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Tropospheric Ozone (O_3) Behaviour in Rural Areas of Italy

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Abstract

Tropospheric Ozone (O_3) is one of the most important pollutants in the atmosphere, causing some damage to human health, climate, vegetation and materials. This pollutant presents different behaviours in urban and rural environments. High levels of nitrogen oxides (precursor of O3) in urban areas have an important role in photochemical production of O3 in the atmosphere. However, O3 concentrations tend to be higher in rural areas. For better understanding this phenomenon, the O3 data at 52 rural sites in Italy were analysed in this study. It aimed the assessment of the trend and distribution of O3 concentrations; the evaluation of the exceedances of the standard values for human health protection; the analysis of the daily maximum values of O3 concentrations at all monitoring sites; the analysis of the annual average profiles of O3 concentrations; the application of cluster analysis to group the monitoring sites according to the respective O3 behaviour. The ongoing environmental monitoring data obtained from 52 monitoring stations during the period 2008-2012 were used in this study and the O3 data analysis was performed for each year of the mentioned period. It concluded from the results that the O3 concentration at the different rural sites and the daily the maximum concentrations had different behaviour over the study period. Cluster analysis divided the monitoring sites in six groups according to their O3 concentration behaviour. The observed differences for the different groups related to the geographical location and altitude of the monitoring sites. All these results will provide a physical basis for accurately predicting ozone concentration in extensive future research.

Keywords: O3 concentration; pollutant; cluster analysis.

1. Introduction

Over the past few years, air pollution has become a serious problem on a global scale due to changes in human activities which have a significant importance on the alteration of the atmosphere characteristics and consequently in ecosystems and human health. In this way, there has been seen an increasing concern of many institutions, governments, scientific community and the world population in general about the effects of photochemical pollution and particles [7].

Tropospheric ozone, characterized as a photochemical pollutant and a strong oxidant is generator of various impacts on human health, vegetation and materials. Even though the contribution of hydrocarbons released from plants and soil and the ozone migration from the stratosphere is low, ground-level ozone as a byproduct of human activities contributes significantly to both air quality and environment degradation [1].

Italy which is a country in Southern Europe, part of the Mediterranean Basin, is generally affected in the spring and summer by episodes of photochemical pollution. Italy is an important economic center in the world which has serious air pollution problems derived from emissions of various pollutants from large urban centers and industrial clusters. The typical climate of this region and its geographic features characterize the appropriate environment for the occurrence of photochemical pollution episodes [8].

In this regard, the European Union has made efforts in order to issue a number of laws with the aim to protect human health, inform and alert the population. The European Union also aims that the authorities use the database as a decision-making support on strategic plans and programs to reduce emissions and improve air quality [2]. The present work is a contribution to the understanding of ozone behavior in Italy.

2. Material and Methods

In this study is presented the O_3 behavior at 52 rural sites in Italy, during the fiscal years of 2008 and 2012, aiming: I) the assessment of the trend and distribution of O_3 concentrations; II) the evaluation of the exceedances of the standard values for human health protection; III) the analysis of the annual average profiles of O_3 concentrations; IV) the analysis of the daily maximum values for O_3 concentrations at all monitoring sites; V) the application of cluster analysis (CA) to group the monitoring sites according to the respective O_3 behaviors. Regarding the last objectives (IV and V) we are going to discuss in a future paper, because the data are still in processing.

2.1. The selection of the air quality stations

At an early stage, based on the central objective of this study, were selected fifty-two rural monitoring stations but after the application and verification of the compliance with a legal requirement which set the annual collection efficiency higher or equal to 60% for each monitoring station, the sample of fifty-two monitoring stations was reduced to thirty. The monitoring data were obtained from the Superior Institute for Protection and Environmental Research´s website [3].

