Analysis of the Tropospheric Ozone Content in the Air from Targu-Jiu and Rovinari Areas

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The measurements of the hourly ground-level ozone (O_3) concentration of two monitoring stations from Târgu Jiu and Rovinari area was analysed because elevated O_3 concentrations have a negative impact to humans, vegetation, animals and materials. The temporal distribution pattern of ozone in relation to solar radiation intensity was observed. The measurements performed revealed that ozone has an annual variation with a typical spring maximum for Rovinari area, and a typical summer maximum for Târgu-Jiu area due to increased solar radiation. Ozone has a daily pattern driven by levels of ozone precursors with a peak in the afternoons.The possible sources for the variability in the O_3 concentrations between these two stations were evaluated based on the available O_3 precursors and meteorological data. Higher concentrations of ozone recorded in the Tg-Jiu, compared with the Rovinari are due to the major contribution of NOx and hydrocarbons from vehicle traffic to the obtaining of tropospheric ozone. There were determined the daily maximum 8 h average ozone concentrations. The results show that during 2013, there were not registered values higher than the target value of 120µg/m^3 for both monitoring stations.

Keywords: tropspheric ozone level, daily maximum 8-h average ozone concentration

In the last two hundred years, there have been remarkable changes of our environment, the atmosphere being one of those environmental factors most affected by these changes. Reasons of damage of air quality are the result of the rapid growth of emissions of the specific gases as a result of the intensification of human activities [1-5]. Many human activities have a negative impact on thermal and energy balance.

While ozone layer located at the upper limit of the stratosphere is exhausted due to emissions of ozone-depleting substances (ODS), the global climate has been disrupted by emissions of greenhouse gases (GHS), weathers phenomena are becoming increasingly difficult to be predicted. Uncontrolled global warming and ozone depleting will have direct and irreparable consequences on life on the planet.

Through the Vienna Convention (1985) on the protection of the ozone layer have been established appropriate measures to protect human health and the environment against adverse effects resulting or those that could result from human activities which affect the ozone layer. Convention opens the way for the adoption of the Montreal Protocol in 1987 regarding the production and consumption of ODS - ozone depleting substances.

The Kyoto Protocol of 1987 of the United Nations Framework Convention on Climate Change requires signatory states to regulate emissions of a group of six greenhouse gases: carbon dioxide (CO_2), methane (CH_4), perfluorocarbons (PFCs), hydrofluorocarbons (HFCs), nitrous oxide (N_2O) and sulfur hexafluoride (SF_6).

Scientific evidence and the experience gained in the implementation of the two protocols have highlighted a number of links between depreciation ozone layer and global warming. It has been shown that some phenomena can amplify or diminish the other, and interdependence of these phenomena motivate the need to harmonize the foresights of the two protocols. For example, there are differences between the two protocols on the stages of phasing out the chemicals and their regulation. Some of the substances that have to be eliminated under the Montreal Protocol have as alternative substances that are covered by the Kyoto Protocol, and for them Kyoto Protocol provides measures to reduce emissions. As a result, causes and effects of ozone depleting and global warming are related. Both phenomena have negative and positive effects. CFCs and other ODS are also greenhouse gases whose global warming potential is much higher than CO_2 gas reference for measuring global warming potential (GWP).

Despite the differences between the two protocols, there have been made good progress in policies and measures to reduce emissions.

Ozone is spread in the atmosphere to a height of about 50 – 55 km. At the bottom, the atmosphere is rich in ozone, especially in areas where the temperature is low, since this gas is very unstable at high temperatures. Therefore, the amount of ozone is higher on the mountains than the sea, or in the polar regions compared to the equatorial regions.

NO_x (NO and NO_2) and volatile organic compounds (VOC) are precursors for the ground-level ozone (O_3). It is primarily produced by complex photochemical reactions. Accumulation of the ozone in the troposphere is influenced by physical and chemical processes, and by the meteorological conditions [6].

Balance between production and dissociation of the stratospheric ozone was deteriorated with the emergence

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of chemical compounds called ozone depleting substances (ODS).

Depending on the field of use of, ODS are divided into several categories refrigerants used in air conditioning and other cooling equipments (CFCs - chlorofluorocarbons, and HCFC - hydrochlorofluorocarbons); substances used for firefighting (halons); substances for the manufacture of foam insulation (CFC and HCFC); solvents used as cleaning agents in the electronic industry (CFCs, HCFCs, methyl chloroform and carbon tetrachloride); substance used as fumigants (methyl bromide); substances used in various fields such as paints and coatings, inks, medical applications (CFCs, HCFCs, methyl chloroform and carbon tetrachloride).

These substances are released as a result of human activities, and they are stable in the troposphere. Because they are not soluble in water, are not removed by decreasing of the precipitation. Their presence in the atmosphere has a strong negative impact on ozone. Since many of them have a long life (eg CFC between 45 and 1700 years), they are transported by vertical convective processes in the stratosphere, where they are dissociated by the action of UV radiation. By their dissociation is resulting chlorine that destroys ozone.

Ozone depletion has negative effects not only on aquatic and terrestrial ecosystems, but also on materials, chemical processes in the atmosphere, influencing the whole balance of life on earth. Numerous studies have highlighted the complex response of managed grasslands to ozone [7-9].

The effects of ozone on human health are skin sunburns (erythema), skin peeling, cellular necrosis, different types of skin cancer, damage to the cornea (photo keratitis), cataracts, blindness or ocular cancer, impairments in airway function, weakened immune system [10, 11].

Effects of ozone on the environment are reducing photosynthesis, growth and flowering, especially of the plants susceptible to increased UV radiation (wheat, barley, oats, corn, peas, tomatoes), negative influence on nitrogen fixation in the soil, impaired reproductive capacity and vitality of small and unicellular organisms, harmful effects on sensitive organisms, especial phytoplankton and zooplankton [12].

In this study, ground level ozone data measured from two different urban locations in Jiu county for one year were analyzed to assess the temporal distribution patterns of ozone in relation to relevant meteorological parameters. Our analysis was made to describe the general features of the ozone pattern, and to compare data collected from two monitoring stations.

