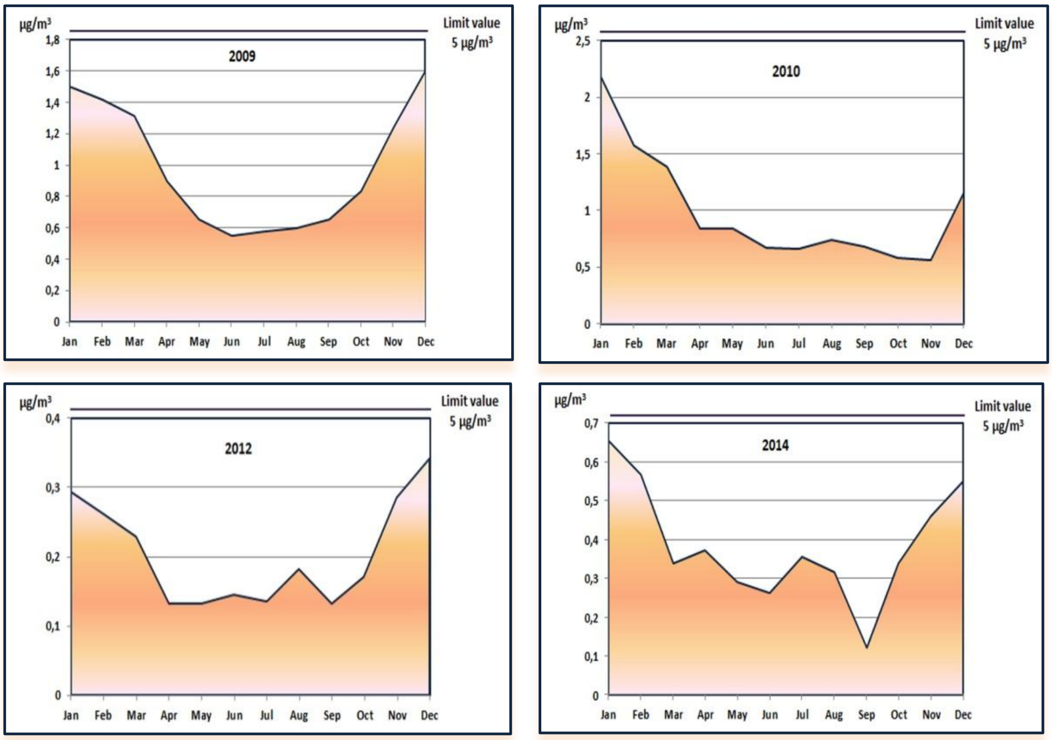


Fig. 5. Seasonal dynamics of benzene at an urban background station

The diurnal variations of benzene complement the seasonal dynamics and allocate the main sources of air pollution. In January (CP) the concentrations of benzene during the night and in the early morning hours are relatively low and vary from 0.557 to 0.622µg/m^3. During the day no significant changes are observed, with the exception of 11:00h – 0.934µg/m^3. However, after 17:00h, the concentrations of benzene gradually rise up to 2.057µg/m^3 (18:00h), 2.098µg/m^3 (19:00h), 2.101µg/m^3 (21:00h), 2.099µg/m^3 (22:00h) and they are maintained until 24:00h (fig.6). The seasonal differences in the concentrations of benzene depend mainly on the emissions from domestic heating and cooking, when burning firewood in the small domestic stoves. The higher values are also caused by the infavourable meteorological conditions during the cold months of the year (low wind speeds, fogs and temperature inversions), which hinder atmospheric dispersion.