2.2 The characterization of the monitoring sites

After the selection of the monitoring sites, the next step was to collect information concerning their location, the altitude and the main pollution source (traffic, industrial or background). Most of the data were obtained from information available in the respective websites of the Regional Agencies for Environmental Protection in Italy, while the remainder from environmental reports published by these agencies. In table 1. are presented the geographical coordinates, altitude and the date of activation for each monitoring site:

Table 1- Geographical coordinates and altitude of the monitoring sites and their starting date (SD) of O_3

	Site	Region	Latitude	Longitude	Altitude	SD
TTP	PIANA ROTALIANA	Trentino-Alto Adige	46° 11' 49"	11° 06' 48"	227	2008
VVA	ASIAGO - CIMA EKAR	Veneto	45° 50' 56"	11° 34' 09"	1366	
VTM	MANSUE'	Veneto	45° 24' 32"	11° 09' 41"	14	2004
FGD	DOBERDO DEL LAGO	Friuli Venezia Giulia	45° 14' 31"	13° 27' 22"	125	
LLA	ABBADIA CERRETO	Lombardia	45° 13' 26"	9° 35' 09"	64	
LLB	BERTONICO	Lombardia	45° 14' 01"	9° 39' 59"	65	
LBC	CASIRATE D'ADDA	Lombardia	45° 29' 54"	9° 33' 22"	108	
LPC	CORNALE	Lombardia	45° 2' 24"	8° 54' 51"	74	
LBG	GAMBARA	Lombardia	45° 14' 58"	10° 17' 57"	47	
LMS	SCHIVENOGLIA	Lombardia	45° 1' 01"	11° 4' 34"	11	
PTD	Druento- La Mandria	Piemonte	45° 10' 33"	7° 33' 37"	335	05/09/2001
PCS	Saliceto – Moizo	Piemonte	44° 24' 50"	8° 10' 03"	388	01/12/1999
PAV	Vinchio- San Michele	Piemonte	44° 48' 29"	8° 18' 37"	250	30/01/2009
VAD	DONNAS	Valle Di Aosta	45° 35' 48 "	7° 45' 59"	341	01/10/1994
VAE	ETROUBLES	Valle Di Aosta	45° 49' 07"	7° 14' 02"	1339	
VAL	LA THUILE	Valle Di Aosta	45° 43' 47"	6° 58' 01"	1637	01/10/1994
EMG	GAVELLO	Emilia - Romagna	44° 55' 44"	11° 10' 44"	4	30/05/2008
ERS	SAN CLEMENTE	Emilia - Romagna	43° 55' 55"	12° 37' 38"	179	23/01/2008
LSC	CENGIO - CAMPO DI CALCIO	Liguria	44° 23' 23"	8° 12' 07"	400	01/04/1999
TGG	GR-MAREMMA	Toscana	42° 40' 16"	11° 05' 39 "	232	
MMC	Civitanova IPPODROMO S. MARONE	Marche	43° 20' 11"	13° 40' 28"	110	20/02/2006
MAG	Genga -Parco Gola della Rossa	Marche	43° 28' 08"	12° 57' 07"	541	01/10/2006
UPB	BRUFA	Umbria	43° 4'4.20"	12° 28' 05"	315	2008
LRC	CASTEL DI GUIDO	Lazio	41° 53' 22"	12° 15' 59"	61	
LFF	FONTECHIARI	Lazio	41° 41' 24"	13° 15' 01"	388	
MCG	GUARDIAREGIA	Molise	41°25′08″	14° 31′ 32″	884	2006
MIV	VASTOGIRARDI	Molise	41°45′34″	14° 12′ 32″	954	2007
PLL	LECCE - S. M. Cerrate	Puglia	40° 27' 35"	18° 06' 59"	18	01/05/2004
CCF	Firmo	Calabria	39° 42' 51"	16° 11' 32"	325	01/01/2004
CCS	Saracena	Calabria	39° 44' 33"	16° 12' 13"	387	

The main pollution source of the monitoring sites is background. CCS is the only monitoring site with industrial source pollution. Figure 1 shows a map with the spatial distribution of the monitoring sites in Italy.

Figure 1. Map with the spatial distribution of the monitoring sites in Italy

2.3. Data processing

Initially, we proceeded to the organization of data in Excel spreadsheets. Afterwards was carried out a statistical approach, including the calculation of averages, maximums, minimums, medians, daily profiles, annual profiles and exceedances to the EU limit values. This process was quite time consuming and required the development and application of macros in Excel, in order to reduce the probability of committing calculation errors and to accelerate the execution time of all the implemented processing.

