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Slant column MAX-DOAS measurements of nitrogen dioxide, formaldehyde, glyoxal and oxygen dimer in the urban environment of Athens

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HIGHLIGHTS

- Slant column densities retrieved for the first time in Athens using a MAX-DOAS system.
- Diurnal and seasonal variability of NO_2 suggest link to anthropogenic emissions.
- Temporal variability of HCHO and CHOCHO suggests stronger link to photochemistry.
- Elevated NO_2 levels when W winds are prevailing, low levels under N-NE winds.
- The cloud influence is weak at the $+1^{\circ}$ elevation angle.

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ABSTRACT

Slant column (SC) densities of nitrogen dioxide (NO_2), formaldehyde (HCHO), glyoxal (CHOCHO) and oxygen dimer (O_4) were successfully retrieved for the first time in Athens, by using spectral measurements from a ground-based multi-azimuth Multi-AXis Differential Optical Absorption Spectroscopy (MAX-DOAS) system. The data span the period from October 2012 to March 2014 and measurements were conducted at NOA's (National Observatory of Athens) station in Penteli (38.0°N, 23.9°E, 527 m a.s.l.) at eight azimuth angles and eight off-axis elevation angles. The SC_{NO2}, SC_{HCHO} and SC_{CHOCHO} measurements at $+1^{o}$ elevation angle, pointing towards the urban area, range from 0.6 to $24 \cdot 10^{16}$, $0.8–9.6 \cdot 10^{16}$ and $0.3–5.2 \cdot 10^{15}$ molec cm^{-2} (mean daily values throughout the whole period), respectively. Seasonal modulation characterised by summertime maximum and wintertime minimum was observed for HCHO and CHOCHO, while for NO_2 the maximum values were recorded during winter. Changes in the diurnal variability of all trace gases with season and day of the week are investigated suggesting a strong link to primary anthropogenic sources for NO_2 and a weaker one, compared to photochemistry, for HCHO and CHOCHO. In addition, the impact of the reduced anthropogenic emissions during weekends on the measured SC values was quantified and 30%–50% lower SC_{NO2} values were found during weekends. The contribution of local urban emissions to the overall recorded amounts of the selected species was assessed. Using meteorological data from NOA's station in Penteli, the impact of the local circulation patterns on the SC levels was estimated, and a strong relation between western wind direction, which is related to the industrial area, and enhanced SC measurements was found.

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1. Introduction

Urban smog, a term coined from smoke and fog, is a frequent phenomenon in Athens since the 1980s, resulting from pollution emitted by anthropogenic activities related to intense urbanization and road traffic as well as partial industrialisation. During the last few decades, several studies have been carried out in Athens focusing on air pollution. These studies used in-situ measurements (e.g. Lalas et al., 1983; Barde and Button, 1990; Viras and Siskos, 1992; Ziomas et al., 1998; Kalabokas et al., 1999; Kalabokas and Repapis, 2004), ground-based remote-sensing techniques, such as active DOAS and LIDAR (e.g. Avdikos et al., 2006; Kalabokas et al., 2012; Papagiannis et al., 2012; Psiloglou et al., 2013) and space-based observations (e.g. Vrekoussis et al., 2013). Here, we report on measurements performed in Athens with a novel passive Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) instrument. In contrast to previous ground-based remote observations monitoring air composition at a fixed viewing direction, the deployed MAX-DOAS has the advantage of sequentially pointing at multiple azimuth angles. The instrument installed at the premises of National Observatory of Athens in Penteli (527m a.s.l., Fig. 1), scans the whole urban area of Athens providing information on both the vertical and the horizontal distribution of important trace gases in the troposphere above the Athens basin. In this work, MAX-DOAS slant column retrievals of nitrogen dioxide (NO_2), the oxygen dimmer (O_4), formaldehyde (HCHO) and glyoxal (CHOCHO) are presented for the time period from October 2012 until March 2014. The importance of these species is summarized below.

Nitrogen dioxide (NO_2) is an important tropospheric pollutant, participating among others, in catalytic cycles leading to ozone formation; it is destroyed by oxidation to nitric acid (Seinfeld and Pandis, 2006). It affects human health increasing the risk of respiratory symptoms (Chaloulakou et al., 2008; Schwartz et al., 1991). In urban environments, its main source is fossil fuel combustion (e.g. Noxon, 1978). Although combustion processes emit NO_2 only in small quantities, they also emit nitrogen monoxide (NO) which rapidly forms NO_2 when reacting with ozone molecules. Over 50% of NO_x (NO plus NO_2) emissions in the urban environment of Athens are attributed to road transport (Markakis et al., 2010). Additional important NO_x sources in Athens are the industrial area (Elefsina) to the West-Southwest of the city center and the Piraeus port to the South-Southwest (Kassomenos et al., 1995). A large (31%) reduction in tropospheric NO_2 levels has been observed since 2008, as a result of the economic crisis (Vrekoussis et al., 2013). Due to its strong absorption lines in the visible region of the spectrum, NO_2 is readily observed using optical absorption spectroscopy (e.g. Brewer et al., 1973; Solomon et al., 1987).

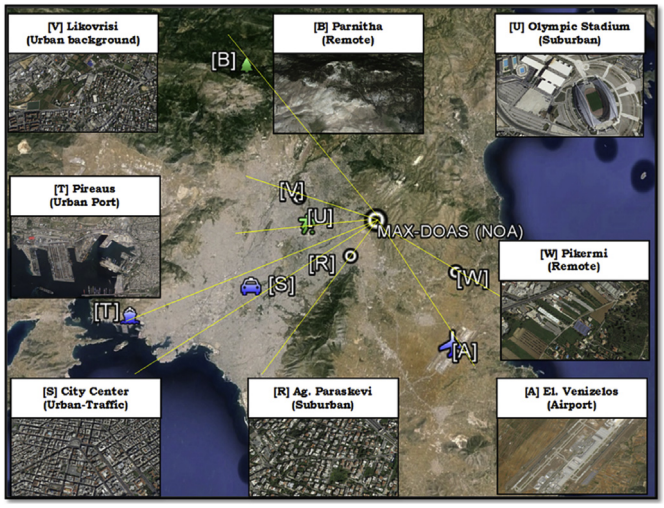

Fig. 1. MAX-DOAS location at NOA's premises in Penteli mountain, and viewing directions over Athens.

Formaldehyde (HCHO) is an intermediate short-lived (Arlander et al., 1995) product of the oxidation of volatile organic compounds (VOCs) and of many hydrocarbons, including methane (CH_4) (Levy, 1971; Finlayson and Pitts, 1976). Consequently, it can be used as an indicator for the presence of hydrocarbons and volatile organic compounds (VOCs) (Finlayson and Pitts, 2000). Under particular meteorological conditions, an abundance of NO_x and VOCs with sufficient UVB radiation may lead to the development of photochemical smog (Seinfeld and Pandis, 2006). HCHO also contributes to the radical budget of the atmosphere mainly as a primary source for the hydroperoxy radical (HO_2) (Platt et al., 1979). Prior to this study there have been only sporadic measurements reported concerning formaldehyde amounts in Athens (Amanatidis et al., 1997; Klemm et al., 1998), with the exception of a study by Bakeas et al., (2003) where measurements for a six month time period are reported.

Glyoxal's (CHOCHO) presence in the atmosphere is attributed to the oxidation of VOCs (Calvert et al., 2000), since its primary emissions are believed to be small compared to its secondary sources (Volkamer et al., 2005). High concentrations of glyoxal have been reported in polluted urban environments (Volkamer et al., 2005) as well as over areas with high biogenic emissions (Wittrock et al., 2006; Vrekoussis et al., 2009, 2010). Moreover, glyoxal is a short-lived species, so it can be used as an indicator of VOC oxidation processes (Volkamer et al., 2005). Thus far, to our knowledge there are no reported CHOCHO measurements conducted in Athens.

The oxygen dimmer (O_4) is the collision complex of two oxygen molecules $(O_2)_2$. It has several absorption bands in the near ultraviolet (UV), visible (VIS) and near infrared (IR) and it absorbs weakly under clear sky conditions (Perner and Platt, 1980). Given that the O_4 has a well known and almost constant vertical concentration profile, the absorption enhancement by O_4 can be used to calculate the mean optical path of the transmitted light (Pfeilsticker et al., 1997). MAX-DOAS measurements of O_4 at different elevation angles can provide information about the atmospheric aerosol profile, since aerosols change the optical path in a way which depends on their vertical distribution (Wittrock et al., 2004; Heckel et al., 2005; Wagner et al., 2004).

This paper is structured as follows: in Section 2 a presentation of the topography of the Athens basin is given followed by the description of the MAX-DOAS instrument and the DOAS technique used. Time series of the measurements, seasonal and diurnal cycles and the impact of wind fields on pollutants levels are presented in Section 3. The cloud influence on the measured SC densities is also investigated. Finally, in Section 4, the main conclusions of this study are presented.

