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OZONE AND OZONE PRECURSORS IN URBAN ATMOSPHERE

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ABSTRACT: *Monitoring of atmospheric air at an urban background station in the city of Varna, Bulgaria between 2007 and 2014 to evaluate the levels of the secondary pollutants O_3 and its precursors – NO, NO_2, NMHC and CO. Annual, monthly and diurnal variations were studied. The results show that O_3 and the precursors do not exceed the norms that threaten human health. As compared with the start of the monitoring, the O_3 concentrations have risen from 32.22 to 52.04 μg/m³ and the differences have high statistical significance ($0.025 \leq P \leq 0.05$). The maximum concentrations of the secondary pollutant O_3 are achieved several hours after the peak precursor levels.*

Measures are proposed for reduction of the emissions of the O_3 precursors with the aim to reduce the concentrations of the secondary pollutant in the lower atmosphere.

KEY WORDS: *O_3, ozone precursors, NO, NO_2, NMHC, CO, atmospheric air*

INTRODUCTION

The ozone in the lower atmosphere is a secondary pollutant which is formed as a result of photochemical reactions of volatile organic compounds (VOC), nitrogen oxides and CO under the influence of high temperatures and ultraviolet solar radiation. The ozone is not directly emitted by different sources, but is formed as a result of photochemical reactions in the atmosphere. For that reason the short-term peak concentrations of O_3 are not reached in close proximity to the source but at a given distance from the sources of the emissions of the substances which are precursors of ozone, so that a secondary pollutant can form. [6, 10].

The spatial distribution of O_3 concentrations is complex and depends on a number of factors, for instance: photochemical formation of ozone, its horizontal and vertical transport, the depletion of ozone by NO and dry deposition. These factors, on their part, are strongly influenced by meteorological conditions, topographic characteristics and the presence of other pollutants – dominated mainly by VOC, as well as NO_x and CO. These processes determine particular

characteristics in the distribution of O_3 concentrations in a European, subregional and local scale. The distribution structure of O_3 in urban areas is quite complicated. In the main source regions and around roads with heavy traffic, the O_3 levels are insignificant. The maximum peak concentrations are frequently observed in the suburbs and even in clean remote rural regions – i.e. at a great distance from the pollution sources [8, 14]. Because of that, the monitoring stations are located in territories with background pollution outside regions which are in close proximity with heavy traffic roads or industrial sources, because the local NO emissions can be the reason for ozone depletion and lead to disturbance in the spatial representativeness of its concentrations – the location is in housing and commercial urban areas, large streets or squares with low or no traffic, open areas with sports and recreational facilities.

Over the past years, different satellite methods have been used for obtaining information on the content of gaseous components in the atmosphere, such as O_3, CO, SO_2, greenhouse gases CO_2, N_2O, CH_4 etc., which increases the possibility to study the spatial variations of the gaseous components [17].

Ozone irritates the eyes, nose and throat. It affects the nervous system and leads to weakness, vertigo, nausea, agitation and other disturbances. It affects the immune system and decreases immunity towards respiratory diseases. Most frequently, people with asthma working in the open are the most affected by the hazardous influence of O_3 [11, 13].

The aim of this survey is to estimate the levels of urban area air pollution with the secondary pollutant O_3, study the levels of ozone precursors, the seasonal and diurnal variations, as well as the keeping of the norms for human health safety.

MATERIAL AND METHODS

The ambient Air Quality Directive 2008/50/EO [8] and Ordinance № 12 on the norms for sulfur dioxide carbon oxide, fine dust particles and ozone in atmospheric air [14] delineate the necessity of measuring ozone precursors – mainly nitrogen oxides and suitable volatile organic compounds, such as ethane, ethylene, n-butane, i-pentane, l-pentane, isoprene, ethylbenzene, etc., as well as total non-methane hydrocarbons.

In conformity with the normative requirements, the measuring of the concentrations of ozone and its precursors in atmospheric air were made in an urbanized area, the city of Varna – the third largest city in Bulgaria, with population of over 350 000. The monitoring period is 2007-2014 in one urban station for the following indicators: O_3, NO, NO_2, CO and non-methane hydrocarbons (NMHC). The station functions as an automatic measuring station with 24-hour operating mode, with geographical coordinates: +043.13.27.80; +027.54.56.64. The station has been classified as urban background station with a range of 100 m to 2 km.

