Reply to anonymous reviewer#1

We gratefully acknowledge anonymous reviewer#1 for his/her comments, that helped us improve the manuscript substantially. We tried to address all reviewer's comments. In the following, analytical replies are provided to each of the reviewer's comments. Reviewer's comments are written in bold font. Line numbers, when provided refer to the version with track changes.

General comments

The manuscript by Fountoulakis et al. correlates total ozone columns (TOC) and surface UV radiation at 307.5 and 324 nm with geopotential height at 250 hPa (GPH). While the anti-correlation between tropopause height and TOC has long been known, using GPH instead of tropopause height is a novel idea. Using GPH, the authors then explore the effect of atmospheric pressure patterns on short- and long-term variations in ozone and UV radiation. The results are interesting and worth publishing in ACP. In the second part of the paper, the authors then analyze UV measurements at three Italian stations for long-term trends and use TOC and GPH data to interpret these trends.

Most of the analyses are sound, with the exception of two issues: the effect of the atmospheric ozone profile on UV radiation and the effect of changes in aerosol and clouds on trends, as described in "Mayor Comments" below. The presentation is generally clear, although the Summary at the end is too long; too much detail distracts from the main messages. I recommend publication of the manuscript, provided that my Mayor and Minor comments below are addressed appropriately.

Reply

We tried to shorten the Summary at the end of the manuscript as suggested by the reviewer. After further analysis we found that the reviewer was right about the two issues described above, and we tried to correct the manuscript properly. More details are provided in the replies to the reviewer's specific comments.

Major Comments:

The authors mention multiple times that the vertical redistribution of ozone in the atmosphere has an important effect on the global irradiance at 307.5 nm and that changes of this distribution over time can explain some trends in their UV measurements. My model calculations (see below) suggests that this effect is not important for the solar zenith angles (SZAs) of 45° and 67° considered in this study. The authors should perform their own model calculations and adjust their assertions accordingly.

Reply

We performed model simulations as recommended by the reviewer, and indeed, the effect of changes in total ozone is larger at the SZA of 67° with respect to 45°, independently from the vertical distribution of changes in total ozone (at least for changes up to 10% with respect to the average levels of total ozone in Italy). However, as also suggested by the reviewer, we repeated the analysis of the long-term changes of the spectral UV irradiance, more carefully this time, and our new findings are in agreement with the modelling simulations.

Along the same lines, the authors imply that clouds and aerosols have a larger effect on surface UV radiation at a SZA of 45° compared to 67°. For example, they report that there are no significant trends in UV radiation at 67° at Rome while significant trends were calculated for 45° (their Figure 7). They attribute this difference to cloud and aerosol effects. My model calculations

(also below) confirm that aerosol effects are larger at 67° than 45°. It is therefore unlikely that there is no trend at 67° but a signficant trend at 45° because of cloud or aerosol effects. Instead, I suspect that there is a problem in the UV radiation data at 45°. However, the data presented do not allow me to confirm this suspicion.

Reply

Under certain conditions attenuation by clouds and aerosols can be larger at lower SZAs (see Figures S1 and S2 in the supplement), especially in UVB wavelengths. However, this was not the case in our study. As correctly suggested by the reviewer there was a problem with the derived UV trends (they were significantly affected by gaps in the series), but at SZA=67°. In order to solve this issue, we tried to improve the filtering of the data used in the analysis. Furthermore, for Rome and Lampedusa we performed the analysis for the SZA of 65° instead of 67°, which gave more reliable results (see lines 196-206 of the manuscript). For Aosta data availability was better at 67°, thus analysis was performed for the particular SZA. Despite the small difference in the SZA for which the data were analyzed results for the three stations are comparable to each other as explained in the manuscript.

Minor Comments:

L54: Regarding "avoided extremely high levels of solar UVB radiation". Perhaps give a number here.

Reply

Relative information has been added to the manuscript.

L56: The recent *Nature* paper by Young et al. (https://doi.org/10.1038/s41586-021-03737-3) could also be cited here.

Reply

Done

L70: You could also cite: Ohring & Muench 1960: (https://doi.org/10.1175/1520-0469(1960)017<0195:RBOAMP>2.0.CO;2).

Reply

Done

L72: Please provide a reference that the tropopause rises with warming of the troposphere.

Reply

Done

L152: regarding "standard uncertainty for spectral UV measurements … of the order of 5%" So that would be 10% at the 2-sigma level?

Reply

Yes, this is correct. Throughout the manuscript we refer to 1-sigma (standard) uncertainties, which in our opinion is clear. Thus, we do not believe that further discussion is necessary in the manuscript relative to the 2-sigma uncertainty level.

L156: "smaller than 2.5%" is only half as large as the 5% quoted above. Why?

Reply

The uncertainty of 5% discussed above refers to Brewer spectrophotometers. The 2.5% uncertainty at this point refers to the Bentham spectroradiometer operating at Aosta. We think that this is already clear in the manuscript.

L168: Regarding "available for at least 15 days.": That's only half the days in a month. Significant error in monthly averages could occur if the missing days are biased towards either the start or end of a month. How was this problem addressed? Could this have caused spurious trends?

Reply

The reviewer is right at this point. The threshold of 15 days was used as a compromise between representativeness and availability of data to perform a trend analysis. To make sure that there is no bias issue due to the distribution of gaps we changed the data filtering method for the data used in the revised version of the manuscript. Again, we only consider months for which measurements are available for at least 15 days, with the additional criterion that at least 5 days are available for each of the following sub-periods in the month: day 1 – day 10, day 11 – day 20, day 21 – end of month (see line 208).

L225: The study focuses on anomalies in GPH at 250 hPa rather than tropopause altitude, the parameter frequently in other studies (see line 70). Figure S1 in the Supplement shows that there is a good correlation between the two parameters. Please describe the advantage of using GHP instead of tropopause height considering that the tropopause separates tropospheric and stratospheric ozone and therefore might be the more important parameter.

Reply

In this study we studied the link between the GPH at 250 hPa and total ozone in order to investigate and highlight the relationship between synoptical tropospheric conditions (for which the 250 hPa GPH is more representative relative to the altitude of the tropopause) and total ozone. The same information has been added to the manuscript (lines 224 - 230).

L253: Attributing correlation coefficients between GPH and the other parameters shown in Table 1 to "dynamical stratospheric processes" and "tropospheric processes" is a bit of a stretch. It would be more appropriate to say that a higher GPH emphasizes processes in the troposphere while a lower GPH emphasizes those in the stratosphere.

Reply

We deleted this phrase in the revised version of the manuscript.

L263 - 285: Please structure better: First describe changes at SZA=67° based on Fig 3, then do the same for SZA=45°, based on Fig 4. Lastly, highlight the differences between trends at the two SZA.

Reply

We tried to improve the structure of this section.

L263-270: The text does not fit Figure 3. The whole paragraph is questionable, and while it identifies Figure 3, it should be mentioned that this description refers to the analysis of data at SZA=67°. Specifically, "307.5" in line 263 should be "324"; "324" in line 264 should be "307.5". Regarding "The overall increase of the 307.5 irradiance for 2006 – 2020": Do you refer to an increase averaged over all months? If so, how was the annual anomaly calculated considering the large difference in winter and summer UV radiation?

Reply

Obviously, the manuscript was confusing at this point. In this section trends have been only studied and reported separately for each month of the year, and not as average over all months. We re-wrote this part of the manuscript clearer for the results of the updated analysis.

Lines 271 - 285: The text should be better structured. First, it should be said that this analysis is now for SZA=45° and that data from Aosta, Lampedusa, and Rome are discussed sequentially. For example: "We now discuss changes observed at a SZA of 45°. At Aosta, the irradiance at 324 nm increased by 0.6%/year in August..."

Reply

The 3.2.1 section was structured in a different way following the recommendation of the reviewer.

L275 - 277 and L351 - 353: As already noted above, I find it hard to believe that there were no trends at 67° but significant trends at 45° due to cloud and aerosol effect. Clouds and aerosols typically have a larger effect at 67° compared to 45°. To quantify this, I modeled spectra of global irradiance for 45° and 67°, either without aerosols or by assuming an aerosol layer. I parameterized the aerosol optical depth with Angström's formula, setting alpha=1 and beta=0.25. This is a rather dense aerosol layer. At SZA=45°, global irradiance with aerosols was suppressed relative to the no-aerosols case by 17.5% at 307.5 nm and 16.3% at 324 nm. At 67°, global irradiance was lower by about 20% at both wavelengths, confirming that the effect of aerosols increases with SZA. Hence, I do not believe that clouds or aerosol are responsible for the different trends at 45° and 67°. Instead, I suspect some problems in the data, e.g., due to gaps. This issue should be explored further by the authors with their own model calculations.

Reply

The reviewer has a point here. This issue has been addressed properly as discussed earlier (see replies to the reviewer's general comments). We are thankful to the reviewer, who helped us solve this significant issue and improve the manuscript.

L284: Considering that the changes for April and May are so different, can it be ruled that problems in the data, such as data gaps affecting the calculation of monthly averages, led to the high value in April?

Reply

We checked and did not find data gaps that could be responsible for the differences between April and May. The difference between April and May can be safely attributed to the corresponding difference in the trends of total ozone. Analysis of total ozone series using Brewer and MERRA-2 data for Rome (analysis of the MERRA-2 ozone is not discussed in the manuscript) yielded similar results: no trend in May, and significant decrease in April.

L288 and L294: Why suddenly “SZA of 67.5°”? Up to now the SZA was 67°.

Reply

It was a typo and has been corrected.

L300: Again, I find it hard to believe that the trends for a SZA at 45° and 67° (or 67.5° ?!?) are so different, in particular for April, and to a lesser extent for August and September. The fact that the large trend for April is also present at 324 nm suggests that the trend in ozone (Fig 8a) is not the driving factor.

Reply

After improving and updating the analysis we found similar results for the two SZAs, which were indeed attributed to aerosols and clouds and not ozone.

L310: Regarding: “As the SZA increases the role of ozone at the middle and upper atmosphere becomes more important regarding the attenuation of the UV-B irradiance relative to ozone at the lower stratosphere.” I presume that you refer to the Umkehr effect here. However, that effect is only significant for SZA > 80°. To confirm that the ozone profile has only a minor affect on UV irradiances at 307.5 and 324 nm for SZA of 45° and 67°, I ran model calculations (LibRadtran/UVSPEC) using either the standard mid-latitude profile (afglms.dat) or a modified profile where I increased the ozone concentration by 5% in the upper troposphere and lower stratosphere (between 13 and 20 km). I then scaled the original afglms profile and this modified profile to a TOC of 315 DU. This scaling effectively increased the ozone of the modified profile by 3.8% between 13 and 20 km and lowered it by 1.1% at all other altitudes. The global spectral irradiance at 307.5 nm calculated with the modified profile for SZA=45° was 0.06% larger than the irradiance calculated with the standard profile. The difference for 67° was 0.09%. At 324 nm, the difference was basically zero. These calculations show that the effect of the profile at these SZAs is negligible. So the sentence in line 310 should be removed.

Reply

The reviewer is right. We performed similar analysis and we got similar results as the reviewer. Again, we thank the reviewer for his/her efforts. The manuscript has been corrected.

L326-375: The summary is too long. Please shorten and emphasize the essential numbers and messages rather than repeating the Results section.

Reply

The summary and conclusions section has been shortened significantly as suggested by the reviewer

L355: The sentence “The increase … at Rome” is one example of a sentence that does not add much and could be deleted to make Section 4 more focused.

Reply

It has been deleted

L358: As mentioned above, my model calculations do not support the assertion that the difference at 45° and 67° is due to clouds and aerosols. If the authors feel otherwise, they should support their assertion with their own calculations.

Reply

We have replied to this comment earlier

L359: "SZA decreases" > "SZA increases". ("SZA decreases" means that the Sun is closer to the zenith and the contribution of the direct irradiance becomes larger, not "less significant".)

Reply

Corrected

L364: My model calculations above strongly suggest that the following sentence is either incorrect or greatly overstates the effect: "The difference between the observed and the expected change in the irradiance at 307.5 nm can be attributed to the fact that ozone changed differently at different levels in the atmosphere."

Reply

Appropriate corrections have been applied to the manuscript.

L372: The same can be said about the sentence "… can be explained by the decreasing ozone in the lower stratosphere and the increasing ozone in the upper stratosphere."

Reply

This sentence has been removed

L379: Again, at 67° the effect of the profile is negligible and the sentence "of upper stratospheric ozone to the attenuation of UVB irradiance becomes more significant with increasing SZA" should be removed.

Reply

The sentence has been removed.

L380: I agree that. "More robust statistical analyses and radiative transfer modelling are necessary in order to quantify the relative contribution of different factors to the short- and long-term changes of the surface solar UV irradiance in Italy" but I disagree that these calculations are "out of the scope of the present study." The authors assert multiple times that the vertical redistribution of ozone has an import effect on global UV irradiance for SZA of 45° and 67°, contrary to my calculations. They should make their own calculations to look into this issue in more detail than I did, and perhaps add an additional figure to the manuscript summarizing their results.

Reply

More robust statistical analysis has been performed and the manuscript has been updated according to the findings of this analysis,

Technical suggestions / grammar / typos:

L13: Delete "In this study" (It is obvious that the abstract refers to this study.)

Reply

Done

L14: over Italy > across Italy (Otherwise readers might think that UV was measured in the air above ground.)

Reply

Done

L14: "located at quite different" > "characterized by quite different"

Reply

Done

L16: "307.5 nm, 324 nm" > "307.5 nm and 324 nm"

Reply

Done

L18: "geopotential height at 250 hPa (GPH)." > "geopotential height (GHP) at 250 hPa."

Reply

Done

L28: "It was also showed that" > "It was also shown that" or "We also showed that"

Reply

Done

L31: "period which" > "period, which" ; "aerosols were" > "aerosols, were"

Reply

Done

L42: "is also absorbed" > "is absorbed"

Reply

Done

L43: "ozone dominates on scattering" > "ozone has greater importance than scattering

Reply

We changed the phrase "dominates on" with "is more significant than"

L46: “leading to reduced” > “ but also reduced” (otherwise it sounds as if low- and mid-latitude ozone changes are only the result of high-latitude processes)

Reply

Done

L52: “resulted on decreasing” > “resulted in decreasing”

Reply

Done

L89: “parameters which affect significantly” > “parameters that significantly affect”

Reply

Done

L96: “different latitudes and environmental conditions” > “and affected by differing environmental” (a site cannot be "located at an environmental condition”)

Reply

Done

L97: “extent at which” > “extent to which”

Reply

Done

L118: “referred as IOS standard.” > “referred to as IOS standard.”

Reply

Done

L188: “GPH at 250 hPa” > “GPH at 250 hPa and at 850 hPa”, and delete "and ...850 hPa."

Reply

Done

L243: “For 45°” > “For a SZA of 45° “

Reply

Done

L279: “none” > “any”

Reply

Done

L286: “3.2.1 Long-term variability in the period 1996 – 2020” > “3.2.1 Long-term variability at Rome for the period 1996 - 2020”

Reply

Done

L348: “of the GPH” > “in the GPH”

Reply

Done

L349: I don’t understand “was depicted to”

Reply

We re-wrote the sentence in a clearer way.

Supplement, line 3: “Figure A1” > “Figure S1”

Reply

Corrected

Supplement, line 4: GHP at 250 hPa and 850 hPa are correlated, not “anti-correlated”

Reply

Corrected

Supplement, Caption Figure S1: “tropo-pause” > “tropopause”; delete extra space after 850 hPa

Reply

Corrected

Variability and trends of the surface solar spectral ultraviolet irradiance in Italy: on the combined~~a possible~~ influence of dynamics and lower and upper stratospheric ozone trends

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Abstract. The~~In this study the~~ short- and long-term variability of the surface spectral solar ultraviolet (UV) irradiance is~~are~~ investigated across~~over~~ Italy using high quality ground~~-~~based measurements from three sites characterized by~~located at~~ quite different environmental conditions~~,~~ and covering the full latitudinal extent of the Italian territory: Aosta (45.7° N, 7.4° E, 570 m a.s.l.), Rome (41.9° N, 12.5° E, 75 m a.s.l.), and Lampedusa (35.5° N, 12.6° E, 50 m a.s.l.). The variability of the irradiances at 307.5 nm and~~,~~ 324 nm, and their~~of the~~ ratio are~~between the 307.5 nm and the 324 nm irradiances were~~ investigated with respect to the corresponding variability in total ozone and the geopotential height (GPH) at 250 hPa.~~ (GPH).~~ The study was performed for two periods: 2006 – 2020 for all stations, and 1996 – 2020 only for Rome. A statistically significant correlation between the GPH and total ozone monthly anomalies was found for all stations and all seasons of the year. A corresponding statistically significant correlation was also found in most cases between the GPH and the 307.5 nm irradiance monthly anomalies. The correlation among the~~between~~ GPH monthly anomalies at the three~~different~~ sites was statistically significant, possibly explaining the strong and significant correlation among~~between~~ the corresponding total ozone monthly anomalies.~~ at the three sites.~~ A statistically significant ~~decrease of ~~total ozone decrease, of ~0.1%/year was found for Rome over~~for~~ the period 1996 – 2020, which however at SZA = 65° did not lead to~~induce~~ increasing trends in the annual levels of the irradiance at 307.5 nm (neither increasing trends in the corresponding ratio between the 307.5 nm and the 324 nm irradiances).~~) at SZA = 67°.~~ Further analyses revealed positive trends in the ratio and the 307.5 nm irradiance in particular months~~at smaller solar zenith angles (SZA),~~ which followed negative trends in total ozone. The ~~can be attributed to the fact that ~~total ozone decrease over Rome was mainly attributed to decreasing ~~is driven by a decrease in the ~~lower ~~stratosphere while upper ~~stratospheric ozone. Furthermore, it was shown that over all stations~~ increases, and the effect of changes of upper stratospheric ozone becoming disproportionately larger for increasing SZA. It was also showed that~~ long-term changes in total ozone follow changes in GPH, which is an additional indication that negative trends in total ozone were~~are~~ mainly driven by changes in

lower stratospheric ozone. An anti-correlation between the GPH long-term changes and total ozone was also evident for all stations in the period 2006 – 2020. For specific months positive~~Positive~~ trends in UV irradiance for this latter period, which were mostly~~possibly~~ driven by changes in clouds and/or aerosols rather than total ozone, were found for each of the three sites~~Rome and Aosta~~. This study clearly points out the significance of dynamical processes which take place in the troposphere for the variability of total ozone and surface solar UV irradiance.