2. Data and methodology

2.1. Site description

The particulate and gaseous pollutants levels in Athens are strongly influenced by the special topography of the city (Fig. 1). The city of Athens, along with Piraeus to the south, and their suburbs, is surrounded in a semicircular way by four mountains: Aegaleo (450 m) to the West, Parnitha (1400 m) to the North, Penteli (1100 m) to the Northeast and Hymettus (1050 m) to the East. The basin is open to the South and Southwest. Under specific meteorological conditions, Athens' topography favors the accumulation of atmospheric pollutants (Kassomenos et al., 1995).

2.2. Instrumentation and data retrieval

The MAX-DOAS instrument used in this study is part of the BREDOM network (Bremian DOAS network for atmospheric measurements, http://www.iup.uni-bremen.de/doas/groundbased_data.htm). It is installed in Penteli (38.05°N, 23.86°E, 527m a.s.l) at the premises of the National Observatory of Athens (Fig. 2, left panel).

Briefly, the instrument comprises a telescope unit, connected via an optical fiber bundle to a grating spectrometer (LOT 260S, 600 l/mm ruled grating) equipped with a cooled (−40 °C) CCD detector (Andor, 2048 × 512 pixels). The spectral coverage of the spectrometer is 330–500 nm with a spectral resolution of approximately 0.7 nm. The telescope unit is mounted on a pan-tilt-head (Fig. 2, right panel) in order to be able to point towards any direction in the sky. The field of view of the telescope is about 1°.

During routine operation, measurements are performed at various azimuth and elevation angles as well as to the zenith. Eight elevation angles relative to the horizon were selected: −1°, 0°, +1°, +2°, +4°, +8°, +15° and +30°. Since the greater part of the optical path is in the lower troposphere, measurements at low elevation angles have higher sensitivity to the concentration of absorbing trace species close to the surface (Hönninger et al., 2004; Wittrock et al., 2004). Concerning the azimuthal direction, eight viewing azimuth angles with respect to south were selected: −60°, −30°, 40°, 52.5°, 65°, 77.5°, 100° and 140°. For simplicity we refer to these directions as W, A, R, S, T, U, V and B respectively (Fig. 2). Although there is unobstructed view towards all directions, direction 'B' pointing towards the Parnitha mountain cannot be considered as completely unobstructed since Parnitha's altitude is 1400 m and its distance from Penteli's station is about 15 km. Direction 'V' is characterised as urban background, 'U' and 'R' as suburban, 'T' and 'S' are typical urban directions, 'A' is pointing to the airport and 'W' is a remote unobstructed direction. The duration of one full scanning cycle through all directions is about 15 min. The instrument has been operating continuously since October 2012.

The acquired spectra are analysed using the DOAS technique (Differential Optical Absorption Spectroscopy, Platt and Stutz, 2008), which applies the Beer-Lambert's law. The optical thickness, i.e. the logarithm of the ratio of the observed to a reference spectrum, is separated into two components: a high and a low frequency one. The absorption by trace gas molecules and the signature of rotational Raman scattering (Ring effect) are represented by the high frequency part, while the attenuation by scattering processes in the atmosphere and the low-frequency part of the absorption are represented by the low frequency part. The determination of the differential slant column density (SC), which is the product of the retrievals, is then achieved by fitting to the optical depth (a) the laboratory cross-sections of the retrieved species (Table 1) and (b) a polynomial accounting for the low-frequency component. The polynomial used is of degree 4 for NO_2, HCHO and O_4 and of degree 3 for CHOCHO. Slant column densities for NO_2, HCHO, CHOCHO and O_4 have been retrieved employing specific fitting windows for each trace gas (Table 1). Fig. 3 depicts four characteristic fits for NO_2, HCHO, CHOCHO and O_4. Typical detection limit values for near noon conditions at +1° elevation angle are 2.7×10^{-14} molec/cm^2 for NO_2, 3.5×10^{-15} molec/cm^2 for HCHO and 2.1×10^{-14} molec/cm^2 for CHOCHO.

The spectrum used as reference is the concurrent zenith observation obtained within the same measurement cycle for each measurement in the off-axis viewing angles. Hence, the retrieved SC corresponds to the difference in slant columns between the spectrum observed at lower elevation and the concurrent zenith sky measurement. The concentration as a function of altitude could be estimated by using a profiling algorithm (e.g. Roscoe et al., 2014). In this work, we focus on the spatial and temporal variability of the trace gases, which can already be discussed using the differential slant columns. Similarly, differential slant column densities have also been used in other studies for characterising atmospheric conditions (e.g. Leigh et al., 2007; Heckel et al., 2005; Wagner et al., 2004; Hönninger et al., 2002).

During the period from October 2012 to March 2014, 480 days of MAX-DOAS data were recorded, leading to an overall data capture of 89%. In order to limit the possible impact of stratospheric absorption interferences on the measurements and to simplify the interpretation of results, values corresponding to solar zenith angles (SZA) larger than 75° degrees were not considered.

For the interpretation of the results, detailed meteorological data (wind-speed, wind-direction and temperature) retrieved from the ground-based station of the National Observatory of Athens in Penteli (http://penteli.meteo.gr/stations/penteli/), is also used.

3. Results and discussion

3.1. Data presentation and basic statistical analysis

In order to investigate the spatial homogeneity of the measurements, the correlation coefficients between NO_2

Table 1
Spectral fitting windows and absorption cross sections used in the data analysis.

Molecule	Fitting windows (nm)	Absorption cross sections
NO_2	425–490	Vandaele et al., [1998]
HCHO	336–359	Meller and Moortgat [2000]
CHOCHO	434–458	Volkamer et al., [2005]
O_4	338–380	Hermans et al., [2003]

Fig. 2. Telescope of the MAX-DOAS instrument installed at the premises of the National Observatory of Athens (left panel). Panoramic view of the azimuth scan (right panel).

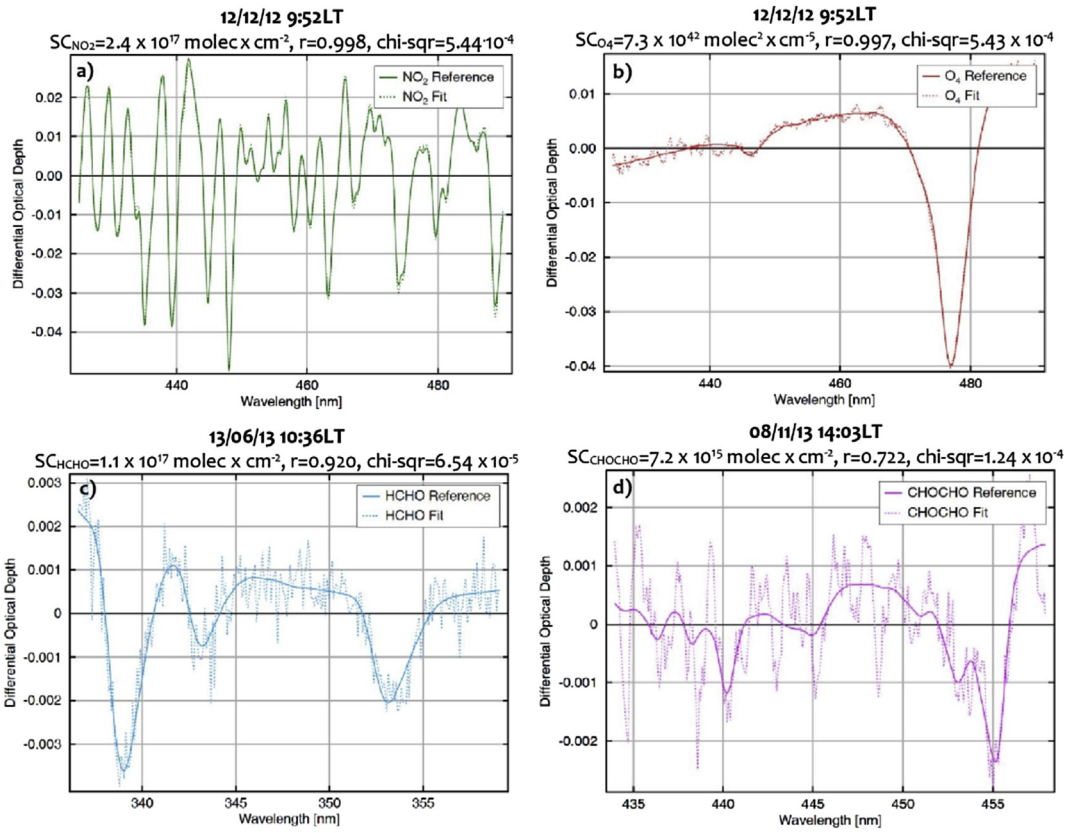

Fig. 3. Example of NO2 (Fig. 3a), O4 (Fig. 3b), HCHO (Fig. 3c) and CHOCHO (Fig. 3d) DOAS fits. The solid line depicts the reference cross section scaled to the slant column values, and the dashed line depicts the fit (sum of scaled cross-section and residual).

measurements at the +1° (representative of the layer close to the surface) and +30° (representative of the integrated tropospheric column including higher layers) elevation angles in all azimuthal directions were calculated (Table 2). As expected, high correlations are revealed between neighboring azimuthal directions. In line with this finding, direction 'S' pointing at the city center, has been chosen as typical to characterise urban air quality in Athens. Respectively, direction 'W', which is a sparsely populated area, has been chosen as characteristic of remote environment conditions. These two directions are henceforth used for the presentation of the results. Measurements at +30° elevation show higher correlation coefficients (not shown here), since at higher elevations the measurements are less sensitive to lower troposphere and boundary layer pollution (Wittrock et al., 2004; Hönninger et al., 2004; Platt and Stutz, 2008) and thus less affected by changes in surface pollution levels. In addition, the spatial separation between the measurement volumes in the lower troposphere is considerably smaller at +30° than at +1° elevation for geometrical reasons, reducing gradients and increasing correlation.

