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Surface ozone concentration and its relation with weather types in NW Italy, 2003–2014

Elisa Giaccone[1,2,*], **Simona Fratianni**[2,3], **Nicola Cortesi**[4], **José Carlos González-Hidalgo**[5]

[1]University of Lausanne, Institute of Earth Surface Dynamics, Géopolis, 1015 Lausanne, Switzerland
[2]University of Turin, Department of Earth Sciences, via Valperga Caluso 35, 10125 Turin, Italy
[3]Research Centre on Natural Risks in Mountain and Hilly Environments (NatRisk), via Leonardo da Vinci 44, 10095 Grugliasco, Italy
[4]Earth Sciences Department (ESS), Barcelona Supercomputing Center, Carrer de Jordi Girona 29, 08034 Barcelona, Spain
[5]Department of Geography, IUCA, University of Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza, Spain

ABSTRACT: In this study, we analyzed the evolution of the surface ozone concentration in northwestern Italy and its relation to weather types (WTs) during the 2003–2014 period, by downloading and processing the ozone data from monitoring stations for the cities of Turin, Asti, Genoa and Savona. The corresponding trends were calculated and the correlation between ozone and the WTs assessed. Specifically, daily surface atmospheric patterns were obtained from sea level pressure data from the NCEP/NCAR reanalysis data set, and the WTs were classified following the Lamb catalogue. Furthermore, the influence of nitrogen dioxide (NO_2), temperature, precipitation and wind speed on ozone values was evaluated on a daily basis. Results showed a cyclical evolution of ozone on a daily, weekly and seasonal scale, with maximum values in daytime and summer, and minimum values at night and during winter. The observed trends were not significant because of strong inter-annual variability. Inland ozone values were generally lower than coastal ones, but fluctuated more. The average ozone concentrations were statistically related to WTs: high ozone values were associated with the eastern type and low values with the cyclonic and western types. Also, temperature and wind speed had a significant influence on the ozone concentration for both inland and coastland cities. More specifically, temperature had a positive correlation with ozone in each city, wind had a positive correlation only in inland areas; the correlation in the coastal zone was negative. Precipitation generally showed a negative and less significant correlation with daily ozone concentrations.

KEY WORDS: Ozone · Weather types · Climatic variables · Northwestern Italy

1. INTRODUCTION

Tropospheric ozone is a powerful greenhouse gas (Forster et al. 2007, IPCC 2013) with high oxidation capacity and well-known negative effects on human and animal health, vegetation and crops (The Royal Society 2008, Cooper et al. 2014). It is generated by atmospheric electric discharge (lightning), anthropogenic emissions (UNEP & WMO 2011) and by the photochemical interaction of nitrogen oxides (NOx) and volatile organic compounds (VOCs) in the presence of light. The process is complex and involves interactions between air mass circulation (transport from the stratosphere to the troposphere), temperature, wind speed, solar radiation, NOx emissions and environmental concentrations of VOCs (Monks 2000, Trainer et al. 2000, Demuzere et al. 2009, Adame Carnero et al. 2010).

The ozone concentration usually exhibits strong inter-annual variability due to various factors affect-

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*Corresponding author: elisa.giaccone@gmail.com ing production and residence time in the atmospheric boundary layer, such as cloudiness, temperature and stability (Jonson et al. 2006, Tørseth et al. 2012). In addition, the spatial and temporal distribution of its precursors, the long-range transport of air pollutants and the increment of global background concentrations in the Northern Hemisphere contributes to ozone's inter-annual variability (Mircea et al. 2014, Monks et al. 2015). In Europe, ozone follows well-recognized daily and seasonal cycles; presenting higher values during daytime and in the spring/summer months and lower concentrations at night and in winter (Nolle et al. 2005, Tarasova et al. 2007). Furthermore, a combination of pollutant emissions and VOCs induces the 'weekend effect', consisting of higher ozone values on Saturdays and Sundays. NOx (particularly NO; Querol et al. 2014) and VOC emissions are generally lower on these days because of lower levels of human activity. For this reason less ozone is consumed to produce NO_2 (Jiménez et al. 2005, Castell-Balaguer et al. 2012).

On a monthly scale, ozone spring maximum values are detected in northern Europe and summer maximum values in the Mediterranean region, particularly in north-western Italy. Generally, this is attributed to differences in its precursors (Monks 2000, Ordóñez et al. 2017). While it is accepted that solar radiation is the major factor responsible for the maximum summer ozone production, the origin of the spring maximum is not so well understood (Sánchez et al. 2008), although it has been attributed to the dominant role of photochemistry in the observed build-up of tropospheric ozone in the winter–spring transition period (Zanis et al. 2007, Monks et al. 2015).

Several studies have been conducted to detect temporal and spatial variability in ozone concentration, especially in relation to meteorological conditions (Di Carlo et al. 2007), large-scale processes (e.g. North Atlantic Oscillation; Pausata et al. 2012) and regional climate characteristics around the Mediterranean basin (Huszar et al. 2012). In this region, due to the high frequency of anticyclone conditions, with high temperatures and stagnant meteorological conditions, frequent peaks in ozone values can be caused by photochemical reactions during summertime (Silibello et al. 1998, Vecchi & Valli 1998, Nolle et al. 2002, Vautard et al. 2005, Jacob & Winner 2009, Schurmann et al. 2009, Gottardini et al. 2010, Zanis et al. 2014). These ozone concentration values around the Mediterranean basin are usually higher than those in northern Europe (EEA 2016). Furthermore, air-mass transport from the stratosphere to lower tropospheric levels has recently been suggested as one of the reasons for summer ozone enhancement in the Mediterranean area, due to high ozone concentration in the stratosphere (Kalabokas et al. 2013, Zanis et al. 2014, Cristofanelli et al. 2015, Monks et al. 2015). Finally, comparison between atmospheric patterns and ozone concentration around the Mediterranean basin have shown differences in both absolute values and monthly peaks between inland (summer peak) and coastal (spring peak) cities (Sánchez et al. 2008, Castell-Balaguer et al. 2012, Santurtún et al. 2015).