3. Results and Discussion

The table 2 shows the monitoring site efficiencies and the number of exceedances of surface O_3 concentrations to EU standards for protection of the human health during the studied period. Missing data for the following monitoring station (i) MAG and (ii) CCF were interpolated from the annual average value of the monitoring station.

The majority of monitoring stations have not exceeded the alert threshold (240 µg m^{-3} for hourly average). Therefore, it is possible to identify the monitoring sites which exceeded the standard limit, specifically (i) VVA, (ii) LBG, (iii) LLM, (iv) LSC, (v) LRC, (vi) LFF, (vii) LRL and (viii) SSS. The LLM site was the only monitoring site that exceeded the standard limit in the first three years of the study period. Most of the monitoring sites exceeded the information threshold (180 µg m^{-3} for hourly average), except (i) VAE, (ii) TAA, (iii) CCS, (iv) TGG, (v) PLL, (vi) MAG, (vii) CCF, (viii) MAM. According to the results, the monitoring sites VAL and LRC only exceeded once the standard limit during all study period. It is seen that the sites VVA and LLM which are located at high altitudes, 1363 and 1194 respectively, showed the highest numbers of exceedances. Regarding the target value for the protection of human health (120 µg m^{-3} for a maximum of daily 8 h averages), in all the monitoring sites were found higher O_3 concentrations than the defined limit. The EU target limit for the human health protection was respected at VAL, LRC, CCS, SSS and CCF. The result revels that previous mentioned sites had lower concentrations when comparing to the target limit which is 25 days a year, averaged over 3 years.

Table 2. Monitoring sites efficiency in percentage (ME) and number of exceedances of surface O_3 concentrations to EU standard values for protection of human health during the study period: (i) information threshold (IT); (ii) alert threshold (AT); and (iii) the target value (TV)