Observation sites and instrumentation

For Rovinari, the main source of ambient air pollution is the Thermal Rovinari, located to the north-east of the village. Except Rovinari power plant, an important contribution to air pollution have also the exploration mining in the area (Pinoasa, Tismana, and Rosia careers), in particular the activities of coal loading, unloading and transport to and from deposits.

These activities contribute to air pollution in the area especially with the powder (in extremely meteorological conditions), and gas emissions (SO_2, NO_x) in the case of self-ignition of coal deposits.

Also, road traffic and domestic activities have a negligible contribution to air pollution in the area, due to the fact that many of the homes in the area use charcoal for heating during the cold season.

Measures on ozone concentrations were concentrated on two layers of the atmosphere: the troposphere, the boundary layer of the Earth’s surface where ozone concentrations over certain limits, constitute a danger to the environment and health; in the stratosphere, where ozone depletion determines increasing of UV radiation entering the earth’s atmosphere with a negative impact to the earth life.

Studies on ozone concentrations were more focused towards agglomeration areas due to the presence of ozone precursors (hydrocarbons and oxides of nitrogen), which can lead to high concentrations of ozone in certain weather conditions [13-15].

Given the fact that about 9% of the total ozone is found in the troposphere, it is important to know its distribution in this atmospheric layer.

Measurements of ozone concentrations in the Tg-Jiu have been performed using an automatic air quality monitoring GJ1, industrial type, located in the northwestern part of the city Tg-Jiu. (fig. 1 - left). Air quality monitoring network in the Rovinari includes an automatic station measuring air quality GJ2, located in the south-east of the village Rovinari (fig. 1 - right).

Both stations performed continuous measurements of the following indicators sulfur dioxide (SO_2), nitrogen oxides (NOx), related to nitrogen dioxide (NO_2), carbon monoxide (CO), ozone (O_3) and particulate matter PM_{10} fraction.

Automatic air quality monitoring stations are equipped with a meteorological station for performing measurements about wind direction, wind speed, atmospheric pressure, temperature, humidity, solar radiation and rainfall.

Measurements of automatic stations are transmitted every hour, as hourly concentrations to a local server, at the Environmental Protection Agency Tg-Jiu, where, after the verification and validation they are forwarded to a central server located at National Agency for Environment Protection Bucharest. The data are used for the production of newsletters, reports and briefings.

The daily maximum 8 h average ozone concentrations shall be considered to verify the compliance with the target value. The daily maximum 8 h average ozone concentration

Fig. 1. Setup of the automatic monitoring station GJ1 (left), and GJ2 (right)

is chosen by examining 8h ozone concentration averages, calculated from hourly data and updated each hour.

Month / Day	J	F	M	A	M	J	J	A	S	O	N	D
1	27.7	22.2	31.1	38.2	45.4	36.09	36.7	35.1	37	31.4	49.9	35.5
2	25.3	13.7	40.4	37.9	43.7	41.8	37.9	36.4	35.8	27.3	45.3	30.4
3	20.7	7.5	38.5	32.6	44.1	40.9	39.5	36.2	32.2	25.6	34.2	38.1
4	17.5	21.4	44.5	34.8	39.6	37.7	39.9		32.2	30.3	33.5	24.1
5	22.4	22.9	40.3	31.4	39.8	35.4	37		33.8	32	33.9	25.4
6	30.5	19.9		43.1	36		40.4	43.2	35.3	35.5	35.3	27.9
7	29.9	12.6		35.7	42.1		42.4	42.2	38.3	31.4	33	34.4
8	28.1	20.3	30	32.6	44.7	41.9	38.1	42.7	39.1	34.2	27.7	33.1
9	26	30.5	31.3	30.2	41	45	37.3	40.3	35.7	30.7	29	33.4
10	22.4	31.7	35	32.9	39.7	40.6	36.3	39.9	40.8	29.4	36.5	31.6
11	14.2	30.4	32.9	44.8	40.7	39.1	37.4	38.2	35.5	36.7	37.8	26.1
12	26.9	34.9	35.4	42.2	41.1	37.3	37.8	43	28.6	37.4	49.8	29.3
13	23.6	28.5	28.9	45.1	33.3	42.2	37.5	39.9	34.3	28.5	51.8	29.6
14	20.5	34.8	26.1	45.7		50	34.5	41.3	34.6		38	29.5
15	15.3	28.9	46.1	44.9	35.3	46.7	35.9	34.3	36.4	18.1	47.1	30
16	10	22.4	47.8	42.9	42.4	46.9	33	32.3	35.7		39.2	26
17	7.4	17.9	44.7	45.5	37.3	47.5	36.6	38.6	37.7	48.9	34.7	23.8
18		30.5	37.6	46.5	41.5	48.6	35.8	40.4	33.7	34.5	35.2	22.8
19	12.4	31.8	33.4	54.2	49.7	51.3	37.5	39	29.4	36.1	49.1	23.6
20	12.4	24.3	42.6	46	47.6	44.2	39.9	39.6	33.7	36.8	37	19.1
21	9	21.5	31.3	52.5	51.8	55.5	37.5	40.5	32.3	28.2	32.9	20
22			45.1	42.8	38.8	56.2	36.3	41.8	39.6	34.3	33	27.3
23	16.1	30.6	47.1	40.6	32.2	51.8	37.2	41.6	33	35.2	35.9	23
24	14.4	28.6	41.2	47.4	34.4	52.7	40.3	36	29	38.9	35.7	25.4
25	13.3	27.7	33.3		42.2		40.9	39.8	34	29.1	41.4	30.1
26	17.7	25.4		50	43.5	25.8	42.3	38.8	39.3	30.7		25.4
27	19.5		38.6	45.7	45.3		41.7	34.1	35.6	32.2		22.5
28	19.6	40.4	45.1	49.5	45.7	34	43	30.8	34.1	30.2	39	21.9
29	16.9		45.7	48.1	42.6	36.5	43.1	35.1	30.6	26.4	29.6	22.1
30			27.4	47.6	41.6	33.7	37.3	32	30.9	31.9	31.3	24.4
31			20.7		31.8		36.5	34.9		35.9		25.6