At a global level, surface ozone trends are difficult to estimate because they are extremely variable. Indeed, ozone values depend on season, elevation, region, meteorological conditions and proximity to precursor emissions (Gaudel et al. 2018). In Europe, a slight reduction in ozone precursor emissions has caused a decrease in extreme ozone levels in rural and urban sites (Derwent et al. 2010, Simpson et al. 2014, EEA 2016). However, it is impossible to draft a generalized statement regarding ozone trends, because of its high spatial and seasonal variability (Gaudel et al. 2018, Yan et al. 2018).

In this research, we analyzed the ozone concentrations in north-western Italy, where regional studies have not yet been carried out. The period analyzed was 2003–2014. Our main objectives were to (1) characterize the ozone concentrations inland in the Piedmont region and coastal areas in the Liguria region, and (2) identify whether any correlations exist between ozone concentration, climate variables and the atmospheric conditions defined by weather types (WTs).

2. MATERIALS AND METHODS

2.1. Site description

Four ozone monitoring stations located in the NW of Italy (Turin, Asti, Genoa and Savona) were analyzed. Turin and Asti were chosen as representative of the Piedmont inland region, while Genoa and Savona were selected for the Liguria coastland area (Fig. 1). The selected stations were those holding long-term measurements with ozone records; 3 of the stations are located in background areas and one station is an industrial areas (Savona).

The stations in the Piedmont area are located in the cities of Turin (243 m a.s.l.) and Asti (149 m a.s.l.). Turin is located on the Po River plain, while Asti is in a hilly area. Both cities are characterized by continental climate conditions with hot summers and cold

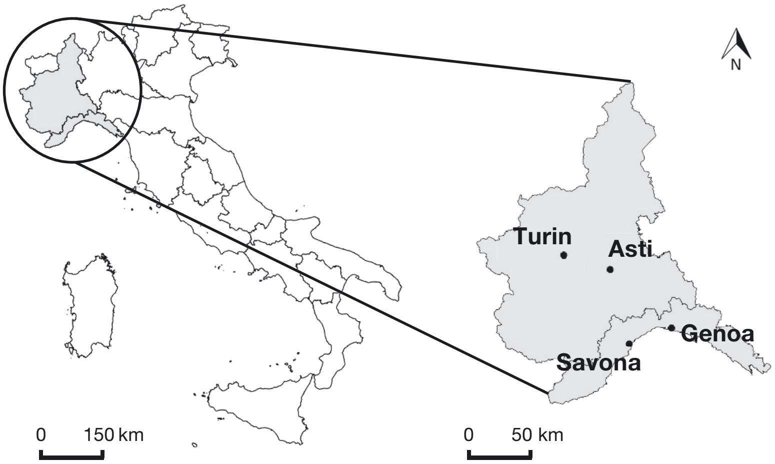

Fig. 1. The 4 monitoring stations analyzed in this study: Turin (45.0249° N, 7.6490° E), Asti (44.9089° N, 8.2054° E), Genoa (44.4181° N, 8.9273° E) and Savona (44.2871° N, 8.4316° E)

winters (i.e. a high annual temperature range), and bimodal precipitation regime (spring and autumn), with higher annual mean precipitation in Turin (847 mm yr^{-1}) than in Asti (662 mm yr^{-1}; Baronetti et al. 2018). Two main factors induce these thermal-pluviometric characteristics: the surrounding orography and the atmospheric circulation (Fazzini et al. 2004, Fratianni & Acquaotta 2017). The dry continental air masses flow from the north-west and the moist air masses are mainly from the eastern part of the Po Valley (Fratianni et al. 2005, Terzago et al. 2012). Moreover, numerous foehn episodes coming from the north, north-west and west occur. They are combined with sunny weather and low precipitation. Southern foehn events are also normal, but less frequent (Fratianni et al. 2009).

The coastal stations in Liguria are located in Genoa (33 m a.s.l.) and Savona (31 m a.s.l.). These cities are characterized by a moderate temperature range, with high precipitation in autumn and winter (ARPAL–CFMI-PC 2013, Brandolini et al. 2017). In Genoa, the annual mean precipitation value is higher than in Savona (1357 and 826 mm yr^{-1} respectively; Acquaotta et al. 2018a,b).

Turin and Genoa are densely populated cities, with well-developed industrial and commercial districts. Furthermore, Genoa has many ports for commercial and tourism activities. Asti and Savona are less populated, but Savona is surrounded by an industrial area. From a climate point of view, the most evident climate differences between Piedmont and Liguria emerge mainly because mountain ranges (Alps and Apennines) isolate the inland (Piedmont) from the coastal areas (Liguria).

2.2. Classification of WTs

Daily WTs were obtained for the 2003–2014 period from the daily mean sea level pressure (SLP) grid of the NCEP/NCAR reanalysis data set (Kistler et al. 2001). Classification followed the original Lamb's WT catalog developed by Jenkinson & Collison (1977) and Jones et al. (1993, 2013), initially developed for the British Isles. The WTs were determined with the methodology described for Portugal by Trigo & DaCamara (2000). The classification applies geometrical and physical characteristics, such as the strength and direction of the airflow and the degree of vorticity. The following geostrophic indices were used: southerly flow (SF), westerly flow (WF), total flow (F), southerly shear vorticity (ZS), westerly shear vorticity (ZW) and total shear vorticity (Z). These were calculated using SLP values acquired from 16 grid points (defined by the coordinates from point p1 to point p16) over southern Europe, centered on Turin (45° N, 7.5° E; Fig. 2). As reported in the methodology proposed by Trigo & DaCamara (2000) and adopted by Cortesi et al. (2013), the following equations, readjusted to our area, were used:

$$SF = SF1\,[0.25(p5 + 2p9 + p13) - 0.25(p4 + 2p8 + p12)] \quad (1)$$

$$WF = [0.5(p12 + p13) - 0.5(p4 + p5)] \quad (2)$$

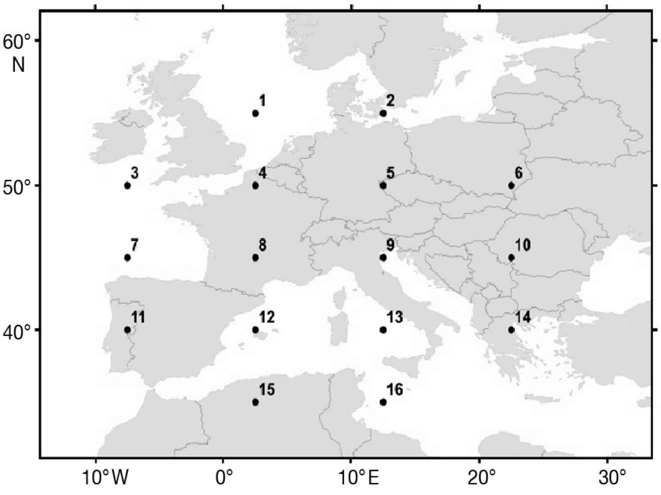

Fig. 2. 16 grid points centered over Turin used to calculate the flow indices and vorticity. Distance between points: 10° longitude and 5° latitude

$$ZS = ZS1\ [0.25(p6 + 2p10 + p14) - 0.25(p5 + 2p9 + p13) - 0.25(p4 + 2p8 + p12) + 0.25(p3 + 2p7 + p11)] \quad (3)$$

$$ZW = ZW1\ [0.5(p15 + p16) - 0.5(p8 + p9)] - ZW2\ [0.5(p8 + p9) - 0.5(p1 + p2)] \quad (4)$$

$$F = (SF^2 + WF^2)^{1/2} \quad (5)$$

$$Z = ZS + ZW \quad (6)$$

where $SF1 = 1 / \cos(PC)$; $ZS1 = 1 / (2 \times \cos^{2[PC]})$; $ZW1 = \sin(PC) / \sin(PS)$; and $ZW2 = \sin(PC) / \sin(PN)$. PC is the latitude of the center of the 16-point grid; PS the latitude of the row of grid points 11, 12, 13 and 14 in Fig. 2; and PN the latitude of the row of grid points 3, 4, 5 and 6 (both rows are at 5° latitudinal distance from the central row). The conditions defining the different types of circulation are the same as those established in Trigo & DaCamara (2000), and are explained as follows:

1. Direction of flow was given by $\tan^{-1}$ (WF / SF), 180° was added if WF was positive. The appropriate direction was calculated using an 8-point compass, allowing 45° sector^{-1}.

2. If $|Z| < F$, the flow is essentially straight and classed as a pure directional type (8 different cases, according to the compass directions).

3. If $|Z| > 2F$, the pattern was classed as a pure cyclonic type if $Z > 0$, or a pure anticyclonic type if $Z < 0$.

4. If $F < |Z| < 2F$, the flow was classed as a hybrid type and was, therefore, characterized by both direction and circulation (8 × 2 different types).

This procedure enabled 26 different WTs to be identified at daily scale: 8 pure directional types (N, NE, E, SE, S, SW, W, NW); 2 pure types, determined by the vorticity strength (cyclonic, C and anticyclonic, A); and 16 hybrid types (8 cyclonic and 8 anticyclonic for each direction). Unlike some other authors (Jenkinson & Collison 1977, Jones et al. 1993), an unclassified class was not defined because we opted to distribute the fairly few cases (<2%) with possibly unclassified situations among the retained classes. Before being correlated with ozone data, the 26 WTs were regrouped into 10 distinct types by classifying hybrid types as purely directional (Russo et al. 2014). This choice stemed from the need to highlight the importance of air mass direction, which is extremely influential in the transport of ozone precursors.

2.3. Statistical analysis

The original hourly data of the surface ozone concentration (1 January 2003–31 December 2014) were obtained from the regional agencies for environmental protection, Arpa Piedmont and Arpa Liguria.

Mean daily data were calculated as a 24 h average (00:00–23:59 h). To identify the daily and weekly cycles, daytime and nighttime ozone concentrations were calculated from hourly data. Diurnal (daytime) was defined as the 12 h average between 08:00 and 19:00 h, and the nocturnal (nighttime) as the average between 19:00 and 08:00 h of the following day. The daily average values of weekdays (Monday to Friday) were compared with the average weekend values (Saturday and Sunday) to detect the 'weekend effect', a well-known process related to change in precursors during Saturdays and Sundays (Querol et al. 2014). Monthly, seasonal and annual aggregations were performed by obtaining an average of the daily values, done only when >85% of original hourly data were available in accordance with Annex I of the 2008/50/EC Directive (Russo et al. 2014). Monthly values are useful to provide an overview about seasonal cyclic behavior and in calculating the annual range.

For the same period (2003–2014), daily data for NO_2 (a well-recognized precursor of ozone), temperature, precipitation and wind speed were downloaded from the Arpa Piedmont and Liguria database. When data availability was >85%, the daily data were aggregated monthly and annually and compared with the ozone data. The percentage of missing daily data was between 7 and 10% for O_3, NO_2 and meteorological variables.

Annual trends were assessed using the Mann-Kendall non-parametric test to verify statistical significance, assuming a 95% probability level (Mann 1945, Kendall 1975). The series were not detrended because their trends were not autocorrelated.

To assess the correlation between daily ozone and the predictor variables (daily values of NO_2, temperature, precipitation and wind speed), linear models were performed in R v.3.2.3 (R Development Core Team 2015).

To investigate the relationship between ozone concentration and WTs, we applied an ANOVA with repeated measurements in time (e.g. Linn et al. 1988, Clark et al. 2000, Cotrozzi et al. 2018). A comparison of marginal mean values was performed between inland stations and coastal stations and the differences in ozone concentration between seasons and WTs were highlighted (e.g Demuzere at al. 2009, Russo et al. 2014). An *a posteriori* Bonferroni test (Dunn 1961) was applied to detect significant differences.

3. RESULTS

3.1. Ozone cycles

In the 4 stations, ozone is characterized by both daily and seasonal cycles, with the concentration being higher during daytime (08:00–19:00 h) than nighttime (19:00–08:00 h) throughout the year (Table 1). Genoa is an exception, because from October to February, the average nighttime values are higher those in daytime. The mean differences between daytime and nighttime values are particularly noticeable in Asti (33 µg m^{-3}) and Turin (24 µg m^{-3}), while they are lower in Savona (18 µg m^{-3}) and non-existent in Genoa (0 µg m^{-3}).

