Diurnal cycle of ozone throughout the troposphere over Frankfurt as measured by MOZAIC-IAGOS commercial aircraft

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Abstract

Ozone is generally assumed to have weak diurnal variations in the free troposphere due to lower production rates than in the boundary layer, in addition to a much lower NO titration and the absence of dry deposition at the surface. However, this hypothesis has not been proven due to a lack of high frequency observations at multiple times per day. For the first time, we take benefit from the frequent O3 vertical profiles measured above Frankfurt in the framework of the MOZAIC-IAGOS program to investigate the diurnal variations of O3 mixing ratios at multiple pressure levels throughout the troposphere. With about 21,000 aircraft profiles between 1994 and 2012 (98 per month on average), distributed throughout the day, this is the only dataset that can allow such a study. As expected, strong diurnal variations are observed close to the surface, in particular during spring and summer (enhanced photochemistry and surface deposition). Higher in altitude, our observations show a decrease of the diurnal cycle, with no diurnal cycle discernible above 750 hPa, whatever the season. Similar results are observed for the different percentiles of the O3 distribution (5th, 25th, 50th, 75th, 95th). An insight of the changes of the diurnal cycles between 1994–2003 and 2004–2012 is also given. We found higher O3 mixing ratios during the latter period, particularly on the lowest pressure levels, despite lower mixing ratios during summer.

1. Introduction

Ozone (O3) is a trace gas of major importance in the atmosphere due to its adverse effects on health, vegetation and climate change. In the troposphere, O3 is produced photochemically by the oxidation of methane, carbon monoxide (CO) and non-methane hydrocarbons (NMHCs) in the presence of nitrogen oxides (NOx=NO+NO2) and sunlight, or transported downward from the stratosphere. It is removed by dry deposition, titration by NO and reactions with hydrogen oxide radicals (HOx=OH+HO2) (Monks, 2005). Ozone is lost in low-NOx environments, such as the marine boundary layer. Halogens also play a role in the ozone chemistry, directly through a reaction with O3 itself, or indirectly through a reaction with NMHCs (production or destruction of O3 depending on the conditions) (Monks et al., 2015).

During the last several decades, numerous studies have investigated the causes and characteristics of the diurnal variation of surface O3 at a wide range of locations (Singh et al., 1978; Oltmans and Levy, 1994; Pryor and Steyn, 1995; Zhang et al., 2004). At low altitudes over continental regions under the influence of anthropogenic emissions, ozone generally exhibits minimum mixing ratios during night, mainly due to dry deposition and titration by NO in the shallow nocturnal boundary layer (BL). During daytime, mixing ratios increase under the combined effect of photochemical production and mixing with O3-rich air masses from the residual BL, reaching a maximum in the afternoon. The diurnal cycle typically has its maximum
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amplitude in summer when photolysis rates are the highest, while diurnal cycles observed in winter are less pronounced. Over regions with a more complex orography, the local dynamics can play a more important, if not dominant, role in the diurnal variability of O₃. At high-altitude mountain sites, observations usually show a reverse cycle, with maximum mixing ratios during night (e.g. Bonasoni et al., 2000; Cristofanelli et al., 2013; Ezcurra et al., 2013; Zhang et al., 2015). This pattern is the result of the mountain peaks being heavily influenced by the lower free troposphere at night where ozone mixing ratios are typically greater than at the surface if the mountain is located in a rural or remote region. During the day upslope flow caused by the heating of the mountain slopes brings ozone depleted air from the BL up to the summit (Oltmans and Komhyr, 1986; Oltmans et al., 2013). In the marine BL, daytime O₃ can be destroyed by photolysis, reactions with HOₓ and halogens or dry deposition (Ganzeveld et al., 2009). During summertime, when low-NOₓ conditions prevail over oceans, these sinks dominate the O₃ production by photolysis of NO₂ and the entrainment from aloft in the free troposphere (FT) usually leading to minimum mixing ratios in the afternoon (Ayers et al., 1992; Monks et al., 1998, 2000).