1 Introduction

The amount of solar ultraviolet radiation (UVR) reaching the Earth's surface is an important environmental, ecological and atmospheric parameter to be measured and studied. The relationship between UVR and biological effects has been well established. Exposure to UVR is vital for many living organisms, including humans, however, overexposure may produce detrimental effects in humans, animal and plants (Paul and Gwynn-Jones, 2003; Caldwell et al., 1998; Bornman et al., 2019; Calkins and Thordardottir, 1980; Williamson et al., 2019; Häder et al., 1998). Photons with wavelengths below 290 nm are absorbed in the higher atmosphere, mainly by molecular oxygen (O_2) and ozone (O_3) and practically do not reach the Earth's surface. Most of the ultraviolet-B (UVB) irradiance (280 – 315 nm) is absorbed by ozone in the stratosphere (Bais et al., 1993; Griggs, 1968; Inn and Tanaka, 1953). Absorption by stratospheric ozone is more significant than scattering by molecules and aerosols in the UVB spectral range, while scattering plays a relatively larger role than ozone absorption in the UVA~~Most of the ultraviolet-B (UVB) irradiance (280 – 315 nm) is also absorbed by ozone in the stratosphere (Bais et al., 1993; Griggs, 1968; Inn & Tanaka, 1953). Absorption by stratospheric ozone dominates on scattering by molecules and aerosols in the UV-B spectral range, while scattering plays a relatively larger role than ozone absorption in the UV-A~~.

In the 1980s and 1990s, the increase of anthropogenic emissions of ozone depleting substances (ODS) enhanced the ozone chemical destruction ~~of ozone~~ in the stratosphere mainly over Arctic and Antarctica, and led~~leading~~ to reduced stratospheric ozone~~ even~~ at mid-latitudes of the Southern and the Northern hemispheres (Solomon et al., 1986; McConnell et al., 1992). In its turn, the ozone reduction resulted~~, and subsequently~~ to higher levels of UVB radiation at the Earth's surface (Madronich et al., 1998; Kerr and McElroy, 1993; Zerefos et al., 1995). Emissions of ODS were regulated after the adoption of the Montreal Protocol in 1987 and subsequent amendments and adjustments, and since the mid-1990s the reduction of stratospheric ozone has decelerated. The first signs of recovery are now evident over higher latitudes (Weber et al., 2018; Solomon et al., 2016). Recent studies show that recovering ozone over Antarctica resulted in~~on~~ decreasing UVB radiation (Bernhard and Stierle, 2020). Over the Arctic, many studies report negative, but in most cases not significant, trends of UVB radiation in spring (Eleftheratos et al., 2015; Lakkala et al., 2017; Svendby et al., 2018).~~Over the Arctic, many studies report negative, but in most cases not significant, trends of UVB radiation in spring (Eleftheratos et al., 2015; Lakkala et al., 2017; Svendby et al., 2018).~~ Due to the successful implementation of the Montreal protocol the world avoided extremely high levels of solar UVB radiation (nearly double with respect to the UVB levels in the 1970s over northern and southern mid-latitudes by 2100) which would have been detrimental for the viability of ecosystems, as well as for human (McKenzie et al., 2019; Morgenstern et al., 2008; Newman and McKenzie, 2011; Young et al., 2021).

However, the future evolution of total ozone levels, and subsequently of UVB radiation is still uncertain. Although decreasing ODS since mid-1990s led to increasing ozone in the upper stratosphere~~ since mid-1990s~~ (Steinbrecht et al., 2017; Sofieva et al., 2017), lower stratospheric ozone in the Northern mid-latitudes has been continuously decreasing, offsetting the increase occurring in the upper stratosphere (Wargan et al., 2018; Ball et al., 2018). Changes in lower stratospheric ozone appear to have a strong spatial and seasonal variability, and the processes that drive them are not clear yet (Szeląg et al., 2020). Furthermore, dynamical phenomena occasionally (once every few years) favor extensive destruction of Arctic stratospheric ozone in early spring (Dameris et al., 2021; Manney et al., 2011; Pommereau et al., 2018; Varotsos et al., 2012; Wohltmann et al., 2020)~~ Furthermore, dynamical phenomena occasionally (once every few years) favor extensive destruction of Arctic stratospheric ozone in early spring (Dameris et al., 2021; Manney et al., 2011; Pommereau et al., 2018; Varotsos et al., 2012; Wohltmann et al., 2020)~~, leading to extremely low ozone over Northern hemisphere high and mid-latitudes (due to the transport of poor-ozone air masses from the poles towards mid-latitudes), and subsequently to very high levels of solar UVB radiation at the Earth's surface (Bernhard et al., 2020; Petkov et al., 2014)~~(Bernhard et al., 2020; Petkov et al., 2014)~~. In addition, low ozone episodes (Siani et al., 2002)~~(Siani et al., 2002)~~ not related to ozone over the poles can be experienced. These episodes are characterized by significant ozone decreases over limited geographical regions and are associated with synoptic weather systems. (at time scales of 1 to 3 days). An increasing frequency of the occurrence of such phenomena in the future could strongly affect the ozone levels in the atmosphere, and subsequently the terrestrial levels of UVB. As discussed in several studies (e.g., Reed, 1950; Ohring and Muench, 1960; Hoinka et al., 1996; Dobson et al., 1946; Varotsos et al., 2004; Vaughan and Price, 1991; Steinbrecht et al., 1998), changes in tropopause altitude are linked to inverse changes in the amount of total ozone. According to the studies by~~(e.g., Dobson et al., 1946; Reed, 1950; Hoinka et al., 1996; Varotsos et al., 2004; Angell and Korshover, 1964; Steinbrecht et al., 1998; Vaughan and Price, 1991), changes in tropopause altitude are linked to inverse changes in the amount of total ozone. Thus, increasing altitude of the tropopause due to climate change related warming of the troposphere~~ Varotsos et al., (2004) and Steinbrecht et al., (1998), positive trends in the height of the tropopause explain 25 – 30% of the reduction of total ozone over Athens in 1984 – 2002, and Hohenpeissenberg in 1967 – 1997 respectively, due to the pushing up of air with the change of tropopause altitude (Vaughan and Price, 1991). Thus, an increasing altitude of the tropopause due to climate change related to the warming of the troposphere (e.g., Lin et al., 2017) would induce negative trends in lower stratospheric ozone, and subsequently positive trends in UVB.

Over many mid-latitude stations of the Northern hemisphere, changes in aerosols and clouds – and not ozone - have been found to be the main drivers of the long-term changes of the UVB and the UVA irradiance (Lin et al., 2017; Chubarova et al., 2020; De Bock et al., 2014; Fountoulakis et al., 2016, 2018; Hooke et al., 2017; Fitzka et al., 2012; Zhang et al., 2019).~~(Chubarova et al., 2020; De Bock et al., 2014; Fitzka et al., 2012; Fountoulakis et al., 2016; Fountoulakis et al., 2018; Hooke et al., 2017; Zhang et al., 2019).~~ Aerosols and clouds also play a significant role in the short-term variability of UVA and UVB irradiance (di Sarra et al., 2008; Kazadzis et al., 2009; Mateos et al., 2015, 2011). Two different studies~~(e.g., Mateos~~

~~et al., 2015; Kazadzis et al., 2009; di Sarra et al., 2008; Mateos et al., 2011). Two different studies (Fragkos et al., 2016), and~~ (Raptis et al., 2021; Fragkos et al., 2016)~~Raptis et al., 2021)~~ report moderate or even low erythemal irradiance (McKinlay and Diffey, 1987) during extremely low ozone events, because of remarkably high aerosol load. The trends reported in different studies for the period between mid-1990s to present vary significantly even within a few hundreds of kilometres. Fountoulakis et al., (2020b) reported an average increase of 5% per decade in the 307.5 nm irradiance for Uccle, Belgium in 1996 – 2017, and for the same period an average decrease of 7% per decade for Reading, UK, which is less than 400 km from Uccle. Other, independent studies report similar results for the two stations. Hooke et al. (2017) reported an 8% decrease in erythemal doses for Chilton, UK (located a few kilometers from Reading) in 1991 - 2015, while De Bock et al., (2014) and Pandey et al., (2016) reported positive trends in Uccle (in 1991 – 2013 and 1995 – 2014 respectively).

The UV irradiance spatial variability in Italy is very large, mainly due to the country's long latitudinal extent and complex topography (Meloni et al., 2000). Thus, atmospheric parameters may affect UVB and UVA irradiance in a different way at different locations (e.g., Fountoulakis et al., 2020b). Recent studies have shown that atmospheric parameters that~~(e.g., Fountoulakis et al., 2020). Recent studies have shown that atmospheric parameters which~~ affect significantly solar UV radiation, such as clouds (Manara et al., 2016; Manara et al., 2015; Mateos et al., 2011; Pfeifroth et al., 2018) and aerosol (Orza and Perrone, 2015; Rizza et al., 2019; Di Ianni et al., 2018; Putaud et al., 2014; Masiol et al., 2017; di Sarra et al., 2008) have changed in Italy in the last decades, either on a regional or on a country scale. Although in Italy long-term continuous solar spectral UV (Diémoz et al., 2011) and total ozone measurements (Siani et al., 2018) are available from three different stations across the country, they have never been used to study the long-term changes of UV irradiance at the surface, and how they are affected by changes in total ozone. In this study, the long-term datasets of high-quality spectral UV and total ozone measurements of three Italian sites (Aosta, Rome, and Lampedusa), located at quite different latitudes and affected by differing environmental conditions were used in order to study the changes of solar UV irradiance, and the extent to~~at~~ which they were~~are~~ driven by changes in total ozone. Furthermore, there was an effort to investigate whether, and to what extent changes in synoptical atmospheric circulation affected~~affect~~ the surface solar UV irradiance short- (e.g., yearly) and long-term variability.

The paper is structured as follows. In Sect. 2 the data and methods used for the study are described. In Sect. 3.1 the possible links between the short-term variability of UV irradiance and atmospheric dynamics are studied. In Sect. 3.2 the trends of spectral UV irradiance and total ozone for the three stations are analyzed and discussed with respect to their main drivers. Finally, in Sect. 4 the main findings and the conclusions of the study are summarized.

2 Data and methodology

Long series of high-quality spectral UV measurements are available from three Italian stations, providing a complete latitudinal coverage of Italy (Fig. 1). The Aosta monitoring station at the facilities of Regional Environmental Protection Agency of the Aosta Valley (ARPA Valle d'Aosta) (45.7° N, 7.4° E, 570 m a.s.l.) is a semi-rural site (at Aosta–Saint-Christophe), in the

North-Western Alps. The site of the Physics Department of Sapienza University of Rome (41.9° N, 12.5° E, 75 m a.s.l.) is an urban site at a distance of about 25 kilometres from the Tyrrhenian Sea. The Lampedusa Station for Climate Observations of the Italian Agency for the New Technologies, Energy and Sustainable Economic Development (ENEA), located on the island of Lampedusa (35.5° N, 12.6° E, 50 m a.s.l.) is a background remote (island) site.

At Rome the total column of ozone has been measured by a single monochromator Brewer (MkIV type) with serial number 67 (Brewer#067) since 1992 (Siani et al., 2018). Measurements of the spectral irradiance have been performed by the same instrument since 1996, at wavelengths 290 – 325 nm with a step of 0.5 nm and a resolution of ~0.6 nm (Casale et al., 2000). The world travelling reference standard Brewer (Brewer#017) (maintained by the International Ozone Services Inc.; https://www.io3.ca/index.php) transfers the ozone calibration from the reference triad maintained by Environment and Climate Change Canada (Fioletov et al., 2005; Zhao et al., 2020) to field instruments. Hereafter the travelling reference standard Brewer is referred to as IOS standard. Intercomparisons between Brewer#067 and the IOS standard were~~are~~ performed on an annual or biennial basis since the installation ensuring the optimal quality of total ozone measurements. At Rome UV calibrations were performed using IOS 1000 W lamps (traceable to~~As discussed in the following, regular inter-comparisons between~~ the National Institute of Standard~~IOS standard~~ and Technology - NIST, Maryland, USA). Furthermore, the instrument was also compared~~Brewer spectrophotometers at Lampedusa and Aosta ensure the consistency between the total ozone datasets recorded at the three stations. Inter-comparisons~~ with the traveling spectroradiometer QUASUME (unit for the ~~UV reference standard~~ Quality Assurance of Spectral Ultraviolet Measurements~~assurance of spectral ultraviolet measurements~~ in Europe) (~~through the development of a transportable unit (QASUME;~~ Hülsen et al., 2016; Gröbner and Sperfeld, 2005) during the UV intercomparison campaign in Arosa (Switzerland) in 2012, as well as at Rome in 2003 and 2008. Stability checks using 50 W lamps traceable to the IOS 1000 W lamps were regularly performed ensuring the consistency and homogeneity of the Rome UV time-series during the whole period of study.~~(hereafter referred as QASUME) in 2003 – 2008 and with IOS standard thereafter, performed every 2-3 years, ensure the high quality of the spectral UV measurements. The consistency between the UV spectra measured by QASUME and the IOS standard is ensured by the common participation of both instruments in the inter-comparison campaigns on an annual or biennial basis (e.g., Redondas et al., 2018; Redondas & Rodriguez-Franco, 2015).~~

For the present study measurements of total ozone and spectral UV irradiance for 1996-2020 have been used for Rome. Measurements~~. Note that spectral UV measurements~~ for the first six months of 2018 were not used ~~for Rome~~ because operational problems induced increased uncertainty in the measurements.

At Lampedusa measurements of total ozone and spectral UV irradiance have been performed since 1997 by a double monochromator Brewer (MkIII type) with serial number 123 (Brewer#123) (di Sarra et al., 2002). Solar spectra are measured in the range 286 – 363 nm with a step of 0.5 nm and a resolution of ~ 0.55 nm. Calibrations of spectral UV measurements are performed 4-5 times per year with a field calibrator which uses 1000 W FEL lamps traceable to NIST (di Sarra et al., 2008). Regular inter-comparisons (every 2 – 4 years since 1998) with the IOS standard ensure the good quality of total ozone measurements. The Lampedusa spectral UV dataset has been recently subjected to QA/QC ~~and homogenized~~ for the period

2003 – 2020. For the present study measurements of the total ozone and spectral UV irradiance have been used for the period for which high quality measurements were~~are~~ available for all three sites (i.e., 2006 – 2020).

At Aosta, spectral UV-visible measurements are performed by a double monochromator Bentham DTMc300 with serial number 5541 (Bentham5541) in the range 290 – 500 nm with a step of 0.25 nm and a resolution of ~0.5 nm. Spectral UV measurements began in 2004. Since 2006 inter-comparison with QASUME was~~is~~ performed on an annual or biennial basis ensuring the high quality of the measurements. Recently the spectral UV dataset of Aosta was re-evaluated and homogenized for the period 2006 – 2020 (Fountoulakis et al., 2020a). Measurements of the total ozone are available since 2007 by a single monochromator Brewer (MkIV type) with serial number 66 (Brewer#066). The quality of total ozone measurements was~~is~~ ensured by inter-comparisons with the IOS standard, which have been performed since 2007 on a biennial basis. Total ozone and spectral UV measurements for Aosta have been analysed for 2007 – 2020 and 2006-2020, respectively.

Intercomparisons between the IOS standard and the spectrophotometers at all three stations on annual or biennial basis ensured the consistency between the total ozone datasets recorded at the three stations. The good quality of the total ozone and spectral UV measurements was~~is~~ further ensured by performing stability checks and applying a number of quality control/quality assurance procedures on a regular (daily, weekly, or monthly basis) at each of the three sites described above (Fountoulakis et al., 2020b; Ialongo et al., 2010). The accuracy of total ozone columns retrieved by measuring irradiances of direct sunlight radiation (DS mode) (Kerr, 2010) by well-maintained and calibrated Brewer spectrophotometers, such as those used in the present study, is of the order of 1% (Vanicek, 2006). The consistency between measurements from different instruments (if they are well maintained and calibrated) is also ~1% (Redondas et al., 2018). The standard uncertainty for spectral UV measurements at wavelengths longer than 305 nm from well maintained and calibrated Brewer spectrophotometers is of the order of 5% (Garane et al., 2006). The agreement between synchronous spectra from well maintained and similarly calibrated spectrophotometers is also of the order of 5% (standard deviation of the differences) (Bais et al., 2001). For wavelengths longer than 305 nm and SZAs below 75° the standard uncertainty in the spectral UV measurements of Bentham5541 is smaller than 2.5%. A detailed description of the uncertainties of the spectral UV measurements performed in Aosta can be found in Fountoulakis et al., (2020a).

Spectral measurements at the wavelengths 307.5 nm (306.5 – 308.5 nm average) and 324 nm (323 – 325 nm average) have been analysed for all three sites. Irradiance at 307.5 nm was chosen since it is strongly affected by total ozone, while the irradiance at 324 nm is weakly affected by ozone. Although ozone has a stronger effect on wavelengths shorter than 307.5 nm, the particular wavelength was chosen because it is less affected by noise and spectral straylight (relative to shorter wavelengths). For each spectrum, the ratio between the irradiance at the two wavelengths (307.5 nm and 324 nm) was also calculated (and will be herein referred as 307.5/324 nm ratio) because changes of the ratio should be strongly correlated with changes in total ozone. The ratio is also affected by other atmospheric factors such as high altitude clouds (see Figures S1 and S2 in the supplement) and particular types of organic aerosols (e.g., Mok et al., 2016). However, the role of these latter atmospheric parameters on the variability of the 307.5/324 nm ratio is expected to be minor with respect to the role of ozone. For each day, all spectra measured within +/- 2° around the selected solar zenith angles (SZA) were interpolated to the central

SZAs of 65° and 45°~~and will be herein referred as 307.5/324 nm ratio. Long-term changes of the ratio should be strongly correlated with changes in total ozone. For each day, all spectra measured within +/- 2° around the solar zenith angles (SZA) of 67° and 45° were interpolated to the central SZAs~~ using the empirical relationship proposed by Fountoulakis et al. (2016), and then averaged to calculate the irradiance. For Aosta the~~The~~ SZA of 67° was used instead of 65° because the minimum (noon) SZA in most days of December and January is larger than 65°, while at Rome and Lampedusa the SZA of 65° is reached throughout the ~~whole~~ year. Choosing the SZA of 67° also for Rome and Lampedusa would produce more gaps in their UV series due to the lower availability of measurements at 67° relative to 65°. For months for which measurements at 65° were adequate for the calculation of monthly anomalies in Aosta, we performed the analysis for both SZAs (65° and 67°) and the results were nearly identical (which was expected since monthly UV anomalies were used in the study instead of absolute UV itrradiances). At ~~at~~ all three sites~~, while~~ the SZA of 45° is reached in the period April – September.

Monthly averages of the irradiances and the ratio were calculated for months for which measurements were available for at least 15 days (with the sub-criterion that measurements were available for at least 5 days for each of the following sub-periods: day 1 – day 10, day 11 – day 20, day 21 – end). Total ozone daily averages were~~. Daily averages of the total ozone have been~~ used for the calculation of monthly averages, again when measurements for at least 15 days were available. For all three stations, analyses were performed for the period September 2006 – August 2020 (14 years), i.e., the longest period of overlapping measurements. For Rome, analyses were additionally performed for the period September 1996 – August 2020 (24 years). In all cases, monthly climatological averages of each quantity were calculated for the whole available period (2006 – 2020 or 1996 – 2020). Monthly anomalies were calculated by subtracting the monthly climatological averages from the monthly average values. Calculation of trends was performed by applying a least square linear fit to the monthly anomalies and statistical significance was in all cases estimated by applying the Mann-Kendal test. Trends were not calculated when anomalies were available for less than 50% of the months in the first half and 50% of the months in the second half of each period.