Table 1
THE DAILY MAXIMUM 8-HOUR AVERAGE OZONE CONCENTRATION IN TG-JIU

Month / Day	J	F	M	A	M	J	J	A	S	O	N	D
1		25.4	23.9	24.9	23.9		33.3	39.3	37.7	18.7		17
2		18	27.1	21.6	27.1		35.7	41	31.8	12.6		12.1
3		16.3	26.6	22.2	26.6		36.6	41.4	23	18.2		14.3
4	16.8	23.6		23.9		26.2	39.5	43.9	25.1	22.7		11.4
5	22.7	19.3		23.1		25.4	31.4	45	25.5	28.9		15.4
6	25.5	19.8	26.2	26.6	26.2	26.3	36.9	49	31.2		14	19.5
7	27	17.5	21.3	24.8	21.3	27.4		48.4	28.2		22.2	21.9
8	23.3	16.4		22.3	20.1	31.1	39.9	52.8	35.4		17.8	22.9
9	20.7	14.2	20.1	21.8	20.3	33.5	34.9	55.3	26.6		16.6	19.9
10	11.2	16.6	20.3	20.3	23.9	37.3	30.1	50.7	32		16.1	21.6
11	11.9	19.2	23.9	25.5	21.8	24.7	36	44.3	26.7		17.1	12.8
12	26.8	22.7	21.8	25.2		29	41.2	49.8	14		15.6	15.4
13	22.1	22.5		25.4	16.3	31	37	48.1	26.6		17.3	15.5
14	21.4	22.2	16.3	28.5	14.2	33	32.9	45.6	33.1		16.8	11.3
15	15	17.9	14.2	28.3	29.6	35.1	34.9	35.7	31.7		21.5	11.1
16		18.1	29.6	28.7	28	38.7	31.4		35.7		21.7	11
17	11.1	14.1	28	33.7	26.3	37.8	36.2		28.6		15.2	11.4
18	15.6	17.6	26.3	28.3	22.8	35.8	35		29.6		16	10.4
19	16.7	15.4	22.8	35.3	19.2	35.1	36.4		23.5		19.3	9.1
20	15.2	15.4	19.2	27.9	22.8	32.5	42.2		26.6		18.5	9.1
21	11.2	15.3	22.8	37.7	16.3	41.8	34.1	35.3	23.9		12.8	12.6
22	23.2	17.3	16.3	30.9	20.6	34.9	37.1	39.3	24.1		15.4	13.7
23	20.5	15.3	20.6	26.3	28.4	33.4	39.3	36.5	23.4			10.3
24	15.4	14.3	28.4	29.7	23.8	34.8	45.3	20.6	20.2			10.4
25	19.5	14	23.8	21.6	22.6	29.1	44.6	32.5	32			11.4
26	22.4	17.4	22.6	32.5	22.6	27.6	50.2	26.7	42.7		13	10.4
27	22.7	21.5	23.1	30.6	23.1	24.7	48.7	15.4	42.4		14.1	11.5
28	21.9	24.4	23.8	31.8	23.8	32.9	48.2	10.7	26.6		14.6	11.4
29	17.7		22.7	29.7	22.7	31.1	50.8	26.5	17.8		15.6	11.1
30	15.1		19.6	31.2	19.6	25.8	34.3	22.9	17.4		15.6	10.7
31	23.3		15.2		15.2		42.4	29.7				9.4

Table 2
THE DAILY MAXIMUM 8-HOUR AVERAGE OZONE CONCENTRATION IN ROVINARI

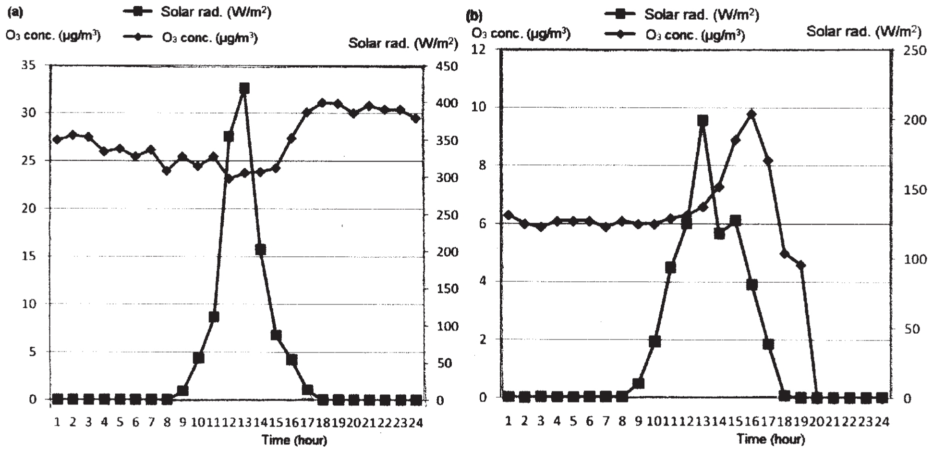

Fig. 2. Hourly average O_3 concentration variation and solar radiation on 06.01.2013 at Tg. Jiu (a) and 17.01.2013 at Tg. Jiu (b)

Results and discussions

Availability of data and the results of monitoring of tropospheric ozone in the Tg-Jiu for 2013 are presented in table 1, and those for ozone content Rovinari area are presented in table 2.

The data were made available by the Tg-Jiu Environmental Protection Agency.

Interpretation of results was done according to Law. 104/2011 on ambient air quality [16]. Under this law, the target value for ozone concentration to protect human health is 120μg/m^3, specifying that it has not to be exceeded more than 25 days per year. To verify compliance with the target value, it shall be considered the maximum daily 8 h averages.

Maximum 8 h averages daily is chosen by examining 8-hour average ozone concentration, calculated from hourly data and updated each hour.

