CHANGEABILITY OF SURFACE OZONE CONCENTRATION IN TBILISI IN LAST 30 YEAR

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Abstract. The increased attention is recently paid to studies of the surface ozone concentration (SOC) in different countries. This first of all is connected to the fact that ozone is the toxic pollutant of the atmosphere, whose concentration frequently exceeds the maximum permissible standard, in consequence of which the World Organization of Public Health included it in the list of five basic pollutants, whose content must be monitored during the determination of the air quality. The regular researches of (SOC) in Tbilisi are conducted by the Mikheil Nodia Institute of Geophysics from 1980 to present time. Thus, since 1984 there are data of the continuous series of ozone observations. The measurements of ozone were conducted by the electro-chemical ozone instrument OMG-200.

In this work some results of the statistical analysis of observational data of the average semi-annual and annual values of the (SOC) in the period from 1984 through 2013 are presented. Observational data for 15 hours are given.

In the proposed work the analysis of data is carried out with the use of the standard statistical analysis methods of random events and methods of mathematical statistics for the non accidental time-series of observations

The statistical structure of the changeability of the mean annual, half year and monthly values of SOC in Tbilisi for the indicated period of time is investigated. Correlation connection between mean annual, half year and monthly values of SOC is established. The special features of the changeability of average monthly values of SOC on the three ten-year-old periods of time are studied.

Trends and random components of time series of mean annual (five order polynomial) and half year (the five order polynomial for cold period and six order polynomial for warm period) values of SOC are eliminated.

Key words: Surface ozone concentration, air pollution.

Introduction

The increased attention is recently paid to studies of the surface ozone concentration (SOC) in different countries. This first of all is connected that ozone is the toxic pollutant of the atmosphere, whose concentration frequently exceeds the maximum permissible standard, in consequence of which the World Organization of Public Health included it in the list of five basic pollutants, whose content must be monitored during the determination of the air quality [1-4]. The regular researches of surface ozone concentration in Tbilisi are conducted by the Mikheil Nodia Institute of Geophysics from 1980 to present time [1, 5-7]. Thus, since 1984 there are data of the continuous series of ozone observations.

In particular, the effect of the meteorological parameters on the surface ozone concentration [1], the climatic effects of SOC [5], the long-term variations of SOC were studied [7-10].

In recent years the large-scale experimental work on a study of photochemical smog and surface ozone and their negative influence on the health of the population of Tbilisi are carried out. Monitoring smog forming and its associated atmospheric parameters both in the regime of stationary measurements on two fixed bases of observation and in irregular mobile regime route measurements on 20 points in different districts of city are carried out (content in air of ozone, of submicron aerosols, radon, light ions; solar radiation intensity, visibility, cloudiness, temperature, humidity, wind, pressure; gamma-radiation of soil; intensity of galactic cosmic rays) [7,11,12].

For example, physical statistical model of the connections of processes of formation of photochemical smog and ozone with different atmospheric parameters is obtained, on the basis of which the conditions for the formation of smog ozone into different seasons of year are established; the maps of the spatial distribution of SOC in Tbilisi are represented; it is shown that according to the data of the stationary point of measurements it is possible to estimate the level of the pollution of air of the Tbilisi city as a whole; ultra-short term (2-5 hours) and short term (12 hours) the statistical models of the prognostications of smog ozone, whose accuracy composes 64-78 %, is developed [7].

The effects of the action of the concentration of surface ozone, and also others determining and associating the photochemical smog of the atmospheric parameters on the health of people are revealed. In particular, it is established that under the conditions of Tbilisi in recent years the maximum day concentration of ozone of 50 mcg/m^3 and above extremely unfavorably influences the health of people. This concentration considerably of those lower (3-5 times) accepted in Europe and USA the maximum permissible concentrations of ozone. It appeared according to data for the years of 1984-2010, that the increased concentrations of surface ozone (and also the associating it harmful for the health people of the components of smog) on the average growth of the average annual mortality of the population in Tbilisi by 1680 people. This composes 14.1% of the average annual mortality of the population of the city, which is 3 times higher than for the same parameters in the developed countries. It is established that in recent years in comparison to the eightieth years of the past century, the population of Tbilisi became more sensitive to air pollution (negative effects for the health of people and the cases of lethal outcome they occur with lower concentrations of surface ozone) [7, 12].