The time series of daily-averaged SC densities for the remote (W) and urban (S) area are presented in Fig. 4. Basic statistical quantities for NO_2, HCHO, CHOCHO and O_4 are presented in Fig. 5. The analysis is based on the daily values and refers to the entire measurement period.

At first, an obvious observation is that the difference in SC_{NO2} densities as a function of elevation angle is greater over the polluted area (Fig. 4a and b), in agreement with earlier findings (Hönninger et al., 2004; Leigh et al., 2007). The enhanced values of SC_{NO2} at lower elevation angles are explained by: a) longer optical light path within the boundary layer (Wittrock et al., 2004; Hönninger et al., 2004; Platt and Stutz, 2008) and b) higher NO_2 levels at lower levels as result of surface emission sources. This is why the difference between the remote and urban direction become more apparent at low elevation angles. In particular, at +1° elevation, the SC_{NO2} densities in the urban direction are on average twice as high as in the remote direction, while for +8° and +30° elevations the excess is 38% and 5%, respectively. Based on daily SC_{NO2} values at +1° elevation angle, the daily SC_{NO2} levels for the urban area vary from $0.6 \cdot 10^{16}$ molec cm^{-2} to $24 \cdot 10^{16}$ molec cm^{-2}, with an average value of $(7.3 \pm 4.7) \cdot 10^{16}$ molec cm^{-2}. The corresponding values for the remote area range from $0.3 \cdot 10^{16}$ molec cm^{-2} to $20 \cdot 10^{16}$ molec cm^{-2} with an average value of $(3.7 \pm 3.5) \cdot 10^{16}$ molec cm^{-2}. The seasonal variation of the SC_{NO2} in the urban and remote area is discussed in detail in Section 3.2.

SC_{HCHO} time series are shown in Fig. 4c and d. Once more, the difference between the remote and urban area is most evident at +1° elevation angle: the SC_{HCHO} densities over the urban area are higher by an average of 13%. Similar difference (9%) is found at +8° elevation while almost no difference is noted at the +30° elevation. Overall, over the urban area the daily SC_{HCHO} values at +1° elevation angle vary from a minimum of $0.8 \cdot 10^{16}$ molec cm^{-2} to a maximum of $9.6 \cdot 10^{16}$ molec cm^{-2}, with an average value of $(3.1 \pm 1.3) \cdot 10^{16}$ molec cm^{-2}. The corresponding values for the remote area range from $0.7 \cdot 10^{16}$ molec cm^{-2} to $8.1 \cdot 10^{16}$ molec cm^{-2} with an average of $(2.8 \pm 1.2) \cdot 10^{16}$ molec cm^{-2} (Fig. 5).

Fig. 4e and f presents daily SC_{CHOCHO} values. CHOCHO measurements at +1° elevation angle are on average 30% higher in the urban direction compared to the remote direction, while the corresponding excess for +8° elevation angle is 16%. Similarly to NO_2 and HCHO measurements, almost no difference is observed for

Table 2
Correlation matrix of SC_{NO2} for all viewing directions at +1° elevation angle. The values in the gray box show the high correlation between all the directions pointing to the city center.

Directions	W	A	R	S	T	U	V	B
W		0.963	0.743	0.732	0.726	0.735	0.751	0.821
A	0.963		0.836	0.810	0.790	0.785	0.773	0.804
R	0.743	0.836		0.985	0.949	0.911	0.826	0.728
S	0.732	0.810	0.985		0.984	0.954	0.877	0.772
T	0.723	0.790	0.949	0.984		0.987	0.931	0.825
U	0.735	0.785	0.911	0.954	0.987		0.966	0.866
V	0.751	0.773	0.826	0.877	0.931	0.966		0.938
B	0.821	0.804	0.728	0.772	0.825	0.866	0.938	

the +30° elevation. The average SC_{CHOCHO} value for the urban area is $(1.8 \pm 0.8)\cdot 10^{15}$ molec cm^{-2} and the corresponding value for the remote is $(1.4 \pm 0.6)\cdot 10^{15}$ molec cm^{-2} (Fig. 5).

From Fig. 4 it is clearly deduced that the difference in SC values between low and higher elevation angles is larger for NO_2 compared to HCHO and CHOCHO, indicating that the NO_2 vertical profile is more strongly weighted to the lower troposphere than that of the secondary VOCs which are produced in the atmosphere itself.

Finally, the daily SC_{O4} values are presented in Fig. 4g and h for the urban and remote directions, respectively. The SC_{O4} of the lower viewing directions are well separated from the +30° elevation, except for specific days when the retrieved SC_{O4} at the different elevation angles converge. This convergence is indicative of increased aerosol load during these days; aerosols decrease the length path of the photons, so the observed O_4 absorption is also reduced. Thus, the slant columns at different elevation angles result in similar levels due to similar light paths (Wittrock et al., 2004; Wagner et al., 2004; Heckel et al., 2005). This pattern appears more frequent during springtime and it is associated to dust transport from North Africa (Gerasopoulos et al., 2006), but also during wintertime due to increased aerosol emissions (domestic heating sources) (Gerasopoulos et al., 2014; Paraskevopoulou et al., 2015). Clouds also play an important role, especially for observations close to the horizon, by changing the average light path and thus the expected actual slant column. The small difference of SC_{O4} levels during the whole period between the +1° and the +8° elevation angle has also been reported, even during clear days, in other studies (e.g. Wagner et al., 2004). The O_4 levels do not seem to vary significantly between the remote and the urban area indicating: a) relatively small gradients in aerosol load and b) that the differences observed in the trace gas SCs for different azimuth angles are not the result of differences in light path length.

3.2. Seasonal variability

The monthly average SC densities for the retrieved species are presented for the typical remote and urban area, for all elevation angles (Fig. 6). A clear seasonal cycle is observed for SC_{NO2}, with winter maxima and summertime minima (Fig. 6a). Winter versus summer shows 80% and 180% higher values for the urban and for the remote area (+1° elevation angle), respectively. Reduced NO_2 levels during summer can be attributed to: (a) lower anthropogenic NO_x emissions during summer vacations (Kalabokas et al., 1999) mainly as result of reduced traffic, and enhanced anthropogenic