As shown in table 1, during 2013 there were not registered values higher than the target 120μg/m^3.

Analysing the daily maximum values it was found that the lowest ozone concentrations were recorded in January, and the highest in April.

Maximum ozone concentration has a value lower than the target with 74.6%, and the minimum ozone concentration has a value lower than the target value with 93.8%.

The data presented in table 2 indicate that in the case of Rovinari area were not recorded values higher than the target value established for tropospheric ozone to protect human health (120 mg/m^3). The lowest ozone concentrations were recorded during December, and the highest in August.

Among the meteorological factors measured, the greatest influence on ozone concentrations has solar radiation.

In urban agglomeration, in the early morning due to heavy car traffic (especially between 6 AM and 8 AM), and other human activities are emitted primary pollutants (NOx and hydrocarbons) in higher concentrations that react with existing ozone causing a slight decrease in ozone concentrations in the atmosphere. With increasing the solar radiation increases ozone, photochemical reactions reaching a maximum level around noon, leading to peak in ozone concentrations variation.

Looking at the hourly average for periods from January with the highest and smaller ozone concentrations, and making a correlation with solar radiation, it is found that in the Tg -Jiu, the highest concentrations of ozone during the day with the maximum value (30.5 μg/m^3 in 06.01.2013) were not recorded in the time period with the largest solar radiation (11 AM – 2 PM), but in the time period 4-7 PM (fig. 2a).

During this period, there may not be a correlation between hourly average ozone concentrations during the day and solar radiation intensity.

However, on 17.01.2013, the daily maximum 8-hour average was the lowest in January (7.4 mg/m^3), the highest hourly average ozone concentrations were recorded in the range time 1 to 5 PM, and solar radiation intensity was highest between 10 AM to 5 PM (fig. 2b).

In the Rovinari, in January there was an 87.7 % data capture. Maximum daily concentration with the highest value was registered on 07.01.2013 and represented 22.5 % of the target, and maximum daily concentration with the lowest value was recorded on 10.01.2013 and accounted for 9 3% of the target value.

Monthly average represented 15.9 % of the target.

In February 2013 was recorded in the Targu -Jiu data capture 92.8% and an increase in the concentration of ozone beside the previous month to 24.4%, without exceeding the target value, and for the Rovinari to recorded 100 % data capture.

Maximum daily concentration with the highest value represented 33.7% of the target value, and the lowest value was only 6.3% in the Tg-Jiu, and the maximum daily concentration Rovinari 21.2 % of target was determined on 01.02.2013, and the lowest daily maximum was determined on 25.02.2013, it represents 11.7% of the target value.

Monthly average maximum concentration values daily in February 2013 from the Rovinari showed a value close to that of January, representing 15.3% of the target value.

For the next month, March, in the Targu Jiu with a data capture 90.3 %, the monthly average concentration of this period was higher than the previous month by 31.7 % and higher with 48.4 % than in January.

Daily maximum concentration represented about one third of the target and it was registered on 16.03.2013, and the lowest was 17.3%.

In Rovinari area, in March was an increase of the maximum daily concentrations representing 18.8% of the target value.

Maximum daily concentration with the highest value represented nearly a quarter of the target value was recorded on 16.03.2013 while the lowest value was 11.8%, being recorded 15.03.2013.

April is the time of year when there were recorded the highest ozone concentrations in the Tg -Jiu, the average of this period representing 35.4 % of the target value.

Daily maximum concentration was recorded on 19.04.2013 and represented 45 % of the target value, and the minimum concentration value was recorded on 09.04.2013.

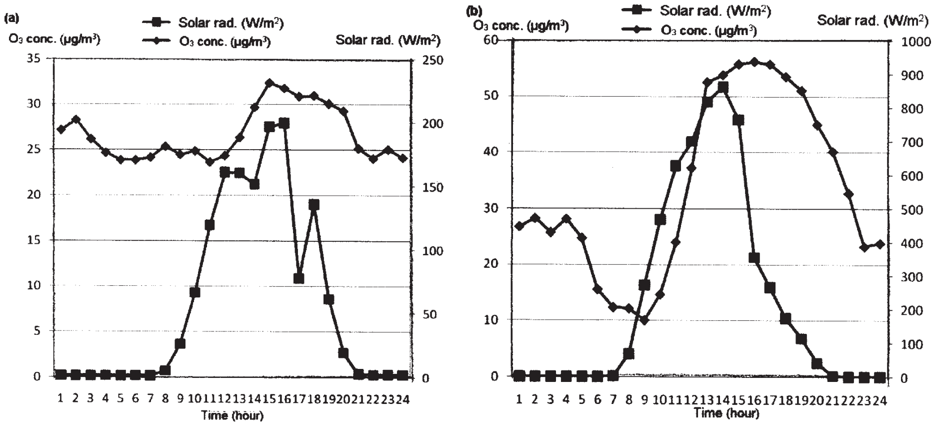

Fig. 3. Hourly average O_3 concentration variation and solar radiation on 09.04.2013 (a), and on 19.04.2013 in Tg. Jiu area (b)

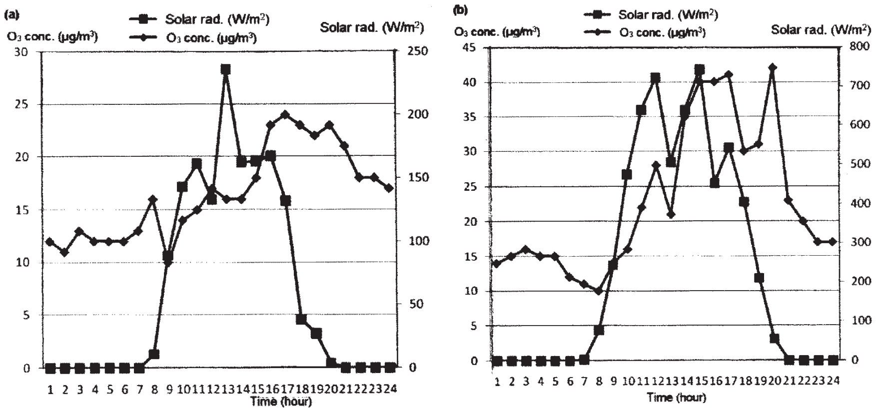

Fig. 4. Hourly average O_3 concentration variation and solar radiation on 02.04.2013 (a), and on 19.04.2013 (b) in Rovinari area

An analysis of hourly values from 09.04.2013 when the maximum daily concentration averages on 8 h was the lowest value of the month (30.2 $\mu g/m^3$), shows that the highest ozone concentrations were measured in the time interval 1 to 7 PM, when the reactions of formation of tropospheric ozone are carried at their maximum level due to solar radiation during this period (fig. 3a).