The statistical structure and trends of the SOC in Tbilisi periodically were established [5, 7-10, 13]. In particular in 1984-2010 and 1984-2012 trends of the mean annual and half year values of SOC had the forms of the polynomial of the fourth power [10,13].
In this work some results of the statistical analysis of observational data of the average semi-annual and annual values of the surface ozone concentration in the period from 1984 through 2013 are represented (for 15 hours on the local time).

Study area and methods
The measurements of ozone were conducted by the electro-chemical ozone instrument OMG-200. Observational data for 15 hours are presented. The unit of the ozone measurement is omitted below (mcg/m^3). In the proposed work the analysis of data is carried out with the use of the standard statistical analysis methods of random events and methods of mathematical statistics for the non accidental time-series of observations [14, 15].
The following designations will be used below: Y_{warm}, Y_{cold} and Y – the mean of six months' (April-September, October-March) and yearly values of surface ozone concentration, Min – minimal values, Max – maximal values, σ – standard deviation, C_v – coefficient of variation (%), R –coefficient of linear correlation, R^2 – coefficient of determination, K_{DW} – Durbin-Watson statistic, α – the two-sided level of significance. The estimation of the difference between the investigated parameters was evaluated according to the Student's criterion ($\alpha \leq 0.2$). According to Student's criterion ($\alpha \leq 0.2$) the significant value of R (for the time-series of observations in 30 years) is 0.24. Gradations of the correlation coefficients: $R \leq 0.39$ – weak, $0.40 \leq R \leq 0.59$ – moderated, $0.60 \leq R \leq 0.79$ – high, $0.80 \leq R \leq 0.1.0$ - strong.
The trend curve was determined by the optimum selection of the regression equation of the dependence of real data on the time and the Durbin-Watson statistic value for the residuals. It was assumed that the *trend + background* component = the values of trend curve - minimum of the absolute value of residuals; *Random components* = value of residuals + absolute value of residuals. As a result: *Real data* = *Trend* + *Background* component + *Random components.*

Results and discussion
The results in table 1-3 and fig. 1-6 are given.
Real data. The standard statistical characteristics of mean monthly, seasonal, semi-annual and annual values of SOC in Tbilisi in the table 1 and upper part of table 2 are represented.
As follows from table 1 mean monthly values of SOC varies from 21.2 (December) up to 58.4 (April); the minimal value of SOC varies from 3 (January) up to 34 (April); the maximal value of SOC varies from 38 (December) up to 107 (March); standard deviation varies from 9.1 (December) up to 20.2 (March); coefficient of variation from 19.3 (June) up to 44.6 (November).
Mean seasonal values of SOC (table 1) vary from 31 (Winter) up to 56 (spring); the minimal value varies from 10.7 (winter) up to 30.7 (summer); the maximal value of SOC varies from 52.7 (winter) up to 85 (spring); standard deviation varies from 9.2 (Summer) up to 15.2 (spring); coefficient of variation from 18 (Summer) up to 35.1 (winter).
Mean semi-annual and annual values of SOC (table 2, upper part) varies from 36.1 in the cold period up to 51.8 in the warm period, the minimal value of SOC varies from 15.2 in the cold period up to 31.5 per warm half-year, maximal - from 55.3 in the cold period to 69.0 in the warm period, standard deviation varies from 9.4 per warm half-year up to 11.5 in the cold season, coefficient of variation from 18.1% per warm half-year up to 31.9 % in the cold period.