As investigating the O₃ diurnal variability requires a sufficiently high frequency of measurements (typically 1 h), all the previous studies have been restricted to the surface. In the FT, neither satellite observations nor ozone soundings are frequent enough to derive a complete diurnal profile of O₃. In principle, Lidar measurements over a sufficiently long period may be used to investigate the diurnal cycle of O₃ at multiple levels in the troposphere (although with more uncertainties than considering in-situ observations) but to our knowledge, no such studies exist (probably because such Lidar observations are complex to operate routinely during long periods). The changes of diurnal variability with altitude have been investigated during some campaigns with several instruments deployed at different altitudes along a mountain slope, showing a decrease of the O₃ diurnal variability with altitude, and a slight reverse at the highest elevations with greater mixing ratios during night (Ezcurra et al., 2013; Burley et al., 2015; Brodin et al., 2010). However, the previously mentioned strong influence of the local dynamics in such environments prevents extrapolation of these results to the FT.

Airborne observations of O₃ (among other species) have been measured by the MOZAIC-IAGOS program since 1994 using commercial aircraft from several airlines. Vertical profiles from the surface to 11–12 km are obtained as the aircraft operationally descend and ascend from airports. Among the 200 airports visited worldwide, the Frankfurt, Germany airport is by far the most frequently visited, with approximately 21,600 flights between 1994 and 2012, which corresponds to 98 flights per month, on average. During this long period, airline schedules have varied enough to have yielded observations that are reasonably well-distributed throughout the day. In this paper, we take advantage of these high-frequency measurements to investigate the diurnal variations of O₃ throughout most of the troposphere (0–12 km).

The observational dataset is described in Sect. 2. Section 3 presents the results, including the diurnal profiles of O₃ in the troposphere and their change over the last two decades. Results are discussed in Sect. 4.

2. Dataset and methods

2.1 MOZAIC-IAGOS observations

The MOZAIC (Measurements of OZone and water vapour on Airbus In-service airCraft) program, initiated in 1994 and incorporated into the IAGOS (In-service Aircraft for a Global Observing System; www.iagos.org) program since 2011 takes advantage of commercial aircraft to provide worldwide in-situ measurements of several trace gases (e.g., O₃, CO) and meteorological parameters (e.g. water vapour) throughout the troposphere and the lower stratosphere (Marenco et al., 1998; Petzold et al., 2015; Nédélec et al., 2015). Ozone measurements are performed using a dual-beam UV-absorption monitor (time resolution of 4 seconds) with an accuracy of ±(2 ppbv+2%) (Thouret et al., 1998). More details on the new IAGOS instrumentation can be found in Nédélec et al. (2015). The continuity of the dataset between the MOZAIC and IAGOS programs has been demonstrated based on the 2-year overlap (2011–2012) (Nédélec et al., 2015).

In this study, we focus on the vertical profiles above the Frankfurt airport where observations are the most frequent. The coverage and density of the datasets are described in Sect. 2.3. Note that the availability of observations at different times of day is due to several MOZAIC-IAGOS aircraft simultaneously serving this destination. Some other airports have also been frequently visited by MOZAIZ-IAGOS aircraft (e.g. New York, Paris, Windhoek, Vienna, Tokyo), but usually by only one aircraft during specific time frames, resulting in too few profiles to properly investigate the diurnal variations of O₃.

2.2 Data treatment

During landing and take-off phases, observations are obtained through most or all of the troposphere, and often part of the lower stratosphere. The time resolution of 4 seconds roughly corresponds to a vertical distance of 30 m. As landing and take-off do not exactly correspond to vertical profiles, only the observations within the 400 km around the Frankfurt airport are considered, which limits the possible spread of O₃ mixing ratios due to horizontal heterogeneity. This study focuses on tropospheric O₃ and observations at the tropopause level and in the stratosphere are thus ignored. However, stratospheric intrusions within the...
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troposphere are retained (i.e. vertical profiles are not purely tropospheric). Here, the tropopause is defined as the 30 hPa-width layer centred on the 2 pvu (potential vorticity units) iso-surface, following the method of Thouret et al. (2006). The PV values are extracted along each vertical profile from the European Centre for Medium-Range Weather Forecasts (ECMWF) operational analysis (00:00, 06:00, 12:00, 18:00 UTC) and forecasts (03:00, 09:00, 15:00, 21:00 UTC). More details on the procedure are given in Petetin et al. (2015).