The differences between diurnal and nocturnal concentration increase in the spring–summer months, particularly in the Piedmont cities, and reach their minimum in winter. The intra-annual range (maximum–minimum difference of monthly mean values) differs between inland/coastal cities and daytime/nighttime average values, being higher in Piedmont inland stations and during daytime (daytime difference in Turin and Asti: 98 µg m^{-3}, nighttime difference: 55 and 46 µg m^{-3}, respectively). For the coastal stations, 2 tendencies were highlighted: Savona has a similar pattern to the inland stations, with a narrower intra-annual range, while Genoa has a single trend with few marked differences and nighttime values higher than daytime in autumn and winter.

The mean daily ozone values prove the existence of the weekend effect: the ozone concentration certainly increases during Saturdays and Sundays, from 6% (Savona) to 11% (Turin) compared to those during weekdays (Fig. 3).

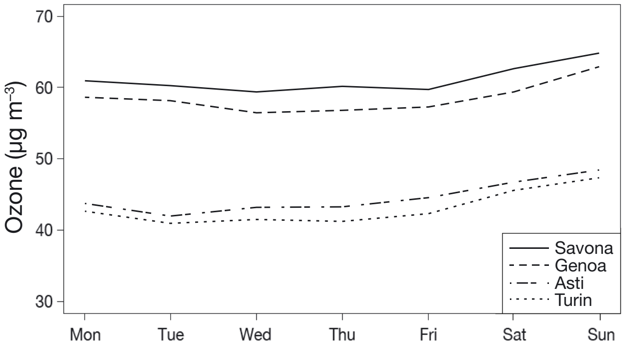

Fig. 3. Mean ozone concentrations at the 4 analyzed monitoring stations during the week

The seasonal ozone cycle is characterized by a winter minimum and a summer maximum. The maximum summer mean value is found in July for the stations of Turin (86 µg m^{-3}), Asti (83 µg m^{-3}) and Savona (83 µg m^{-3}), and in August for the city of Genoa (81 µg m^{-3}). In the coastal cities, a secondary maximum in May was observed. The winter minimum is found in December in Piedmont cities (9 and 12 µg m^{-3} for Turin and Asti, respectively), and in Genoa (35 µg m^{-3}) and in November in Savona (36 µg m^{-3}) (Fig. 4).

As expected, the NO_2 monthly values present a seasonal cycle opposite to that of ozone, with a winter maximum and a summer minimum (Fig. 4).

Annual average values of surface ozone are higher in the coastal cities of Liguria (Genoa 58 µg m^{-3}, Savona 60 µg m^{-3}) than in the cities in Piedmont (Turin 43 µg m^{-3}, Asti 44 µg m^{-3}). The ANOVA with repeated measurements in time reinforces the annual and individual results for each station, showing that there are significant differences in the daily ozone concentration between inland and coastal cities, and among WTs and between sites and seasons ($p < 0.001$; Table 2). In particular, there is a noticeable difference in ozone concentration between coastal and inland stations (i.e. higher concentrations in coastal stations, with an average of 59 µg m^{-3} compared to inland, 43 µg m^{-3}). The highest values of ozone are reached in summer (78 µg m^{-3}), whereas the lowest are in winter (27 µg m^{-3}), confirming the seasonal cycle. Furthermore, at a seasonal level, the ozone values of winter, autumn and spring are

Table 1. Monthly daytime and nighttime ozone values (µg m^{-3}) in northwestern Italy, with annual average and standard deviation

	Daytime (08:00–19:00 h)				Nighttime (19:00–08:00 h)			
	Turin	Asti	Genoa	Savona	Turin	Asti	Genoa	Savona
Jan	13	16	34	42	9	11	41	37
Feb	26	29	44	57	13	11	49	48
Mar	52	60	58	73	27	24	58	59
Apr	66	78	65	83	42	38	65	64
May	83	92	68	90	51	45	69	66
Jun	101	104	75	93	59	50	67	64
Jul	108	112	84	102	63	54	74	67
Aug	95	100	85	93	54	45	78	62
Sep	71	73	70	79	31	27	71	57
Oct	30	33	47	58	11	10	51	42
Nov	12	16	36	39	7	9	43	33
Dec	11	14	33	41	8	10	42	37
Aver.	56	61	58	71	31	28	59	53
St. dev.	37	37	19	23	22	18	13	13

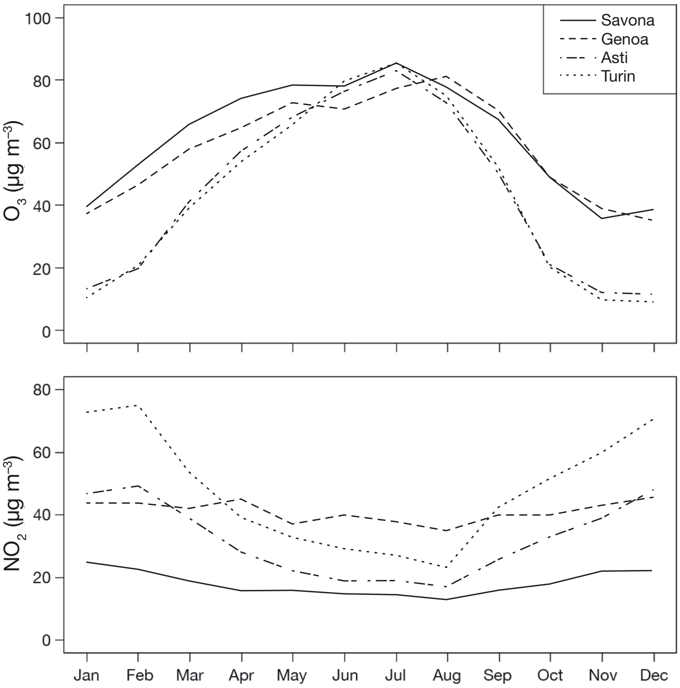

Fig. 4. Monthly mean values of (top) ozone and (bottom) NO_2 at the 4 analyzed monitoring stations