In addition to the ground-based measurements, re-analysis products from Modern-Era Retrospective analysis for Research and Applications version 2 (MERRA-2) have been used, mainly for the investigation of changes in atmospheric conditions, and ozone at different atmospheric levels. All MERRA-2 products used in the present study were provided in a grid resolution of 0.5°x0.625° (latitude x longitude) and were~~have been~~ downloaded from the Giovanni platform maintained by National Aeronautics and Space Administration (NASA) (https://giovanni.gsfc.nasa.gov/giovanni/). Monthly average total ozone (GMAO, 2015a) for 1996 – 2020 and Geopotential Heights (GPH) at 250 hPa and 850 hPa (GMAO, 2015b) were downloaded and analysed for southern Europe. Several studies report a link between tropopause altitude and total ozone (e.g., Steinbrecht et al., 1998; Varotsos et al., 2004). In this study we tried to find the link between the GPH at 250 hPa and total ozone in order to investigate and highlight the relationship between synoptical tropospheric conditions (for which the 250 hPa GPH is a better proxy relative to the tropopause altitude) and total ozone. The 850 hPa GPH was chosen as a proxy for the dynamical conditions near the surface. It was chosen instead of the GPH at a higher pressure level (e.g. 1000 hPa) because it is less affected by the features of the surface. The Geopotential Height (GPH) was~~have been downloaded and analysed for southern Europe. The~~

~~Geopotential Height (GPH) was also~~ linearly interpolated to the co-ordinates of Aosta, Rome and Lampedusa in order to study its variability over these sites. Monthly average ozone mixing ratio (GMAO, 2015b) from MERRA-2, at different pressure levels between 150 and 3 hPa for 1996 – 2020 has been interpolated to the coordinates of the station of Rome. The version 7 Aqua/AIRS L3 Monthly Standard Physical Retrieval (AIRS-only) tropopause height product with 1° x 1° resolution (AIRS3STM) (AIRS project, 2019)~~(AIRS project, 2019)~~ was also interpolated to the coordinates of the three stations for the period 2006 – 2020. The AIRS3STM was also downloaded from the same platform. As shown later, positive/negative anomalies in GPH at 250 hPa ~~generally coincide with positive/negative anomalies of the tropopause altitude and positive/negative anomalies in GPH at 850 hPa. According to the studies of Varotsos et al., (2004) and Steinbrecht et al., (1998), positive trends in the height of the tropopause explain 25 – 30% of the reduction of total ozone over Athens in 1984 – 2002, and Hohenpeissenberg in 1967 – 1997 respectively~~and 850 hPa generally coincide with positive/negative anomalies of the tropopause altitude. ~~.~~

3 Short- and long-term variability of UV irradiance

3.1 Short-term variability of UV irradiance and the role of changes in GPH

In this section we investigate whether there is a correlation between the monthly anomalies of ~~the~~ GPH at 250 hPa (hereafter named as GPH unless something different is specified) and the corresponding anomalies of UV irradiance (at 307.5 nm and~~,~~ 324 nm) and the 307.5/324 nm ratio. Here, and in the following sections, the Pearson (i.e., linear) correlation coefficients are reported. For all cases that a strong correlation was found, it was optimally described by a linear fit. The investigation was performed for all three stations for the period 2006 – 2020. For Rome, the analyses were also performed for the period 1996 – 2020.

Fig. 2 shows the sequence of the correlation analysis among the sites for the different atmospheric parameters. As shown in Fig. 2, the GPH at Aosta and Rome varies in a similar way despite the distance between them and the fact that the two sites are in~~at~~ quite different environments. The correlation coefficient for GPH at the two sites (panel a) is ~0.9 and indicates that to a wide extent the two sites are affected by the same synoptical systems. This strong correlation is also found for the anomalies of total ozone (panel m) and subsequently for the anomalies of the 307.5 nm irradiance (panel d) and the 307.5/324 nm ratio (panel j). The correlation for the 324 nm irradiance (panel g) is statistically significant but weak (~0.28~~26~~). The corresponding correlation between the same variables (with the exception of the 324 nm irradiance) at Rome and Lampedusa was again significant but weaker than for Rome and Aosta, which however was expected since the latitudinal distance between Rome and Lampedusa (6.4°) is larger~~longer~~ than the distance between Rome and Aosta (3.8°). Part of the differences could be also due to the fact that dust outbreaks play a more significant role on the variability of surface UVR over Lampedusa than in Rome and Aosta (e.g., Meloni et al., 2008). A weak but statistically significant correlation between GPH (~0.5) and total ozone (~0.4) in Aosta and Lampedusa was found. However, in this latter case the correlation found for total ozone and GPH is not reflected in the levels of UV irradiance. Further analyses showed that for GPH and total ozone the correlation between different sites was generally stronger in winter and weaker in summer. Even for summer, however, the correlation between the aforementioned parameters for the pairs Aosta – Rome and Rome – Lampedusa was~~is~~ statistically significant (in the case of total ozone the correlation was~~is~~ also significant for the pair Lampedusa – Aosta). What is interesting is that the strongest correlation for the 307.5 nm irradiance and the 307.5/324 nm ratio for all sites was found for summer, which shows that the levels of the 307.5 nm irradiance over all three sites varied~~vary~~ in a similar way, mainly because total ozone also varied~~varies~~ in a very similar way.

In Table 1 the correlation coefficients between GPH and the UV irradiance at 307.5 nm and 324 nm (for SZAs 67° and 45°), GPH and the 307.5/324 nm ratio (for SZA = 67° and SZA = 45°), and GPH and total ozone are presented. The change (in DU) in total ozone and (in %) in the irradiances and the ratio for a 1 m change in GPH are also shown for the cases for which statistically significant correlation or anti-correlation was found. The latter changes were again calculated assuming linear correlation (or anti-correlation) between GPH and the aforementioned parameters. The monthly anomalies for each of the four seasons of the year (December, January, February for winter, March, April, May for spring, June, July, August for summer, and September, October, November for autumn) were used for the calculation of the correlation coefficients. Numbers in bold denote statistical significance (Mann – Kendall method was used to determine statistical significance) at the 95% confidence level (hereafter the statistical significance at the 95% confidence level is referred as statistical significance).

Variations in the GPH at 250 hPa are strongly correlated with variations in the tropopause altitude, as well as with variations in the GPH at 850 hPa (i.e., near the surface) (see Figure S3 in the Supplement).~~Appendix I).~~ Thus, the results presented in Table 1 partially confirm the findings of previous studies reporting correlation between tropospheric dynamics variability and total ozone, since a strong and statistically significant anti-correlation between total ozone and GPH was also found for all Italian stations and all seasons. The correlation was~~is~~ slightly lower in summer relative to other seasons (especially in Aosta). A possible explanation is that the relatively stable synoptical conditions in summer led~~lead~~ to much smaller variability in GPH relative to other seasons of the year, which in turn had~~possibly has~~ a weaker effect on total ozone relative to other phenomena.~~.~~ As discussed in the following sections, changes in GPH also played~~play~~ a significant role in the total ozone long-term changes ~~of total ozone~~ over Italy.

The anti-correlation between total ozone and GPH was associated with, in most cases, a statistically significant correlation between GPH and the 307.5/324 nm ratio. The correlation between the GPH and the ratio was generally stronger for Aosta than for Lampedusa and Rome. This is possibly because variations of the GPH are linked to larger variations of the total ozone at higher latitudes, given that the amount and the variability of total ozone increase with increasing latitude. The correlation between GPH and the 307.5 nm irradiance was also statistically significant in most cases. In some cases (e.g., Aosta in autumn) the correlation between GPH and the 307.5/324 nm ratio was~~is~~ much stronger than the correlation between GPH and the 307.5 nm irradiance. As already discussed, the variability of the ratio was mainly determined by the variability of total ozone, while the 307.5 nm irradiance was also affected by the variations of factors such as clouds and most types of aerosols which have a relatively flat spectral effect in the range 307.5 – 324 nm.

It is interesting to note that in addition to the significant correlation between GPH and the 307.5 nm irradiance, strong and statistically significant correlation was found between GPH and the 324 nm irradiance for Rome. For the SZA of 45° the correlation was significant for spring and summer. For 67° the correlation was significant for all seasons for 2006 – 2020, and for all seasons except summer for 1996 – 2020. The correlation coefficients were generally larger for 2006 – 2020 relative to 1996 – 2020. Statistically significant correlation between the 324 nm irradiance and the GPH has been found for Lampedusa in winter and for Aosta in autumn. The strong link between GPH and the 324 nm irradiance may be related to changes in aerosols and clouds, associated with changes in synoptical meteorological conditions. Aerosol and clouds, in their turn, affect the levels of both UVB and UVA irradiances.~~irradiance levels.~~ Changes in GPH at 250 hPa were strongly anti-correlated with~~to~~ changes in atmospheric pressure near the surface (see Fig. S3~~S.1~~ in the supplement), which were strongly linked to changes in cloudiness and wind patterns (both of which also affect aerosol load).

According to the results shown in Table 1, an increase of 1 m in the GPH induced a decrease of 0.2 – 0.5 DU in total ozone over Italy, and a corresponding increase of 0.02 – 0.07% in the 307.5/324 nm ratio. The increase in the 307.5 nm irradiance due to a 1 m increase in GPH ranged between 0.01 and 0.1% depending on season and station. The results were similar for 324 nm (increase of the irradiance by 0.01 – 0.07% for a 1 m increase in GPH) when a significant correlation with GPH was found.

~~The results presented in Table 1 show clearly that total ozone and surface UVR are affected not only by dynamical processes that take place in the stratosphere (e.g., Monge-Sanz et al., 2003; Neu et al., 2014; Weber et al., 2011), but they can be also affected significantly by processes that take place in the troposphere.~~

3.2 Long-term variability of spectral UV irradiance and total ozone

3.2.1 Long-term variability in the period 2006 – 2020

In this section the results of the analysis of the long-term changes for the same quantities as those discussed in Sect. 3.1 are presented and discussed for the period September 2006 – August 2020, during which, measurements were available for all three stations: Aosta, Rome, and Lampedusa. The estimated trends of the irradiances at 307.5 nm and 324 nm, and the 307.5/324 nm ratio at SZA = 65° (67° for Aosta) are presented in Fig. 3, while the corresponding trends for SZA = 45° are presented in Fig. 4. The trends were~~ also~~ calculated separately and are presented for each month of the year. The estimated trends for total ozone (from ground-based measurements) and GPH are presented in Fig. 5.

For Aosta no significant change of the 307.5 and 324 nm irradiances or of their ratio were found for the SZA of 67°. At the SZA of 45° the 324 nm irradiance increased in August by 0.6%/year.~~Statistically significant change (of 0.15%/year) was found only for the 307.5 nm irradiance in July at Aosta (Fig. 3a). For the same month neither the 307.5/324 nm ratio nor the 324 nm irradiance changed significantly, although they increased with an average rate of ~ 0.7%/year. It is possible here that the natural variability masks the presence of trends. The overall increase of the 307.5 irradiance for 2006 – 2020 is ~2%, and although it is statistically significant, it is less than the standard uncertainty in the measurements. Thus, this result should be treated with~~

~~caution. In November an increase in total ozone over Aosta, of 0.7%/year was found, which again coincides with a decrease of the GPH, which however is not statistically significant. The 307.5 nm irradiance and the 307.5/324 nm ratio also decreased in the same month, but their decrease was again not statistically significant.~~

~~At the SZA of 45° the 324 nm the irradiance in August increased over Aosta by 0.6%/year.~~ An increase of similar magnitude, but not statistically significant, was found for the 307.5 nm irradiance, while the 307.5/324 nm ratio remained relatively stable. In the same month total ozone did not change, which justifies the absence of significant trend in the ratio. However, ~~the~~ GPH increased significantly by 88 m/~~0.07%/~~year, which may be related with changes in cloudiness and/or aerosols (e.g., Manara et al., 2016)). A possible explanation for the fact that in August the UV irradiance at 45° increases while at 67° it remains relatively stable is that the two SZAs correspond to different times of the day, in which cloudiness and/or aerosols may change differently. In November an increase in total ozone over Aosta, of 0.7%/year was found, which again coincides with a GPH decrease, which however is not statistically significant. The 307.5 nm irradiance and the 307.5/324 nm ratio at 67° also decreased in the same month, but their decrease was again not statistically significant. ~~Since changes in aerosols and cloudiness have a stronger effect on the direct component of the solar irradiance (scattered irradiance in the UV is mainly redistributed rather than backscattered by aerosols and clouds) the changes in UV are more pronounced for 45° relative to 67° because direct component has a more significant contribution at smaller SZA.~~

At Lampedusa ~~neither~~ the UV irradiance increased significantly for SZA value of 65° in summer. The irradiance at 324 nm increased by ~ 0.2%/year in June, July and August. The corresponding increase of~~nor~~ the irradiance at 307.5 nm for the same months was ~0.05%/ year, while it was not statistically significant in June. The irradiance did not change significantly at 45°. The detected changes in UV irradiance can be attributed to changes in aerosols (e.g., dust) since clouds are rare at Lampedusa in summer. However, the overall change for the whole period of study (for summer at 65 º) is ~3% for 324 nm and ~1% for 307.5 nm, which is below the standard uncertainty in the measurements (~5%). Thus, the reported trends should be treated with caution.~~ratio changed significantly for both SZAs (45° and 67°).~~ Total ozone ~~also~~ did not change at Lampedusa for none of the twelve months despite the~~. The~~ statistically significant increase in GPH in September. The latter increase did~~ at Lampedusa does~~ not coincide with any statistically significant change in total~~of~~ ozone or UV irradiance.

The UV irradiance in April at Rome ~~did not change significantly at SZA = 67°, but~~ increased significantly ~~for both, 307.5 nm and 324 nm, by ~1%/year~~ at SZA = 65° as well as at SZA=45°, for both, 307.5 nm and 324 nm, by ~0.2%/year and ~0.5%/year, respectively, at 65°, and by ~1%/year for both wavelengths at 45°. The 307.5/324 nm ratio also increased, but the increase was not statistically significant. In the same month total ozone decreased and GPH increased, but ~~again,~~ neither of these latter changes was significant. These results show that changes in total ozone were~~are~~ not the dominant driver of changes in UV irradiance in April in 2006 – 2020, and that other factors such as aerosols and clouds played~~play~~ a more important role. No statistically significant changes were detected for the other months.

3.2.1 Long-term variability at Rome for~~in~~ the period 1996 – 2020

In Fig. 6 the monthly anomalies of the 307.5 nm irradiance, the 324 nm irradiance, the 307.5/324 nm ratio, and the total ozone are presented for Rome for the period September 1996 – August 2020 at the SZA of 65~~67.5~~°. Moving averages and the linear trends for the four quantities are also presented in the same figure. The calculated trends and the corresponding p-values are presented in Table 2. A negative, statistically significant trend of -0.1%/year was found for total ozone, corresponding to a decrease of ~~\~~~2.4% during the 24-year period. Although total ozone decreased~~decreases~~, neither the 307.5 nm irradiance, nor the 307.5/324 nm ratio increased~~increase~~.

The trends for each month were calculated for the 24-year period and are presented in Fig. 7. Analyses were performed for both SZAs, 65~~67.5~~° and 45°. In addition to the trends of spectral irradiance, the results for the 307.5/324 nm ratio are presented. Trends for July at 65° are not shown because of the large number of missing values. The long-term changes of GPH and total ozone (measured by Brewer#067) were also investigated and are presented in Fig. 8.

For the SZA of 65~~67~~° the irradiance at both wavelengths increased~~did not change~~ significantly in April, by 0.2%/year for 307.5 nm and 0.3%/year for 324 nm. In ~~any of~~ the same month the 307.5 nm irradiance at 45° also increased~~12 months of the year. The ratio decreased~~ significantly by 0.5%/year. The ratio changed in the same way for both SZAs and increased significantly in April (by ~0.35%/year), August and September (for both months by 0.2%/year), inversely following the negative ~~only in March, on average by -0.2%/year. In general, significant changes in~~ total ozone trends~~did not correspond to significant changes in the 307.5/324 nm ratio as expected~~. Total ozone decreased significantly in April (with an average rate of -0.4%/year), September (with an average rate of -0.2%/year), and October (with an average rate of -0.15%/year). A decrease in total ozone of -0.15%/year was also found for August, which however was not statistically significant~~However, for the SZA of 45° the 307.5/324 nm ratio increased significantly in April (by \~0.35%/year), August and September (for both months by 0.2%/year), inversely following the negative total ozone trends. Unfortunately, measurements for SZA=45° are available only for the period April – September at Rome due to the geographical position of the station~~.

It can be also perceived from Fig. 8 that trends in total ozone inversely followed~~follow~~ the trends of GPH, which is a strong indication that trends in total ozone are related with dynamical changes in troposphere and the lower stratosphere, which in turn shows that at least part of the trends was~~is~~ due to reduction of ozone at the lower stratosphere. Based on the results shown in Table 1, we estimated that about 50 - 70% of the long-term variability of total ozone and 307.5/324 nm ratio for different months (shown in Figures 7 and 8) is explained from the long-term variability of the GPH (shown in Figure 8). Many recent studies show that at the mid-latitudes of the northern hemisphere ozone increased~~increases~~ at the higher stratosphere and decreased~~decreases~~ at the lower stratosphere (Sofieva et al., 2017; Eleftheratos et al., 2020; Ball et al., 2019; Staehelin et al., 2001). Thus, an explanation of the results presented in Figures 6, 7 and 8 could be that the negative trends in lower stratospheric ozone dominated~~dominate~~ over positive trends in higher stratospheric ozone over~~at~~ Rome, resulting to an overall decrease in total ozone.

~~As the SZA increases the role of ozone at the middle and upper atmosphere becomes more important regarding the attenuation of the UV-B irradiance relative to ozone at the lower stratosphere.~~ Qualitative analysis of the monthly average ozone mixing ratio at different pressure levels between 100 and 3 hPa for the period of study over Rome (see Fig. S4~~S.2~~ in the supplement) confirmed that ozone increased~~increases~~ at lower pressure levels and decreased~~decreases~~ at higher pressure levels, which agrees with~~confirming~~ the findings~~finding~~ of previous studies. A detailed quantitative analysis is however out of the scope of the present study.

Figure 9 shows the trends of total ozone (from MERRA-2) and GPH in a wider spatial scale for the months of April and September for which statistically significant changes in total ozone were found. These plots suggest that changes over Rome were associated with~~are part of~~ changes that took~~taking~~ place over wider spatial scales. Although deriving trends of the total ozone from MERRA-2 is more uncertain than deriving trends from good quality ground-based measurements (Zhao et al., 2021), the graphs in Fig. 9 still show clearly that for the considered months (April and September), negative trends in total ozone coincided~~coincide~~ with positive trends in the GPH (which denotes shift of the tropopause towards higher altitudes) over wide areas. This was not the case for October for which changes in GPH did not coincide spatially with changes in total ozone. Although it is not safe to draw quantitative conclusions from this analysis, it indicates that dynamical changes in the atmosphere could possibly play a significant role in affecting ozone changes.