Data are aggregated on 50-hPa pressure surfaces from 1000 to 300 hPa. For the construction of the diurnal profile, we consider time intervals of 3 hours: 0–3, 3–6, 6–9, 9–12, 12–15, 15–18, 18–21, 21–24 UTC. For convenience, hours in this paper are expressed in UTC; note that in Germany, the local solar time (LST) corresponds to UTC+1 from November to March (included), and UTC+2 otherwise (the 0–3 UTC time interval thus roughly corresponds to the closing times of the airport). Diurnal profiles are calculated at both the seasonal (DJF: December-February, MAM: March-May, JJA: June-August, SON: September-November) and annual scale (ANN: annual). Note that observations are far too sparse during the 0–3 UTC time interval and are therefore ignored in this paper. The procedure is applied to several metrics, including the mean and 5th, 25th, 50th, 75th and 95th percentiles.

2.3 Density and coverage of the dataset

The number of O₃ observations available over the 1994–2012 period for the calculation of the diurnal cycles is reported in Table S1 in the Supplement. On average, each point of the diurnal cycle (corresponding to a given 3-hour time interval and a given 50-hPa pressure level) relies on about 52,000 observations. However, this density strongly varies depending on the time of day. The densest sampling is available between 3 and 12 UTC (above 80,000 observations), followed by 12–15 UTC (around 54,000) and 15–18 UTC (around 29,000). A substantially lower density occurs between 18 and 24 UTC (below 16,000 observations). The sampling is reasonably well balanced between the different seasons, with 29, 22, 29 and 20% of the data obtained in winter, spring, summer and autumn, respectively.

In terms of spatial coverage, observations available before 18 UTC are mostly obtained from flight routes north of Frankfurt, while observations after 18 UTC are typically south of Frankfurt. Considering that (i) the tropopause height decreases as one moves northward and that (ii) there are some uncertainties associated with the estimation of PV, this sampling bias may result in more frequent occurrences of stratospheric contamination before 18 UTC than after. However, due to the fact that only the troposphere is considered in this study and that we take into account only the observations within 400 km of the Frankfurt airport, this source of uncertainty is expected to be low.

It is worth noting that some uncertainties may arise from the temporal discontinuity of this database. Indeed, measurements are not performed continuously throughout the day (as occurs at a surface station), but sporadically between 1994 and 2012 with frequencies that vary from one 3-hour time interval to another. The data coverage at 800 hPa is shown in Fig. 1 for the different time intervals. Between 3 and 15 UTC, observations are available during almost all the 1994–2012 period. At 15–18 UTC, observations are sparse between 2005 and 2010 (inclusive). The least dense coverage concerns the 18–21 UTC time interval, observations are available all along the 1994–2012 period, except during a large part of 2005 and 2010 as well as during a few months in 2003–2004. The coverage is similar at 6–9, 9–12 and 12–15 UTC, while data are the sparsest at 21–24 UTC.

![Figure 1](https://example.com/fig1.png)

Data coverage on a monthly basis at 800 hPa for the different 3-hour time intervals. For each time interval (associated to its own colour for clarity), months with at least one observation in the pressure layer centred around 800 hPa are coloured, while blanks indicate the absence of observations. For instance, during the 3–6 UTC time interval, observations are available all along the 1994–2012 period, except during a large part of 2005 and 2010 as well as during a few months in 2003–2004. The coverage is similar at 6–9, 9–12 and 12–15 UTC, while data are the sparsest at 21–24 UTC.