The monthly and annual changes in the concentrations of O_3 and its precursors have been monitored, as well as the diurnal variations and the dependency on the solar radiation intensity. The monitoring results have been statistically processed using the variation analysis method and the differences have been estimated with A. Fisher-Student's t-distribution test.

RESULTS AND DISCUSSION

The results of the 8-years' monitoring of the quality of atmospheric air at an urban background station show that at the beginning of the survey (2007), the O_3 concentrations were the lowest – 32.22 μg/m^3 and are significantly lower than the human health safety norm of 120 μg/m^3. Over the following years, the O_3 concentrations gradually rise to 49.49 μg/m^3 in 2011, being the highest in 2013 – 52,04 μg/m^3, and the differences have high statistical significance ($0{,}025 \leq P \leq 0{,}05$) (fig. 1).

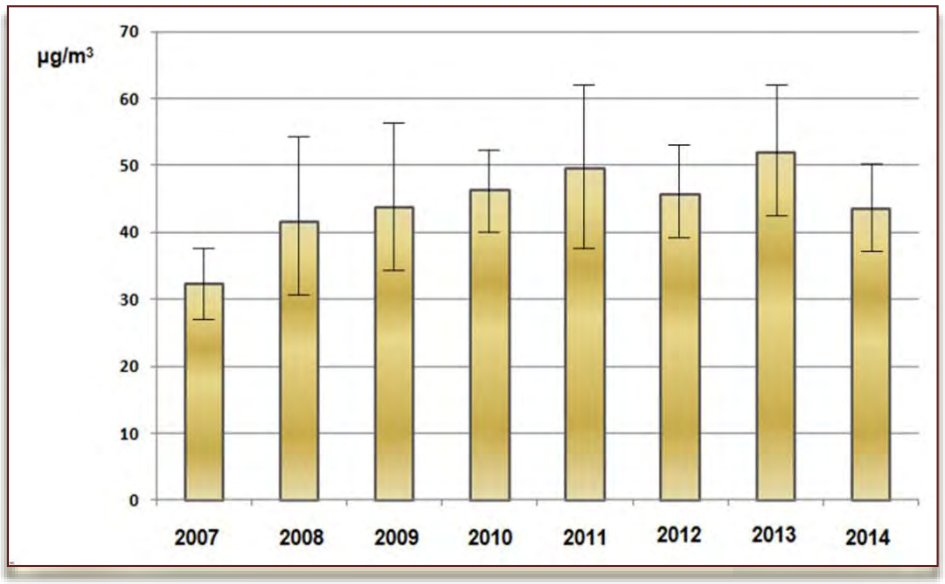

Fig.1. Average annual O_3 concentrations in atmospheric air.

The annual variations over the years determine higher O_3 values during the warm season – from 47.81 to 71.60 μg/m^3 as compared to the cold season of the year – from 22.88 to 44.24 μg/m^3 because of the higher solar radiation intensity. From the data for 2014, the O_3 concentrations during the summer months vary between 50.60 and 58.71 μg/m^3, and during the winter months – between 26.55 and 47.81 μg/m^3 (Fig.2). Some authors who study the seasonal and diurnal variations of O_3 and its precursors, also establish maximum O_3 concentrations during the summer or spring/summer season, and minimum concentrations during the winter. [1, 9, 16]. O_3 levels going above the information threshold of 180 μg/m^3 and the warning threshold of 240μg/m^3 have not been established.