4 Summary and conclusions

In the present study the variability of solar UV irradiance at 307.5 nm and 324 nm, and the 307.5/324 nm ratio was analysed with respect to the variability of total ozone and GPH. Analyses were performed for the sites of Rome, Aosta, and Lampedusa, where long-term and high quality measurements of spectral irradiance and total ozone were~~are~~ available for the period 2006 – 2020. For Rome, analyses were also performed for 1996 – 2020.

Statistically significant anti-correlation was found between the year-to-year variability of GPH and total ozone for all three sites and all seasons of the year, which confirms the findings of studies reporting that variability in troposphere dynamics is strongly correlated with the variability in total ozone (e.g., Ball et al., 2019; Staehelin et al., 2001). The anti-correlation between total ozone and GPH induced a corresponding correlation between GPH and the 307.5 nm irradiance, and between GPH and the 307.5/324 nm ratio, which in most cases was significant. Correlation between GPH and the 307.5 nm irradiance (and GPH and the 307.5/324 nm ratio) was significant for all three sites but slightly stronger for Aosta relative to Rome and Lampedusa, which can be attributed (at least partially) to the fact that total ozone at higher latitudes generally reaches higher values. Thus, variations in GPH induced~~induce~~ larger absolute changes in total ozone and subsequently the UVB irradiance. At Rome, the GPH was also correlated significantly with the 324 nm irradiance (for anomalies in 2006 – 2020 the correlation coefficients for all seasons were ~ 0.4), possibly because changes in GPH were also linked to changes in clouds and aerosols.

The correlation between the GPH at Rome and Aosta was strong (~0.9) and showed that the two sites were frequently affected by the same synoptical systems. The strong correlation between GPH at the two sites corresponded to a strong correlation between total ozone (~0.67), the 307.5 nm irradiance (~0.74), and the 307.5/324 nm ratio (~0.75) at the two sites. ~~Statistically significant, but weak, correlation was also found for the 324 nm irradiance at Rome and Aosta (~0.26).~~ The correlation between GPH at Rome and Lampedusa was again strong and significant (~0.75), while the correlation between GPH at Lampedusa and Aosta was also statistically significant but weaker (~0.48). In both cases the correlation for total ozone was statistically significant, ~0.5 and ~0.4 respectively, but the correlation for the irradiance at 307.5 nm and the 307.5/324 nm ratio was weak, although in some cases it was statistically significant.

In addition to the fact that there was a~~The~~ strong correlation between the monthly anomalies in~~of~~ the GPH (and subsequently between the total ozone anomalies) in Aosta, Rome, and Lampedusa, the~~ was depicted to their~~ long-term trends in 2006 – 2020 in all three sites~~which~~ were toward the same direction (i.e, the GPH was increasing/decreasing at all sites) for most months of the year.

During 2006 – 2020 ~~However, the long-term trends of GPH and total ozone were not statistically significant in most cases. For SZA = 67°~~ the irradiance at 307.5 nm and 324 nm ~~did not change significantly in 2006 – 2020 at none of the three sites. However, the UV irradiance at 307.5 nm and 324 nm~~ increased significantly in April at Rome by~~ ~ ~~0.2 - 1~~7~~%/year depending on wavelength and~~, in Rome at~~ SZA and~~= 45°~~ possibly due to changes in aerosols and/or cloudiness. Positive, statistically significant trends were also found for Lampedusa for summer months, of 0.05%/year and 0.2%/year for 307.5 nm and 324 nm respectively, possibly driven by changes in aerosols. ~~clouds and/or aerosols.~~ At Aosta increases of ~0.7%/year~~similar magnitude~~ were found for the 307.5 nm and the 324 nm irradiances (only the latter was statistically significant) at 45° in August, which were possibly ~~mostly~~ driven mostly by changes in clouds and/or aerosols. Changes in troposphere dynamics in April and September, which took place on a wide spatial scale during 1996 – 2020, led to decreased total ozone over Rome, which in turn resulted to statistically significant increases in the 307.5/324 nm ratio at 45° and 65° SZA. The ratio also increased in August following the (not statistically significant) decrease in total ozone. In October the ratio increased, though not significantly, following the significant decrease in total ozone. In all above cases the changes in total ozone and the 307.5/324 nm ratio were in good agreement with the RAF (Radiation Amplification Factor) of ~1 for SZAs 45° – 65° reported by di Sarra et al., (2002).~~The increase in UV irradiance in August at Aosta coincided with a statistically significant increase in the GPH, which was not however the case for the changes in UV irradiance in April at Rome. Changes possibly driven by clouds and/or aerosols were found at SZA = 45° and not at SZA = 67°, which can be explained by the fact that clouds and aerosols, both have a stronger effect on the direct relative to the diffuse component of the solar irradiance. The direct component becomes less significant as the SZA decreases, leading to less significant trends of the irradiance.~~

~~The large, statistically significant increase of total ozone at Aosta in November (during 2006 - 2020), by ~0.8%/year induced a negative trend of ~1%/year in the 307.5/324 nm ratio at 67° SZA, which was not however statistically significant. According to di Sarra et al., (2002) a change of ~1% in total ozone at that SZA should induce a change of 2 – 3% in the irradiance at 307.5 nm. The difference between the observed and the expected change in the irradiance at 307.5 nm can be attributed to the fact that ozone changed differently at different levels in the atmosphere.~~

~~Changes in troposphere dynamics in April and September, which took place on a wide spatial scale during 1996 – 2020, led to decreased total ozone over Rome, which in turn resulted to statistically significant increases in the 307.5/324 nm ratio at 45° SZA. Total ozone also decreased in October, although no statistically significant change of GPH was found, resulting again in a significant increase in the 307.5/324 nm ratio at 45° SZA. In all above cases the changes in total ozone and the 307.5/324 nm ratio were in good agreement with the RAF (Radiation Amplification Factor) reported by (di Sarra et al., 2002). The 307.5/324 nm ratio at 67° SZA decreased significantly in March at the same site and for the same period, although no statistically significant change of total ozone was found. In general, the results for Rome for 1996 – 2020 can be explained by the decreasing ozone in the lower stratosphere and the increasing ozone in the upper stratosphere. The two processes are competitive to each other regarding their effect on UVB irradiance, with a stronger influence on UVB of the lower stratospheric ozone decrease at the small SZA.~~

Concluding, the present study shows that total ozone over the Northern part of Italy decreased in the last decades mainly because of changes in the dynamics of the troposphere, the effect of which is dominant over the ozone recovery in the upper stratosphere. In particular months, total ozone decrease induced reduction of the UVB irradiance over Rome during 1996 - 2020. In 2006 – 2020 the levels of UV irradiance at Aosta, Rome, and Lampedusa generally increased due to changes in clouds and/or aerosols. This~~The overall decrease of total ozone has a stronger effect on the irradiance at 307.5 nm at smaller SZAs, since the relative contribution of upper stratospheric ozone to the attenuation of UVB irradiance becomes more significant with increasing SZA. Changes in cloudiness and/or aerosols also may alter the levels of UV irradiance at Aosta and Rome. More robust statistical analyses and radiative transfer modelling are necessary in order to quantify the relative contribution of different factors to the short- and long-term changes of the surface solar UV irradiance in Italy, which however is out of the scope of the present study. In any case, this~~ study shows very clearly that changes in the troposphere can play a key role in the formulation of the levels of total ozone and surface UV radiation. Synoptical circulation patterns and changes were found to be linked, not only to changes in total ozone, but also in UVB, and in some cases in UVA, irradiance. Since significant changes~~change~~ in the dynamics of the troposphere are projected for the future (e.g., IPCC, 2013), thorough investigation is necessary in order to determine their possible impact on the future levels of surface solar UV radiation.

Data availability

The ground based total ozone and spectral UV measurements used in this study can be made available upon request to the PIs of the stations. All re-analysis and satellite products used in the present study have been downloaded from the Giovanni platform maintained by National Aeronautics and Space Administration (NASA) (https://giovanni.gsfc.nasa.gov/giovanni/).

Author contributions

IF and HD conceptualized the paper and~~.~~ IF led the paper preparation. IF, HD and AMS performed the data analysis. HD is responsible for the ground-based total ozone and spectral UV measurements in Aosta. AMS is responsible for the ground-based total ozone and spectral UV measurements in Rome. AdS, DM, and DS are responsible for the ground-based total ozone and spectral UV measurements in Lampedusa. All authors contributed to the writing of the paper.

Acknowledgements

Measurements at Lampedusa~~Lampeudusa~~ were maintained thanks to support from the Italian Ministry for University and Research through projects NextData and Marine Hazard, and the Italian Space Agency through the PRISCAV project. Observations also contribute to the Aerosol, Clouds and Trace Gases Research Infrastructure. Contributions by Francesco Monteleone and Giandomenico Pace are gratefully~~grate-fully~~ acknowledged.~~-~~ Part of the analyses used in this paper were produced with the Giovanni online data system, developed and maintained by the NASA GES DISC.

References

AIRS project: Aqua/AIRS L3 Monthly Standard Physical Retrieval (AIRS-only) 1 degree x 1 degree V7.0, Greenbelt, MD, USA, Goddard Earth Sciences Data and Information Services Center (GES DISC), Accessed: 25/06/2021, https://doi.org/10.5067/UBENJB9D3T2H, 2019.

Angell, J. K. and Korshover, J.: Quasi-biennial variations in temperature, total ozone, and tropopause height, J. Atmos. Sci., 21, 479–492, 1964.

Bais, A. F., Zerefos, C. S., Meleti, C., Ziomas, I. C., and Tourpali, K.: Spectral measurements of solar UVB radiation and its relations to total ozone, SO2, and clouds, J. Geophys. Res. Atmos., 98, 5199–5204, https://doi.org/https://doi.org/10.1029/92JD02904, 1993.

Bais, A. F., Gardiner, B. G., Slaper, H., Blumthaler, M., Bernhard, G., McKenzie, R., Webb, A. R., Seckmeyer, G., Kjeldstad, B., Koskela, T., Kirsch, P. J., Gröbner, J., Kerr, J. B., Kazadzis, S., Leszczynski, K., Wardle, D., Josefsson, W., Brogniez, C., Gillotay, D., Reinen, H., Weihs, P., Svenoe, T., Eriksen, P., Kuik, F., and Redondas, A.: SUSPEN intercomparison of ultraviolet spectroradiometers, J. Geophys. Res. Atmos., 106, 12509–12525, https://doi.org/https://doi.org/10.1029/2000JD900561, 2001.

Ball, W. T., Alsing, J., Mortlock, D. J., Staehelin, J., Haigh, J. D., Peter, T., Tummon, F., Stübi, R., Stenke, A., Anderson, J., Bourassa, A., Davis, S. M., Degenstein, D., Frith, S., Froidevaux, L., Roth, C., Sofieva, V., Wang, R., Wild, J., Yu, P., Ziemke, J. R., and Rozanov, E. V: Evidence for a continuous decline in lower stratospheric ozone offsetting ozone layer recovery, 18, 1379–1394, https://doi.org/10.5194/acp-18-1379-2018, 2018.

Ball, W. T., Alsing, J., Staehelin, J., Davis, S. M., Froidevaux, L., and Peter, T.: Stratospheric ozone trends for 1985–2018:

sensitivity to recent large variability, 19, 12731–12748, https://doi.org/10.5194/acp-19-12731-2019, 2019.

Bernhard, G. and Stierle, S.: Trends of UV Radiation in Antarctica, https://doi.org/10.3390/atmos11080795, 2020.

Bernhard, G. H., Fioletov, V. E., Grooß, J.-U., Ialongo, I., Johnsen, B., Lakkala, K., Manney, G. L., Müller, R., and Svendby, T.: Record-Breaking Increases in Arctic Solar Ultraviolet Radiation Caused by Exceptionally Large Ozone Depletion in 2020, Geophys. Res. Lett., 47, e2020GL090844, https://doi.org/https://doi.org/10.1029/2020GL090844, 2020.

De Bock, V., De Backer, H., Van Malderen, R., Mangold, A., and Delcloo, A.: Relations between erythemal UV dose, global solar radiation, total ozone column and aerosol optical depth at Uccle, Belgium, 14, 12251–12270, https://doi.org/10.5194/acp-14-12251-2014, 2014.

Bornman, J. F., Barnes, P. W., Robson, T. M., Robinson, S. A., Jansen, M. A. K., Ballaré, C. L., and Flint, S. D.: Linkages between stratospheric ozone, UV radiation and climate change and their implications for terrestrial ecosystems, Photochem. Photobiol. Sci., 18, 681–716, https://doi.org/10.1039/C8PP90061B, 2019.

Caldwell, M. M., Björn, L. O., Bornman, J. F., Flint, S. D., Kulandaivelu, G., Teramura, A. H., and Tevini, M.: Effects of increased solar ultraviolet radiation on terrestrial ecosystems, J. Photochem. Photobiol. B Biol., 46, 40–52, https://doi.org/https://doi.org/10.1016/S1011-1344(98)00184-5, 1998.

Calkins, J. and Thordardottir, T.: The ecological significance of solar UV radiation on aquatic organisms, Nature, 283, 563–566, https://doi.org/10.1038/283563a0, 1980.

Casale, G. R., Meloni, D., Miano, S., Palmieri, S., Siani, A. M., and Cappellani, F.: Solar UV-B irradiance and total ozone in Italy: Fluctuations and trends, J. Geophys. Res. Atmos., 105, 4895–4901, https://doi.org/https://doi.org/10.1029/1999JD900303, 2000.

Chubarova, N. E., Pastukhova, A. S., Zhdanova, E. Y., Volpert, E. V, Smyshlyaev, S. P., and Galin, V. Y.: Effects of Ozone and Clouds on Temporal Variability of Surface UV Radiation and UV Resources over Northern Eurasia Derived from Measurements and Modeling, https://doi.org/10.3390/atmos11010059, 2020.

Dameris, M., Loyola, D. G., Nützel, M., Coldewey-Egbers, M., Lerot, C., Romahn, F., and van Roozendael, M.: Record low ozone values over the Arctic in boreal spring 2020, 21, 617–633, https://doi.org/10.5194/acp-21-617-2021, 2021.

Diémoz, H., Siani, A. M., Casale, G. R., di Sarra, A., Serpillo, B., Petkov, B., Scaglione, S., Bonino, A., Facta, S., Fedele, F., Grifoni, D., Verdi, L., and Zipoli, G.: First national intercomparison of solar ultraviolet radiometers in Italy, 4, 1689–1703, https://doi.org/10.5194/amt-4-1689-2011, 2011.

di Sarra, A., Cacciani, M., Chamard, P., Cornwall, C., DeLuisi, J. J., Di Iorio, T., Disterhoft, P., Fiocco, G., Fuá, D., and Monteleone, F.: Effects of desert dust and ozone on the ultraviolet irradiance at the Mediterranean island of Lampedusa during PAUR II, J. Geophys. Res. Atmos., 107, PAU 2-1-PAU 2-14, https://doi.org/https://doi.org/10.1029/2000JD000139, 2002.

di Sarra, A., Fua, D., Cacciani, M., Di Iorio, T., Disterhoft, P., Meloni, D., Monteleone, F., Piacentino, S., and Sferlazzo, D.: Determination of ultraviolet cosine-corrected irradiances and aerosol optical thickness by combined measurements with a Brewer spectrophotometer and a multifilter rotating shadowband radiometer, Appl. Opt., 47, 6142–6150, https://doi.org/10.1364/AO.47.006142, 2008.

Dobson, G. M. B., Brewer, A. W., and Cwilong, B. M.: Meteorology of the lower stratosphere, Proc. R. Soc. London, Ser. A, 185, 144–175, 1946.Eleftheratos, K., Kazadzis, S., Zerefos, C. S., Tourpali, K., Meleti, C., Balis, D., Zyrichidou, I., Lakkala, K., Feister, U., Koskela, T., Heikkilä, A., and Karhu, J. M.: Ozone and Spectroradiometric UV Changes in the Past 20 Years over High Latitudes, 53, 117–125, https://doi.org/10.1080/07055900.2014.919897, 2015.

Eleftheratos, K., Kapsomenakis, J., Zerefos, C. S., Bais, A. F., Fountoulakis, I., Dameris, M., Jöckel, P., Haslerud, A. S., Godin-Beekmann, S., Steinbrecht, W., Petropavlovskikh, I., Brogniez, C., Leblanc, T., Liley, J. B., Querel, R., and Swart, D. P. J.: Possible Effects of Greenhouse Gases to Ozone Profiles and DNA Active UV-B Irradiance at Ground Level, https://doi.org/10.3390/atmos11030228, 2020.

Fioletov, V. E., Kerr, J. B., McElroy, C. T., Wardle, D. I., Savastiouk, V., and Grajnar, T. S.: The Brewer reference triad, Geophys. Res. Lett., 32, https://doi.org/https://doi.org/10.1029/2005GL024244, 2005.

Fitzka, M., Simic, S., and Hadzimustafic, J.: Trends in spectral UV radiation from long-term measurements at Hoher Sonnblick, Austria, Theor. Appl. Climatol., 110, 585–593, https://doi.org/10.1007/s00704-012-0684-0, 2012.

Fountoulakis, I., Bais, A. F., Fragkos, K., Meleti, C., Tourpali, K., and Zempila, M. M.: Short- and long-term variability of spectral solar UV irradiance at Thessaloniki, Greece: effects of changes in aerosols, total ozone and clouds, 16, 2493–2505, https://doi.org/10.5194/acp-16-2493-2016, 2016.

Fountoulakis, I., Zerefos, C. S., Bais, A. F., Kapsomenakis, J., Koukouli, M.-E., Ohkawara, N., Fioletov, V., De Backer, H., Lakkala, K., Karppinen, T., and Webb, A. R.: Twenty-five years of spectral UV-B measurements over Canada, Europe and Japan: Trends and effects from changes in ozone, aerosols, clouds, and surface reflectivity, Comptes Rendus Geosci., 350, 393–402, https://doi.org/https://doi.org/10.1016/j.crte.2018.07.011, 2018.

Fountoulakis, I., Diémoz, H., Siani, A. M., Hülsen, G., and Gröbner, J.: Monitoring of solar spectral ultraviolet irradiance in Aosta, Italy, Earth Syst. Sci. Data, 12, 2787–2810, https://doi.org/10.5194/essd-12-2787-2020, 2020a.

Fountoulakis, I., Diémoz, H., Siani, A.-M., Laschewski, G., Filippa, G., Arola, A., Bais, A. F., De Backer, H., Lakkala, K., Webb, A. R., De Bock, V., Karppinen, T., Garane, K., Kapsomenakis, J., Koukouli, M.-E., and Zerefos, C. S.: Solar UV Irradiance in a Changing Climate: Trends in Europe and the Significance of Spectral Monitoring in Italy, https://doi.org/10.3390/environments7010001, 2020b.

Fragkos, K., Bais, A. F., Fountoulakis, I., Balis, D., Tourpali, K., Meleti, C., and Zanis, P.: Extreme total column ozone events and effects on UV solar radiation at Thessaloniki, Greece, Theor. Appl. Climatol., 126, 505–517, https://doi.org/10.1007/s00704-015-1562-3, 2016.