Table 2. Main results of the Bonferroni post hoc test. Weather types: directional (E, N, NE, NW, S, SE, SW, W) and pure (cyclonic, C; anticyclonic, A)

Variable		Mean (µg m^{-3})	Error	95% CI Lower bound	95% CI Upper bound
Localization					
Coastal		58.9	0.5	57.9	59.8
Inland		43.2	0.5	42.3	44.1
Season					
Winter		27.0	0.7	25.7	28.3
Autumn		39.7	0.7	38.4	41.1
Spring		61.1	0.6	59.8	62.3
Summer		78.2	0.7	76.7	79.6
Weather types					
A		51.6	1.0	49.6	53.6
C		39.1	1.2	36.7	41.6
E		62.0	1.3	59.4	64.6
N		52.6	1.0	50.6	54.5
NE		53.7	1.0	51.7	55.6
NW		49.2	1.0	47.1	51.2
S		50.0	1.0	48.0	51.9
SE		55.8	1.0	53.9	57.8
SW		49.0	1.0	47.0	51.1
W		43.2	1.4	40.4	46.0
Localization × season					
Coastal	Winter	40.3	0.9	38.4	42.1
	Autumn	51.6	1.0	49.7	53.6
	Spring	67.6	0.9	65.8	69.5
	Summer	77.0	1.1	74.8	79.1
Inland	Winter	13.8	0.9	12.0	15.6
	Autumn	27.9	1.0	25.9	29.8
	Spring	54.5	0.9	52.8	56.3
	Summer	79.4	1.0	77.4	81.3

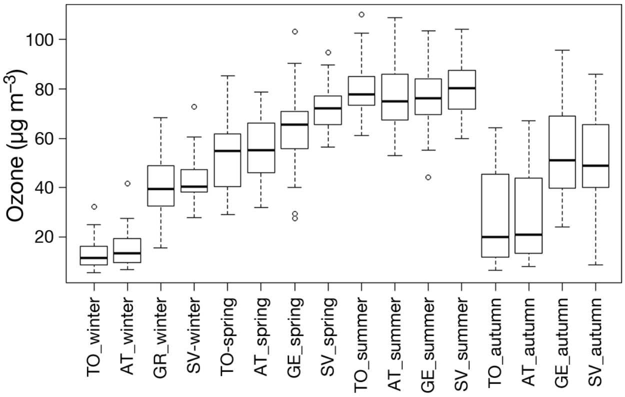

Fig. 5. Seasonal pattern of mean daily ozone concentrations (µg m^{-3}) in all 4 monitoring stations, regrouped based on seasons. Box and whiskers present the median, first and third quantiles, minimum and maximum value and possible outliers. Winter: DJF; spring: MAM; summer: JJA; autumn: SON. TO: Turin; AT: Asti; GE; Genoa; SV: Savona

lower in Piedmont than Liguria, unlike in the summer, when the measurements are reversed (Fig. 5).

The annual trends are not significant, because of the high variability in ozone concentration. Also, the series is too short to have significant statistical trends.

3.2. Relationship between ozone, WTs, climatic variables and NO_2

In the NW of Italy, the most frequent WT is the anticyclonic type (A; 19%) with an annual average of around 69 d yr^{-1}, generally associated with medium-high values of SLP. The second most frequent is the northeasterly type (NE; 16%) with 58 d yr^{-1} and medium-high values of SLP; the third is the northerly type (N; 12%) with 43 d, characterized by low SLP. Type A is most frequent in August, NE is the most frequent in June and N in July (Figs. 6 & 7).

Based on ANOVA and Bonferroni tests, the differences in ozone concentration under the 10 WTs analyzed are significant ($p < 0.001$). The highest average for daily ozone concentration occurs within the easterly and southeasterly circulation patterns (62.0 and 55.8 µg m^{-3}, see Table 2). The minimum ozone concentration values are found under the influence of the cyclonic (39.1 µg m^{-3}) and westerly types

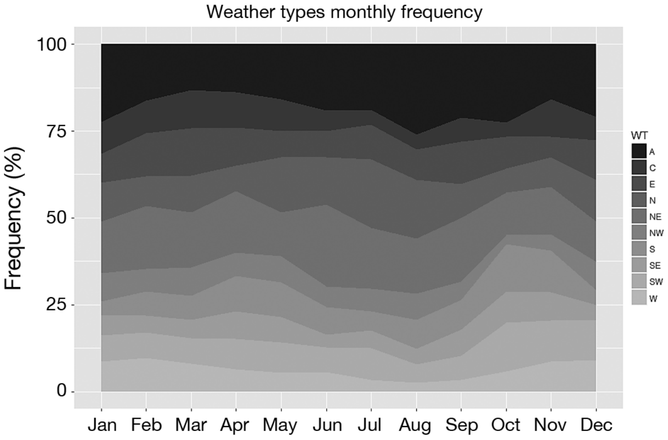

Fig. 6. Monthly frequency of the 10 weather types (WTs): directional (E, N, NE, NW, S, SE, SW, W) and pure (C: cyclonic; A: anticyclonic)

(43.2 μg m^{-3}). In Fig. 8, the box and whiskers plots help us to better understand the ozone distribution based on WTs, separately for each station and each season and then regrouped into inland (Turin and Asti) and coastal (Genoa and Savona) regions. In general, it is evident that ozone has wider range in Turin and Asti, even if many outliers are present in Genoa and Savona (Fig. 8a–d). In Turin (Fig. 8a), the highest maximum concentrations of ozone can be observed under NE and A types, while the highest median values are seen under N and NW types. In Asti (Fig. 8b), the highest maximum concentrations are under S and SE types, and the highest median values under N and NE types. In Genoa (Fig. 8c), SW and N types are responsible for the most elevated maximum concentrations; however, N, E, NE and NW give rise to the highest median values. In Savona (Fig. 8d), S and E types cause the highest maximum values of ozone, E and NE types the highest median values. NE, N, E and A types increase the ozone concentration in winter, SE and E mainly during spring and autumn, E and S in summer (Fig. 8e–h). In the inland stations, the highest maximum ozone is reached with S and NE types, the highest median with N and NE types. In coastland cities, the highest maximum values are recorded with S and SE types, the highest median values with E, N and NE.