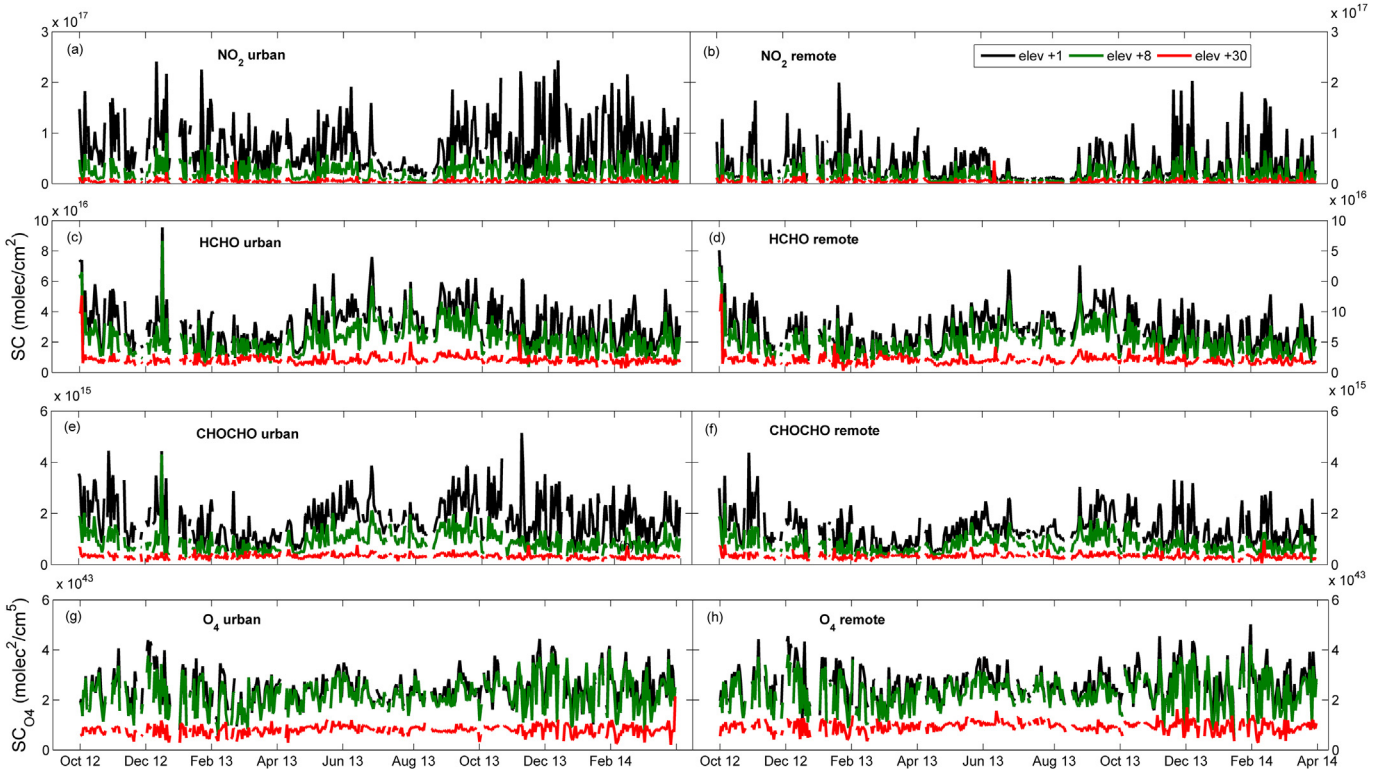

Fig. 4. Time series of daily-mean SC density values for three elevation angles (black, green and red lines represent +1°, +8° and +30° elevation angles, respectively) for urban (left panels) and remote (right panels) area for NO_2, HCHO, CHOCHO and O_4. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

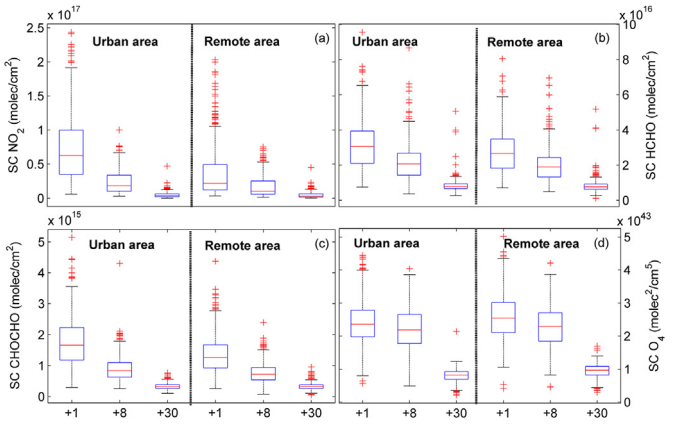

Fig. 5. Whisker plots for three elevation angles (+1°, +8° and +30°) for urban (left triplet on each subplot) and remote (right triplet on each subplot) area for NO_2, HCHO, CHOCHO and O_4 resulting from daily values. On each box the central red line is the median, the edges of the box are the 25th and 75th percentiles. The whiskers extend to the most extreme data points, not considering outliers which are represented by the red crosses. The value considered as outlier is any value that lies more than one and a half times the length of the box from either end of the box. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

emissions during winter due to fossil fuel burning for heating purposes, (b) the prevailing Etesian Northern winds encountered mainly during July and August (e.g. Pezzoli, 2005) characterising 54 out of the 62 days and leading to efficient removal of pollution from the Athens' basin, (c) lower dispersion efficiency in winter due to near surface thermal inversion resulting in shallower boundary layer with high NO_2 concentrations and (d) longer NO_2 lifetime in winter due to decreased NO_2 photolysis rate, along with reduced hydroxyl radical levels, which leads to reduced conversion of NO_2 to HNO_3.

A clear seasonal variation is also observed for HCHO (Fig. 6b). The increased summer levels of SC_{HCHO} are attributed to the photochemical production of HCHO. It has been previously estimated that the photochemical production of HCHO in Athens represents 83% of the measured formaldehyde during summer, while the corresponding ratio for winter is 33% (Bakeas et al., 2003). The average SC_{HCHO} at +1° elevation angle are 37% higher during summer months (June to August) compared to winter months (December to February), both for the urban and the remote direction. During summer, lower SC_{HCHO} values are encountered in July and August. Although the solar irradiation is still high during these two months, the efficient ventilation by the strong Etesian Northern winds, which favors the effective dispersion of pollutants, along with lower primary HCHO emissions, can result in reduced HCHO levels. Similar seasonal variation of HCHO has been reported for urban areas in several studies (e.g. Tanner and Mong, 1984; Ho et al., 2002; Possanzini et al., 1996). However, only sporadic measurements of HCHO have been reported for Athens in the past (Klemm et al., 1998; Amanatidis et al., 1997) and just two works which report on the seasonal variation (Kalabokas et al., 1997; Bakeas et al., 2003). In particular, Kalabokas et al. (1997) found no clear seasonal variation of HCHO in Athens, in agreement with the later observations of Bakeas et al. (2003). At first, the relatively small difference in SC_{HCHO} values between remote and polluted areas in this study (Fig. 6b), suggests that the impact of direct anthropogenic sources on HCHO levels is small. However, after taking into account the different photochemical production of HCHO in winter and summer (33% and 83% respectively), as calculated by Bakeas et al. (2003) for distinguishing photochemical from anthropogenic HCHO production, a potential link between HCHO levels and anthropogenic sources can be deduced. More specifically, for the urban area the calculated average SC_{HCHO} value attributed to non photochemical sources is $1.89 \cdot 10^{16}$ molec cm^{-2} in winter and $0.65 \cdot 10^{16}$ molec cm^{-2} in summer. This indeed suggests the potential impact of anthropogenic sources on SC_{HCHO} levels, reflecting the intensification of human activities during winter.

A similar to HCHO seasonal pattern is also observed for CHOCHO (Fig 6c). CHOCHO is only produced by VOCs having at least 2C atoms, whereas HCHO is produced by the oxidation of methane as well by VOC having 2 or more carbons. They are both removed from the boundary layer and the lower troposphere by photolysis and reaction with OH. However, CHOCHO reacts with OH and is photolysed more rapidly than HCHO, thus it has shorter chemical lifetime. Provided that the source of VOCs is at the surface and that the production of HCHO is dominated by VOCs, then both HCHO and CHOCHO have practically the same source, and their seasonal variability is likely to be similar close to source regions. However their horizontal and vertical distributions are expected to be different in a transported and chemically transformed pollution plume. The average SC_{CHOCHO} densities are about 23% and 15% higher during summer compared to winter, for the urban and the remote area (+1° elevation angle), respectively. CHOCHO presents a more distinct difference between the remote and the polluted direction compared to HCHO, which indicates a potentially stronger relation to direct anthropogenic sources. The link to direct anthropogenic sources is also supported by the smaller difference found between summer and winter months.

The O_4 seasonal variation is not so pronounced (Fig 6d). From February to April the difference between low and high elevation measurements is smaller indicating stronger extinction, which could be attributed to high aerosol load in the atmosphere. Stronger extinction is also reflected by the slightly (approximately 10%) lower levels of SC_{O4} during these months. No considerable difference regarding the levels between remote and urban area is noted and this could be attributed to the fact that O_4 absorption depends on many factors (clouds, dust, visibility) apart from anthropogenic aerosols, which are characteristic of the urban area. Clouds and Saharan dust affect the remote and urban measurements almost in the same way, since most of the time their horizontal distribution is uniform. Additionally, the small difference could also be attributed to efficient aerosol transport from the city to the background areas throughout the day.

3.3. Cloud screening

During the 1.5 year of MAX-DOAS observations, days with high cloud and aerosol load have occurred, possibly «contaminating» the obtained SC densities by influencing the atmospheric radiative transfer and thus affecting the analysis of the observations. To address this restriction for further analyses, meteorological observations from the National Observatory of Athens for cloud coverage were used to screen out cases with large cloudy cover. Overall, 30% of the measurements were removed by the cloud screening. Fig. 7 shows the monthly means of SC densities for all four retrieved trace gases with and without cloud screening at the +1° elevation.

In general, no significant differences are observed, suggesting that uncertainties in the following analyses for the +1° elevation due to cloud influences are small and do not affect the findings. This can be understood by the fact that most clouds are above the main light path of the 1° viewing direction which is nearly horizontally. Greater influence was found, as expected, during winter months. In general, for NO_2 the mean difference for the urban area is 5%, for HCHO, CHOCHO and O_4 the difference is 6%, 8% and 3%, respectively.