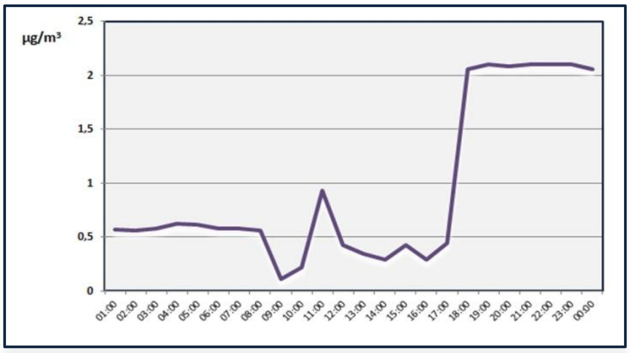


Fig.6. Diurnal variations of benzene at an urban background station, CP

Other authors' research shows concentrations of 39 volatile organic compounds (incl. benzene) in air in urban and industrial regions, and considerable seasonal differences are established in the benzene levels, and the diurnal variations are connected mainly with changes in the meteorological parameters. [17]. At the traffic oriented station in the city of Varna, clear cut seasonal dynamics are observed. In 2011, the concentrations of benzene during the cold months move between 0.398 and 1.840µg/m^3, and during the warm months – between 0.175 and 0.407 µg/m^3 (fig.7). Analogous variations are observed in other years as well. In 2013, the average monthly concentrations of benzene vary from 0.689 to 3.986µg/m^3 (CP) and from 0.411 to 0.656µg/m^3 (WP); in 2014 – from 0.554 to 1.179µg/m^3 (CP) and from 0.218 to 0.337µg/m^3 (WP) (fig.7). The human health safety norm is not exceeded. Certain differences are observed in 2012 – high concentrations of benzene are registered during the summer months – до 1.381µg/m^3. The high values are mainly the result of emissions from the exhausts of vehicles, because of the intensive traffic during the summer.

Added to petrol, C_6H_6 improves its detonation stability and is an important part of unleaded petrol. Because of that, 80-85% of C_6H_6 emissions in Europe are the result of automobile traffic. [1]. Some authors studying the emissions of harmful substances from automobile transport (CO, NO, NO_2, NO_x, SO_2, HC, PM_{10}) recommend strict control over emissions and keeping the environmental norms with the aim of reducing the pollutants and improving air quality [9].

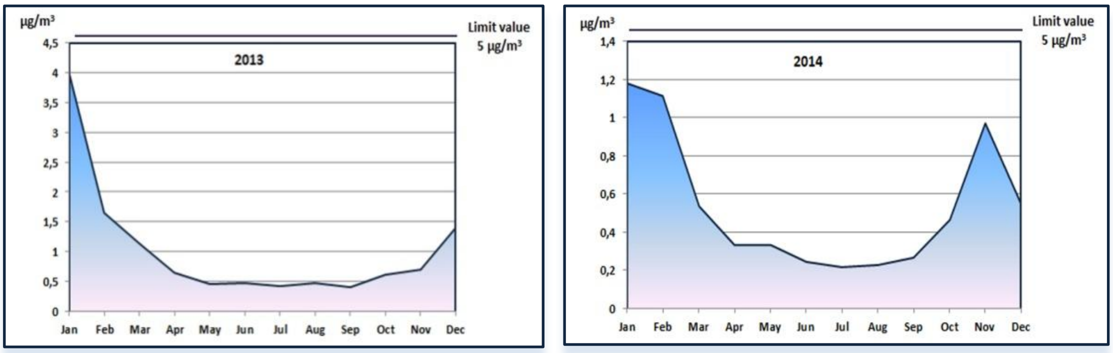
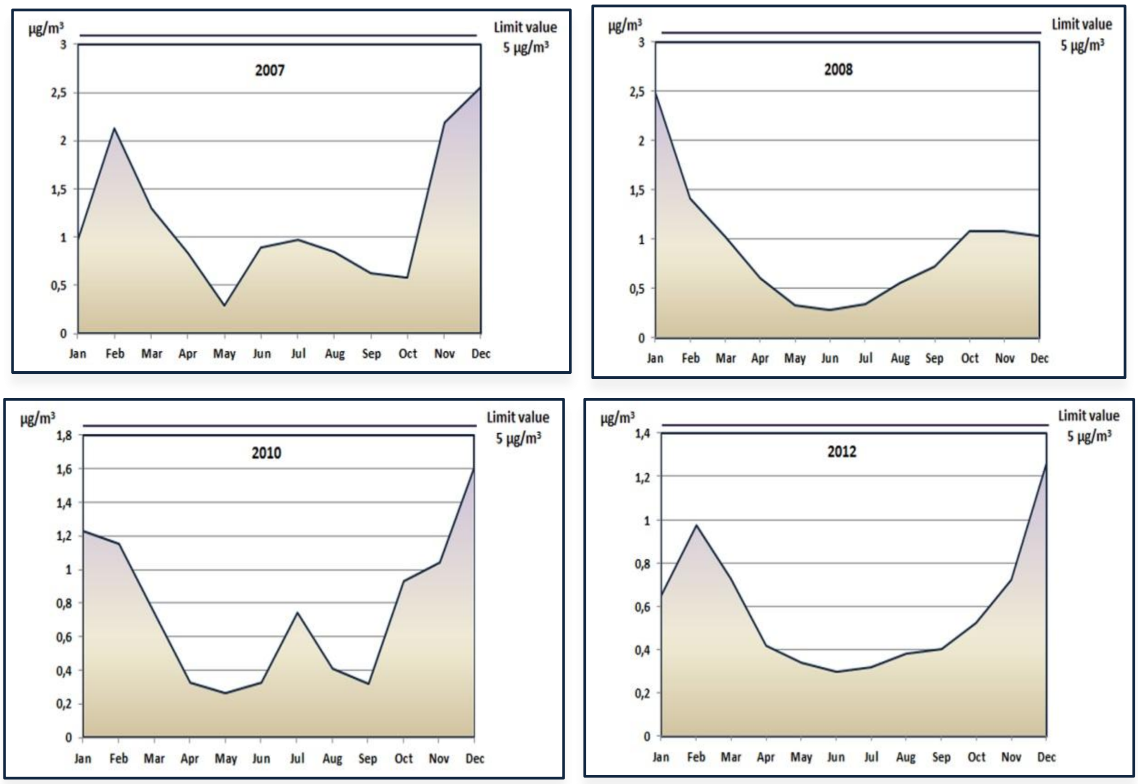