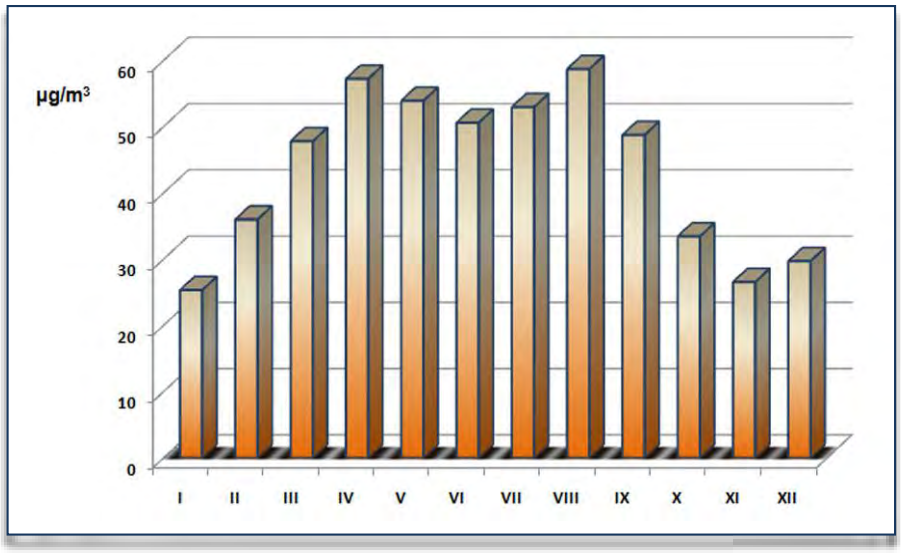

Fig. 2. Average monthly O_3 concentrations in 2014.

The correlation of the formed secondary pollutant O_3 on the solar radiation intensity in August (warm season) is given in Fig.3a. From the data, the night and early morning hour O_3 concentrations are relatively low and vary from 15.25 to 60.85µg/m^3. After 08:00 LT, though, a gradual rise of O_3 concentrations is observed – up to 113.74 µg/m^3 at 11:00 LT; 114.99 µg/m^3 at 12:00 LT, with a peak at 13:00 LT – 123.11 µg/m^3, after which a gradual fall is observed in the levels of the secondary pollutant – down to 113.24 µg/m^3 (15:00 LT), 107.90 µg/m^3 (16:00 LT), 105.08 µg/m^3 (18:00 LT) and until the end of the day the O_3 levels move between 10.13 and 39.55 µg/m^3. In their studies of the diurnal ozone variations, other authors establish maximum O_3 concentrations within the 13:00-15:00 LT time interval. [12].

The diurnal fluctuation in the intensity of the global solar radiation is analogous. During the night, zero values are registered, at 06:00 LT the solar radiation is 17.39 W/m^2. After 07:00 LT the intensity grows gradually until it reaches 285.71 W/m^2 (08:00 LT), 617.07 W/m^2 (10:00 LT), with a peak at 12:00 LT – 735.45 W/m^2, after which it gradually falls down to 375.17 W/m^2 (15:00 LT), 194.98 W/m^2 (17:00 LT) and 3.86 W/m^2 (19:00 LT). After that hour, zero values were once again registered until the end of the day.