Between 11 AM and 6 PM, the intensity of solar radiation showed values from 78 to 200W/m^2, and at 3 to 4 PM when solar radiation intensity was highest (196 and 200W/m^2 respectively) were recorded the highest hourly average ozone concentrations.

The same situation is also found on 19.04.2013 in Targu-Jiu where maximum daily 8 h averages concentration presented the highest value of the month (54.2 $\mu g/m^3$).

In this period, the highest ozone concentrations were recorded in the time interval 12 AM to 7 PM, and the most intense solar radiation was registered between 10 AM and 4 PM (fig. 3b).

On 02.04.2013, in the Rovinari the highest hourly average ozone concentrations (23-24 $\mu g/m^3$) were recorded in the time interval 3 PM to 8 PM, and the solar radiation with the highest values were recorded between 9 AM and 7 PM (fig. 4a).

On 19.04.2013, in the Rovinari when maximum daily concentration presented the highest value of the month, the highest hourly average ozone concentrations (31-44 $\mu g/m^3$) were recorded in the time interval 3 to 8 PM, and solar radiation with the highest values were registered between 9 AM to 7 PM (fig. 4b).

In May and June, in the Târgu-Jiu the maximum daily 8-hour averages were quite close, monthly averages were almost identical (41.2 and 41.3 $\mu g/m^3$ respectively).

In June the highest value was recorded daily during the year 2013 (56.2 μg /m^3) on 22.06.2013. At this time of the month, the highest hourly average concentrations of the year were recorded, some of them representing almost half of the target value. These were recorded in the time

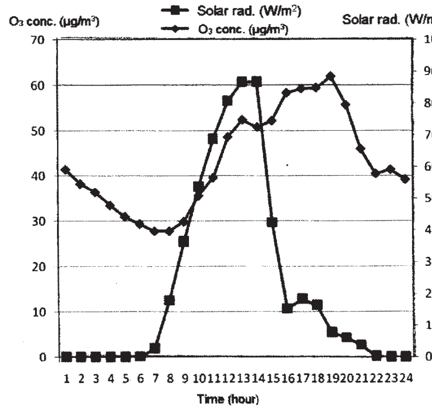

Fig. 5. Hourly average O_3 concentration variation and solar radiation on 22.06.2013 in Tg. Jiu

interval 4 PM to 8 PM, while the intensity of solar radiation had the highest values between 9 AM to 3 PM (fig. 5).

In the Rovinari area, in May the ozone concentrations in the air had a decreasing tendency compared to April, the monthly average daily maximum concentrations representing 18.8% of the target, at a 90.3% data capture.

Maximum daily concentration with the lowest value was recorded on 14.05.2013 and it represented of 11.8% of the target value, and the highest value registered was on 15.05.2013 being a quarter of the target.

The following month, June is characterized by increasing of ozone concentrations in the air by almost 29% from the previous month, the average daily maximum concentrations representing 26.4% of the target at a 90% data capture.

Maximum daily concentration with the highest value represented 34.8% of the target value, and that with a minimum value 20.6%.

Since July, we assist in the Targu-Jiu to a gradual decrease of ozone concentrations.

Thus, in July and August, the average monthly values showed almost identical (38.3 and 38.2$\mu g/m^3$), which were lower than those in June with about 7 % and nearly

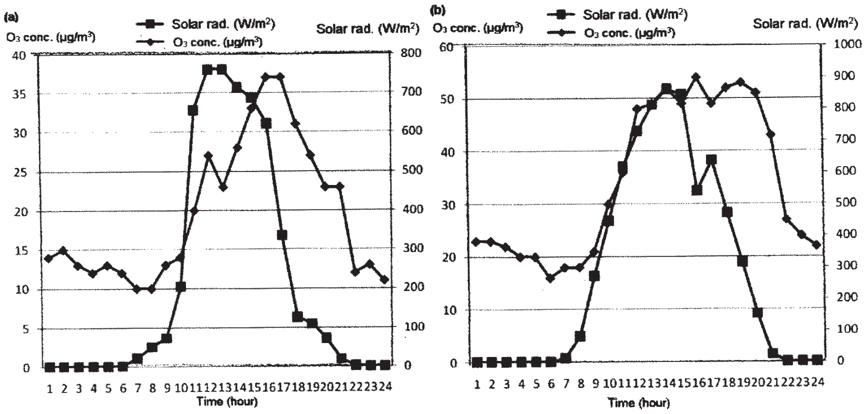

Fig. 6. Hourly average O_3 concentration variation and solar radiation on 10.07.2013 (a), and on 29.07.2013 (b) in Rovinari area

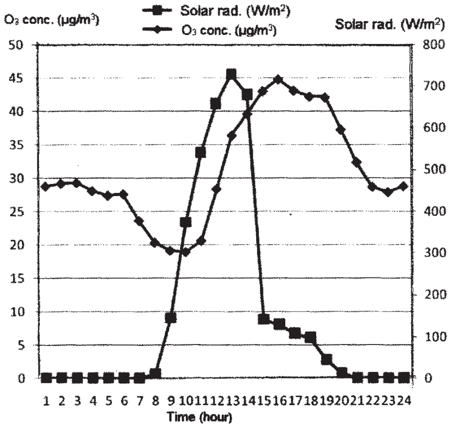

Fig. 7. Hourly average O_3 concentration variation and solar radiation on 10.09.2013 at Tg. Jiu

10 % than in April, the period with the highest daily average concentrations of ozone in the year.