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Diurnal cycle of ozone throughout the troposphere to December 2012. The seasonal and annual diurnal cycles are then calculated over 3-hour time intervals (as explained in Sect. 2.2) using this surface $O_3$ dataset, but with three different types of data selection. First, as a reference case, we use all the available data between 1994 and 2012 (hereafter referred as REF). Second, we consider only the months with at least 1 observation available at 1000 hPa at the corresponding 3-hour time interval in the Frankfurt MOZAIC-IAGOS database (hereafter referred as SUB1). Third, similarly to SUB1, we consider only the months with at least 50 observations available at 1000 hPa in the Frankfurt MOZAIC-IAGOS database (hereafter referred as SUB50). In both the SUB1 and SUB50 cases, we thus artificially create the same data gaps present in the MOZAIC-IAGOS dataset in our surface $O_3$ dataset. Comparing the REF diurnal cycles with the SUB1 and SUB50 allows us to quantify the bias introduced by the absence of observations during some periods. Results are shown in Fig. S1 in the Supplement. Whatever the season and the station, the differences of 3-hour mean mixing ratios between the REF and SUB1 (SUB50) diurnal cycles remain below ±3% (±13%). They are usually greatest at 18–21 UTC, when the MOZAIC-IAGOS data coverage is sparsest. These low differences demonstrate that the data gaps in the MOZAIC-IAGOS dataset likely have a limited impact on the diurnal cycles calculated at Frankfurt, at least close to the surface where these stations are expected to be reasonably well representative (in particular the rural background ones). Similar results are obtained when considering the data coverage of MOZAIC-IAGOS at the other pressure levels. However, it is worth noting that at altitude, these surface observations cannot be considered to be representative.

3. Results

3.1 Diurnal profile of mean tropospheric $O_3$

The diurnal profiles of mean tropospheric $O_3$ over the 1994–2012 period are shown in Fig. 2 at both the seasonal and annual scale. Note that compared to the uncertainty associated with each individual measurement (estimated at ±(2 ppb +2%), see Sect. 2.1), the uncertainties associated with the mean $O_3$ mixing ratios are largely reduced due to the large number of points (see Table S1 in the Supplement), all values remaining below 0.1 ppb.

As expected, the strongest diurnal variations occur in the BL due to the more active $O_3$ production and loss processes close to the surface. The BL diurnal cycle reaches its highest amplitude in summer (25 ppb at 1000 hPa) when the photochemical production is at a maximum, followed by spring (17 ppb) and autumn (12 ppb), while very low variations are observed in winter (4 ppb). The diurnal variation propagates higher in altitude in summer due to the development of a deeper convective BL. In particular, the $O_3$ maximum at 15–18 UTC extends to all pressure levels up to 800 hPa. At 1000 hPa and to a lesser extent at 950 hPa, mixing ratios quickly decrease after 18 UTC, down to 20 ppb at 3–6 UTC, close to the surface. This is likely due to the combined effect of dry deposition and titration by NO (both sinks being enhanced in the shallow nocturnal BL), as suggested by the much lower decrease in the next level. In the early morning (6–9 UTC), the $O_3$ vertical gradient between 1000 and 950 hPa is slightly reduced compared to the night. This is likely due to the turbulence that starts to mix low-$O_3$ air masses from the nocturnal BL with high-$O_3$ air masses from the residual BL (Zhang and Rao, 1999). Later, this $O_3$ vertical gradient keeps decreasing as the turbulent mixing increases, which progressively homogenizes the $O_3$ mixing ratios in the BL.

**Figure 2**

Diurnal variations of the mean $O_3$ mixing ratios in the troposphere above Frankfurt.

The diurnal variations of the mean $O_3$ mixing ratios are calculated by aggregating all the observations obtained above Frankfurt between 1994 and 2012. Results are shown at 15 pressure level in the troposphere, at both the seasonal and annual scale (DJF: winter, MAM: spring, JJA: summer, SON: autumn, ANN: annual). Diurnal variations appear strong in the first levels, but quickly decrease higher in altitude.

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Higher in altitude, there is an absence of strong O\textsubscript{3} diurnal variations, regardless of season. Some variations are still observed at some pressure levels after 18 UTC, and in particular an increase at 18–21 UTC above 350 hPa. This may be an artefact related to the sparser observations at this time of day. Interestingly, based on the observations at the Waldhof station, we previously highlighted (in Sect. 2.3) that this lower frequency of measurement may introduce a moderate positive bias in the diurnal cycle at 18–21 UTC. However, it is not possible to draw definitive conclusions on this point since this bias was mainly observed during the winter and is likely limited to the lower troposphere (i.e. the representativeness of the Waldhof surface station). In any event, coefficients of variation (CV) – defined as the standard deviation of the diurnal cycle normalized by its mean – quickly decrease from 10–30\% at 1000 hPa to less than 4\% above 950 hPa in winter, 850 hPa in spring, 800 hPa in summer and 900 hPa in autumn. Above 800 hPa, CV range between 0.6 and 3.3\%. The highest values are found during the winter at the uppermost pressure levels while most of the CV values elsewhere remain around 1–2\%.