Garane, K., Bais, A. F., Kazadzis, S., Kazantzidis, A., and Meleti, C.: Monitoring of UV spectral irradiance at Thessaloniki (1990–2005): data re-evaluation and quality control, Ann. Geophys., 24, 3215–3228, https://doi.org/10.5194/angeo-24-3215-2006, 2006.

GMAO: No Title, Glob. Model. Assim. Off. (GMAO), MERRA-2 tavgM_2d_slv_Nx 2d,Monthly mean,Time-Averaged,Single-Level,Assimilation,Single-Level Diagnostics V5.12.4, Greenbelt, MD, USA, Goddard Earth Sci. Data Inf. Serv. Cent. (GES DISC), https://doi.org/10.5067/AP1B0BA5PD2K, 2015a.

GMAO: No Title, Glob. Model. Assim. Off. (GMAO), MERRA-2 instM_3d_ana_Np 3d,Monthly mean,Instantaneous,Pressure-Level,Analysis,Analyzed Meteorol. Fields V5.12.4, Greenbelt, MD, USA, Goddard Earth Sci. Data Inf. Serv. Cent. (GES DIS, https://doi.org/10.5067/V92O8XZ30XBI, 2015b.

Griggs, M.: Absorption Coefficients of Ozone in the Ultraviolet and Visible Regions, J. Chem. Phys., 49, 857–859, https://doi.org/10.1063/1.1670152, 1968.

Gröbner, J. and Sperfeld, P.: Direct traceability of the portable QASUME irradiance scale to the primary irradiance standard of the PTB, 42, 134–139, https://doi.org/10.1088/0026-1394/42/2/008, 2005.

Häder, D.-P., Kumar, H. D., Smith, R. C., and Worrest, R. C.: Effects on aquatic ecosystems, J. Photochem. Photobiol. B Biol., 46, 53–68, https://doi.org/https://doi.org/10.1016/S1011-1344(98)00185-7, 1998.

Hoinka, K.P., Claude H., and Köhler, U.: On the correlation between tropopause pressure and ozone above Central Europe, Geophys. Res. Lett., 23, 1753-1756, 1996.

Hooke, R. J., Higlett, M. P., Hunter, N., and O’Hagan, J. B.: Long term variations in erythema effective solar UV at Chilton, UK, from 1991 to 2015, Photochem. Photobiol. Sci., 16, 1596–1603, https://doi.org/10.1039/C7PP00053G, 2017.

Hülsen, G., Gröbner, J., Nevas, S., Sperfeld, P., Egli, L., Porrovecchio, G., and Smid, M.: Traceability of solar UV measurements using the Qasume reference spectroradiometer., Appl. Opt., 55, 7265–7275, https://doi.org/10.1364/AO.55.007265, 2016.

Ialongo, I., Buchard, V., Brogniez, C., Casale, G. R., and Siani, A. M.: Aerosol Single Scattering Albedo retrieval in the UV range: an application to OMI satellite validation, 10, 331–340, https://doi.org/10.5194/acp-10-331-2010, 2010.

Di Ianni, A., Costabile, F., Barnaba, F., Di Liberto, L., Weinhold, K., Wiedensohler, A., Struckmeier, C., Drewnick, F., and Gobbi, G. P.: Black Carbon Aerosol in Rome (Italy): Inference of a Long-Term (2001–2017) Record and Related Trends from AERONET Sun-Photometry Data, https://doi.org/10.3390/atmos9030081, 2018.

Inn, E. C. Y. and Tanaka, Y.: Absorption Coefficient of Ozone in the Ultraviolet and Visible Regions, J. Opt. Soc. Am., 43, 870–873, https://doi.org/10.1364/JOSA.43.000870, 1953.

IPCC: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, 2013.

Kazadzis, S., Kouremeti, N., Bais, A., Kazantzidis, A., and Meleti, C.: Aerosol forcing efficiency in the UVA region from spectral solar irradiance measurements at an urban environment, Ann. Geophys., 27, 2515–2522, https://doi.org/10.5194/angeo-27-2515-2009, 2009.

Kerr, J. B.: The Brewer Spectrophotometer BT - UV Radiation in Global Climate Change: Measurements, Modeling and Effects on Ecosystems, edited by: Gao, W., Slusser, J. R., and Schmoldt, D. L., Springer Berlin Heidelberg, Berlin, Heidelberg, 160–191, https://doi.org/10.1007/978-3-642-03313-1_6, 2010.

Kerr, J. B. and McElroy, C. T.: Evidence for Large Upward Trends of Ultraviolet-B Radiation Linked to Ozone Depletion, Science (80-.)., 262, 1032 LP – 1034, https://doi.org/10.1126/science.262.5136.1032, 1993.

Lakkala, K., Heikkilä, A., Kärhä, P., Ialongo, I., Karppinen, T., Karhu, J. M., Lindfors, A. V., and Meinander, O.: 25 years of spectral UV measurements at Sodankylä, AIP Conf. Proc., 1810, 110006, https://doi.org/10.1063/1.4975568, 2017.

Madronich, S., McKenzie, R. L., Björn, L. O., and Caldwell, M. M.: Changes in biologically active ultraviolet radiation reaching the Earth’s surface, J. Photochem. Photobiol. B Biol., 46, 5–19, https://doi.org/https://doi.org/10.1016/S1011-1344(98)00182-1, 1998.

Manara, V., Beltrano, M. C., Brunetti, M., Maugeri, M., Sanchez-Lorenzo, A., Simolo, C., and Sorrenti, S.: Sunshine duration variability and trends in Italy from homogenized instrumental time series (1936–2013), J. Geophys. Res. Atmos., 120, 3622–3641, https://doi.org/https://doi.org/10.1002/2014JD022560, 2015.

Manara, V., Brunetti, M., Celozzi, A., Maugeri, M., Sanchez-Lorenzo, A., and Wild, M.: Detection of dimming/brightening in Italy from homogenized all-sky and clear-sky surface solar radiation records and underlying causes (1959–2013), 16, 11145–11161, https://doi.org/10.5194/acp-16-11145-2016, 2016.

Manney, G. L., Santee, M. L., Rex, M., Livesey, N. J., Pitts, M. C., Veefkind, P., Nash, E. R., Wohltmann, I., Lehmann, R., Froidevaux, L., Poole, L. R., Schoeberl, M. R., Haffner, D. P., Davies, J., Dorokhov, V., Gernandt, H., Johnson, B., Kivi, R., Kyrö, E., Larsen, N., Levelt, P. F., Makshtas, A., McElroy, C. T., Nakajima, H., Parrondo, M. C., Tarasick, D. W., von der Gathen, P., Walker, K. A., and Zinoviev, N. S.: Unprecedented Arctic ozone loss in 2011, Nature, 478, 469–475, https://doi.org/10.1038/nature10556, 2011.

Masiol, M., Squizzato, S., Formenton, G., Harrison, R. M., and Agostinelli, C.: Air quality across a European hotspot: Spatial gradients, seasonality, diurnal cycles and trends in the Veneto region, NE Italy, Sci. Total Environ., 576, 210–224, https://doi.org/https://doi.org/10.1016/j.scitotenv.2016.10.042, 2017.

Mateos, D., di Sarra, A., Meloni, D., Di Biagio, C., and Sferlazzo, D. M.: Experimental determination of cloud influence on the spectral UV irradiance and implications for biological effects, J. Atmos. Solar-Terrestrial Phys., 73, 1739–1746, https://doi.org/https://doi.org/10.1016/j.jastp.2011.04.003, 2011.

Mateos, D., di Sarra, A., Bilbao, J., Meloni, D., Pace, G., de Miguel, A., and Casasanta, G.: Spectral attenuation of global and diffuse UV irradiance and actinic flux by clouds, Q. J. R. Meteorol. Soc., 141, 109–113, https://doi.org/https://doi.org/10.1002/qj.2341, 2015.

McConnell, J. C., Henderson, G. S., Barrie, L., Bottenheim, J., Niki, H., Langford, C. H., and Templeton, E. M. J.: Photochemical bromine production implicated in Arctic boundary-layer ozone depletion, Nature, 355, 150–152, https://doi.org/10.1038/355150a0, 1992.

McKenzie, R., Bernhard, G., Liley, B., Disterhoft, P., Rhodes, S., Bais, A., Morgenstern, O., Newman, P., Oman, L., Brogniez, C., and Simic, S.: Success of Montreal Protocol Demonstrated by Comparing High-Quality UV Measurements with “World Avoided” Calculations from Two Chemistry-Climate Models, Sci. Rep., 9, 12332, https://doi.org/10.1038/s41598-019-48625-z, 2019.

Mckinlay, A. F. and Diffey, B. L.: A reference action spectrum for ultraviolet induced erythema in human skin., 6, 17–22, 1987.

Meloni, D., Casale, G. R., Siani, A. M., Palmieri, S., and Cappellani, F.: Solar UV Dose Patterns in Italy, Photochem. Photobiol., 71, 681–690, https://doi.org/https://doi.org/10.1562/0031-8655(2000)0710681SUDPII2.0.CO2, 2000.

Meloni, D., di Sarra, A., Monteleone, F., Pace, G., Piacentino, S., and Sferlazzo, D. M.: Seasonal transport patterns of intense Saharan dust events at the Mediterranean island of Lampedusa, Atmos. Res., 88, 134–148, https://doi.org/https://doi.org/10.1016/j.atmosres.2007.10.007, 2008.

Monge-Sanz, B., Casale, G. R., Palmieri, S., and Siani, A.: An investigation on total ozone over western Mediterranean, Nuovo Cim. C, 26, 2003.

Morgenstern, O., Braesicke, P., Hurwitz, M. M., O’Connor, F. M., Bushell, A. C., Johnson, C. E., and Pyle, J. A.: The World Avoided by the Montreal Protocol, Geophys. Res. Lett., 35, https://doi.org/https://doi.org/10.1029/2008GL034590, 2008.

Neu, J. L., Flury, T., Manney, G. L., Santee, M. L., Livesey, N. J., and Worden, J.: Tropospheric ozone variations governed by changes in stratospheric circulation, Nat. Geosci., 7, 340–344, https://doi.org/10.1038/ngeo2138, 2014.

Newman, P. A. and McKenzie, R.: UV impacts avoided by the Montreal Protocol, Photochem. Photobiol. Sci., 10, 1152–1160, https://doi.org/10.1039/C0PP00387E, 2011.

Orza, J. A. G. and Perrone, M. R.: Trends in the aerosol load properties over south eastern Italy, IOP Conf. Ser. Earth Environ. Sci., 28, 12011, https://doi.org/10.1088/1755-1315/28/1/012011, 2015.

Pandey, P., Gillotay, D., and Depiesse, C.: Climatology of Ultra Violet (UV) irradiance as measured through the Belgian ground-based monitoring network during the time period of 1995-2014, in: EGU General Assembly Conference Abstracts, EPSC2016-13080, 2016.

Paul, N. D. and Gwynn-Jones, D.: Ecological roles of solar UV radiation: towards an integrated approach, Trends Ecol. Evol., 18, 48–55, https://doi.org/https://doi.org/10.1016/S0169-5347(02)00014-9, 2003.

Petkov, B. H., Vitale, V., Tomasi, C., Siani, A. M., Seckmeyer, G., Webb, A. R., Smedley, A. R. D., Casale, G. R., Werner, R., Lanconelli, C., Mazzola, M., Lupi, A., Busetto, M., Diémoz, H., Goutail, F., Köhler, U., Mendeva, B. D., Josefsson, W., Moore, D., Bartolomé, M. L., Moreta González, J. R., Mišaga, O., Dahlback, A., Tóth, Z., Varghese, S., De Backer, H., Stübi, R., and Vaníček, K.: Response of the ozone column over Europe to the 2011 Arctic ozone depletion event according to ground-based observations and assessment of the consequent variations in surface UV irradiance, Atmos. Environ., 85, 169–178, https://doi.org/https://doi.org/10.1016/j.atmosenv.2013.12.005, 2014.

Pfeifroth, U., Sanchez-Lorenzo, A., Manara, V., Trentmann, J., and Hollmann, R.: Trends and Variability of Surface Solar Radiation in Europe Based On Surface- and Satellite-Based Data Records, J. Geophys. Res. Atmos., 123, 1735–1754, https://doi.org/https://doi.org/10.1002/2017JD027418, 2018.

Pommereau, J.-P., Goutail, F., Pazmino, A., Lefèvre, F., Chipperfield, M. P., Feng, W., Van Roozendael, M., Jepsen, N., Hansen, G., Kivi, R., Bognar, K., Strong, K., Walker, K., Kuzmichev, A., Khattatov, S., and Sitnikova, V.: Recent Arctic ozone depletion: Is there an impact of climate change?, Comptes Rendus Geosci., 350, 347–353, https://doi.org/https://doi.org/10.1016/j.crte.2018.07.009, 2018.

Putaud, J. P., Cavalli, F., Martins dos Santos, S., and Dell’Acqua, A.: Long-term trends in aerosol optical characteristics in the

Po Valley, Italy, 14, 9129–9136, https://doi.org/10.5194/acp-14-9129-2014, 2014.

Raptis, I.-P., Eleftheratos, K., Kazadzis, S., Kosmopoulos, P., Papachristopoulou, K., and Solomos, S.: The Combined Effect of Ozone and Aerosols on Erythemal Irradiance in an Extremely Low Ozone Event during May 2020, https://doi.org/10.3390/atmos12020145, 2021.

Redondas, A. and Rodriguez-Franco, J.: Eighth Intercomparison Campaign of the Regional Brewer Calibration Center for Europe (RBCC-E), GAW Report- No. 223, WMO - GAW report, Geneva, Switzeland, 2015.

Redondas, A., Carreño, V., León-Luis, S. F., Hernández-Cruz, B., López-Solano, J., Rodriguez-Franco, J. J., Vilaplana, J. M., Gröbner, J., Rimmer, J., Bais, A. F., Savastiouk, V., Moreta, J. R., Boulkelia, L., Jepsen, N., Wilson, K. M., Shirotov, V., and Karppinen, T.: EUBREWNET RBCC-E Huelva 2015 Ozone Brewer Intercomparison, 18, 9441–9455, https://doi.org/10.5194/acp-18-9441-2018, 2018.

Reed, R.J.: The role of vertical motions in ozone-weather relatinships, J. Meteorol., 7, 263-267, 1950.

Rizza, U., Mancinelli, E., Morichetti, M., Passerini, G., and Virgili, S.: Aerosol Optical Depth of the Main Aerosol Species over Italian Cities Based on the NASA/MERRA-2 Model Reanalysis, https://doi.org/10.3390/atmos10110709, 2019.

Siani, A., Casale, G. R., and Galliani, A.: Investigation on a low ozone episode at the end of November 2000 and its effect on ultraviolet radiation, Opt. Eng., 41, 3082–3089, https://doi.org/10.1117/1.1516821, 2002.

Siani, A. M., Frasca, F., Scarlatti, F., Religi, A., Diémoz, H., Casale, G. R., Pedone, M., and Savastiouk, V.: Examination on total ozone column retrievals by Brewer spectrophotometry using different processing software, 11, 5105–5123, https://doi.org/10.5194/amt-11-5105-2018, 2018.

Sofieva, V. F., Kyrölä, E., Laine, M., Tamminen, J., Degenstein, D., Bourassa, A., Roth, C., Zawada, D., Weber, M., Rozanov, A., Rahpoe, N., Stiller, G., Laeng, A., von Clarmann, T., Walker, K. A., Sheese, P., Hubert, D., van Roozendael, M., Zehner, C., Damadeo, R., Zawodny, J., Kramarova, N., and Bhartia, P. K.: Merged SAGE II, Ozone_cci and OMPS ozone profile dataset and evaluation of ozone trends in the stratosphere, 17, 12533–12552, https://doi.org/10.5194/acp-17-12533-2017, 2017.

Solomon, S., Garcia, R. R., Rowland, F. S., and Wuebbles, D. J.: On the depletion of Antarctic ozone, Nature, 321, 755–758, https://doi.org/10.1038/321755a0, 1986.

Solomon, S., Ivy, D. J., Kinnison, D., Mills, M. J., Neely, R. R., and Schmidt, A.: Emergence of healing in the Antarctic ozone layer, Science (80-.)., 353, 269 LP – 274, https://doi.org/10.1126/science.aae0061, 2016.

Staehelin, J., Harris, N. R. P., Appenzeller, C., and Eberhard, J.: Ozone trends: A review, Rev. Geophys., 39, 231–290, https://doi.org/https://doi.org/10.1029/1999RG000059, 2001.

Steinbrecht, W., Claude, H., Köhler, U., and Hoinka, K. P.: Correlations between tropopause height and total ozone: Implications for long-term changes, J. Geophys. Res. Atmos., 103, 19183–19192, https://doi.org/https://doi.org/10.1029/98JD01929, 1998.

Steinbrecht, W., Froidevaux, L., Fuller, R., Wang, R., Anderson, J., Roth, C., Bourassa, A., Degenstein, D., Damadeo, R., Zawodny, J., Frith, S., McPeters, R., Bhartia, P., Wild, J., Long, C., Davis, S., Rosenlof, K., Sofieva, V., Walker, K., Rahpoe, N., Rozanov, A., Weber, M., Laeng, A., von Clarmann, T., Stiller, G., Kramarova, N., Godin-Beekmann, S., Leblanc, T., Querel, R., Swart, D., Boyd, I., Hocke, K., Kämpfer, N., Maillard Barras, E., Moreira, L., Nedoluha, G., Vigouroux, C., Blumenstock, T., Schneider, M., García, O., Jones, N., Mahieu, E., Smale, D., Kotkamp, M., Robinson, J., Petropavlovskikh, I., Harris, N., Hassler, B., Hubert, D., and Tummon, F.: An update on ozone profile trends for the period 2000 to 2016, 17, 10675–10690, https://doi.org/10.5194/acp-17-10675-2017, 2017.

Svendby, T., Hansen, G. H., Bäcklund, A., and Dahlback, A.: No Title, Oslo, Norway, 39 pp., 2018.

Szeląg, M. E., Sofieva, V. F., Degenstein, D., Roth, C., Davis, S., and Froidevaux, L.: Seasonal stratospheric ozone trends over 2000–2018 derived from several merged data sets, 20, 7035–7047, https://doi.org/10.5194/acp-20-7035-2020, 2020.

Vanicek, K.: Differences between ground Dobson, Brewer and satellite TOMS-8, GOME-WFDOAS total ozone observations at Hradec kralove, Czech, Atmos. Chem. Phys., 6, https://doi.org/10.5194/acpd-6-5839-2006, 2006.

Varotsos, C., Cartalis, C., Vlamakis, A., Tzanis, C., and Keramitsoglou, I.: The long-term coupling between column ozone and tropopause properties, J. Clim., 17, 3843–3854, 2004.

Varotsos, C. A., Cracknell, A. P., and Tzanis, C.: The exceptional ozone depletion over the Arctic in January–March 2011, Remote Sens. Lett., 3, 343–352, https://doi.org/10.1080/01431161.2011.597792, 2012.