Table1. The statistical characteristics of mean values of SOC in Tbilisi
in different month and seasons in 1984-2013

Parameter	January	February	March	April	May	June	July	August
Mean	31.2	40.6	55.1	58.4	54.4	52.7	52.5	48.5
Min	3	11	19	34	28	30	29	27
Max	66	68	107	99	80	76	79	72
σ	13.4	14.5	20.2	17.3	14.1	10.2	11.8	11.9
C_v(%)	42.8	35.7	36.6	29.6	26.0	19.3	22.4	24.5
Parameter	September	October	November	December	Winter	Spring	Summer	Autumn
Mean	44.5	37.8	30.2	21.2	31.0	56.0	51.2	37.5
Min	23	18	11	4	10.7	30.3	30.7	20.3
Max	70	68	59	38	52.7	85.0	66.3	59.3
σ	10.5	11.7	13.5	9.1	10.9	15.2	9.2	10.2
C_v(%)	23.7	31.0	44.6	42.8	35.1	27.1	18.0	27.1

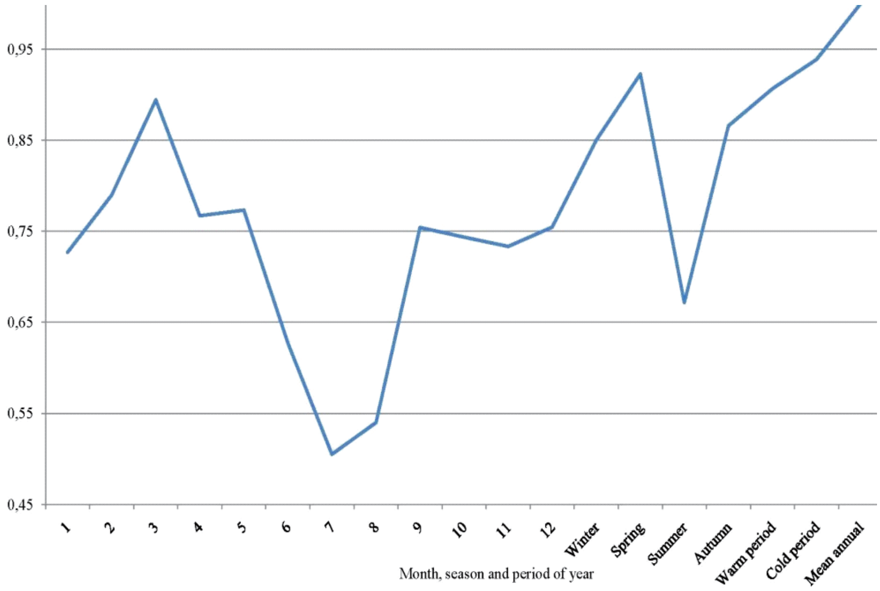

Figure 1. Coefficient of linear correlation between the mean annual values of surface ozone concentration and SOC in different periods of year