Although small in amplitude, these diurnal variations in the free troposphere may still be statistically significant. For each season and each pressure level, between each pair of points of the diurnal cycle (21 possible combinations among the 7 time intervals), a Smith/Welch/Satterthwaite (SWS) t-test (Smith, 1936; Welch, 1938; Satterthwaite, 1946) (also referred as the unequal variance t-test in the literature) is performed to compare the mean O\textsubscript{3} mixing ratios. Ruxton (2006) explained why this SWS t-test should always be used in preference to the Student’s t-test or Mann-Whitney U test (in particular, it does not assume equal variances between the two populations). Results indicate that most of the differences are statistically significant at a 95\% confidence level. On average over all the pressure levels and 3-hour time intervals, about 85, 87, 79, 81 and 74\% of the SWS t-tests performed gives significant differences in the DJF, MAM, JJA, SON and ANN diurnal cycles, respectively. This proportion of statistically different mixing ratios varies with altitude, from about 90–95\% below 950 hPa to 72–78\% around 650–350 hPa. Therefore, throughout the whole troposphere, most of the diurnal variations of O\textsubscript{3} mixing ratios are statistically significant, but both the relative amplitude of these variations and the proportion of significant differences are reduced higher in altitude.

3.2 Diurnal profile of the distribution of tropospheric O\textsubscript{3} mixing ratios

The diurnal profiles of the O\textsubscript{3} 5\textsuperscript{th}, 25\textsuperscript{th}, 50\textsuperscript{th}, 75\textsuperscript{th} and 95\textsuperscript{th} percentiles at the annual scale are shown in Fig. 3. As for the mean O\textsubscript{3} mixing ratios, strong diurnal variations are observed at the lowest levels but quickly decrease with altitude. Qualitatively, a similar picture emerges at the seasonal scale, although variations are usually higher (see Fig. S2–S5 in the Supplement). This is particularly true in summer for the O\textsubscript{3} 95\textsuperscript{th} percentile (Fig. 4), for which the mixing ratios at 21–24 UTC are 5–15 ppb higher than during the rest of the day at several pressure levels in the FT (600–300 hPa). However, the corresponding CVs remain below 6\%.

Whatever the season or the metric, most of the O\textsubscript{3} vertical gradients – defined as positive when O\textsubscript{3} increases with altitude – in the troposphere are positive or only slightly negative. However, as illustrated in Fig. 4, a noticeable exception is the O\textsubscript{3} 95\textsuperscript{th} percentile in summer. During the afternoon, the vertical gradients are -0.22 ppb hPa\textsuperscript{-1} between 850 and 800 hPa (i.e. likely within the BL). At this time of year and day, the solar radiation reaches its maximum and is expected to enhance both the vertical transport and the photolysis rates. These negative gradients may thus suggest that the photochemical production of O\textsubscript{3} is faster than the vertical mixing.

Figure 3
Diurnal variations of several O\textsubscript{3} percentiles in the troposphere above Frankfurt.

Results are shown for the O\textsubscript{3} 5\textsuperscript{th}, 25\textsuperscript{th}, 50\textsuperscript{th}, 75\textsuperscript{th} and 95\textsuperscript{th} percentiles, at the annual scale. As for the mean O\textsubscript{3} mixing ratios, diurnal variations are strong in the first levels but greatly reduced higher in altitude.

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3.3 Changes of the diurnal profile over the two past decades

We now investigate how the O\textsubscript{3} diurnal profile has changed over the past two decades. The dataset is split into two periods, 1994–2003 and 2004–2012. Fig. 5 shows the diurnal profiles of mean O\textsubscript{3} at the annual scale for both periods, and the relative differences between them (the difference being normalized by the mixing ratios observed during the first period). Note that in this section, we investigate only the changes of O\textsubscript{3}, not the trends for which uncertainties would have to be estimated. Overall, the mean O\textsubscript{3} mixing ratios have slightly increased in most of the troposphere and during most of the day. The highest increases are found during the night close to the surface (changes between +21 and +41%). The much lower increase between 9 and 18 UTC (< +7%) leads to a strong decrease of the amplitude of the diurnal cycle, from 15 to 10 ppb. These changes quickly attenuate with altitude, the increase at 950 hPa remaining below +7%. In the second part of the day (after 15 UTC), a slight decrease of the O\textsubscript{3} mixing ratios is observed at some pressure levels, with values ranging between -3 and -1%.