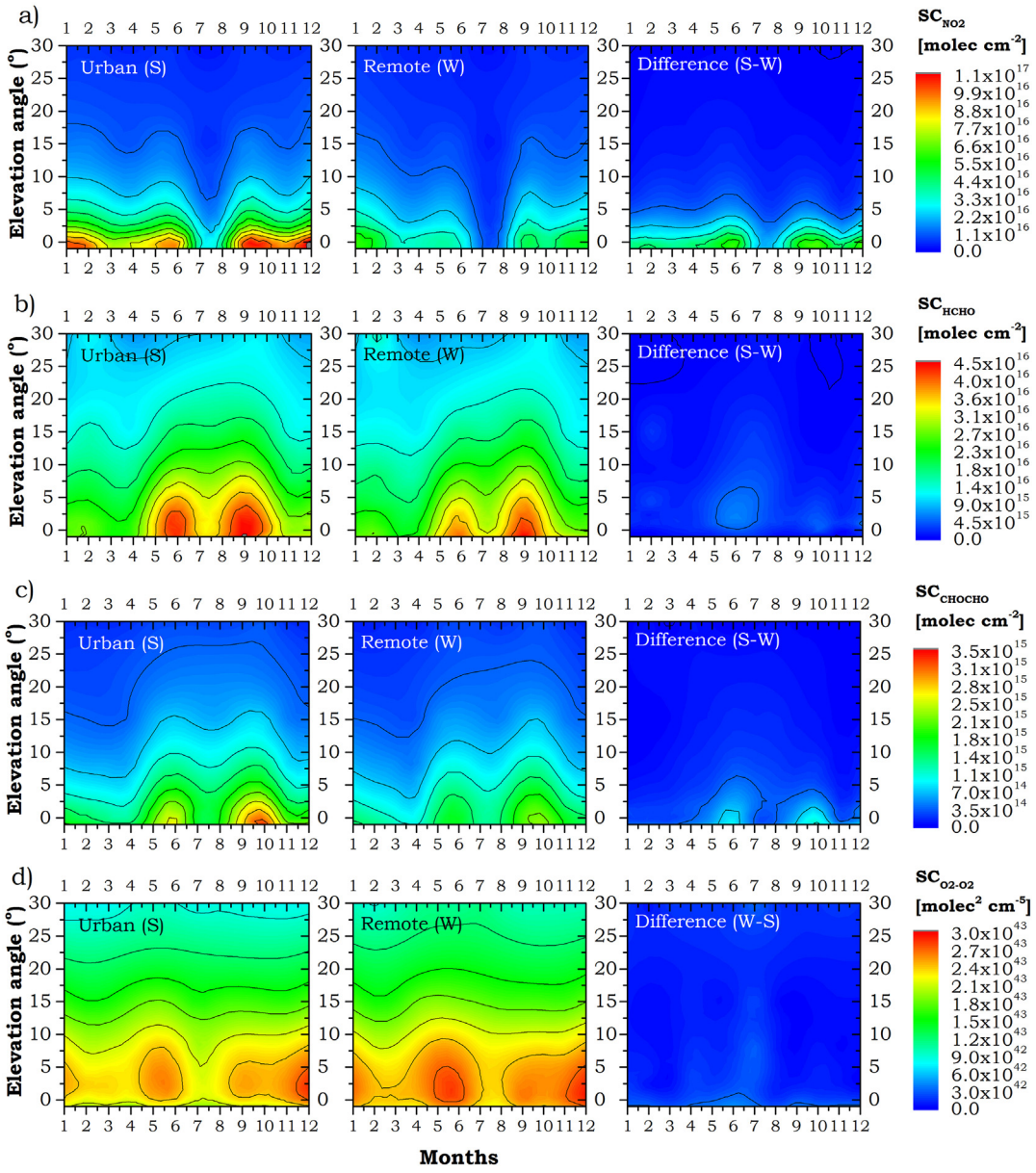

Fig. 6. Monthly average SC densities for NO_2 (a), HCHO (b), CHOCHO (c) and O_4 (d) for all elevation angles for polluted (left column) and remote (central column) areas. The right column depicts the difference between the remote and the urban area.

No difference exceeding 20% was found, even during months with frequent heavy cloud conditions (November–December). Concluding, the effect of clouds on SC retrieved for the +1° elevation does not considerably alter the interpretation of the results. Therefore, the following analyses focus on +1° elevation measurements.

3.4. Diurnal variation and weekend effect

The mean diurnal course of the retrieved species SC densities at +1° elevation angle was calculated separately for the cold (November–March) and the warm period (April–October). The mean daily temperature value of the cold and the warm period was 9.8 °C and 20.6 °C, respectively. The diurnal profiles were obtained by averaging data of 215 days for the warm period and of 265 days for the cold period. Additionally, taking into account that air pollution in Athens is influenced by wind conditions, we examine the effect of air masses originating from polluted (S-SW) and rural (N) areas to the MAX-DOAS observations towards the urban and the remote area respectively. For that purpose, diurnal profiles were calculated separately considering data just for days when wind direction was between 180° and 270° (S-SW) for the urban area and between 315° and 45° (N) for the remote area. This separation gives us more detailed information about the influence of the origin of the air masses on the MAX-DOAS observations. Local time (LT) is used for drawing conclusions about the effect of human activities on the results (cold period LT = UTC+2, warm period LT = UTC+3).

The diurnal cycle of SC_{NO2} (Fig. 8) seems to be rather different between the cold and the warm period, with the main discrepancy found in the afternoon. In all cases, a morning maximum at around 10:00 LT is observed due to increased traffic related NO_x emissions (rush hours in Athens are estimated to be from 08:00 LT until 11:00 LT, Katsoulis, 1996, Kourtidis et al., 1999). The steady build up of NO_2 starts with the beginning of the morning rush hour until noon. The

diurnal maximum of NO_2, emerging 2 h after the beginning of the traffic rush hour, is explained by NO_x chemistry; vehicles emit NO which then reacts with ozone or peroxy radicals and produces NO_2. Later in the day, the NO_2 dissociation due to photochemical processes (Boersma et al., 2008), along with the growth of the boundary layer, lead to NO_2 decline. In the evening, a second maximum appears around 15:00 LT during winter, while in summer NO_2 keeps reducing until late evening. This could be attributed to the different winter and summer boundary layer evolution, along with more intense photochemistry occurring during summer. In winter the photochemical processes start to decelerate soon afternoon, while NO_x is still being emitted, producing the second maximum of the day, both in the remote and in the urban area. It is worth noting that the warm and cold period diurnal cycles of SC_{NO2} exhibit the typical urban daily pattern (e.g. Bigi and Harrison, 2010) and are in agreement with other in-situ measurements for Athens (e.g. Kalabokas and Bartzis, 1998; Moussiopoulos et al., 1997; Rappenglück et al., 1998; Katsoulis, 1996). Peaks are more distinct during weekdays compared to weekends, in both remote and urban area, and this is related to higher anthropogenic activity, mainly traffic.

Many factors such as hydrocarbons and VOCs emissions by motor vehicles, photo-oxidation of hydrocarbons as well as photolysis of HCHO could impact the observed HCHO diurnal course. The observations point out that during the cold and warm periods the diurnal patterns differ (Fig. 9). In the cold period, there is a small morning peak, indicative of the presence of anthropogenic sources (vehicular exhaust and central heating), and a broader afternoon peak in the urban area. Although the statistical significance of the morning peak cannot be supported due to the large error bars, it should be noted that its presence is repeated in both areas. The increase of HCHO begins much earlier in the cold (peak at 09:00 LT) than in the warm (peak at 11:00 LT) period in the urban area. This is possibly due to high ambient humidity during winter, which triggers the formation of HONO (heterogeneous hydrolysis of NO_2 on aerosol surfaces) initiating urban photochemistry (Atkinson, 2000). During the warm period there is a maximum around noon and a steady decrease afterwards, especially in the remote area, suggesting that photochemistry plays a dominant role in HCHO production during summer. Regarding to the weekend effect on HCHO, there is almost no difference between weekdays and weekends, which is an indication of weak link to direct anthropogenic sources. The only exception to this is the winter morning maximum during weekdays, which is repeated in both site types.

SC_{CHOCHO} increases rapidly shortly after sunrise both in the warm and in the cold period (Fig. 10). This increase highlights intense VOC oxidation processes during morning hours. The persisting high CHOCHO levels during the cold period, even after solar noon, reflect either a higher glyoxal production rate compared to the photochemical loss or a reversible partitioning into the aerosol phase (e.g. Knote et al., 2014). In contrast, during the warm period there is a clear maximum at 12:00 LT followed by a sharp decrease. This pattern reflects that CHOCHO photochemical loss begins to be dominant during the warm period at small SZAs and continues to be important for the rest of the day after solar noon (Volkamer et al., 2005). No distinct difference is observed in the patterns between weekdays and weekends, with SC_{CHOCHO} levels being slightly lower during winter weekends, while in summer the peak is more intense during weekdays. More detailed discussion about the weekend effect on the retrieved species is provided in the next two paragraphs.