Fig. 7. Seasonal dynamics of benzene at a traffic oriented station

The presented results show that the sources of benzene in the region of the traffic oriented station in Varna relate to combustion processes – from domestic heating and cooking on the one hand, and from road traffic on the other. The analysis of the results and the pronounced seasonal variations reveal the traffic oriented station as an urban background one rather than as a typical traffic oriented station. At the industrially oriented station in the town of Devnya, the monthly concentrations of benzene yet again show seasonal differences. During the CP of 2007, the average monthly concentrations of benzene vary between 0.978 and 2.561μg/m^3, and during the WP – between 0.290 and 0.980μg/m^3, not exceeding the human health safety norm (5μg/m^3). Analogous variations are observed in other years as well. In 2008, the average monthly concentrations of benzene vary from 1.030 to 2.482μg/m^3 (CP) and from 0.320 to 0.722μg/m^3 (WP); in 2010 – from 0.931 to 1.619μg/m^3 (CP) and from 0.265 to 0.743μg/m^3 (WP); in 2012 – from 0.648 to 1.264μg/m^3 (CP) and from 0.297 to 0.403μg/m^3 (WP); in 2013 – from 0.727 to 1.194μg/m^3 (CP) and from 0.150 to 0.804μg/m^3 (WP); in 2014 – from 0.676 to 1.112μg/m^3 (CP) and from 0.231 to 0.505μg/m^3 (WP) (fig.8).



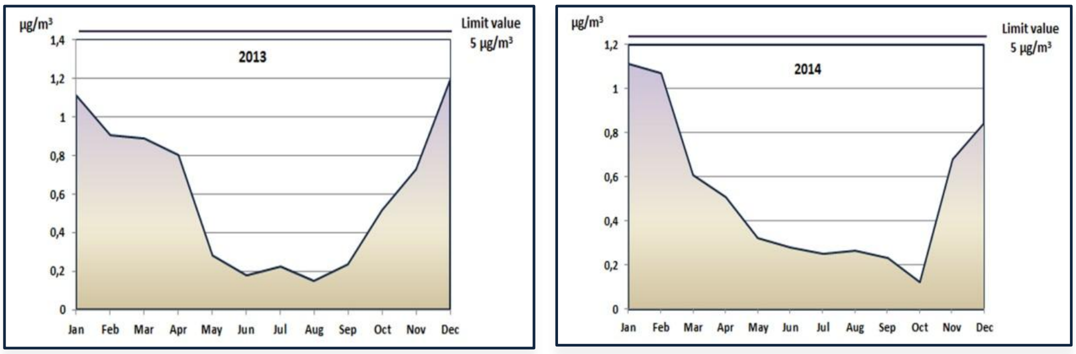


Fig. 8. Seasonal dynamics of benzene at an industrially oriented station

The seasonal dynamics once more reveal the combustion processes in the region as the main source of benzene. This is supported by the results of the diurnal variations of benzene levels during the CP of the year. It is obvious that during the night and in the early morning hours the concentrations of benzene vary between 1.09 and 1.68µg/m^3 (fig.9). After 8:00h a gradual increase of is observed in benzene pollution and the first peak is formed at 11:00h – 2.88µg/m^3. After 12:00h the concentrations of benzene gradually fall down until 17:00h. After 18:00h, however, a sharp rise in the concentrations of benzene is observed with a second peak at 20:00h – 3.67µg/m^3, and the values remain high until the end of the day.