Ozone concentrations continue to decrease also in September and October 2013 in the Târgu-Jiu, thus the monthly average ozone concentrations are lower in October than in September by about 6 %, at a data capture 100 % in September, and 93.5 % in October.

Daily average concentrations of the two months had values close to each other.

The period from 2013 with the highest concentrations of ozone in the atmosphere of the Rovinari was July, when the monthly average was 32.2% of the target value at the data capture 96.8%.

Maximum daily concentration with the lowest was recorded on 10.07.2013 and was a quarter of the value calculated on the 29.07.2013 that represented 42.3% of the target.

Analyzing the hourly average concentrations of ozone in these two days shows that the highest values were recorded in the hours with the most intense solar radiation.

Thus, on 10.07.2013, the highest concentrations of ozone in air (23-27 µg/m^3) were registered in the time interval 12 AM to 7 PM, and solar radiation showed the highest values (205 - 761W/m^2) in the time interval 10 AM to 6 PM (fig. 6a).

On 29.07.2013, when the highest daily maximum concentration was registered, the highest hourly average concentrations (36-54 µg/m^3) were recorded between 11 AM and 9 PM, and solar radiation with the highest values (273 - 862W/m^2) were registered between 9 AM to 7 PM (fig. 6b).

August was characterized by ozone concentrations whose daily averages were within a fairly wide range. The daily maximum 8-hour average with the lowest value represented 8.9 % of the target and was registered on 28.08.2013, and the highest value was recorded on 08.09.2013 and represented 46.1 % of the target. Monthly average concentration of ozone in the Rovinari air represented 31.6 % of the target value being close to that of the previous month.

In Targu Jiu, in September the lowest daily average ozone concentration represented nearly 24% of the target value, and the highest daily average ozone concentration represented 34%.

In October, the lowest daily average concentration was 15.1% of the target value, and the highest about 41%, with specification that these values were isolated values , so that the monthly average was lower than that of September.

It can be concluded that, the hourly average concentrations during September with the highest average daily concentration on 10.09.2013 and the highest hourly average ozone concentrations were recorded in the time interval 1 PM to 7 PM, and solar radiation presented maximum values between 10 AM to 2 PM (fig. 7).

In September, the ozone concentrations in the air of the Rovinari continues to decrease, thus the monthly average of daily maximum concentration represented 23.4% of the target at 96.8% data capture.

Lowest daily maximum concentration was recorded on 12.09.2013, it represents 11.7% of the target value. Maximum daily concentration with the highest value was

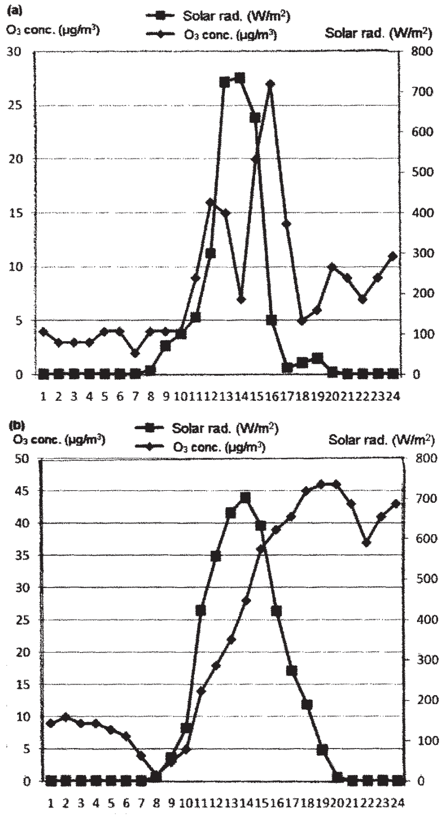

Fig. 8. Hourly average O_3 concentration variation and solar radiation on 12.09.2013 (a) and on 26.09.2013 (b) in Rovinari area

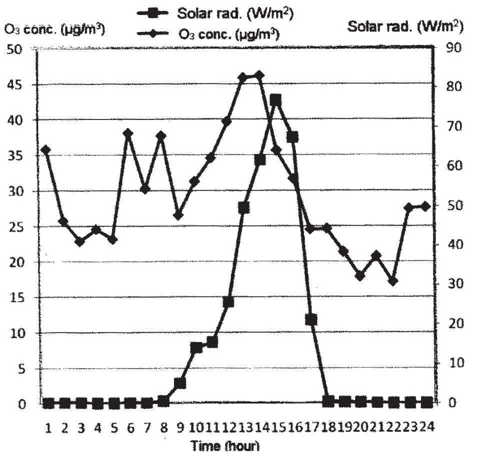

Fig. 9. Hourly average O_3 concentration variation of and solar radiation on 03.12.2013 at Tg. Jiu

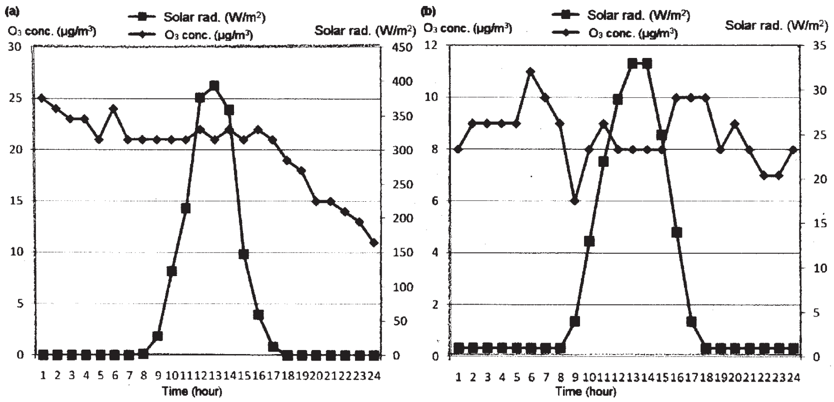

Fig. 10. Hourly average O_3 concentration variation and solar radiation on 08.12.2013 (a) and on 19.12.2013 (b) in Rovinari area

measured on 26.09.2013 and represented 35.6% of the target.