The influence of the frequent strong northern winds (Etesian winds) blowing during July and August, dispersing the pollutants, is

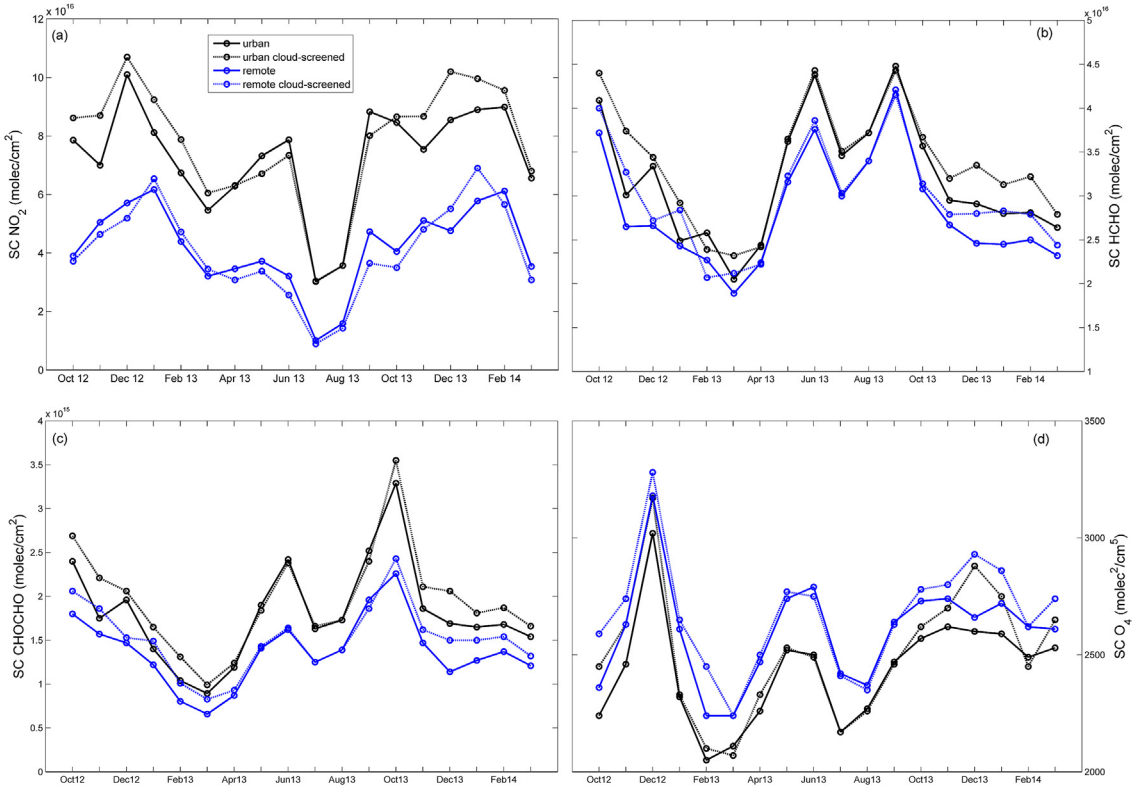

Fig. 7. Monthly average SC densities for NO_2 (a), HCHO (b), CHOCHO (c) and O_4 (d) for the $+1^\circ$ elevation angle for urban (black lines) and remote (blue lines) areas with (dashed lines) and without (solid lines) cloud screening. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

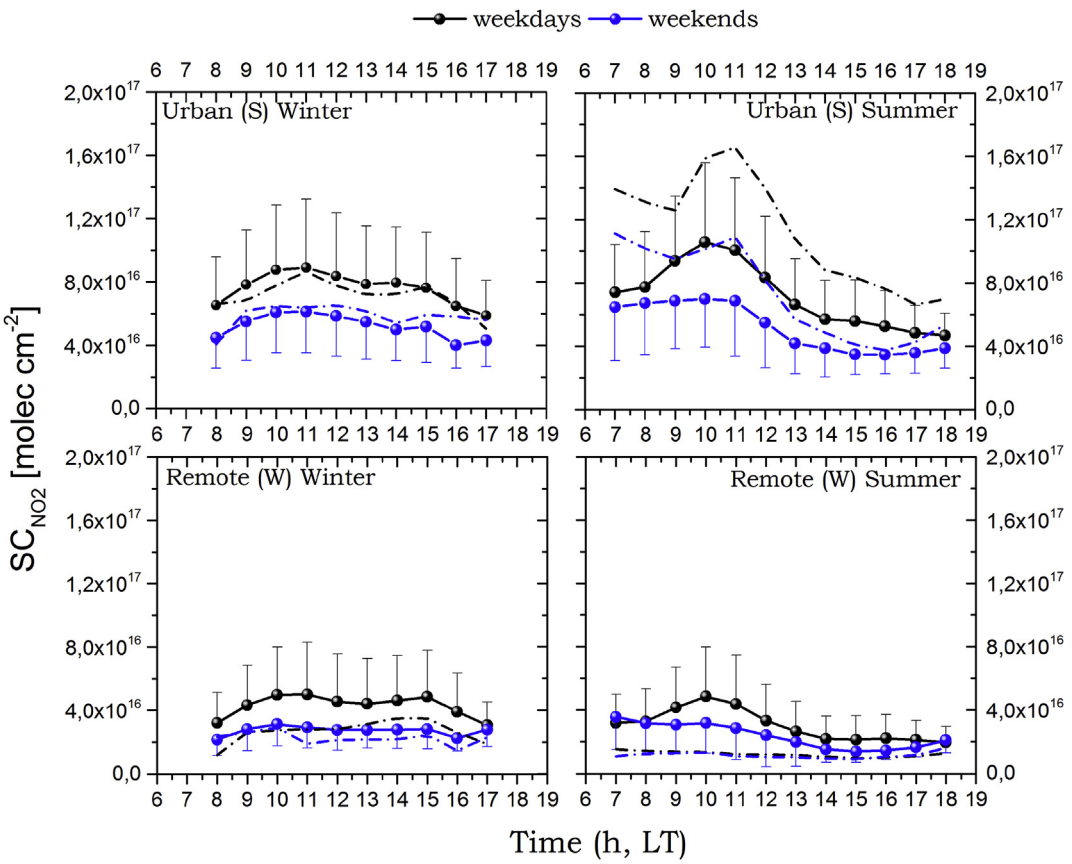

Fig. 8. Average diurnal variation of SC_{NO2} densities, at +1° elevation angle, for each period (warm and cold) for the observations towards the remote and the urban areas. The black and blue lines represent the weekdays and the weekends respectively. The solid lines represent the diurnal variation as obtained by averaging all data for the warm and the cold period separately. The dashed lines depict the result in diurnal variation considering data just for days when wind direction is between 180° and 270° for the urban area and between 315° and 45° for the remote area. The vertical lines represent the standard deviation of the variable for each point. To avoid busy graphs, only one part of the bar is presented, implying similar size in both sides. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

clearly seen in all cases. In the urban area, when these winds were excluded from the analysis and only the S-SW conditions were considered, the SC densities almost double for all trace gases, while the patterns remain the same. Similarly, in the remote direction, when the northern winds were the only ones to be considered in the analysis, the levels of the trace gases are significantly reduced. The case of HCHO during summer in the urban area where the diurnal variation changes with wind direction is interesting, highlighting the dominant role of photochemistry in HCHO production (Fig. 9 right top panel). The wind effect does not seem to be significant during winter.

Monthly averaged SC_{NO2} density values were also calculated separately for weekdays and weekends (not shown here). Higher values are observed during weekdays due to higher traffic emissions and this is in agreement with results reported in other studies for Athens (e.g. Kanakidou et al., 2011; Psiloglou et al., 2013). The average SC_{NO2} density values for the remote area for weekdays and weekends are $3.7 \cdot 10^{16}$ and $2.5 \cdot 10^{16}$ molec/cm^2 respectively (32% difference). The corresponding values for the urban area are $7.7 \cdot 10^{16}$ and $5.2 \cdot 10^{16}$ molec cm^{-2} (32% difference). The observed weekend effect is more pronounced during winter when weekdays exceed weekend's levels by 30–50%. Smaller difference is encountered during April–July and is more evident in the remote area.

For HCHO and CHOCHO the weekend effect is not so pronounced. In particular, for HCHO the difference ranges between 3% and 17% for both site types while the corresponding values for CHOCHO are between 3% and 33%. However, there are some cases, in April and May, when the weekend values are much higher than during weekdays. For HCHO this difference is 20% for April and 25% for May, both in the remote and the urban area. The corresponding values for CHOCHO for the remote area are 25% and 17% and for the urban area 8% and 10%. The results demonstrate similarities regarding the weekend effect on HCHO and CHOCHO. Assuming that the degree of difference between weekends and weekdays is an indicator of the impact of anthropogenic sources on the levels of certain pollutants (the greater the difference, the greater the impact), it can be deduced that HCHO and CHOCHO levels are linked in almost the same way to anthropogenic sources.