Results at the seasonal scale (Fig. S6–S9 in the Supplement) indicate that the increase of night-time O\textsubscript{3} is observed during all seasons, at least at the first pressure level. It is more accentuated in winter/autumn (from +27 to +95%) than in spring/summer (from +3 to +28%). This increase is likely mainly due to the reduction of NO\textsubscript{x} emissions in Europe over the last decades, leading to a lower titration of O\textsubscript{3} by NO (Derwent et al., 2003; Solberg et al., 2005; Jonson et al., 2006). In fact, the wintertime O\textsubscript{3} has increased in the whole troposphere and during the whole day, although at very different extents (from +1 to +20% above the 950-hPa pressure level). A similar picture emerges in spring, although with lower changes. Conversely, the increase in autumn appears confined to the BL (below the 600-hPa pressure level) and is observed throughout the day.
day except at 15–18 UTC where mixing ratios have decreased (from -3 to -9% above the 950-hPa pressure level). Contrary to the other seasons, the O₃ mixing ratios have decreased during summer (apart from the night-time increase at 1000 hPa), in particular below the 700-hPa pressure level where changes from 1994–2003 to 2004–2012 range between -16 and -2%. Above, the decrease is observed only after 18 UTC, although not at all pressure levels. This decrease of summertime O₃ in the BL during daytime partly compensates the increase observed during the other seasons.

The changes of the 5th and 95th percentiles at the annual scale are given in Fig. S10–S11 in the Supplement. Interestingly, the relative increase of the 5th percentile is substantially higher than for the mean O₃ (in particular close to the surface), while the 95th percentile is shown to decrease in large parts of the troposphere.

4. Discussion and conclusion

The diurnal variations of O₃ mixing ratios are well characterized at the surface in many different environments (e.g., urban, coastal, mountain, marine). However, due to the absence of continuous measurements at higher altitudes, both in the boundary layer and the FT, our knowledge of the O₃ diurnal variations relies on assumptions and/or numerical simulations. One generally assumes that O₃ mixing ratios in the free troposphere remain relatively constant throughout the day (in comparison to the surface). This assumption relies on the fact that the O₃ production rates are expected to be lower at altitude. In the free troposphere, a major part of the NOₓ is tied up as peroxyacyl nitrate (PAN) where it is stable at cold temperatures (Singh et al., 1990; Ridley et al., 1990). Besides narrow plumes of lightning NOₓ in which mixing ratios can reach several ppbv, NOₓ mixing ratios remain low, typically ranging between 10 and 1000 pptv (Emmons et al., 1997; Huntrieser et al., 1998; Brunner et al., 2001; Cooper et al., 2006). Over central-western Europe, the NOₓ mixing ratios measured close to thunderstorms in summer were mostly below 150 pptv at 3–8 km and below 400 pptv at 8–11 km (Huntrieser et al., 2002). As highly reactive hydrocarbons also have relatively low mixing ratios in the free and upper troposphere (Singh et al., 2000; Balzani Lööv et al., 2008; Helmig et al., 2008), a larger portion of the Oₓ production (or consumption depending on the NOₓ mixing ratio) relies on the slower oxidation of CO or CH₄. Using the GEOS-Chem model, Zhang et al. (2009) showed Oₓ production rates of only about 1 ppbv d⁻¹ in pollution plumes crossing the North Pacific in the FT.

Even above the south-eastern United States where a large amount of lightning NOₓ is available in summer, Cooper et al. (2006) reported Oₓ production rates of only 3–4 ppbv d⁻¹ in upper troposphere.