Temperature, precipitation and wind speed daily values for the 4 stations were analyzed to search for a correlation with the ozone concentration during the same period (2003–2014). The full results are shown in Table 3. The ozone is signifi-

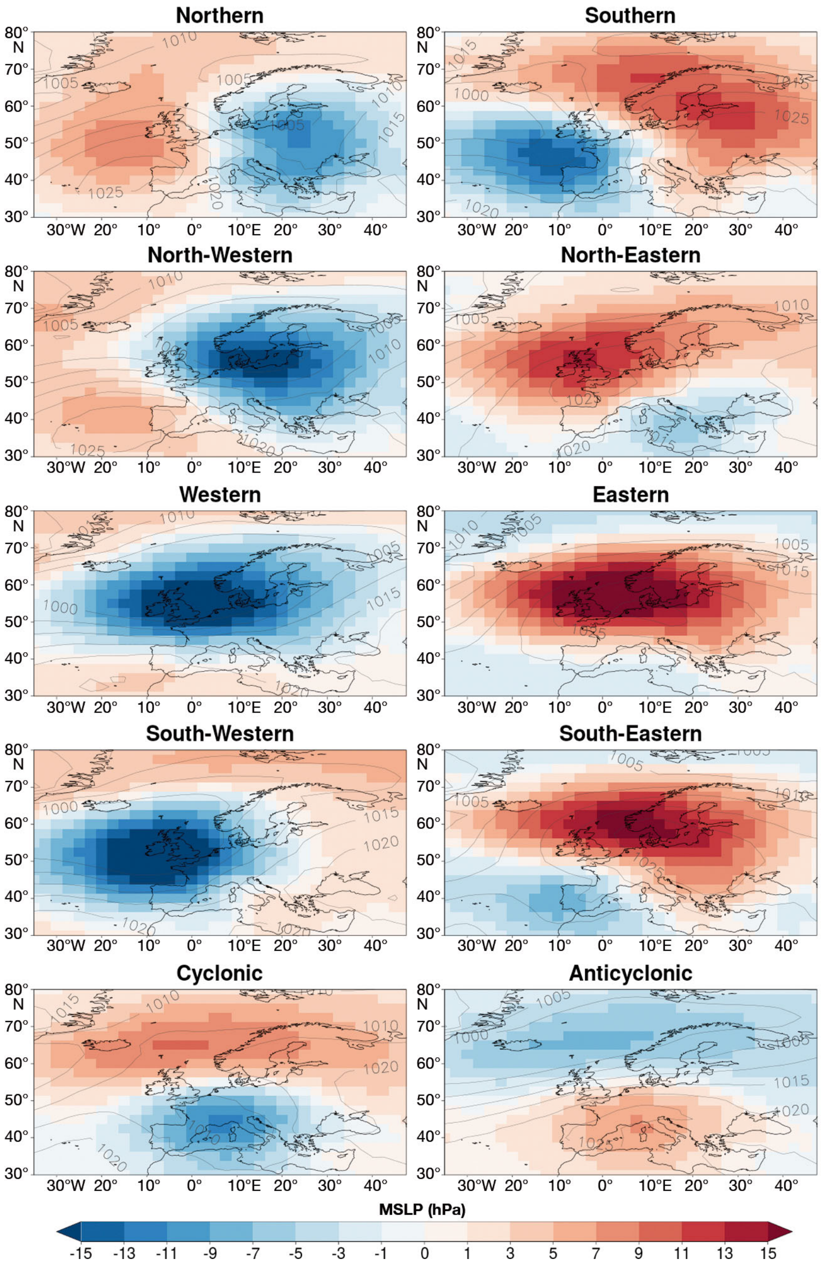

Fig. 7. Multi-panel maps of the mean sea-level pressure (MSLP) and its anomalies during the selected weather types (WTs) based on winter (DJF). The WTs were calculated centered on Turin, also for the other 3 cities. Lines display MSLP levels (hPa); colors are the anomalies. The patterns of other the seasons are similar to the winter pattern, but show less intensity