3.5. Estimation of urban sources contribution

To estimate the contribution of local NO_x sources to the urban area's NO_2 levels, the SC_{NO2} density measurements at the +1° elevation over the remote area were subtracted from those of the urban area. The days were first divided into three characteristic time periods: i) morning (07:00–11:00 LT), ii) noon (11:00–14:00 LT) and iii) evening (14:00–18:00 LT). Before presenting the results, the limitations of this analysis are unfolded: (a) the remote area is also affected by urban pollution through short range transport patterns and (b) the light path for a given elevation angle is different for the urban and for the remote azimuthal viewing direction. In order to address the first limitation, we excluded from the analysis the days when western winds (225°–315°) with

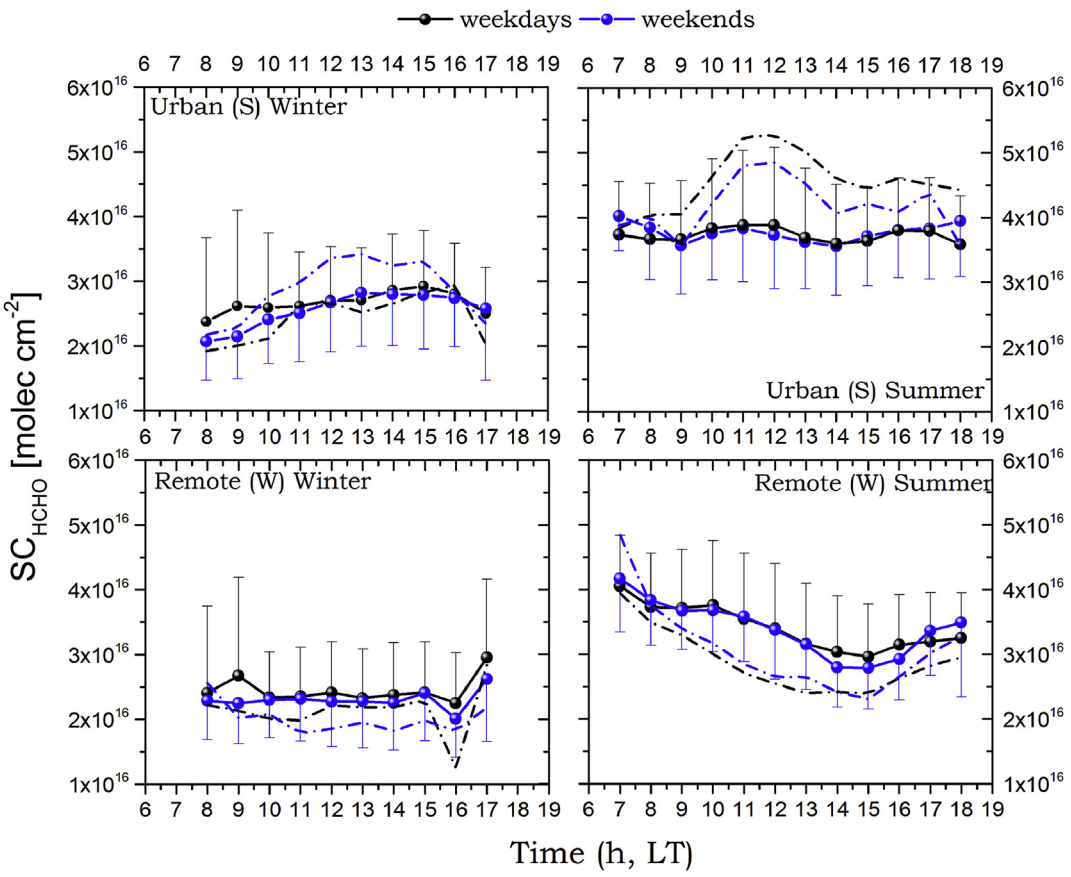

Fig. 9. Average diurnal variation of SC_{HCHO} densities, at +1° elevation angle, for each period (warm and cold) for the observations towards remote and urban areas. The black and blue lines represent the weekdays and the weekends respectively. The solid lines represent the diurnal variation as obtained by averaging all data for the warm and the cold period separately. The dashed lines depict the result in diurnal variation considering data just for days when wind direction is between 180° and 270° for the urban area and between 315° and 45° for the remote area. The vertical lines represent the standard deviation for each point as described in Fig. 7. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

velocity greater than 3 m/s (light breeze wind threshold) were prevailing, conditions which favour the transport of polluted air masses from the urban to the remote area. As already shown in Section 3.1, the O_4 levels do not seem to vary significantly between the remote and the urban area, indicating similar light paths for these two azimuthal viewing directions and giving us the opportunity to keep on with the analysis despite the second limitation.

The contribution of the urban NO_2 sources is calculated to be around 45% and 60% during winter (November–March) and summer months (April–October) respectively and it does not seem to change significantly throughout the day (Table 3). Similar results are reported by Markakis et al., (2010), showing that in the urban environment of Athens 50% of the NO_x emissions are due to road transport. Their outcomes are based on an emission inventory developed using activity and statistical data from national sources. The urban NO_2 sources seem to contribute more during summer and that could be attributed to frequent pollution episodes during the warm period due to high temperatures and intense photochemistry which lead to high ozone production which in turn converts more produced NO into NO_2 in the urban area where high NO emissions are present.

For HCHO the urban sources contribution is not so intense as in the NO_2 case and seems to exhibit a diurnal variation with lower values in the morning and higher levels during noon and evening (Table 3). More specifically, at the +1° elevation angle, the morning contribution is around 5% and 15% for the rest of the day for both seasons.

The urban CHOCHO sources contribution has been calculated to be around 25% in the morning and 15% at noon and evening at the +1° elevation during the cold period. During the warm period, the contribution is 30% in the morning and noon and slightly lower (~20%) in the evening. The latter could be attributed to the CHOCHO photolytic loss which gains importance against CHOCHO production towards lower SZAs (Volkamer et al., 2005). It should be noted that the primary contribution of CHOCHO from local sources to the VOC levels at urban environments is not expected to be high in view of other possible sources (Volkamer et al., 2005).

3.6. Impact of local circulation patterns

The influence of local and regional circulation patterns on the measured NO_2, HCHO and CHOCHO levels over Athens basin is being investigated in this study by using wind speed and direction records from NOA's meteorological station, collocated at MAX-DOAS installation location. The average daily wind vectors were computed from measurements obtained during daytime, and in particular during the same time span as MAX-DOAS' measurements.

The influence of the wind direction on the daily SC_{NO2} density values at +1° elevation angle is presented separately for the urban and remote area (Fig. 11a-b). It is evident that N-NE winds are related to low NO_2 slant column density values, mainly due to lack of pollution sources close to the Athens basin from this sector. The results are in agreement with past studies (e.g. Bakeas and Siskos,