Vaughan, G. and Price, J. D.: On the relation between total ozone and meteorology, Q. J. R. Meteorol. Soc., 117, 1281–1298, https://doi.org/https://doi.org/10.1002/qj.49711750208, 1991.

Wargan, K., Orbe, C., Pawson, S., Ziemke, J. R., Oman, L. D., Olsen, M. A., Coy, L., and Emma Knowland, K.: Recent Decline in Extratropical Lower Stratospheric Ozone Attributed to Circulation Changes, Geophys. Res. Lett., 45, 5166–5176, https://doi.org/https://doi.org/10.1029/2018GL077406, 2018.

Weber, M., Dikty, S., Burrows, J. P., Garny, H., Dameris, M., Kubin, A., Abalichin, J., and Langematz, U.: The Brewer-Dobson circulation and total ozone from seasonal to decadal time scales, 11, 11221–11235, https://doi.org/10.5194/acp-11-11221-2011, 2011.

Weber, M., Coldewey-Egbers, M., Fioletov, V. E., Frith, S. M., Wild, J. D., Burrows, J. P., Long, C. S., and Loyola, D.: Total ozone trends from 1979 to 2016 derived from five merged observational datasets – the emergence into ozone recovery, 18, 2097–2117, https://doi.org/10.5194/acp-18-2097-2018, 2018.

Williamson, C. E., Neale, P. J., Hylander, S., Rose, K. C., Figueroa, F. L., Robinson, S. A., Häder, D.-P., Wängberg, S.-Å., and Worrest, R. C.: The interactive effects of stratospheric ozone depletion, UV radiation, and climate change on aquatic ecosystems, Photochem. Photobiol. Sci., 18, 717–746, https://doi.org/10.1039/C8PP90062K, 2019.

Wohltmann, I., von der Gathen, P., Lehmann, R., Maturilli, M., Deckelmann, H., Manney, G. L., Davies, J., Tarasick, D., Jepsen, N., Kivi, R., Lyall, N., and Rex, M.: Near-Complete Local Reduction of Arctic Stratospheric Ozone by Severe Chemical Loss in Spring 2020, Geophys. Res. Lett., 47, e2020GL089547, https://doi.org/https://doi.org/10.1029/2020GL089547, 2020.

Zerefos, C. S., Bais, A. F., Meleti, C., and Ziomas, I. C.: A note on the recent increase of Solar UV-B radiation over northern middle latitudes, Geophys. Res. Lett., 22, 1245–1247, https://doi.org/https://doi.org/10.1029/95GL01187, 1995.

Zhang, H., Wang, J., Castro García, L., Zeng, J., Dennhardt, C., Liu, Y., and Krotkov, N. A.: Surface erythemal UV irradiance in the continental United States derived from ground-based and OMI observations: quality assessment, trend analysis and sampling issues, 19, 2165–2181, https://doi.org/10.5194/acp-19-2165-2019, 2019.

Zhao, X., Fioletov, V., Brohart, M., Savastiouk, V., Abboud, I., Ogyu, A., Davies, J., Sit, R., Lee, S. C., Cede, A., Tiefengraber, M., Müller, M., Griffin, D., and McLinden, C.: The world Brewer reference triad – updated performance assessment and new double triad, 2020, 1–34, https://doi.org/10.5194/amt-2020-324, 2020.

Zhao, X., Fioletov, V., Brohart, M., Savastiouk, V., Abboud, I., Ogyu, A., Davies, J., Sit, R., Lee, S. C., Cede, A., Tiefengraber, M., Müller, M., Griffin, D., and McLinden, C.: The world Brewer reference triad – updated performance assessment and new double triad, 14, 2261–2283, https://doi.org/10.5194/amt-14-2261-2021, 2021.

Figures

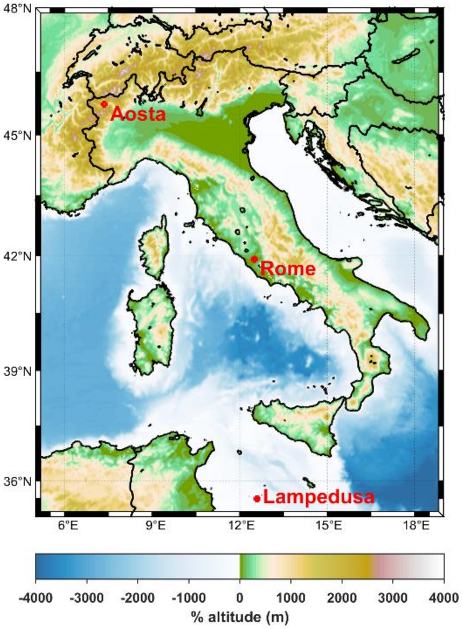
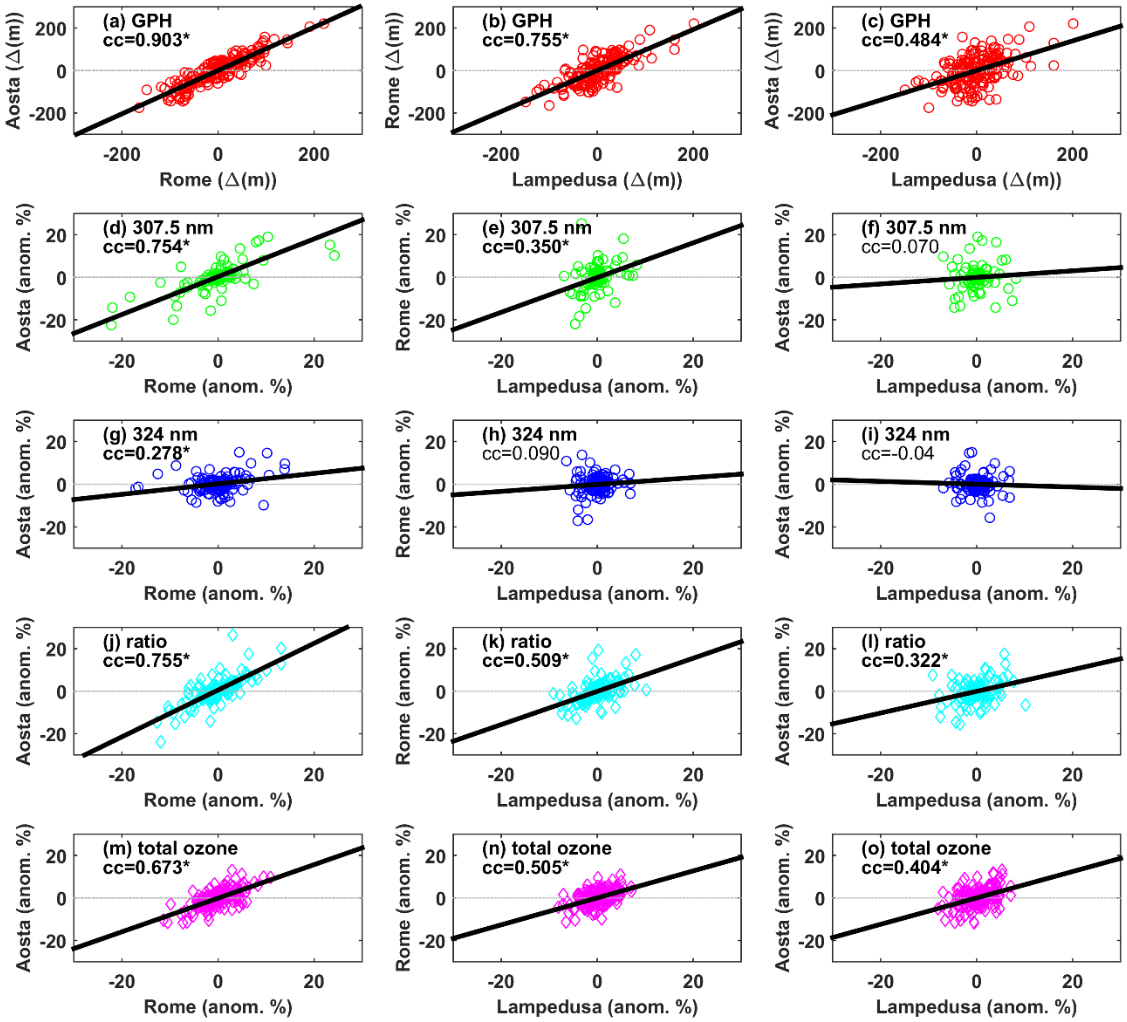


Figure 1: Topographic map of Italy and the three sites for which measurements are analysed in the study.


(a) GPH
cc=0.903*
(b) GPH
cc=0.755*
(c) GPH
cc=0.484*
Aosta (Δ(m))
Rome (Δ(m))
Lampedusa (Δ(m))
200
0
-200
(d) 307.5 nm
cc=0.754*
(e) 307.5 nm
cc=0.350*
(f) 307.5 nm
cc=0.070
(g) 324 nm
cc=0.278*
(h) 324 nm
cc=0.090
(i) 324 nm
cc=-0.04
(j) ratio
cc=0.755*
(k) ratio
cc=0.509*
(l) ratio
cc=0.322*
(m) total ozone
cc=0.673*
(n) total ozone
cc=0.505*
(o) total ozone
cc=0.404*
Aosta (anom. %)
Rome (anom. %)
Lampedusa (anom. %)
20
0
-20

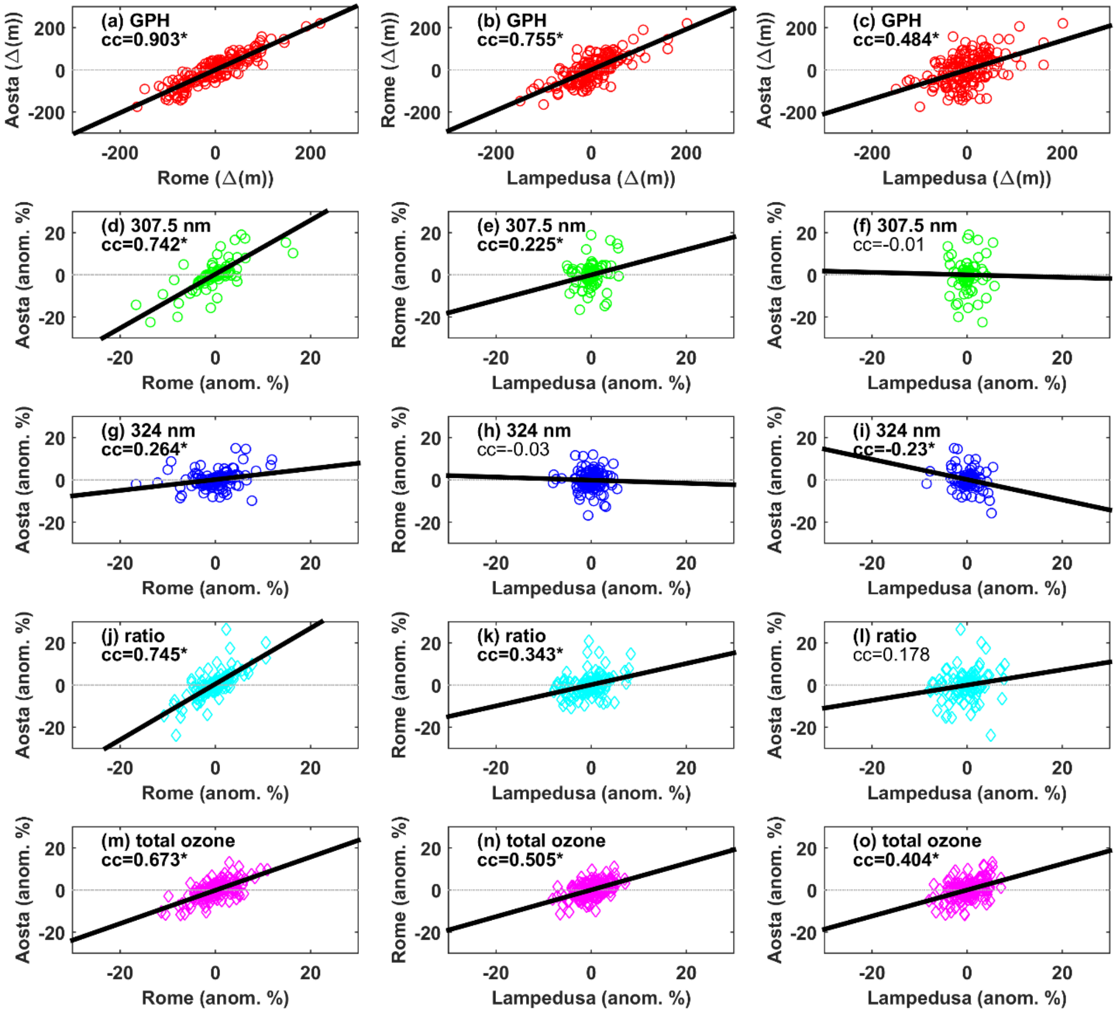
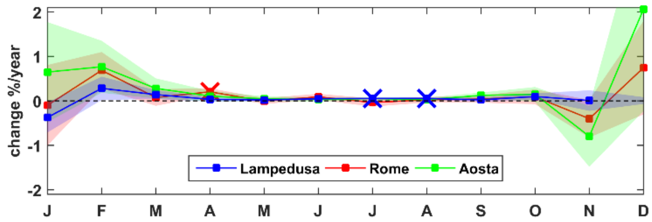
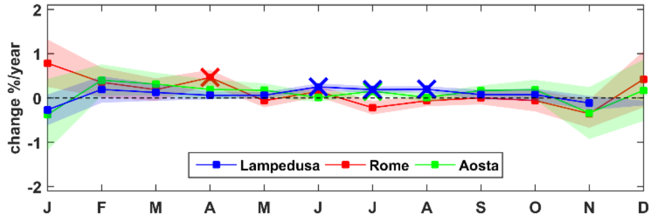


Figure 2: Scatter plots and correlation coefficients (cc) between the monthly anomalies of GPH (first row), irradiance~~irra-diance~~ at 307.5 nm (second row), irradiance 324 nm (third row), 307.5/324 nm ratio (fourth row), and total ozone (fifth row) in terms of anomalies for the pairs Rome – Aosta (first column), Lampedusa – Rome (second column), and Lampedusa – Aosta (third column). Numbers in bold with asterisk denote statistical significance.

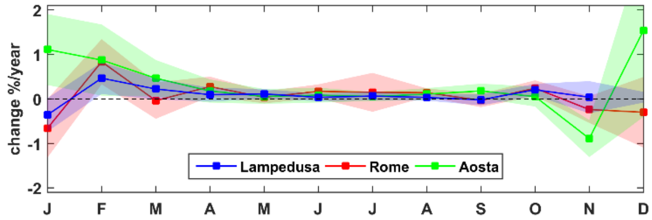
(a) I(307.5 nm)

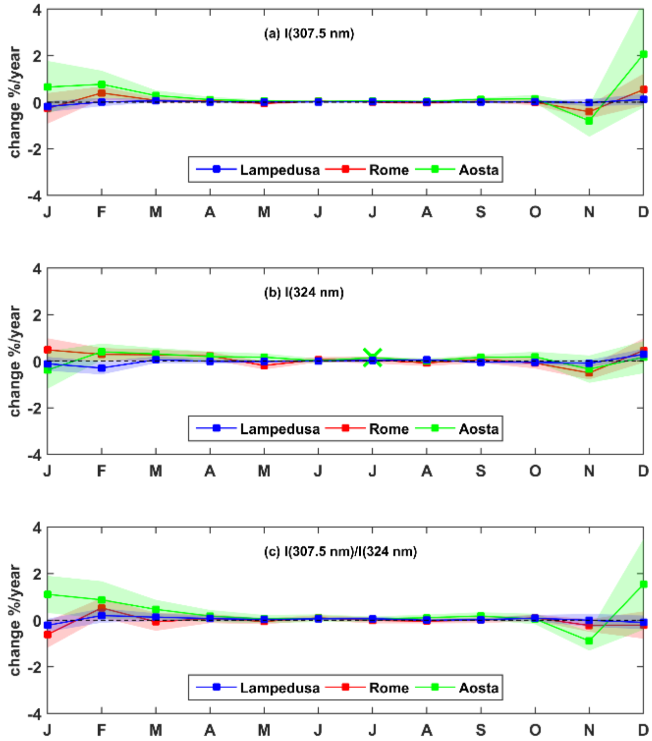


(b) I(324 nm)

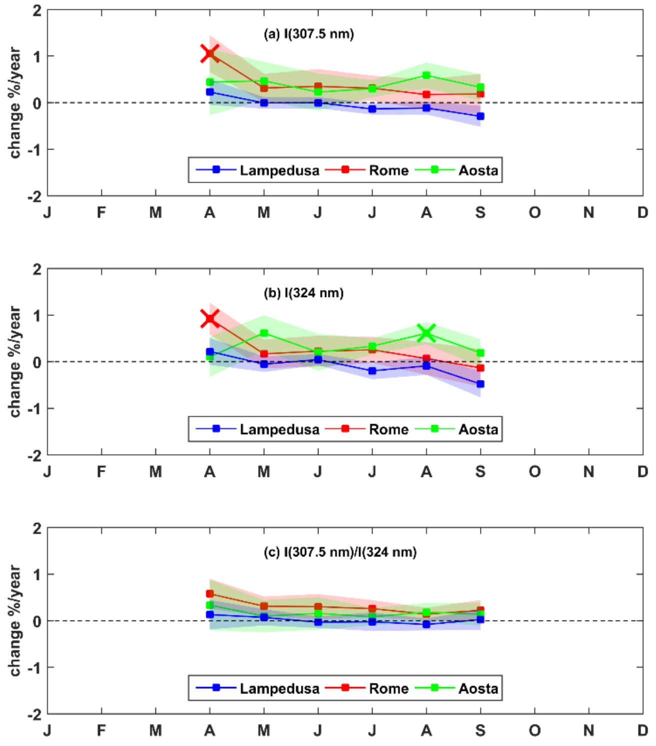


(c) I(307.5 nm)/I(324 nm)





775 **Figure 3: Average change (%) per year of (a) irradiance at 307.5 nm, (b) irradiance at 324 nm, and (c) the 307.5/324 nm ratio. Results are for SZA=67° for the period September 2006 – August 2020. Statistically significant changes have been marked with x. Shaded areas correspond to the 1-sigma standard deviation.**


(a) I(307.5 nm)
(b) I(324 nm)
(c) I(307.5 nm)/I(324 nm)
change %/year
2
1
0
-1
-2
J
F
M
A
M
J
J
A
S
O
N
D
Lampedusa
Rome
Aosta

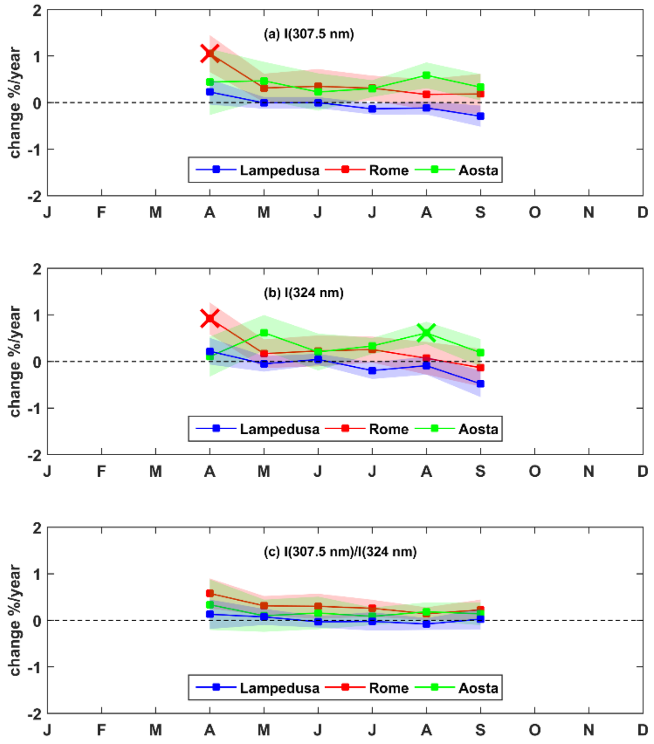
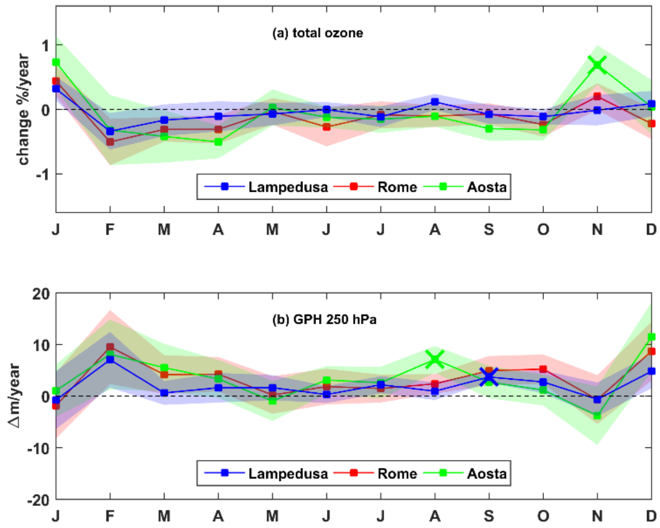


Figure 4: Average (%) change per year of (a) irradiance at 307.5 nm, (b) irradiance at 324 nm, (c) the ratio between the irradiances at 307.5 nm and 324 nm. Results are for 45° the period 2006 – 2020. Statistically significant changes have been marked with x. Shaded areas correspond to the 1-sigma standard deviation.