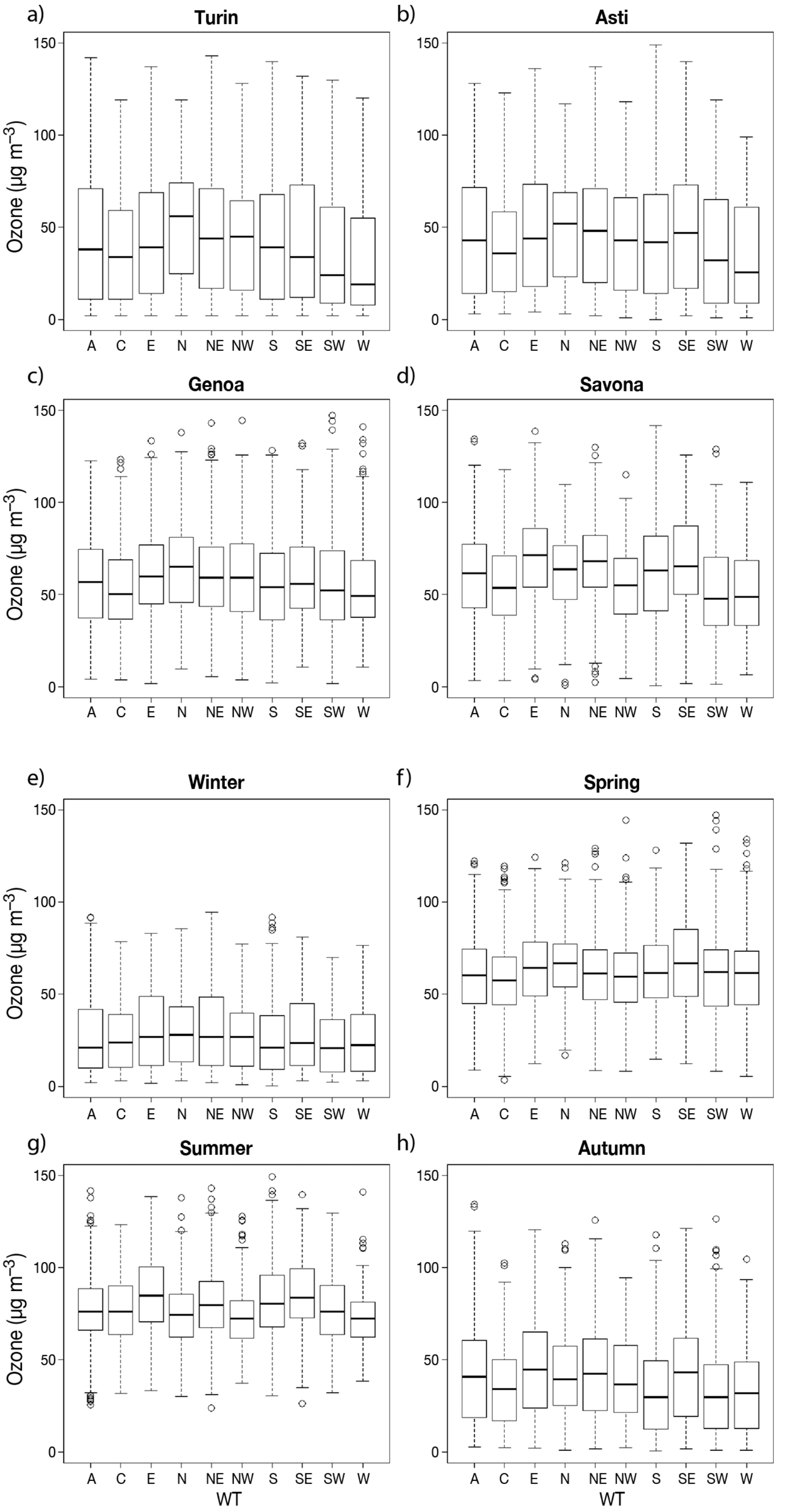

Fig. 8. Daily mean of ozone concentration (µg m^{-3}) based on the selected 10 weather types (WTs) separately for the (a–d) stations and (e–h) seasons. Box and whiskers present the median, first and third quantiles, minimum and maximum value and possible outliers. Winter: DJF; spring: MAM; summer: JJA; autumn: SON

cantly and positively correlated with the temperatures in all stations ($p < 0.001$). Precipitation has a significant negative influence on the ozone concentration, even if the correlation is weak ($p < 0.001$) in Asti, Genoa and Savona. In Turin, there is no correlation or statistical significance ($p = 0.96$).

Different relationships between wind speed and ozone were found: the inland stations recorded positive and significant correlations ($p < 0.001$), while in the coastland they were negative and significant ($p < 0.003$).

The daily NO_2 values are negatively and significantly correlated with the ozone concentration for all analyzed cities ($p < 0.001$; Table 3).

4. DISCUSSION

The ozone concentration follows both a daily and weekly cycle, influenced by solar radiation which affects its formation processes (Zvyagintsev et al. 2008), and by the production of pollutants and VOCs (Castell-Balaguer et al. 2012, Jiménez et al. 2005). Ozone levels are normally higher in daytime and lower during nighttime throughout the year, except in Genoa where the nighttime values are higher than in daytime in the autumn and winter months (Table 2). A similar pattern has also been reported for the northern Spanish coastal stations (Santurtún et al. 2015). This situation could be connected to the differences in commercial activities between the cities, as explained in Section 2.1. The intensity of port activities also causes a higher concentration of ozone precursors at night. The weekend effect is present in all 4 stations. As these are located in or near cities, this effect is more noticeable due to the reduction in NOx emissions (Castell-Balaguer et al. 2012, Jiménez et al. 2005).

The wide range of ozone values in inland cities could be caused by the diurnal temperature range because of their inland location, photochemical activity, air stagnation in the Po river

Table 3. Relationships between ozone (µg m^{-3}) and temperature (°C), precipitation (mm), wind speed (m s^{-1}) and NO_2 (µg m^{-3}). All values employed to calculate the relationships are daily. Equation of linear correlation, coefficient of determination (R^2) and p-value (indicating significance)

	Linear correlation	R^2	p-value
Temperature (°C)			
Asti	$2.89x + 5.79$	0.63	<0.001
Turin	$3.09x - 1.76$	0.66	<0.001
Genoa	$2.09x + 23.84$	0.28	<0.001
Savona	$1.89x + 30.09$	0.27	<0.001
Precipitation (mm)			
Asti	$-0.33x + 45.13$	0	<0.001
Turin	$-0.00x + 43.31$	0	0.96
Genoa	$-0.29x + 59.33$	0.01	<0.001
Savona	$-0.37x + 62.83$	0.03	<0.001
Wind speed (m s^{-1})			
Asti	$19.18x + 16.75$	0.15	<0.001
Turin	$33.17x + 0.97$	0.21	<0.001
Genoa	$-1.3x + 64.88$	0	<0.003
Savona	$-3.04x + 71.1$	0.02	<0.001
NO_2 (µg m^{-3})			
Asti	$-1.28x + 85.51$	0.43	<0.001
Turin	$-0.86x + 84.44$	0.47	<0.001
Genoa	$-0.46x + 78.49$	0.08	<0.001
Savona	$-1.3x + 84.85$	0.2	<0.001

plain and precursor production in local areas (Gabusi & Volta 2005, Russo et al. 2014). Furthermore, as previously noted, ozone has a high spatial variability, which has also been observed in other studies (e.g. Dueñas et al. 2002, Gottardini et al. 2010).

Regarding the seasonal cycle (Fig. 4), the minimum values in winter have also been recorded in other research (e.g. Cristofanelli et al. 2015). The summer maximum is typical of southern Europe and the Mediterranean basin (Scheel et al. 1997, Steiner et al. 2014), because of high insolation rates which can facilitate photochemical action on regional emissions (Zanis et al. 2007, Monks et al. 2009).