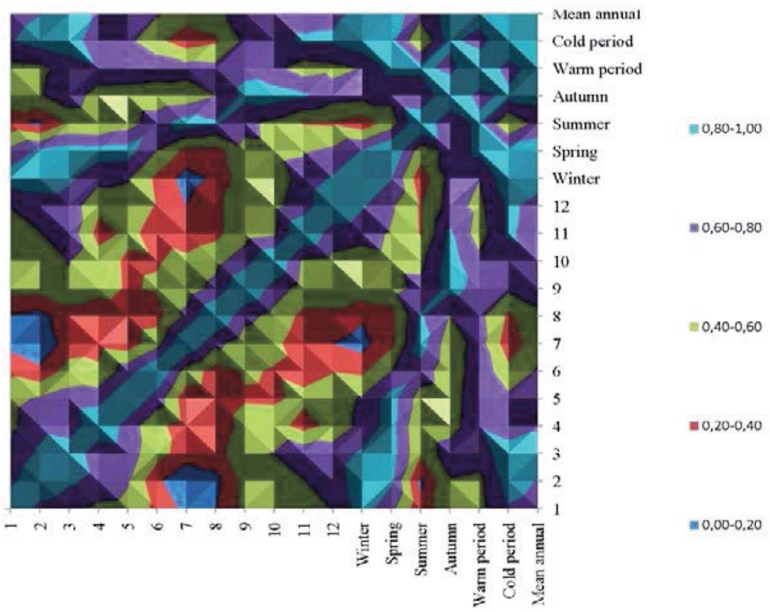

Figure 2. Correlation field of the coefficient of linear correlation of the mean values of surface ozone concentration with each other in the different periods, seasons and months of year

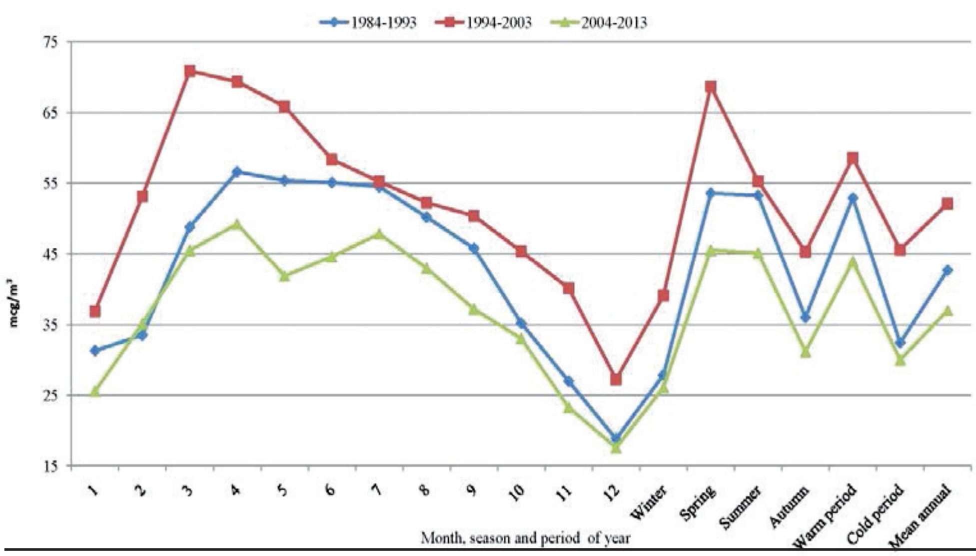

Figure 3. Mean surface ozone concentration in different months, seasons and periods of year in Tbilisi in three ten-year spells of time

Table 2. Difference between the mean concentrations of surface ozone in three ten-year periods of time in different months, seasons and periods of year

Period of year	(1994-2003) - (1984-1993)		(2013-2004) - (1984-1993)		(2013-2004) - (1994-2003)	
	SOC	α	SOC	SOC	α	SOC
January	5.6	No sign	-5.8	No sign	-11.3	0.03
February	19.6	0.0015	1.6	No sign	-18.0	0.002
March	22.1	0.02	-3.3	No sign	-25.4	0.002
April	12.8	0,1	-7.4	0.2	-20.1	0.03
May	10.5	0.05	-13.5	0.02	-24.0	0.001
June	3.3	No sign	-10.5	0.02	-13.8	0.002
July	0.7	No sign	-6.7	No sign	-7.4	0.1
August	2.0	No sign	-7.2	No sign	-9.3	0.15
September	4.6	No sign	-8.6	0.05	-13.2	0.002
October	10.2	0.05	-2.2	No sign	-12.3	0.05
November	13.1	0.05	-3.7	No sign	-16.9	0.002
December	8.5	0.05	-1.2	No sign	-9.7	0.002
Winter	11.2	0.05	-1.8	No sign	-13.0	0.002
Spring	15.1	0.015	-8.1	0.15	-23.2	0.001
Summer	2.0	No sign	-8.1	0.05	-10.1	0.03
Autumn	9.3	0.03	-4.8	0.15	-14.1	0.002
Warm per.	5.6	0.1	-9.0	0.03	-14.6	0.001
Cold per.	13.2	0.015	-2.4	No sign	-15.6	0.001
Year	9.4	0.015	-5.7	0.1	-15.1	0.001