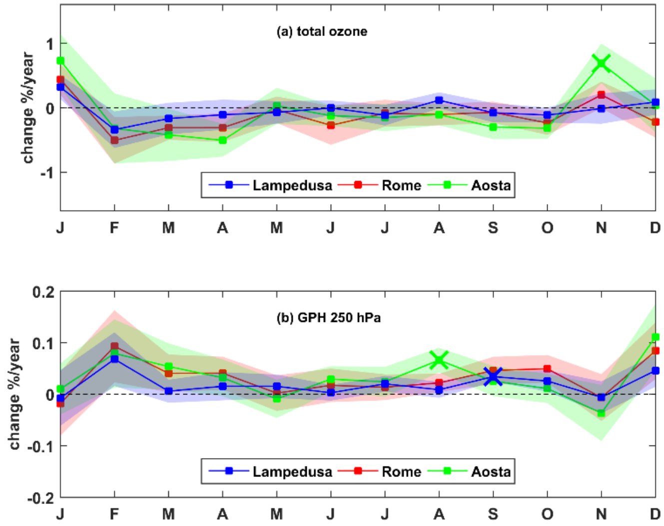
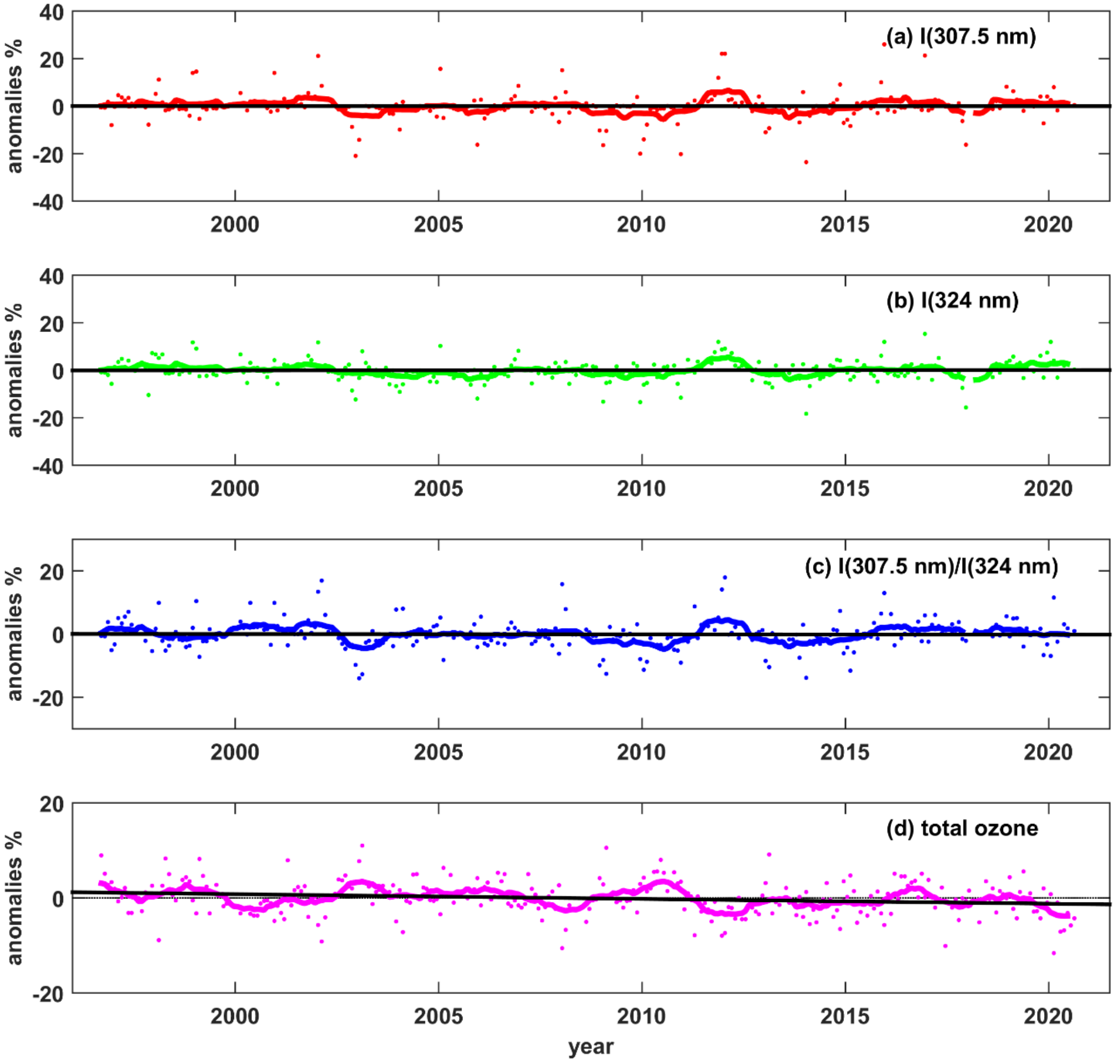


Figure 5: Average (%) change per year of (a) total ozone, and (b) GPH for the period 2006 – 2020. Statistically significant changes have been marked with x.



(a) I(307.5 nm)
(b) I(324 nm)
(c) I(307.5 nm)/I(324 nm)
(d) total ozone
anomalies %
40
20
0
-20
-40
2000
2005
2010
2015
2020
year

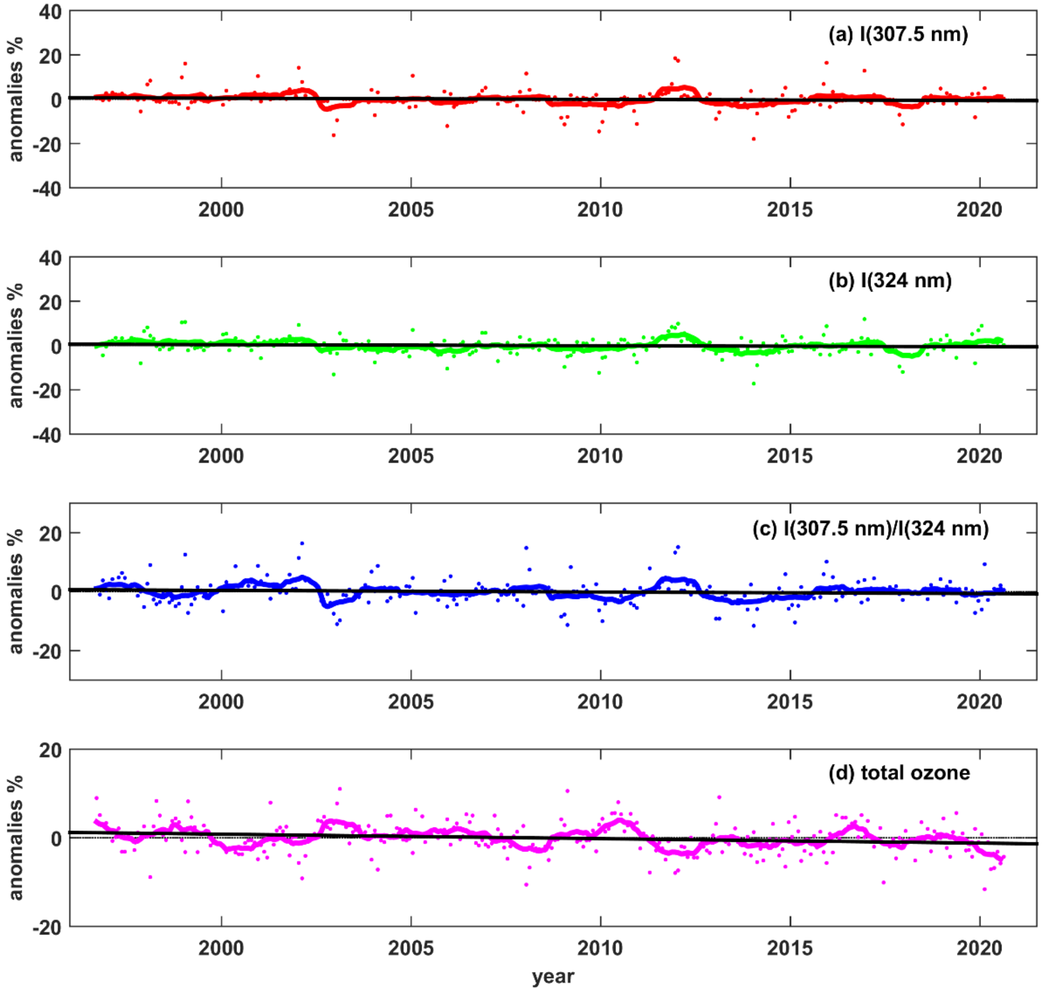
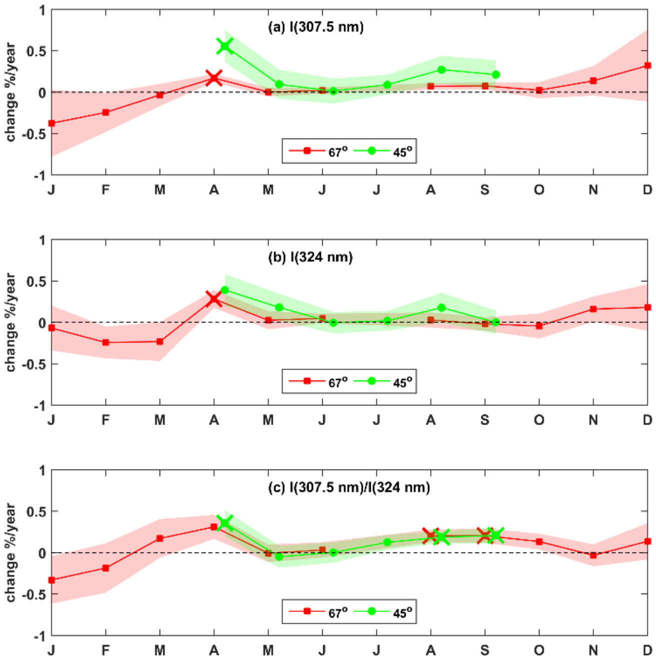


Figure 6. Anomalies (% differences relative to the monthly climatological values, represented by dots), 12-month moving averages (thick coloured lines), and trends (black lines) for Rome, for the monthly averages of (a) the irradiance at 307.5 nm, (b) the irradiance at 324 nm, (c) the ratio between the 307.5 nm and 324 nm irradiances, and (d) the total ozone.


(a) I(307.5 nm)
(b) I(324 nm)
(c) I(307.5 nm)/I(324 nm)
change %/year
1
0.5
0
-0.5
-1
J F M A M J J A S O N D
67°
45°

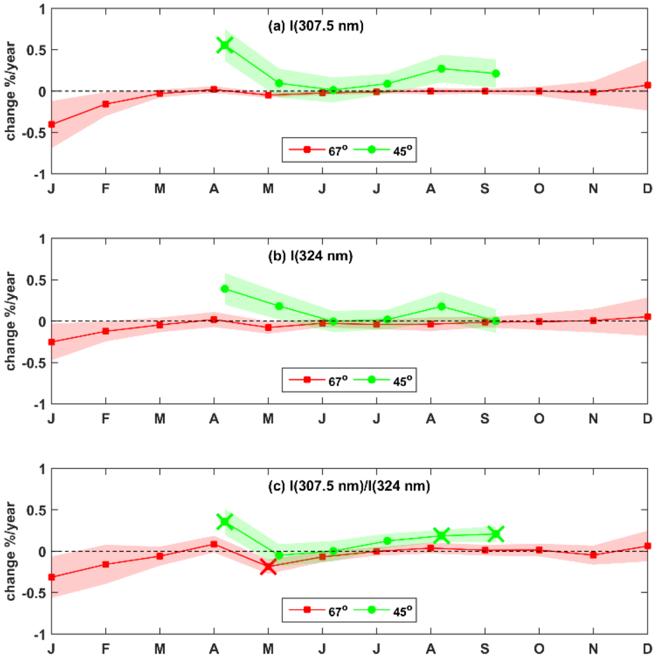

(a) I(307.5 nm)
(b) I(324 nm)
(c) I(307.5 nm)/I(324 nm)
change %/year
1
0.5
0
-0.5
-1
J F M A M J J A S O N D
67°
45°

Figure 7: Average (%) change per year of (a) irradiance at 307.5 nm, (b) irradiance at 324 nm, (c) the ratio between the irradiances at 307.5 nm and 324 nm, for Rome. Trends of the irradiances and the ratio are presented for the 45° and 67.5° SZAs. Statistically significant trends have been marked with x. Shaded areas correspond to the 1-sigma standard deviation.

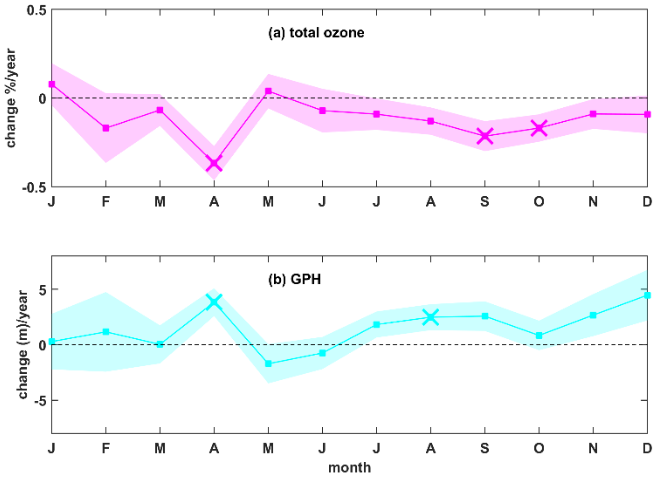
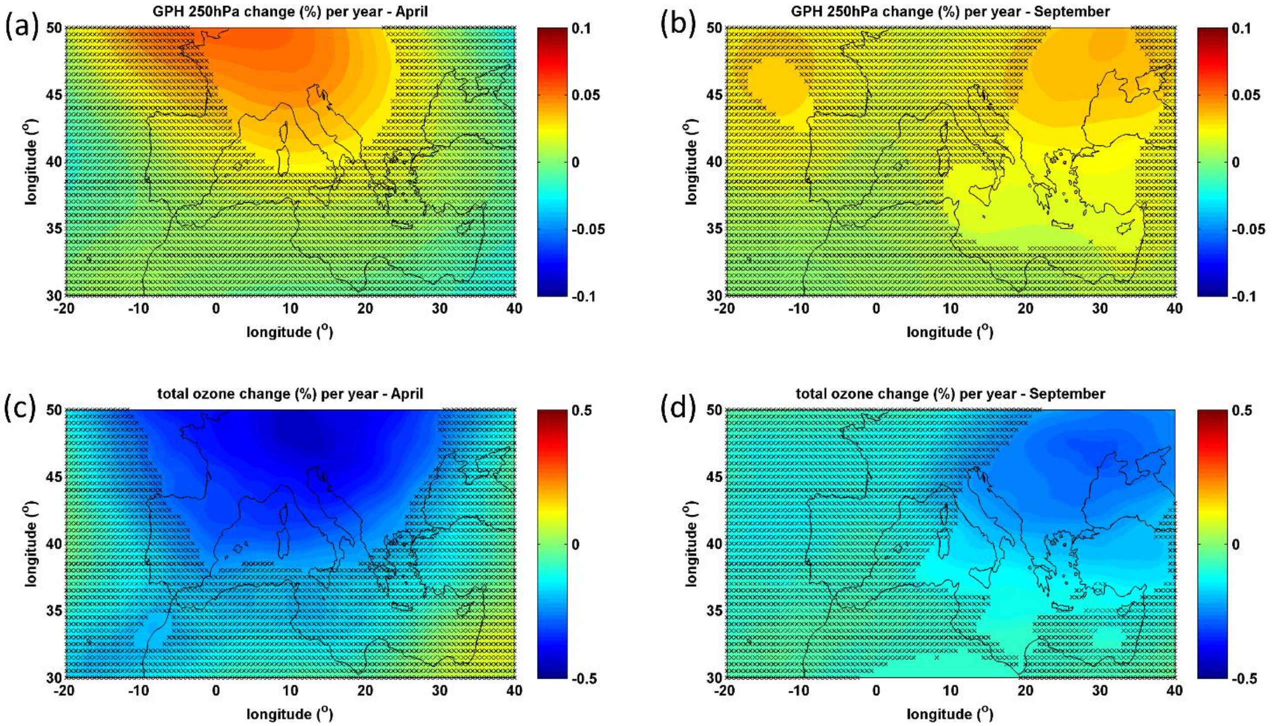


Figure 8: Average (%) change per year of (a) total ozone, and (b) GPH, for Rome. Statistically significant trends have been marked with x. Shaded areas correspond to the 1-sigma standard deviation.



