

Atmos. Chem. Phys. Discuss., 12, 28385-28450, 2012
www.atmos-chem-phys-discuss.net/12/28385/2012/
doi:10.5194/acpd-12-28385-2012
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Assessment of atmospheric processes driving ozone variations in the subtropical North Atlantic free troposphere

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Author response to the Referee comments

Reply to Referee#1

The authors are grateful for the review time and for the good suggestions given by the referee. We incorporate most (practically all) of those comments into our revised manuscript, which has led to substantial improvements. Some sections have improved and enriched their scientific information and others have been clarified.

Our responses to all comments are given hereafter. Attached is the draft revised manuscript where added information or rewritten paragraphs have been marked in yellow.

1. Introduction: There is a recent article on European ozone trends by Logan et al. (JGR, 2012) relevant to the topic of this manuscript which could be cited.

We have cited Logan et al. (2012), as well as another recent paper of ozone trends on a global scale (Oltmans et al., 2013), in the Introduction section. Logan et al. (2012) is indeed an interesting paper that has been also referenced in the first paragraph of Section 3.8.

Logan, J.A., J. Staehelin, I. A. Megretskaia, J.-P. Cammas, V. Thouret, H. Claude, H. De Backer, M. Steinbacher, H.-E. Scheel, R. Stübi, M. Fröhlich, R. Derwent, Changes in ozone over Europe: Analysis of ozone measurements from sondes, regular aircraft (MOZAIC) and alpine surface sites, J. Geophys. Res., Vol. 117, Issue D9, May 2012.

Oltmans, S.J., A.S. Lefohn, D. Shadwick, J.M. Harris, H.E. Scheel, I. Galbally, D.W. Tarasick, B.J. Johnson, E.-G. Brunke, H. Claude, G. Zeng, S. Nichol, F. Schmidlin, J. Davies, E. Cuevas, A. Redondas, H. Naoe, T. Nakano, T. Kawasato, Recent tropospheric ozone changes - A pattern dominated by slow or no growth, Atmos. Environ., 67, 331-351, 2013.

2. Page 28392, line 4: Although there is the relevant reference to the MCAR method, a short description would be useful for the reader.

We have rewritten the part corresponding to the MCAR plots in Section 2.3 as follows:

“

“Source-receptor relationships of atmospheric composition can be investigated with backward trajectory techniques, tracing forward from a defined geographical origin to arrive at measurement sites where the composition may have altered during transport (Fleming et al., 2012). One of these techniques is the so called as MCAR (Mean Concentrations At Receptor). For each pixel of our geographical domain, we select the backward trajectories which arrive to IZO and pass over that pixel. The daily mean O₃ concentrations of the corresponding days are averaged for that pixel. MCAR plots allowed the identification of pathway regions with high and low O₃.

The methodology has been described by Rodriguez et al. (2011). Monthly MCAR plots of surface O₃ were determined using daily 5-day backward trajectories calculated at 00:00UTC and daily (nocturnal) surface O₃ data at IZO for the period 1988-2009.”

We have included the following reference:

Fleming, Z.L., P. S. Monks, A. J. Manning: Untangling the influence of air-mass history in interpreting observed atmospheric composition, Atmospheric Research, Volumes 104–105, Pages 1–39, 2012.

3. Page 28397, lines 6-10: It can be also mentioned the existence of common characteristics in the shape of summertime ozone diurnal cycle (day-time lower ozone values due to thermally driven upslope winds) with other high-altitude European stations such as Jungfraujoch or Zugspitze (see e.g. Schupbach et al., JGR, 2001).

We have added the following text at the end of Section 3.1.:

The “ozone valley” in the daytime is a feature also observed in other high mountain stations: Mauna-Loa (Oltmans et al. ,1994) and Jungfraujoch (Schuepbach et al., 2001).