Result of correlation analysis of the mean values of surface ozone concentration in the different periods, seasons and months of year in fig. 1 and 2 are presented.

As follows from these figures, according to Student's criterion non significance value of R four pair are observed: January – July, January –August; February – July, February –August, February – summer season; July – December, July – winter season; August – winter season. High value of R (≥0.8) for pair: January – winter season; February – March, February – winter season, February – spring season, February – cold period; March - winter season, March – spring season, March – cold period, March – annual; April – spring period; May - spring period; July – summer period; August – summer period; September – autumn season; October – autumn season; November – autumn season, November – cold season; December - winter season, December - cold period; winter season – spring season, winter season – cold period, winter season – mean annual; spring season – warm season, spring season – cold period, spring season – mean annual; summer season – warm period; autumn season – cold period, autumn season – mean annual; warm period - mean annual; cold period – mean annual.

As a whole the distribution of the values of R on the gradations is the following: non signification – 4.7%, weak – 15.8%, moderated – 28.7%, high – 32.7%, strong – 18.1%.

The data about mean surface ozone concentration in different months, seasons and periods of year in Tbilisi in three ten-year spell of time: I) 1984 - 1993, II) 1994 - 2003, III) 2004 – 2013, in fig. 3 are presented. As follows from fig. 3, the intra-annual motion of the mean monthly values of SOC in the first and second periods of time took the single-modal form. In the first period of time the max of SOC in April was observed, in the second period of time – in March. In the third period of time, the intra-annual motion of the mean monthly values of SOC took the bimodal form (extremes in April and July). Seasonal distribution of SOC in the first and third periods of time is similar to each other - in spring and in summer mean values of SOC approximately are identical. In contrast to this, in the second period of time in the spring the clearly expressed maximum of SOC is observed.

The greatest values of the surface ozone concentration in the second period of time, smallest - in the third period and intermediate - into the first period were observed (fig. 3, table 2). In particular, most of all mean values of SOC in the third period in comparison with the second period decreased during March (-25.4), least of all - during July (-7.4). In the third period in comparison with the first period in January - March, July, August, October – December, winter season and cold six-month the values of SOC did not change. In the second period in comparison with the first period in January, July - September, and summer season the values of SOC did not change. The growth effect of SOC in the second period of time, in all likelihood, is connected with the meteorological conditions and the sharp decrease of the emission of the admixtures of anthropogenic nature soiling the atmosphere, caused by the considerable decrease of industrial production and truck transport after the decay of the Soviet Union.

Table 3. The statistical characteristics of mean six months and yearly values of SOC in Tbilisi (1984-2013)