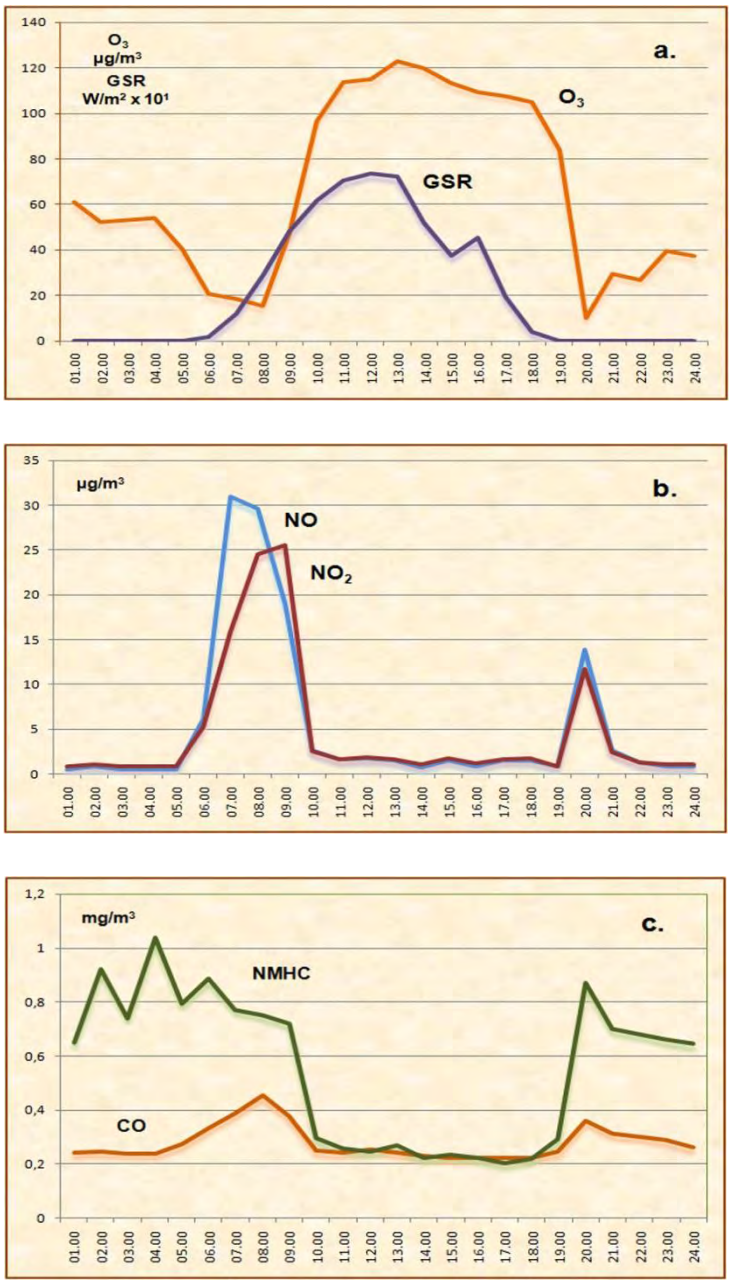

Fig. 3. The diurnal cycle of O_3 formation as related to the global solar radiation and the precursor levels

The diurnal cycle of O_3 formation in the atmospheric air as relating to the precursor levels is given in Fig.3, b and c. The peak hour for O_3 (Fig.3.a) appears after the rising of the concentrations of its precursors – NO, NO_2, CO and NMHC. With the increasing of the solar radiation, photochemical processes speed up. The concentrations of NO reach their peak in the morning hours (07:00 LT), to form peak values of NO_2 at 09:00 LT, followed by maximum O_3 concentrations in the early afternoon (13:00 LT). Non-methane hydrocarbons and CO also reach their highest levels in the morning (08:00 LT), necessary so

that later ozone can form. Since O_3 is a secondary pollutant, the maximum concentrations generally form between 3 and 5 hours after the maximum levels of its precursors have been reached. [3].

The results from the annual dynamics of NO in atmospheric air at the urban station show that the highest average annual concentration at the beginning of the survey (2009) was 17.70 μg/m^3, with a gradual trend of decrease with the NO pollutant over the following years – 4.62 μg/m^3 (2013) and 4.46 μg/m^3 (2014) (Fig.4). The difference in NO levels at the start if the monitoring and at the end of the period have high statistical significance. ($0{,}001 \leq P \leq 0{,}002$).

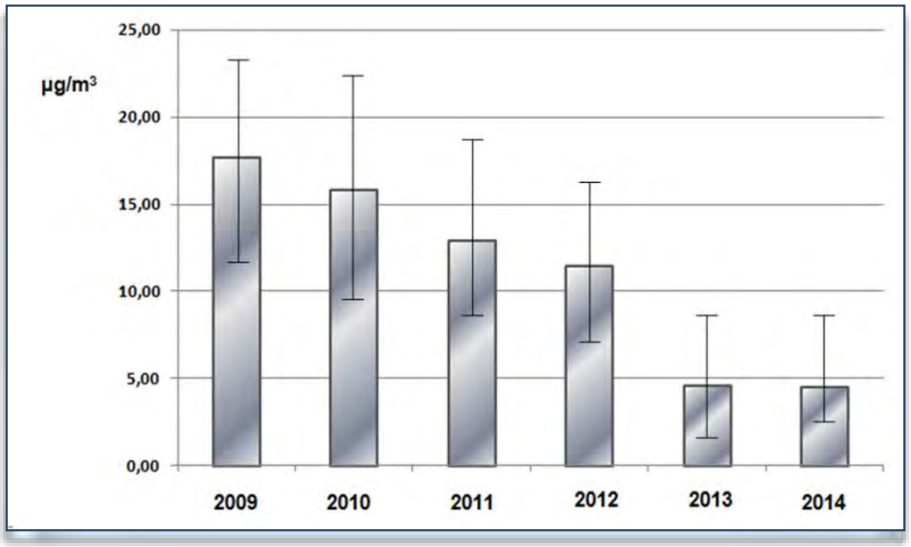

Fig. 4. Average annual concentrations of NO in atmospheric air.