Analyzing the hourly average ozone concentrations on 12.09.2013, it was found that the highest concentrations were recorded between 12 AM to 5 PM, and solar radiation showed increased intensity between 10 AM and 4 PM (fig. 8a).

On 26.09.2013, the maximum daily concentration showed the highest value (42.7 $\mu g/m^3$), average hourly ozone concentrations with highest values were recorded between 12 AM to 2 PM, and solar radiation presented the highest values between 10 AM to 6 PM (fig. 8b).

In October 2013, because of the technical reasons the Rovinari ozone analyzer didn't work.

In November, in the Targu-Jiu ozone concentrations were more elevated than those registered in October and September, the highest daily average was recorded on 13.11.2013, and the lowest were recorded on 08.11.2013.

Monthly average concentration of this period represented 31.4% of the target value.

In December, in the Targu-Jiu was a 100% data capture and monthly average ozone concentration approximately 28% lower than the one of the previous month, this being the second largest after the one in January, when they recorded the lowest concentration of ozone in the year. In this month, the intensity of solar radiation was also greatly reduced. For example, on 03.12.2013 when it recorded the highest daily average concentration, the solar radiation intensity showed the highest values between 1 PM to 4 PM, and hourly average ozone concentrations were highest between 11 AM to 4 PM (fig. 9).

In November, in Rovinari area it was observed a decrease of ozone concentrations in the air, and the average of this period representing approximately 14% of the target values at the data capture of 73.3 %.

The highest daily concentration was recorded on 07.11.2013 and represented 18.5 % of the target, and maximum daily concentration with the lowest value was registered on 21.11.2013 and represented 10.7% of target value.

In the Rovinari, December represented period of 2013 with the lowest ozone concentrations in the air, the monthly average representing 11.2 % of the target.

Maximum daily concentration with the highest value represented about 19 % of the target value, being recorded on 8.12.2013.

During this time of the month, it can not be made a correlation between hourly average ozone and solar radiation. Hourly average concentrations of ozone in this day had fairly close values, the highest concentration (25$\mu g/m^3$) was recorded at 1 AM and lowest (11$\mu g/m^3$) at 12 PM.

Solar radiation presented the highest values between 10 AM and 5 PM (fig. 10a).

Maximum daily concentration with the lowest value was recorded on 19.12.2013 and represented only 7.6 % of the target value. Not this time there is no correlation between the hourly average concentrations of ozone and solar radiation (fig. 10b).

Hourly average ozone concentrations showed very similar values (6-11 $\mu g/m^3$) all of the day, and solar radiation was registered the highest values between 10 AM and 5 PM.

If in the cities, especially in urban agglomerations, responsible for the production of substances that cause the formation of tropospheric ozone are vehicles (NOx and hydrocarbons), in other areas industrialization is responsible for ozone pollution.

A comparative study regarding ozone levels in these two areas analyzed outstanding number of issues related to the ozone presence in ambient air.

The first observation is that the maximum daily values were higher in Tg-Jiu than Rovinari, this can be attributed to the major contribution of vehicle traffic to the formation of tropospheric ozone by air pollution by ozone precursors (NOx and hydrocarbons).

Figure 11 shows the evolution of monthly average concentrations of maximum ozone daily concentrations in the two areas studied.

The biggest differences between the two areas in terms of ozone concentrations in the air have been observed in November, when the monthly average concentration Tg -

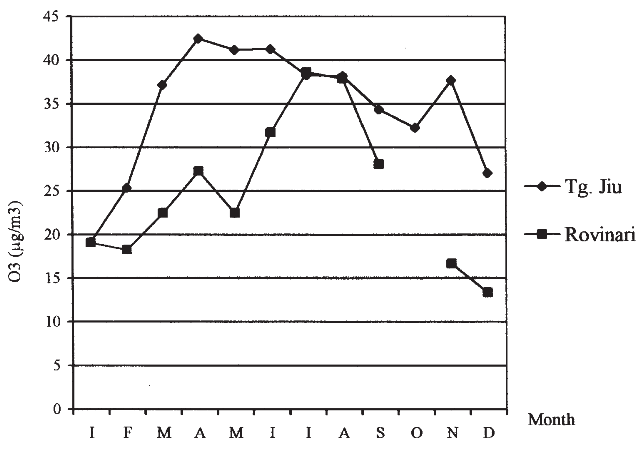

Fig. 11. Variation of monthly average ozone concentrations in areas Tg-Jiu and Rovinari in 2013