Parameter	Warm period	Cold period	Year
	Real data		
Mean	51.8	36.1	43.7
Min	31.5	15.2	26.3
Max	69.0	55.3	61.8
σ	9.4	11.5	9.9
C_v (%)	18.1	31.9	22.6
	Correlation Matrix (between Y_{warm}, Y_{cold} and Y)		
Warm period	1	0.70 (α<0.001	0.91 (α<0.001)
Cold period	0.70	1	0.94 (α<0.001)
Year	0.91	0.94	1
	Trend + background ($Y = a·X^6 + b·X^5 + c·X^4 + d·X^3 +$		
a	-0.000014	0	0
b	0.00122	-0.00012	-0.000095
c	-0.04094	0.010	0.00819
d	0.623	-0.299	-0.2476
e	-4.31	3.555	3.013
f	12.80	-12.82	-11.88
g	29.68	20.43	39.29
R^2	0.63	0.82	0.73
(α) R^2	<0.001	<0.001	<0.001
K_{DW}	1.51	2.24	1.53
(α) K_{DW}	0.05	0.05	0.05
Mean	42.7	22.5	34.7
Min	30.4	6.7	24.7
Max	55.2	39.6	48.9
σ	7.4	10.5	8.4
C_v (%)	17.4	46.4	24.3
Share of real	82.4	62.4	79.4
	Random components		
Mean	9.1	13.6	9.0
Max	20.5	23.5	17.7
σ	5.8	4.8	5.1
C_v (%)	63.2	35.4	56.9
Share of real	17.6	37.6	20.6
	Correlation Matrix (between Y_{warm}, Y_{cold} and Y)		
Warm period	1	0.28 (α=0.1)	0.71 (α<0.001)
Cold period	0.28	1	0.79 (α<0.001)
Year	0.71	0.79	1

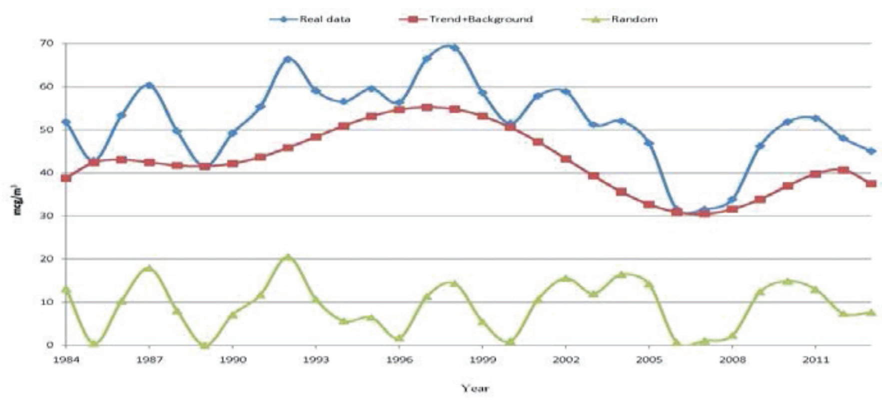

Fig. 4, Trend of mean values of surface ozone concentration in warm period in Tbilisi (1984-2013)

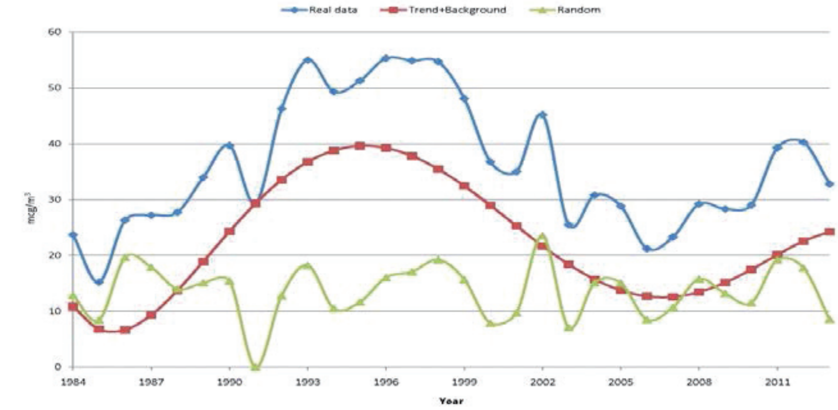

Figure 5. Trend of mean values of surface ozone concentration in cold period in Tbilisi in 1984-2013