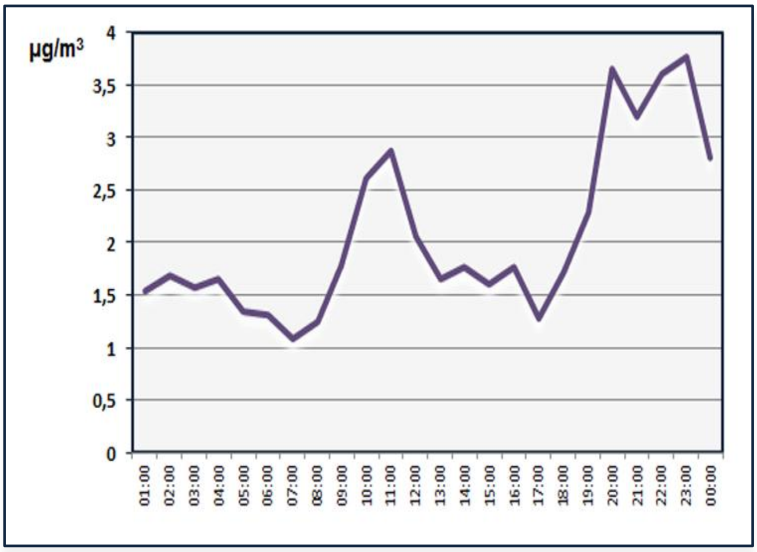


Fig. 9. Diurnal variations of benzene levels in at an industrially oriented station

The diurnal dynamics reveal the main sources of air pollution with benzene – the combustion processes during the cold season in the domestic and public sector, as well as traffic emissions in the region – automobiles, buses and lorries. Other research we have done has revealed that the manufacturing and combustion installations in Devnya, after the issuing of the IPPC permits: (№ 74/2005 – *Solvey sodi AD*, valid as of 01.2006; № 93/2006 – *Deven* Thermal Power Station valid as of 05. 2006; № 68/2005 – *Agropolychim AD* valid as of 01.2006; № 63-H1/2007 – *Devnya cement AD* valid as of 03. 2008) and the introduction of measures for implementation of new facilities in accordance with the best available techniques and environmental standards, a definite improvement in air quality is observed in the region [4] [5] [14]. For that reason currently air pollution is dominated by domestic heating and cooking and road traffic. Seasonal variations of BaP at the traffic oriented station in the city of Varna are given in fig.10. For 2012, the different concentrations of BaP for both periods are very clearly seen. During the winter months, the levels of BaP vary from 1.25 to 6.38 ng/m^3, exceeding the target norm in the PM_{10} fraction for one calendar year (1ng/m^3) [11]. For BaP, there is no daily norm to compare with. During the summer months, the concentrations of BaP vary from zero to 0.65 ng/m^3. In 2014, the seasonal variations is preserved, once more with higher concentrations during the cold months – from 0.74 to 6.10 ng/m^3, exceeding the average annual target norm for human health safety, and during the warm months – from zero to 1.32 ng/m^3. In 2013 the levels of BaP are high, with up to 2.45 ng/m^3 during the summer months, exceeding the target norm for human health safety. The results from the seasonal variations reveal the main sources of BaP in the region of the traffic oriented station in the city – road traffic on the one hand, and on the other hand –domestic heating and cooking and heating of public buildings with coal, firewood and other biomass. The input of BaP emissions from domestic heating and cooking to air pollution on a national scale is impressive – 93.8% of the total emissions for 2013 comes from domestic combustion [10]. When testing 16 PAHs in the $PM_{2.5}$ fraction (including BaP) in an urban region in different seasons, M. F.

Khan et al. established the main source of PAHs – petrol combustion (65%), diesel and fuel oil (19%), natural gas and coal (15%) [7]. Other authors, having studied the seasonal BaP variations in air, prove higher levels during the winter season, because of the wider use of firewood for domestic heating and cooking and the deteriorated dispersion conditions during the cold months of the year [5].

IV. CONCLUSIONS

There is a descending trend in air pollution with benzene at the urban background station in the city of Varna and the industrially oriented station in the town of Devnya for the period 2007-2014, and the decrease holds high statistical value. At the traffic oriented station in the city of Varna, the concentrations of benzene and BaP vary, without having a clear cut tendency. There are also seasonal variations in benzene and BaP pollution – higher concentrations during the cold months, as compared to the warm months of the year. The seasonal dynamics are supported by the diurnal variations of carcinogenic pollutants.