However, several O₃ sources including lightning NOₓ and stratospheric intrusions may introduce some diurnal variability in the free and upper troposphere. The lightning NOₓ emissions represent only 10% (4%) of the total NOₓ emissions at the global scale (at northern midlatitudes) (Schumann and Huntrieser, 2007), but are known to contribute substantially to the formation of O₃ in the FT (DeCaria et al., 2005; Cooper et al., 2006, 2007, 2009). At midlatitudes above continents, a large part of these emissions occur in the middle and upper troposphere (Ott et al., 2010). Based on a lightning detection network of 30 antennas in Germany, Wapler (2013) highlighted a strong diurnal variation of the lightning activity, with a frequency of occurrence peaking at 14–18 UTC (whatever the season). Concerning troposphere-stratosphere exchange, to our knowledge, no previous study has investigated the existence of diurnal variations. However, during the Deep Convective Clouds and Chemistry (DC3) experiment (central United States, summer 2012), Pan et al. (2014) recently reported downward transport of stratospheric Oₓ-rich air masses in the vicinity of overshooting mesoscale convective systems. The thunderstorm activity is generally higher in the afternoon. Based on observations over Europe from the Spinning Enhanced Visible and Infrared Imager (SEVIRI) instrument aboard the Meteosat satellites, Bedka (2011) showed that over land, the frequency of occurrence of these overshooting cloud tops strongly varies throughout the day, with a maximum around 14–17 UTC. As for the formation of Oₓ from lightning NOₓ, this source may thus increase the Oₓ mixing ratios during the late afternoon.

Based on the frequent profiles of MOZAIC-IAGOS aircraft above Frankfurt since 1994, the diurnal variations of the mean Oₓ mixing ratios appear statistically significant regardless of pressure level. However, we demonstrate that these diurnal variations quickly decrease with altitude in the troposphere, and remain small in the middle and upper troposphere. Besides the fact that the photochemically-driven diurnal cycle of Oₓ in the BL extends higher in altitude during the summer, we show that these low diurnal variations in the free and upper troposphere are observed regardless of season. Similar results are obtained for the different percentiles (5th, 25th, 50th, 75th, 95th) of the Oₓ distribution.

Comparing the diurnal cycles between 1994–2003 and 2004–2012, we found an increase of Oₓ in most of the troposphere and during most of the day. This change appears stronger close to the surface during the night, which leads to a decrease of the amplitude of the diurnal cycle in the BL. At the seasonal scale, this increase occurs mainly in winter, and to a lesser extent in spring and autumn while Oₓ is shown to decrease during the summer, although only in the BL. Such changes are consistent with the shift of the Oₓ seasonal cycle toward earlier maxima recently reported at several surface stations over Europe (Parrish et al., 2013) and observed mainly in the lower troposphere around Frankfurt (Petrin et al., 2015).
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This result applies to central/western Europe but may be different at other locations, for instance in the inter-tropical convergence zone (ITCZ) where the deep convection is stronger and more frequent. While no other location has the high sampling frequency of Frankfurt, in the near future, more aircraft will join the IAGOS program, which may allow investigations of the diurnal ozone variations in other regions of the world.

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Contributions

- Contributed to conception and design: HP, OC
- Contributed to acquisition of data: HP, VT, GA, RB, DB, J-MC, PN
- Contributed to analysis and interpretation of data: HP, VT, AG, OC
- Drafted and/or revised the article: HP
- Approved the submitted version for publication: HP, VT, GA, RB, DB, J-MC, AG, PN, OC

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Competing interests

The authors have declared that no competing interests exist.

Data accessibility statement

No new measurements were made for this review article. All ozone datasets mentioned in the text were obtained from existing databases. The MOZAIC-IAGOS data are available on http://www.iagos.fr. The O₃ observations at surface stations around Frankfurt are available on request from the German Federal Environment Agency (Umweltbundesamt, UBA; contact immission@uba.de).