In the coastal stations (Savona and Genoa), a secondary peak is visible in spring (Fig. 4). This situation is similar to Spain, where coastal cities have an ozone peak in spring and inland cities have it during the summer (Santurtún et al. 2015). Taking global and local factors into consideration, the differences in the monthly maxima are understood to be a combination of background 'hemispheric-scale' impact, the influence of the sea (which decreases the temperature range) and early photochemical activity in spring (Atlas et al. 2003, Fernández-Fernández et al. 2011).

In the coastal areas, ozone has the highest annual average concentrations compared to the inland cities, because of greater solar radiation (Table 2). This has been observed in the AMS-MINNI (Atmospheric Modelling System-Italian Integrated Assessment Modelling System) modelling system adopted for the year 2005 by Mircea et al. (2014), along with elevated concentrations of NO_2 in the cities of the Po plain (e.g. Turin and Milan) and other polluted cities (e.g. Genoa, Rome and Naples). Thus, places such as Turin, with high industrial activity, a well-developed tertiary sector and a large population, do not necessarily show higher values of ozone concentration.

Since ozone is dangerous for the health of people and animals, as well as having detrimental effects on vegetation (e.g. Cooper et al. 2014), it is very important to identify its climate drivers, to assess the associated risk for the human population and to adopt the necessary political measures. In this research, we found a significant correlation between ozone concentration and atmospheric circulation patterns (Fig. 8, Table 2), which enhances ongoing research on the relationship between the circulation of weather types and atmospheric pollutants (e.g. Demuzere et al. 2009, Huszar et al. 2012, Saavedra et al. 2012, Russo et al. 2014).

Maximum ozone levels are generally linked to the NE, E and SE WTs, which carry air from the Po valley and the Gulf of Liguria. These conditions are correlated with a high-pressure zone in northern Europe which reaches the north-central part of Italy, and can be present in all seasons. Normally, this is characterized by stable, sunny conditions and dry air masses, which reduce pollution dispersion and deposition (e.g. Rao et al. 2003, Santurtún et al. 2015). Turin is an exception, because high median values are registered under N–NW WTs. These phenomena can be associated with foehn episodes, which are frequent during the winter (Fratianni et al. 2009).

Differences reported between maximum and median values of ozone based on 10 WTs in each city depend on regional and long-distance transport of pollutants and ozone precursors, in particular for the maxima values (Saavedra et al. 2012, Russo et al. 2014). The high values during the summer could be related to the presence of subtropical ridges in the European sector, at longitude 0–15° E. According to research carried out by Ordóñez et al. (2017), this synoptic condition is responsible for the rise in ozone above the local 90th percentile of its seasonal distribution, especially in the Po basin, where the increase occurs on >60% of days. The minimum values correlate to cyclonic and westerly types. During the cyclonic type, a low-pressure zone is centered in Italy. During the westerly type, a strong low pressure zone is centered in northern Europe, extending to northern and central Italy (see Fig. 8). These WTs are usually connected to atmospheric perturbations, cool conditions and precipitation, which reduce ozone concentration (e.g. Comrie & Yarnal 1992).

Climatic variables affect ozone values in different ways (see Table 3). Warmer temperatures cause an ozone increase everywhere, as reported in the literature; e.g. Demuzere et al. (2009) reported a clear relationship between temperature and ozone during the summer in the Netherlands. In fact, temperature enhances the propagation rate of the radical chain that leads to ozone formation (Ruiz-Suárez et al. 1995). Meanwhile, the relationship with precipitation is apparently negative, because on rainy days, cloud cover and atmospheric instability lower the temperature and the amount of solar radiation reaching the ground (Camalier et al. 2007).

From our results, it seems evident that wind (speed and direction) is a triggering factor for the dispersion of ozone precursors from local hotspots and for ozone transport from the stratosphere. Sea/land breeze systems also play a significant role in the transport of ozone from urban to coastal and mountain areas, contributing significantly to high ozone episodes in the coastal regions (Liu et al. 2002), all which could explain the negative relationship with wind detected in Savona and Genoa. On the other hand, in Turin the positive relationship between ozone and wind could be associated with winter foehn episodes generally linked to N and NW WTs, coupled with an adiabatic increase in temperature. For example, in the foehn event of 16–18 December 2005 which reached the Po plain and Turin from the Western Alps, the meteorological station registered a maximum temperature increase of >5°C and an ozone increase of 16 µg m^{-3} compared to the previous and following days (see Fratianni et al. 2009). Indeed, the foehn conditions caused a clear sky and a higher maximum temperature, together with greater solar radiation and a reduction in NO_2. These conditions facilitated the generation of ozone, which increased by up to 30 µg m^{-3} compared to the previous days.

5. CONCLUSIONS

In this research we analyzed the surface ozone concentration and its relationship with atmospheric conditions and climate variables in north-western Italy, where regional studies have not yet been carried out. The period analyzed was 2003–2014. In the study area, we detected the well-known daily, weekly and seasonal ozone cycles: ozone concentration is generally higher during daytime (08:00–19:00 h) than nighttime (19:00–08:00 h) and during weekends. The ozone levels reach a winter minimum in December and January, and a summer maximum in July and August. In the coastal cities, a secondary maximum in May has been observed. In the studied period, no significant trends in ozone concentration were assessed because of strong inter-annual variability.

The WT analysis indicates that the most frequent WT is the anticyclonic type, followed by north-easterly and northerly type. Relationships between ozone and WTs were significant. The highest values of daily ozone concentration occur within the easterly and south-easterly WTs, which are typically associated with stable, sunny conditions and lack of precipitation. The minimum ozone concentration values are found under the influence of the cyclonic and westerly types, which are usually connected to atmospheric perturbations and precipitation in our study area.

Temperature has a positive influence on the ozone concentration, while precipitation has a negative one. Wind affects ozone values positively in Piedmont (especially during the foehn winter episodes reaching Turin) and negatively in Liguria.

This study adds a crucial component to better understand the daily behavior of ozone, including the differences in this between coastal and inland regions in north-western Italy. However, supplementary integration with a longer data series would be useful to expand our knowledge regarding ozone variability. Furthermore, it would be advisable to carry out additional research into peak hourly concentrations, to verify the critical level of ozone pollution in the research area, according to the threshold proposed by the Air Quality Directive (2008/50/EC) of the European Union.

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