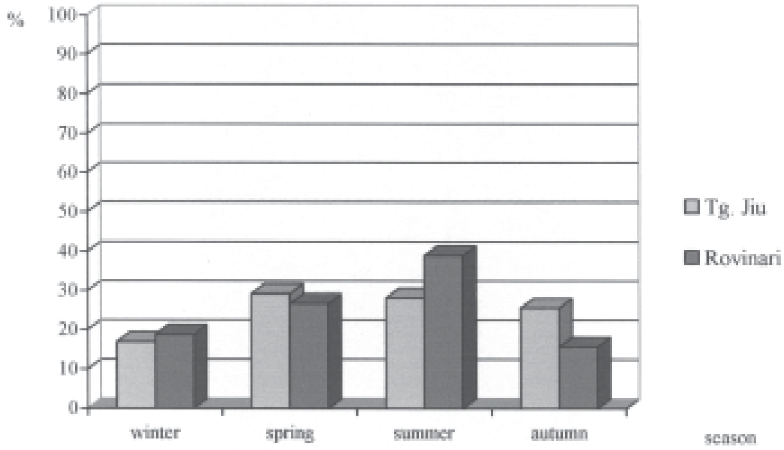

Fig. 12. Seasonal variation of ozone concentration in Tg. Jiu and Rovinari areas

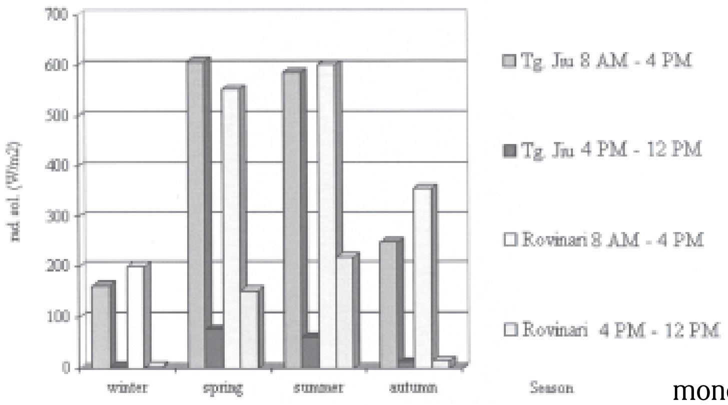

Fig. 13. Seasonal variation of solar radiation in Tg. Jiu and Rovinari areas

Jiu was about 2.3 times higher than in Rovinari. An almost equally large difference was registered in December, when the ozone concentrations in Tg - Jiu were 2 times higher than in the Rovinari.

Differences quite large (over 1.5 times) were observed in the period from March to May.

January, July and August were the times of the year when differences between ozone concentrations were insignificant.

For the Tg - Jiu area, the highest ozone concentrations in the air were recorded in April, and the average of this period represented 34.4% of the target. Instead, for the Rovinari, the highest concentrations were recorded in July, the average of this period represented 32.2% of the target.

Regarding the lowest daily maximum values , these were registered in January for the Tg-Jiu, monthly average concentration representing 16% of the target, and the lowest daily maximum values were registered in December for the Rovinari, and monthly average concentration represented 11 2% of the target value.

Following the further seasonal variation of ozone concentrations in the air in the two areas, it was observed that higher values of ozone were recorded in spring when solar radiation was more intense than in other seasons (fig. 12).

For the Tg -Jiu, the amount of ozone concentrations in spring and summer seasons represented 57.5 % of the total, and 65.6 % for Rovinari area.

For the Tg-Jiu, the highest concentrations were recorded in the summer season, the lowest ozone concentrations were recorded in the winter season.

Variations of the concentration of ozone in the atmosphere depend not only on the sources of emission of pollutants ozone precursors, but also on weather conditions.

Sunlight is one of the factors that influence variation of the ozone concentrations in the air. Under the influence of light, nitrogen dioxide dissociates with obtaining of nitrogen monoxide and oxygen atoms. The dissociation rate of nitrogen dioxide and that of oxygen atoms forming is directly proportional to the light intensity. Since the concentration of ozone is related to the atomic oxygen concentration, it means that the formation of ozone depends on the intensity of solar radiation.

Measurements of solar radiation showed that the highest intensity of solar radiation was recorded between 9 AM to 4 PM.

Figure 13 presents the solar radiation intensity (average) in one day of each season for time periods between 8 AM to 4 PM, 4 PM to 12 PM in Tg- Jiu and Rovinari areas, in 2013.

Values represent the averages of solar radiation for the time period 8 AM – 4 PM and 4 PM- 12 PM for the following days January 16, April 19, July 22 and September 12, both in Tg. Jiu and Rovinari on 2013.

The intensity of solar radiation showed high values in the time period 8am - 4pm, the highest values were recorded in the spring and summer seasons, and lowest values were recorded in winter.

A less obvious correlation between the concentrations of ozone and solar radiation intensity was observed during the month of December in the Rovinari, even if the solar radiation presented high values between 10am to 3pm, average ozone concentrations had values close throughout the day.

Conclusions

The following conclusions can be drawn based on those presented, and based on the results of the measurements of the ozone content in tropospheric air in 2013 in Targu-Jiu and Rovinari areas.

Depending on the ozone presence, in the troposphere or the stratosphere, ozone effects are different. The tropospheric ozone has negative effects on the environment and human health, and the one in the stratosphere has positive effects.

Ozone presents in the troposphere is not emitted direct by factories or cars, but is a secondary air pollutant resulting from the reaction of hydrocarbons and nitrogen oxides under the action of solar radiation.

Measures that have been taken in Tg-Jiu and Rovinari areas during 2013, revealed that ozone concentration values were lower than the target set by the regulations in force.

For Tg-Jiu, the lowest ozone concentrations were recorded in January and the highest in April.

Tropospheric ozone concentrations had values increasingly starting with January to the summer season, followed by their progressive decrease until December.

The highest ozone concentrations during the day were recorded in the time period when the intensity of solar radiation showed the highest values .

Seasons with the highest ozone concentrations were spring and summer, followed by autumn, and the lowest were recorded in the winter season.

For Rovinari area, the ozone concentrations in the air were below the target value.

The highest values of ozone concentration were registered on July in 2013, and the lowest were recorded on December, without one registering of progressive increasing and decreasing as were found in Tg-Jiu area.

Correlations between the concentrations of ozone and solar radiation intensity were possible to be made in the most periods of the year.

Higher concentrations of ozone have been recorded in the Tg-Jiu, compared with the Rovinari, this may be due to the major contribution of vehicle traffic to the obtaining of tropospheric ozone air pollution by ozone precursors (NOx and hydrocarbons).

The highest concentrations of ozone for the Tg-Jiu was observed in the spring season, and in the summer season for Rovinari area.

The lowest ozone concentrations for the two areas analyzed were recorded in winter season.

In urban areas it is found that the transport and vehicles are the main sources of air pollution, mainly due to their large number.

Improving air quality by reducing pollution from vehicles is achieved by optimizing the combustion process and the use of anti-pollution devices, but also by territorial systematic measures.

In the case of companies and organizations, improving air quality can be achieved through implementation of measures to reduce emissions of gaseous and particulate pollutants.

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