During the cold season higher levels of NO are observed – between 10.50 and 45.22 μg/m^3 as compared to the warm season in the year – between 1.13 and 12.89 μg/m^3, relating mainly to combustion processes in the region of the urban background station.

The NO_2 dynamics is analogous. The highest average annual concentration at the beginning of the survey (2008) is 30,22 μg/m^3, without exceeding the average annual human health safety norm (40μg/m^3). Afterwards the NO_2 levels gradually fall down to 26.73 μg/m^3 (2011), 11.39 μg/m^3 (2012) and to 4.44 μg/m^3 (2013), and these differences have high statistical significance ($0{,}001 \leq P \leq 0{,}01$) (Fig. 5). Over the past years, no exceeding the average hourly human health safety norm (200μg/m^3) has been registered. The seasonal dependency gives higher NO_2 concentrations during the cold season – between 18.40 and 45.87 μg/m^3, as compared to the warm season – between 1.21 and 29.30 μg/m^3. Other research on atmospheric air pollution from nitrogen oxides has established seasonal variations, relating mainly to combustion processes during the winter months [2, 5, 6].

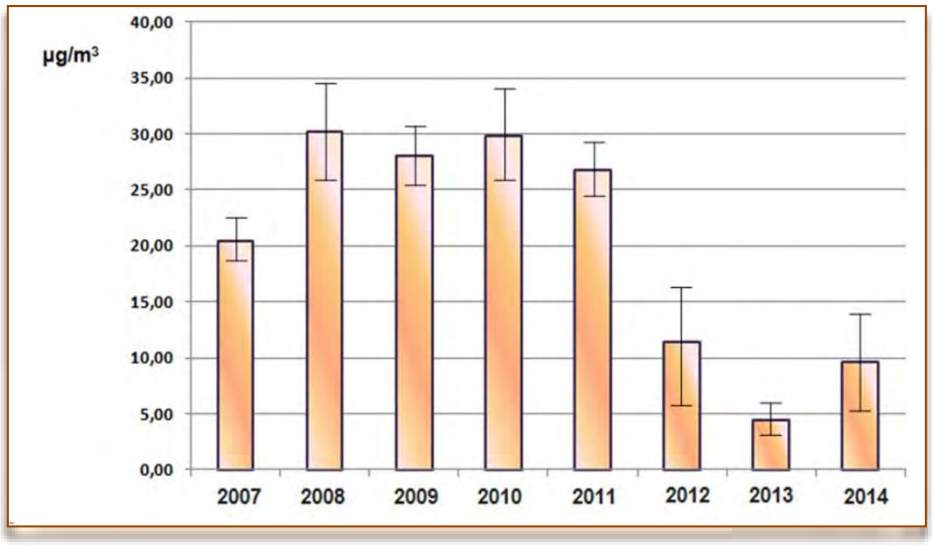

Fig. 5. Average annual NO_2 concentrations in atmospheric air

None-methane hydrocarbons (in annual dynamics) are given in Fig.6. From the data, the lowest concentrations are at the beginning of the survey (2008) – 0.148 mg/m^3. Afterwards concentrations are quite higher – between 0.342 and 0.489 mg/m^3, and the differences have high statistical significance ($P < 0.001$). The monthly NMHC variations show higher levels during the cold season – between 0.402 and 0.738 mg/m^3 as compared to the warm months of the year – between 0.202 and 0.357 mg/m^3. The seasonal dependency at the urban background station relates mainly to the residential wood burning.

The carbon oxide results show that between 2007 and 2011, the average annual CO concentrations vary between 0.594 and 0.854 mg/m^3, without exceeding the human health safety norms (10 mg/m^3) (Fig.7). After 2011 the concentrations gradually fall and by the end of the survey they reach between 0.343 and 0.456 mg/m^3, and these differences have high statistical significance ($P < 0.001$). The monthly variations show higher levels during the cold season– between 0.463 and 2.011 mg/m^3 as compared to the warm season in the year – between 0.142 and 0.549 mg/m^3.