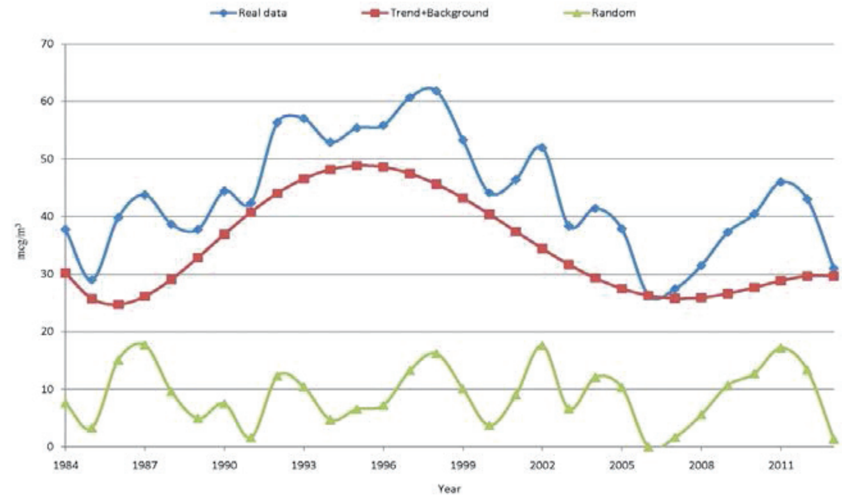

Figure 6. Trend of mean annual values of surface ozone concentration in Tbilisi in 1984-2013

The trend of the mean annual and mean values of SOC in cold season by the five power polynomial are described, trend of the mean values of SOC in warm season by the six power polynomial is described (table 3, fig. 4-6). In table 1 the data of characteristics of trend + background and random components are presented.

Trend + background components. The average values of SOC vary from 22.5 in the cold period up to 42.7 in the warm season, the minimal value of SOC varies from 6.7 in the cold period up to 30.4 per warm half-year, maximal - from 39.6 in the cold period to 55.2 in the warm period, standard deviation - from 7.4 per warm half-year up to 10.5 in the cold season, coefficient of variation from 17.4% per warm half-year up to 46.4 % in the cold period.

A share of the mean values of the components of trend + background from the mean values of real data constitutes: year - 79.4 %, warm season - 82.4%, cold season - 62.4%. Thus, the long-term variations of SOC in Tbilisi are mainly caused by the component of trend + background.

Random components. The average values of SOC varies from 9.0 in the year up to 13.6 in the cold season, the maximal - from 17.7 in the year to 23.5 in the cold period, standard deviation - from 4.8 per cold season up to 5.8 in the warm period, coefficient of variation from 35.4 per cold half-year up to 63.2 in the warm period. Coefficient of linear correlation between Y and Y_{warm} equal 0.71, between Y and Y_{cold} equal 0.79 and between Y_{warm} and Y_{cold} equal 0.28.

As follows from fig. 4-6 an increase in the surface ozone concentration in the period from 1984 through 1995-1996 was observed, then – decrease up to 2006-2007 and in the period from 2008 to 2012-2013 - newly increase.

Conclusions

The long-term variability of the surface ozone concentration in Tbilisi has a complex nature. Range the changeability of the mean values of the surface ozone concentration in different months, seasons and periods of the year is sufficiently great. High and strong correlations are observed between the values of SOC at indicated time intervals in the majority cassis.

The greatest values of the surface ozone concentration in 1994-2003, smallest - in 2004-2013 and intermediate – in 1984-1993 were observed.

The trend of the mean half year and annual values of surface ozone concentration in Tbilisi in 1984-2013 has a nonlinear nature and by the five and six order power polynomial (mean annual, cold period and warm period accordingly) are

described. An increase in the surface ozone concentration in the period from 1984 through 1995-1997 was observed, then – decrease up to 2007 and in the period 2008-2010 - newly small increase.
Taking into account the significant influence of surface ozone on the biosphere, climate and human health (especially in the large cities), subsequently it is provided the intensification of the above-indicated studies.

Acknowledgments
The authors express appreciation to the chief of the department of physics of the atmosphere Dr. A. Amiranashvili for the assistance in the fulfillment of this work.

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