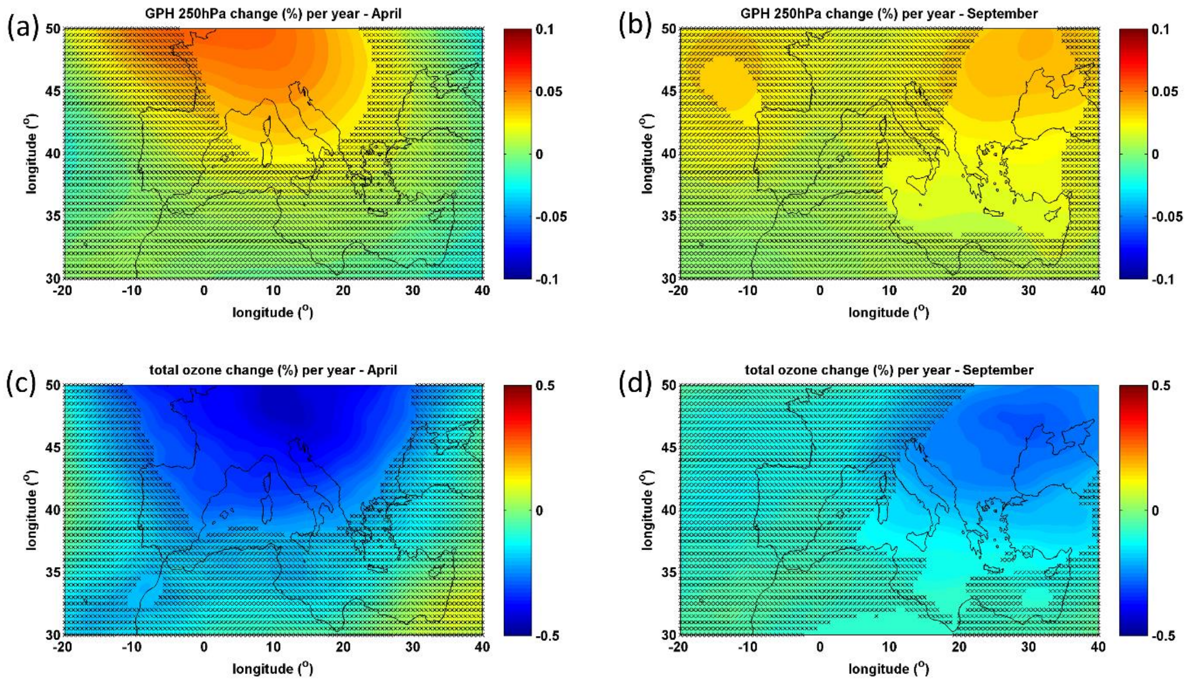


Figure 9: Changes (%) of GPH at 250 hPa (a,b) and total ozone (c,d) and for April (a,c), and September (b,d). Areas over which changes are not statistically significant are covered by x.

Tables

Table 1: Correlation coefficients between the anomalies of GPH and other parameters (total ozone, irradiance at 307.5 and 324 nm and 307.5/324 nm ratio) for four different seasons of the year. Values in bold denote~~de note~~ statistically significant correlation or anti-correlation. Values in the parentheses represent the change (in DU for total ozone and in % for irradiance, for each parameter for which a statistically significant correlation or anti-correlation was found) for a 1 m change in GPH.

	Lampedusa	Rome (2006-2020)	Rome (1996-2020)	Aosta
	Total ozone			
Winter	**-0.69 (-0.03 DU)**	**-0.69 (-0.03 DU)**	**-0.74 (-0.04 DU)**	**-0.63 (-0.04 DU)**
Spring	**-0.64 (-0.05 DU)**	**-0.46 (-0.03 DU)**	**-0.56 (-0.04 DU)**	**-0.68 (-0.05 DU)**
Summer	**-0.54 (-0.04 DU)**	**-0.56 (-0.05 DU)**	**-0.49 (-0.04 DU)**	**-0.30 (-0.02 DU)**
Autumn	**-0.51 (-0.04 DU)**	**-0.62 (-0.03 DU)**	**-0.70 (-0.04 DU)**	**-0.70(-0.04 DU)**
	307.5 nm irradiance (45°)			
Winter	-	-	-	-
Spring	**0.51 (0.06%)**	**0.59 (0.10%)**	**0.57 (0.10%)**	**0.60 (0.07%)**
Summer	**0.41 (0.03%)**	**0.55 (0.07%)**	**0.46 (0.05%)**	**0.44 (0.04%)**
Autumn	**0.49 (0.08%)**	0.33	**0.58 (0.06%)**	0.26
	307.5 nm irradiance (67°)			
Winter	**0.56 (0.03%)~~55~~**	**0.55 (0.07%)~~52~~**	**0.59 (0.08%)~~53~~**	**0.55 (0.07%)**
Spring	**0.55 (0.01%)~~51~~**	**0.42 (0.01%)~~40~~**	**0.61 (0.02%)~~47~~**	**0.58 (0.02%)**
Summer	**0.62 (0.01%)~~58~~**	**0.51 (0.01%)~~49~~**	0.29~~19~~	**0.38 (0.01%)**
Autumn	**0.57 (0.03%)~~52~~**	**0.64 (0.05%)**	**0.52 (0.04%)~~48~~**	**0.64 (0.06%)**
	324 nm irradiance (45°)			
Winter	-	-	-	-
Spring	0.09	**0.49 (0.07%)**	**0.42 (0.06%)**	0.36
Summer	-0.03	**0.48 (0.06%)**	**0.42 (0.04%)**	0.24
Autumn	0.12	0.14	0.34	-0.42
	324 nm irradiance (67°)			
Winter	**0.50 (0.03%)**	**0.44 (0.04%)**	**0.38 (0.04%)**	0.10
Spring	0.08	**0.44 (0.03%)**	**0.40 (0.03%)**	0.31
Summer	0.10	**0.42 (0.01%)**	0.20	-0.02

Autumn	0.07	**0.42** (0.03%)	**0.33** (0.02%)	**0.41** (0.03%)
	307.5/324 nm ratio (45°)			
Winter	-	-	-	-
Spring	**0.65** (0.07%)	-	**0.52** (0.05%)	**0.69** (0.06%)
Summer	**0.61** (0.05%)	**0.52** (0.04%)	**0.39** (0.03%)	**0.54** (0.04%)
Autumn	**0.62** (0.08%)	0.24	**0.53** (0.03%)	**0.76** (0.06%)
	307.5/324 nm ratio (67°)			
Winter	**0.54** (0.03%)	**0.44** (0.06%)	**0.62** (0.06%)	**0.67** (0.07%)
Spring	**0.44** (0.04%)	0.19	**0.39** (0.04%)	**0.66** (0.04%)
Summer	**0.59** (0.03%)	**0.50** (0.03%)	0.17	**0.55** (0.02%)
Autumn	**0.54** (0.06%)	**0.69** (0.04%)	**0.51** (0.04%)	**0.83** (0.06%)

Table 2: Trends and statistics for the 307.5 nm irradiance, the 324 nm irradiance, the 307.5/324 nm ratio, and the total ozone for Rome in 1996 - 2020. Significance level is set at 0.05. Statistically significant trends are in bold.

	Change %/year	Standard deviation	T-statistic	p-value
307.5 nm	~~-~~0.01~~04~~	0.07~~04~~	0.16~~-1.30~~	0.87~~20~~
324 nm	~~-~~0.01~~04~~	0.05~~04~~	0.26~~-1.30~~	0.79~~20~~
307.5/324 nm	~~-~~0.03~~06~~	0.05~~04~~	0.57~~-1.42~~	0.57~~16~~
TOC	**-0.10**	0.03	-3.21	<0.01

Supplement

Attenuation by clouds

In order to investigate the spectral effect of different cloud types on spectral solar UV irradiance in the range 305 – 324 nm we performed simulations with the model uvspec of the libRadtran package (Mayer and Kylling, 2005). Simulations were performed for total ozone equal to 330 DU, AOD=0.1, and for two types of clouds: typical high altitude cirrus clouds (base altitude=10 km, width=1km, effective radius=20 μ m) and typical low altitude water clouds (base altitude=2 km, width=2 km, effective radius=10 μm). The ratio between the spectral irradiance simulated for cloudless and cloudy conditions is presented in Figures S1 and S2.

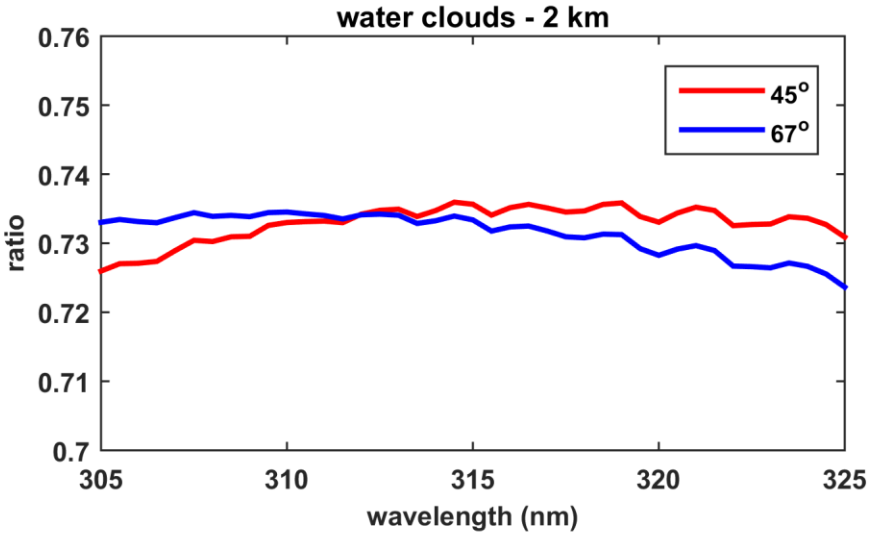


Figure S1: Ratio between the surface solar spectral irradiance at 305 – 325 nm reaching the Earth surface with and without low altitude clouds.

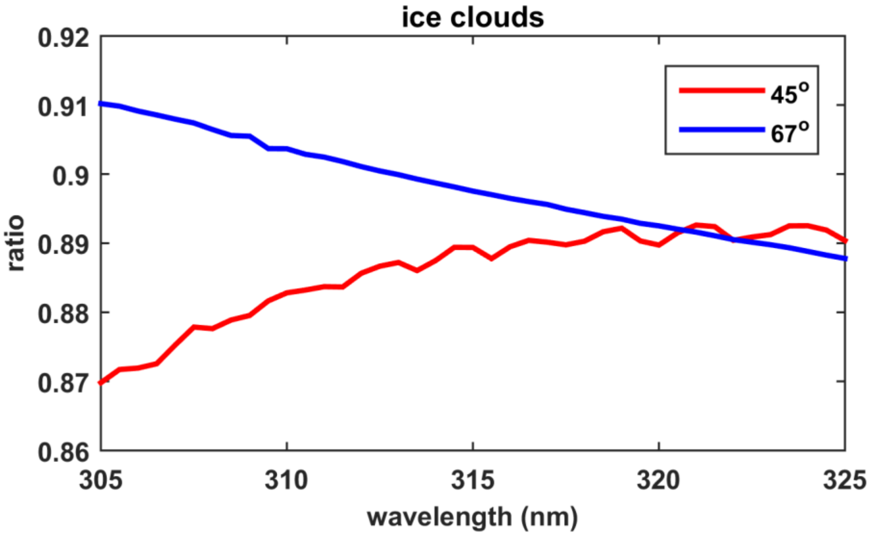


Figure S2: Ratio between the surface solar spectral irradiance at 305 – 325 nm reaching the Earth surface with and without high altitude clouds.

A Cloud Optical Depth (COD) of 1 was considered for the cirrus cloud (Figure S1), while a COD of 6 was considered for the low altitude cloud (Figure S2). For the low altitude clouds, the spectral shape of the attenuation is similar for the SZAs of 45° and 67° and the dependence from wavelength is in both cases small. For the high altitude clouds the attenuation decreases with wavelength at 45° and increases with wavelength at 67°. Attenuation of the irradiance at wavelengths larger than 320 nm is similar at both SZAs. At wavelengths that are affected stronger by ozone attenuation by high altitude clouds is significantly stronger at 45°. Performing the same analysis for different CODs ranging from 1 to 30 for the two cloud types resulted to similar conclusions. From the above discussion it is evident that changes in the occurrence of cirrus would result to more pronounced effects on the levels of UVB irradiance at smaller SZAs.

Correlation between GPH at 250 hPa, GPH at 850 hPa and tropopause altitude

As shown in Figure S3, there is a strong, statistically significant correlation between the GPH at 250 hPa and the tropopause altitude over Aosta, Rome and Lampedusa. As also shown in Figure S1 (panels d- f) GPH at 250 hPa is strongly correlated with GPH at 850 hPa.

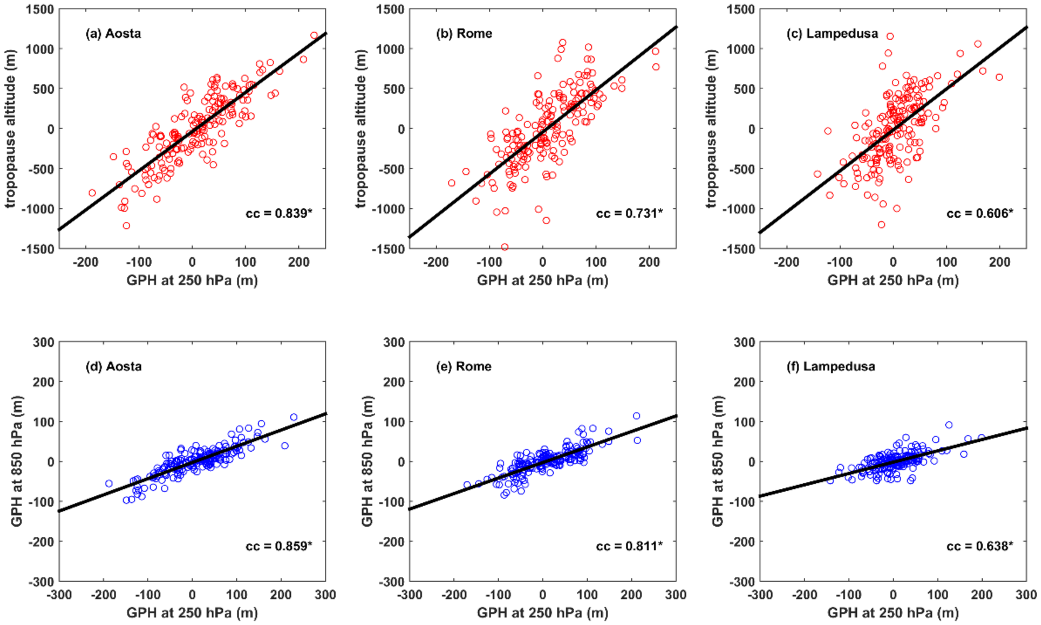


Figure S3: Correlation between the absolute anomalies (in m) between GPH at 250 hPa and tropopause altitude for (a) Aosta, (b) Rome, and (c) Lampedusa, and correlation between the GPH at 250 hPa and 850 hPa for (d) Aosta, (e) Rome, and (f) Lampedusa. The correlation coefficients (cc) are shown at the lower right side of each graph. Values in bold marked with an asterisk denote statistically significant correlation.

Ozone trends at different pressure levels

As shown in Figure S4, ozone over Rome increases significantly at higher stratospheric levels and decreases significantly at lower stratospheric levels.

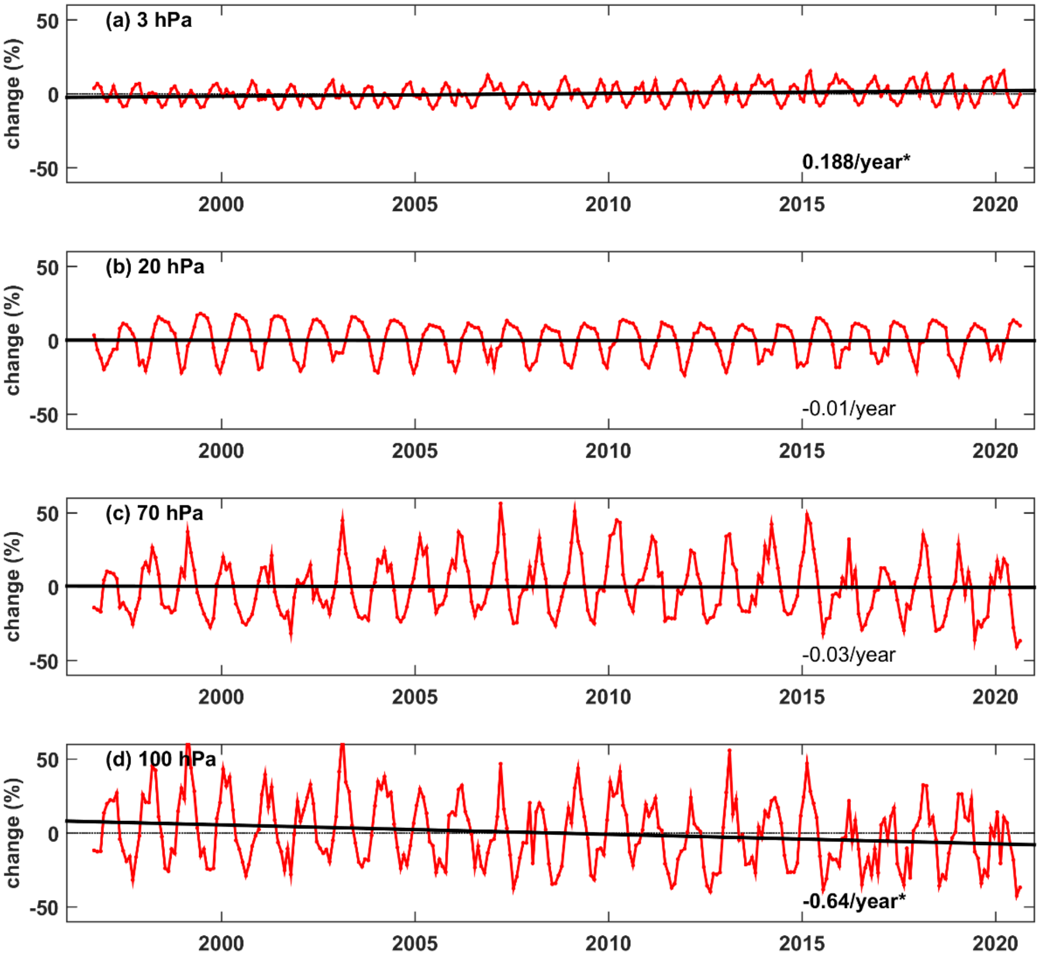


Figure S4: Variability and long-term trends (in %) of the ozone mixing ratio at different atmospheric pressure levels over Rome. Average change per year is shown at the lower right of each graph. Values in bold marked with an asterisk denote statistically significant changes.

References

Mayer, B. and Kylling, A.: The libRadtran software package for radiative transfer calculations-description and examples of use, Atmos. Chem. Phys., 5, 1855–1877, 2005.