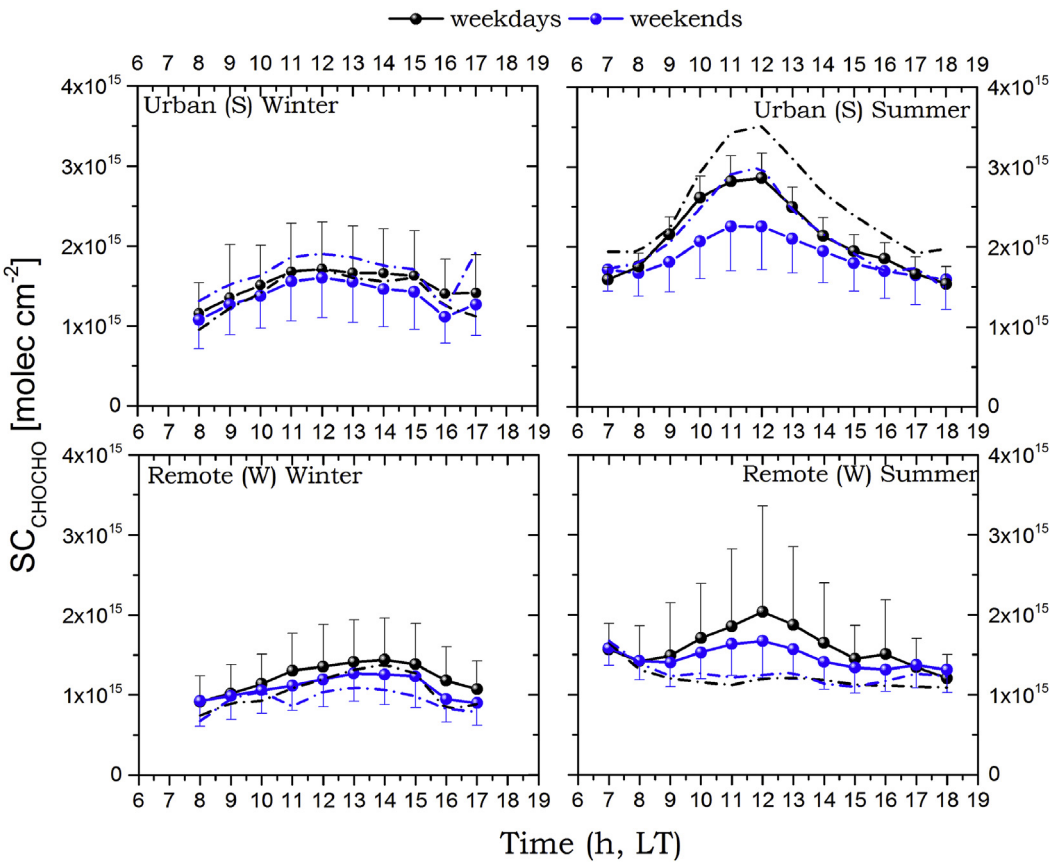

Fig. 10. Average diurnal variation of SC_{CHOCHO} densities, at +1° elevation angle, for each period (warm and cold) for the observations towards remote and urban areas. The black and blue lines represent the weekdays and the weekends respectively. The solid lines represent the diurnal variation as obtained by averaging all data for the warm and the cold period separately. The dashed lines depict the result in diurnal variation considering data just for days when wind direction is between 180° and 270° for the urban area and between 315° and 45° for the remote area. The vertical lines represent the standard deviation for each point as described in Fig. 7. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2002; Kassomenos et al., 1995), where the influence of Northern winds on the ventilation of the Athens area is mentioned. The maximum values of SC_{NO2} occur when the prevailing wind direction is from west. Westerly winds bring the urban emitted NO_2 towards the MAX-DOAS installation in Penteli and at the same time they favor the accumulation of pollutants in the Athens basin due to the special topography of the area. Westerly winds also favor the transport of polluted air-masses from the industrial area (Elefsina) towards the Athens basin, through the existing passage between Parnitha and Aegaleo mountains. The impact of westerlies on pollution episodes has been highlighted in several studies (e.g. Bakeas and Siskos, 2002; Rappenglück et al., 1998; Kallos et al., 1993). The SC_{NO2} density values in the urban area are less influenced by wind direction. This can be attributed to the continuous and intense emissions in the city center due to traffic, resulting in more uniform NO_2 spatial distribution compared to the remote areas.

The retrieved SC_{HCHO} amounts for the urban area show only weak dependance on the prevailing wind direction (Fig. 11c-d). In contrast, the same analysis for the remote area revealed enhanced SC_{HCHO} amounts during westerlies, due to primary and secondary anthropogenic emissions from the city center. Lastly, the SC_{CHOCHO} present a homogenous distribution of values for all directions except for westerlies suggesting formation pathways from anthropogenic precursors (e.g. acetylene, aromatics) (Fig. 11e-f).

Table 3
Urban sources contribution for NO_2, HCHO and CHOCHO.

		Urban sources contribution		
		NO_2	HCHO	CHOCHO
Winter	7:00–11:00LT (UTC+2)	0.46	0.05	0.24
	12:00–14:00LT (UTC+2)	0.45	0.16	0.17
	14:00–18:00LT (UTC+2)	0.41	0.17	0.16
Summer	7:00–11:00LT (UTC+3)	0.57	0.02	0.30
	12:00–14:00LT (UTC+3)	0.61	0.15	0.27
	14:00–18:00LT (UTC+3)	0.60	0.17	0.22

4. Summary and conclusions

First results from MAX-DOAS measurements in Athens were presented covering a period of 18 months (Oct 2012–Mar 2014). Slant column (SC) densities of NO_2, HCHO, CHOCHO and O_4, have been retrieved, covering eight different azimuthal viewing directions, spread over the extended Athens agglomeration, and eight elevation angles. The slant column observations at low elevation angles provide important information for examining the horizontal spatial inhomogeneity of pollution levels in Athens basin. Although the light path is different for each azimuthal direction, the directions representing the remote and the urban area ('W' and 'S' respectively) are both pointing southwards, thus the difference is not significant. The calculation of airmass factors (AMF) and the further derivation of vertical column (VC) densities are beyond the scope of this study. VC densities as well as trace gases' profile

information will be part of future work.

The data was cloud screened, excluding heavy cloudy days, and only a small impact of clouds on the 1° elevation data was found. Thus the retrieved SC densities were used to investigate the temporal variability (seasonal and diurnal) of the selected species. A clear NO_2 seasonal variation is observed with winter maximum and summer minimum. For the polluted urban area, the average winter levels are about 145% higher than summer levels. Seasonal variation is also observed for HCHO and CHOCHO but with summer maximum due to photochemical production.

The observed daily variability of the NO_2 (morning maximum at 10:00 LT and a winter secondary evening peak at 15:00 LT) was attributed to anthropogenic emissions and photochemical sinks. Formaldehyde's diurnal pattern is dominated by a broad afternoon peak during winter in the urban area, while during summer there is a morning maximum (12:00 LT) and a steady decrease then after. During winter the glyoxal's diurnal pattern is characterised by a steady increase after sunshine reaching a maximum value at 14:00LT. In summer a strong maximum appears at noon followed by a sharp decrease. The results for HCHO and CHOCHO suggest a strong link to photochemistry and a weaker link to primary anthropogenic emissions. The influence of Etesians winds, dispersing the pollutants, is evident in all cases and highlights the dominant role of HCHO photochemical production.

For NO_2, a clear weekly pattern was found; 30%–50% lower SC_{NO2} values recorded during weekends. This highlights the significant contribution of local anthropogenic emissions (mainly traffic) to the observed NO_2 columns. The weekend effect is not so intense for HCHO and CHOCHO levels which are 3%–17% and 3%–33%, respectively, lower during weekends. This is to be expected for VOCs which have significant biogenic sources.

By subtracting the NO_2 amounts of the remote area from the ones of the urban area, the NO_2 contribution from local urban emission sources was assessed. The contribution was found to be as large as 45% and 60% (during winter and summer respectively) at the +1° elevation angle with no distinct diurnal variability. The corresponding contribution of the urban HCHO sources is 5% in the morning and 15% during the rest of the day, for both seasons. The CHOCHO urban source contribution is 25–30% in the morning and 15–20% in the evening.

The wind direction does not influence significantly the levels of SC_{HCHO} and SC_{CHOCHO}, especially in the urban area. The SC_{NO2} densities present lower values under N-NE winds, while westerlies result in elevated SC_{NO2} levels. This finding is explained by the local topography of Athens and the location of the main emission sources relative to the instrument.

Concluding, our analysis of the automated multi-azimuth MAX-DOAS measurements over the Athens basin provided detailed temporal and spatial distributions of NO_2, HCHO and CHOCHO for more than a year. They yield a consistent picture of the diurnal, weekly and seasonal variations of these species and their vertical and horizontal distribution around the measurement location. The temporal and spatial patterns point towards: (a) the dominance of anthropogenic sources on NO_x levels, (b) the fact that the VOCs are largely secondary products having additional sources and (c) the significantly active role of photochemistry in Athens. Some of the findings though, need further analysis: formaldehyde's and glyoxal's significantly higher levels during weekends in April and May need to be investigated and checked for sampling effects. Future work will concentrate on applying profile inversions on the data set to investigate the vertical distribution of the trace gases in more detail. Furthermore, the SC_{O4} measurements will be used to obtain quantitative information on the aerosol load and aerosol extinction profiles during cloud free time periods.

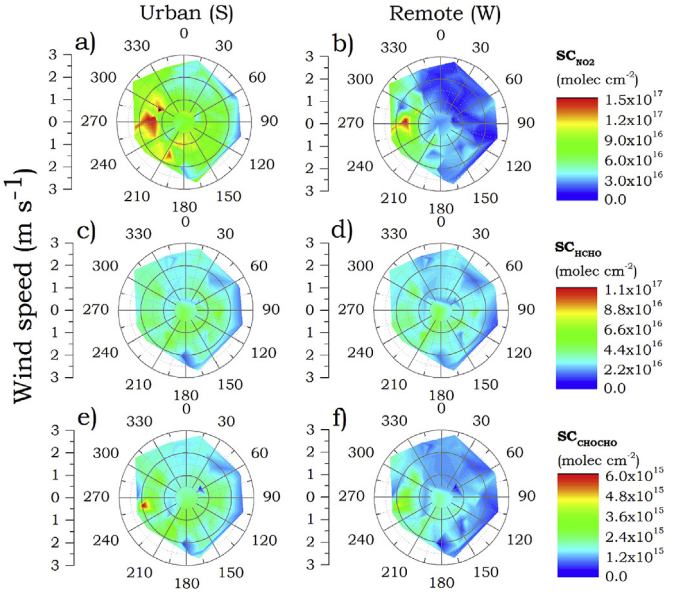

Fig. 11. Daily SC density values for NO_2 (a, b), HCHO (c, d) and CHOCHO (e, f) as a function of wind direction, for remote (right column) and urban (left column) directions.

Acknowledgements

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