Sites	2009				2010				2011				2012			
	ME	IT	AT	TV	ME	IT	AT	TV	ME	IT	AT	TV	ME	IT	AT	TV

TTM	94%	3	0	62	84%	77	0	103	91%	32	0	140	91%	72	0	104
TTP	98%	9	0	63	98%	25	0	67	96%	6	0	82	95%	7	0	54
VVA	94%	132	0	123	96%	133	0	109	94%	85	0	137	98%	117	1	115
VVB	94%	14	0	86	94%	81	0	92	94%	12	0	77	95%	81	0	102
VTM	92%	21	0	71	91%	14	0	59	95%	24	0	94	95%	14	0	60
VPP	94%	8	0	78	95%	0	0	33	96%	2	0	82	95%	7	0	69
FPC	92%	19	0	55	92%	6	0	42	89%	2	0	45	76%	2	0	37
FGD	92%	1	0	87	85%	29	0	61	87%	0	0	81	84%	36	0	79
LLA	97%	7	0	64	82%	26	0	57	89%	25	0	103	93%	16	0	62
LLB	77%	39	0	86	91%	27	0	55	93%	10	0	72	98%	9	0	48
LBC	99%	23	0	72	97%	3	0	52	96%	33	0	101	95%	12	0	78
LPC	95%	36	0	81	90%	48	0	65	79%	28	0	74	95%	19	0	61
LBG	96%	27	0	81	94%	8	0	47	97%	4	0	75	97%	2	0	64
LLM	92%	97	4	107	95%	66	1	68	95%	129	6	129	95%	101	0	84
LMS	91%	0	0	35	90%	32	0	77	91%	4	0	93	97%	12	0	79
PTC	-	-	-	-	-	-	-	-	-	-	-	-	95%	5	0	80
PAD	95%	0	0	51	88%	9	0	79	98%	0	0	69	98%	17	0	78
PTD	82%	45	0	54	94%	22	0	60	97%	19	0	96	97%	63	0	89
PCS	99%	1	0	62	96%	0	0	30	95%	0	0	26	99%	10	0	54
PAV	86%	3	0	69	96%	0	0	73	99%	2	0	105	98%	8	0	97
VAD	98%	2	0	48	81%	0	0	25	100%	4	0	50	99%	3	0	61
VAE	98%	0	0	34	97%	0	0	35	97%	0	0	27	99%	0	0	25
VAL	99%	0	0	1	98%	0	0	9	97%	0	0	21	98%	0	0	11
EPB	89%	43	0	77	93%	42	0	87	94%	15	0	98	95%	41	0	82
ERB	*	0	0	0	99%	0	0	15	99%	0	0	37	98%	5	0	43
EMB	83%	2	0	51	93%	13	0	57	93%	2	0	60	94%	7	0	67
ERF	89%	6	0	73	90%	0	0	45	99%	8	0	89	95%	1	0	72
EMG	99%	9	0	74	97%	18	0	69	89%	13	0	93	100%	6	0	75
EFG	98%	10	0	72	94%	3	0	37	95%	2	0	64	95%	21	0	77
EFO	93%	5	0	68	94%	0	0	23	99%	0	0	65	94%	7	0	60
ERS	98%	0	0	35	94%	1	0	40	94%	0	0	11	99%	10	0	70
EBS	94%	1	0	71	92%	10	0	59	94%	1	0	70	93%	2	0	57
ENS	96%	6	0	70	97%	21	0	55	92%	0	0	83	98%	27	0	80
LSC	92%	0	0	28	92%	0	0	21	95%	0	0	9	98%	0	0	26
TAA	88%	0	0	8	92%	0	0	2	91%	0	0	52	93%	0	0	66
TGG	93%	0	0	6	96%	0	0	29	89%	0	0	51	94%	0	0	42
TPP	92%	15	0	69	93%	19	0	58	84%	4	0	73	89%	0	0	36
MMC	83%	0	0	61	70%	2	0	36	70%	2	0	25	89%	0	0	9
MAG	-	-	-	-	97%	0	0	17	94%	0	0	6	81%	0	0	54
MAM	-	-	-	-	-	-	-	-	-	-	-	-	97%	0	0	42
UPB	93%	3	0	32	92%	0	0	10	95%	2	0	16	95%	0	0	51
LRA	-	-	-	-	85%	0	0	38	98%	0	0	56	97%	0	0	50
LRC	98%	0	0	5	95%	0	0	3	98%	0	0	7	98%	0	0	12
LFF	98%	9	0	53	98%	0	0	52	96%	104	0	141	99%	18	0	99
LRL	89%	3	0	42	98%	0	0	36	99%	1	0	61	97%	9	0	65
MCG	96%	2	0	42	97%	0	0	11	94%	3	0	54	89%	2	0	54
MIV	86%	2	0	41	93%	0	0	6	87%	1	0	47	79%	0	0	78
PLL	63%	0	0	3	91%	0	0	19	90%	0	0	69	89%	0	0	62
PFM	*	0	0	9	92%	0	0	24	89%	1	0	32	83%	0	0	48
CCF	-	-	-	-	90%	0	0	3	99%	0	0	9	69%	0	0	1
CCS	86%	0	0	12	66%	0	0	0	93%	0	0	15	79%	0	0	4
SSS	91%	2	0	8	71%	0	0	9	92%	1	0	7	94%	0	0	3

The figure 2 shows the annual average O_3 concentrations at the studied rural sites, the following monitoring sites presented the highest concentrations in 2012, (i) VVA, (ii) CCS, (iii) MAG, (iv) MCG, (v) VAL, (vi) LFF, (vii) MIV and (viii) CCF.