Supplemental material

- Table S1. Total number of O₃ observations over the 1994–2012 period. (DOC)
  Results are given per pressure level and per 3-hour time period. The 0–3 UTC time period is ignored due to too sparse data. The largest number of data are found at 3–6, 6–9 and 9–12 UTC, with more than 1.2 millions observations along the tropospheric column. This number is reduced to about 0.8 million at 12–15 UTC, and below 0.5 million during the other time periods. Data are the sparsest at 18–21 UTC with about 0.2 million observations along the tropospheric column.
- Figure S1. Influence of the sub-sampling related to the MOZAIC-IAGOS dataset. (PDF)
  The diurnal variations of mean O₃ mixing ratios are calculated at several surface stations around Frankfurt (see text in Sect. 2.3 for details on these stations), both at the seasonal and annual scale (DJF: winter, MAM: spring, JJA: summer, SON: autumn, ANN: annual). The REF diurnal cycles (in black) represent the true diurnal cycles obtained at the surface when considering all the data available between 1994 and 2012. The SUB1 diurnal cycles (in red) represent the diurnal cycles obtained when considering only the months with at least one MOZAIC-IAGOS observation at 1000 hPa at Frankfurt at a given pressure level and season. Similarly, the SUB50 diurnal cycles (in green) correspond to the diurnal cycles based on months with at least 50 MOZAIC-IAGOS observations at Frankfurt. Except for the 0–3 UTC time interval that is ignored in our study, the different diurnal cycles are very similar.
- Figure S2. Diurnal variations of several O₃ percentiles in the troposphere above Frankfurt, in winter (DJF). (PDF)
  Results are shown for the O₃ 5th, 25th, 50th, 75th and 95th percentiles. Diurnal variations are slightly more noisy than at the annual scale (see Fig. 3), likely due to the lower number of points considered. These noisy variations are higher during the second half of the day (in particular for the 5th and 95th percentiles) when less data are available.
- Figure S3. Same as in Fig. S2 but for spring (MAM). (PDF)
- Figure S4. Same as in Fig. S2 but for summer (JJA). (PDF)
- Figure S5. Same as in Fig. S2 but for autumn (SON). (PDF)
- Figure S6. Changes of the O₃ diurnal variations between 1994–2003 and 2004–2012 in winter (DJF). (PDF)
  Diurnal profiles of mean tropospheric O₃ mixing ratios are given for 1994–2003 (left panel) and 2004–2012 (middle panel). The relative differences of mixing ratio between the two periods are shown in the right panel. Crosses indicate the pressure levels and time interval at which the differences are statistically significant regarding the SWS t-test (see text in Sect. 3.1 for details on this test). The increase of O₃ mixing ratios is the strongest during winter, in particular close to the surface where changes exceed +20% while changes range between +5 and +15% higher in altitude during most of the day.
- Figure S7. Same as Fig. S6 in spring (MAM). (PDF)
  Compared to winter (see Fig. S6), the changes of O₃ mixing ratios between 1994–2003 and 2004–2012 are weaker in spring, with values ranging between -5 and +10% in most of the troposphere (except in the first pressure level where the increase remain above +20% during the night).
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- **Figure S8. Same as in Fig. S6 but for summer (JJA). (PDF)**
  Contrary to the other seasons, results in summer show substantially lower O₃ mixing ratios in 2004–2012 than in 1994–2003 below 700 hPa (again except in the first pressure level during the night), with changes up to -15 and -20%, in particular during the middle of the day.

- **Figure S9. Same as in Fig. S6 but for autumn (SON). (PDF)**
  The changes of O₃ mixing ratios in autumn show an increase below 700 hPa during most of the day (except at 15–18 UTC when mixing ratios are shown to increase), although changes all remain below ±20%.

- **Figure S10. Changes of the diurnal variations of the O₃ 5th percentile at the annual scale (ANN). (PDF)**
  As for the previous figures, diurnal profiles are shown for 1994–2003 (left panel) and 2004–2012 (middle panel), while the relative differences of mixing ratios between the two periods is shown in the right panel. Compared to the changes of the mean O₃ mixing ratios (see Fig. 5), the increase of the O₃ 5th percentile appears stronger, with changes above +15% in a large part of the troposphere, in particular below 700 hPa. The changes are reduced higher in altitude.

- **Figure S11. Same as in Fig. S10 but for the O₃ 95th percentile. (PDF)**
  Contrary to the O₃ 5th percentile previously described in Fig. S10, results here indicate a decrease of the O₃ 95th percentile at the annual scale between -5 and -15% below 700 hPa, mostly during the middle of the day. The picture is more contrasted higher in altitude where changes range between -10 and +10%.

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