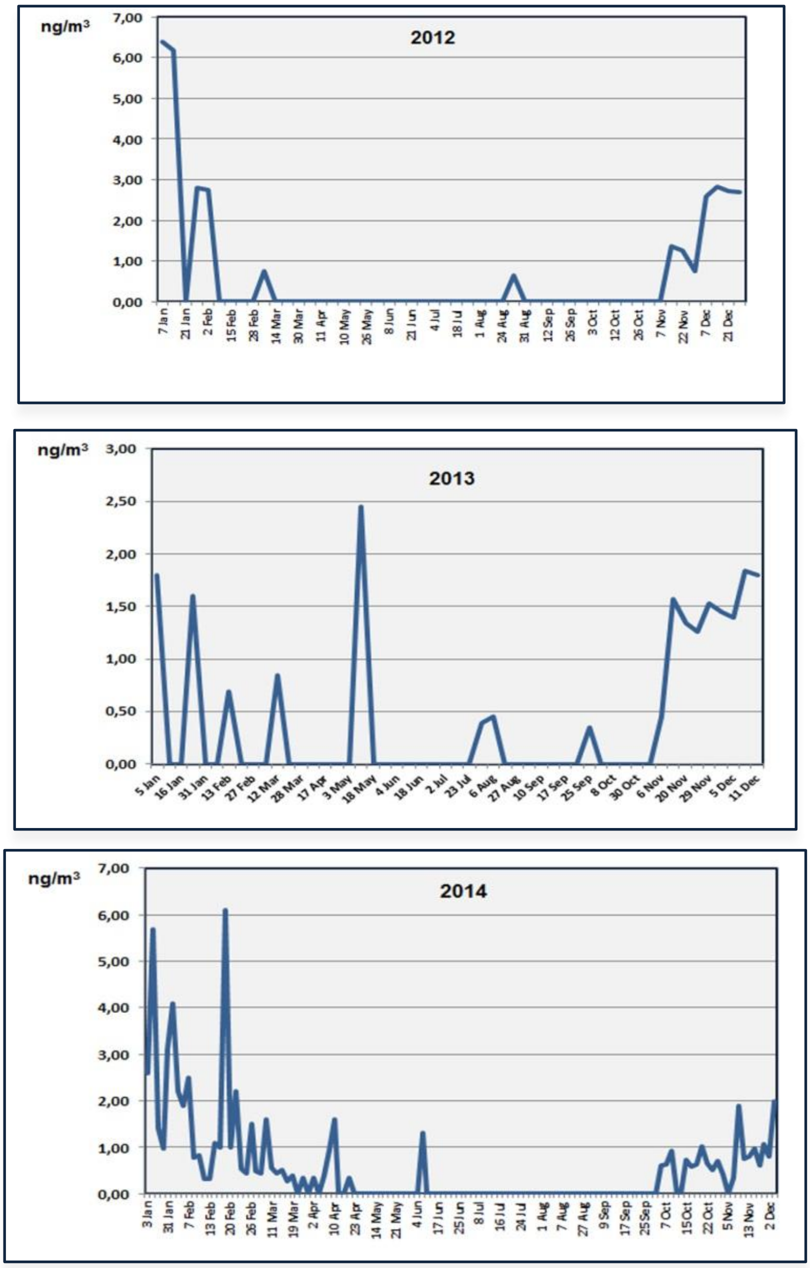


Fig. 10. Seasonal dynamics of BaP at a traffic oriented station

An updating is required of the environmental programs of the municipalities in the North-East Planning Region, especially Varna and Devnya Municipalities, relating to the existence of carcinogenic pollutants. It is also necessary to implement a system of measures for lowering coal and firewood consumption by the population, in order to lower benzene and BaP emissions from domestic heating and cooking. These measures need to be permanent in character and to be directed at densely populated quarters and regions. Despite of the fact that this is a national issue, local authorities, within their prerogatives, can stimulate the raising of energy efficiency of the buildings as a measure for lowering solid fuel consumption.

It is necessary to launch information campaigns for advising the public on energy efficiency rules, maintain a system for annual updating of the information on the used fuels for domestic heating, as well as supply the homes and public buildings with central thermal or gas heating. It is also necessary to optimize road traffic along the municipal roads with the most intensive traffic in order to reduce benzene and BaP emissions from exhaust fumes from vehicles. Information campaigns are necessary aiming at inciting the use of bicycles and public transport, as is modernizing the public transport pool and promoting the use of environmentally friendly fuels.

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