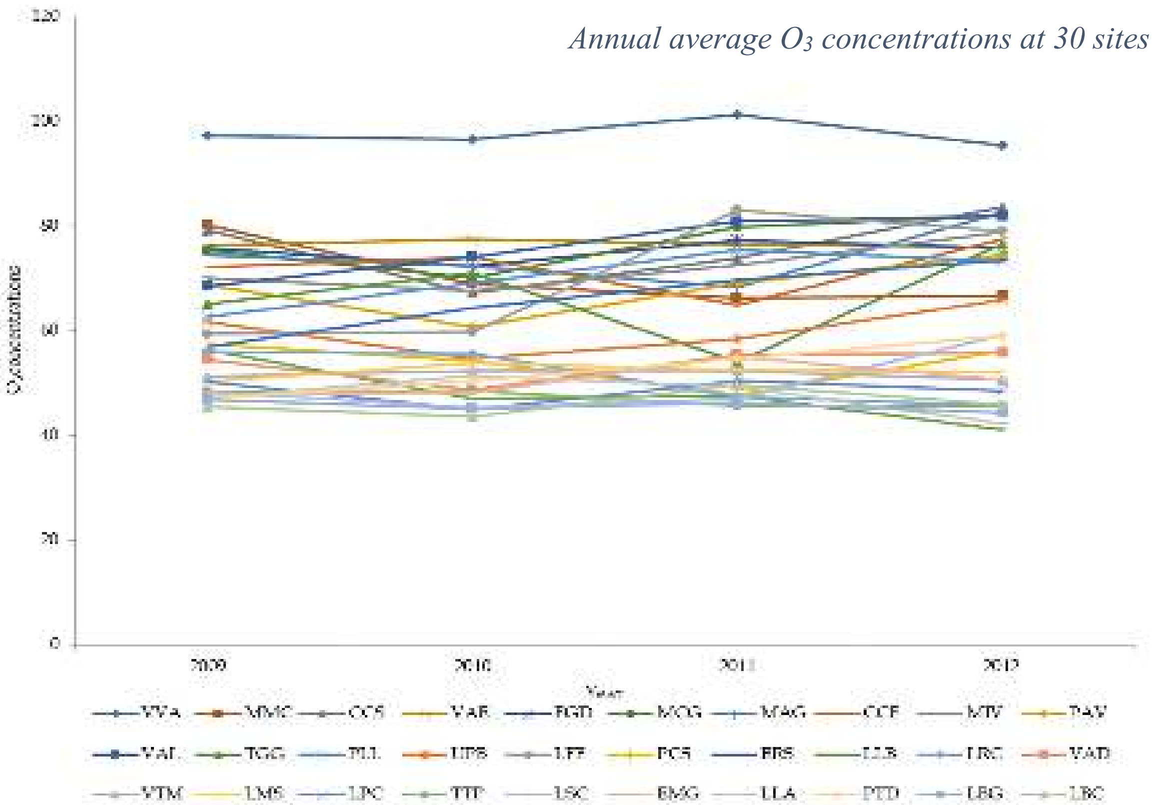

Figure 2. Annual average O_3 concentrations ($\mu g\ m^{-3}$) at the different rural sites during the studied period

It also shows that the ozone behavior varies depending on the monitoring stations. For instance, the MMC site showed a decreasing trend during the study period, having achieved a reduction of -11 µg m−3 between 2009 and 2010 as well as a reduction of -3 µg m−3 between 2010 and 2011, remaining constant for the following year.

4. Conclusions

- During the study period, O_3 concentrations presented the highest values in 2011 and 2012, periods when high concentrations were recorded.
- Concerning the exceedances of the thresholds defined in the European Directives, to protect human health, we can see that the alert threshold has been exceeded from (i) VVA, (ii) LBG, (iii) LLM, (iv) LSC, (v) LRC, (vi) LFF, (vii) LRL and (viii) SSS sites, among which LLM site was the only monitoring site that exceeded the standard limit in the first three years of the study period.
- The information threshold was exceeded from most of the monitoring sites. VVA and LLM sites, which are located at high altitudes, 1363 and 1194 respectively, showed the highest numbers of exceedances, while Regarding the target value for the protection of human health, in all the monitoring sites were found higher O3 concentrations than the de-fined limit except VAL, LRC, CCS, SSS and CCF.
- The study carried out in this rural areas may contribute to improve the knowledge of ozone dynamics in Italy, which is part of the Mediterranean basin.
- All these results will provide a physical basis for accurately predicting ozone concentration in extensive future research.

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