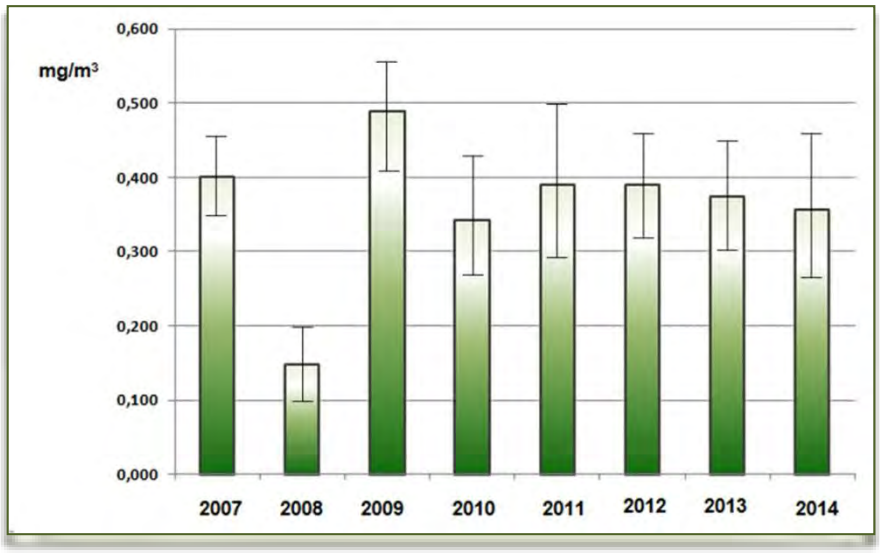

Fig. 6. Average annual NMHC concentrations in atmospheric air

The increased levels during the winter months are mainly due to combustion processes. During the cold season the atmospheric air gets polluted with CO as a result of the incomplete residential wood burning. The home coal/fire burning stoves achieve relatively low temperatures, thus creating conditions for incomplete burning of solid fuels.

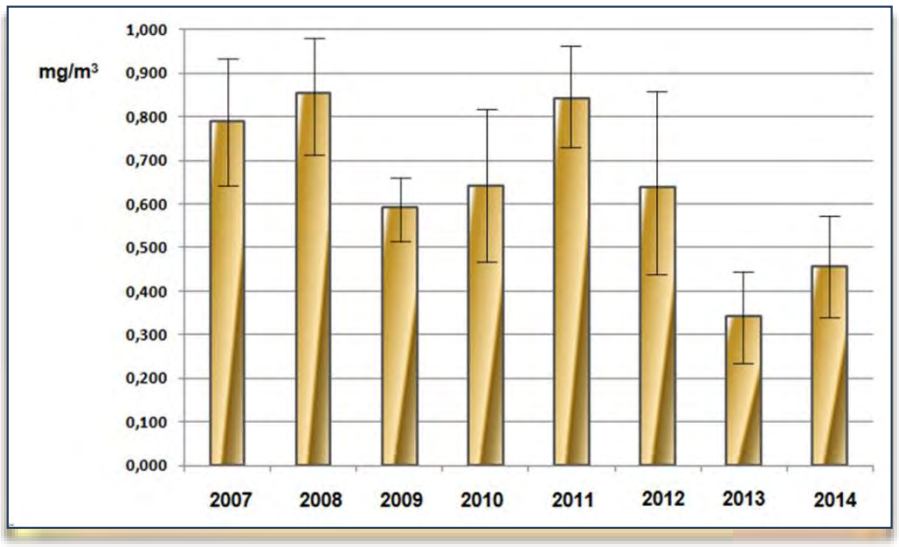

Fig. 7. Average annual CO concentrations in atmospheric air

CONCLUSIONS

The concentrations of the secondary pollutant O_3, as well as its precursors in the atmospheric air of the city of Varna (measured at the urban background station) do not exceed the human health safety norms during the whole monitoring period. The ozone formation depends directly on the intensity of the solar radiation and is the result of the higher concentrations of the precursors.

Varna Municipality works with programs for decreasing the emissions and reaching the established norms for harmful substances in atmospheric air: 2009-2014 and 2014-2016 [4, 15]. They provide measures for decreasing O_3 precursor levels, so as to decrease the concentrations of the secondary pollutant – ozone in the surface layers of the atmosphere. The measures are directed at reducing the emissions from heating public buildings and the homes and include: stage-by-stage gasification of housing quarters and the homes of the citizens, increasing energy efficiency via renovation of buildings, etc.

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