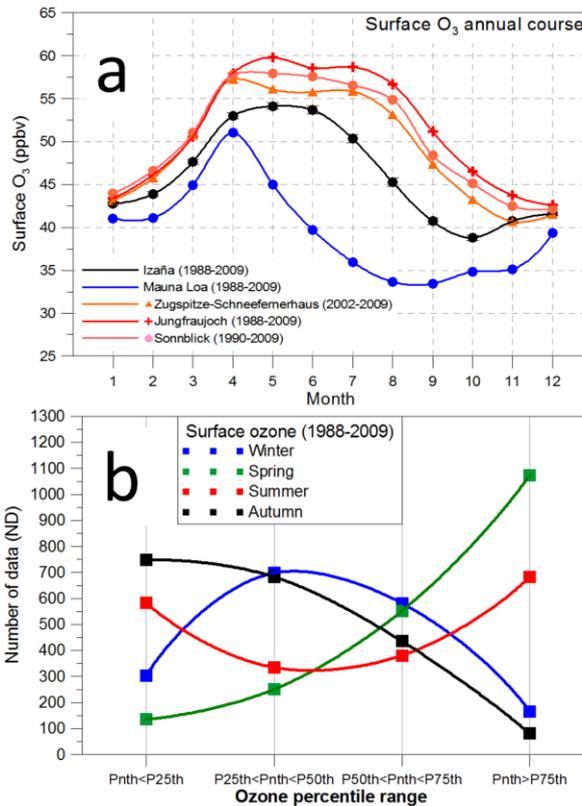
We have included the following two references in Section 3.1:

Oltmans, S.J., and Levy II.H., Surface ozone measurements from a global network, Atmos. Environ., Vol. 28, No 1, 9-24, 1994.

Schuepbach, E., T. K. Friedli, P. Zanis, P. S. Monks, and S. A. Penkett, State space analysis of trends and seasonalities of lower free tropospheric ozone (1988 – 1997) at the high elevation site at Jungfraujoch, J. Geophys. Res., 106(D17), 20,413 – 20,427, 2001.

4. Page 28398, lines 27-29: I think that a note comparing the ozone seasonal cycle at Izaña with the respective one at other high altitude European stations (Jungfraujoch, Zugspitze, Sonnblick) could be added.

This is a good suggestion. In Figure 4a we have introduced a comparison of the O₃ annual course at Izaña station with those of other high mountain stations: Mauna-Loa, Zugspitze-Schneefernerhaus, Jungfraujoch and Sonnblick.



The following text has been included in Section 3.2:

Figure 4a shows non detrended monthly means for surface O₃ at IZO, Mauna-Loa (Oltmans et al., 1994), Zugspitze-Schneefernerhaus (Nienerowski, 2004), Jungfrauoch (Logan et al., 2012), and Sonnblick (Federal Environment Agency Austria). Data from Mauna-Loa and the alpine stations have downloaded from the World Data Centre for Greenhouse Gases (WDCGG; <http://ds.data.jma.go.jp/gmd/wdcgg/>). IZO shows characteristics intermediate to those recorded at Mauna-Loa and the alpine stations. Rodriguez et al. (2004) compared the O₃ annual course at IZO with that observed at Mauna-Loa, noting that in summer O₃ monthly means sharply decrease in the latter, while high O₃ events (daily mean values of 60-70 ppbv) are recorded at IZO. However, the typical continental annual cycle, with a broad spring/summer maximum observed in the alpine stations, is not seen at IZO where the annual cycle peaks in late spring (May-June). This is an indication that IZO is not affected by photochemical production from regional emissions in summer.

5. Page 28400, lines 8-10: The authors state that "It is noticeable the fact that trajectories from the Sahel, and those originated over North Africa and the Mediterranean Basin, travel at mid-high altitudes, mainly in July and August." It would be better to specify that these low-level trajectories originate from Northwest Africa and Western Mediterranean.

We have changed this sentence as follows:

"It is noticeable that in July and August low-level trajectories originate from Western Sahara, while trajectories from the Sahel, and those originated over Western North African countries and the Mediterranean Basin travel at mid-high altitudes."

6. Page 28401, lines 23-25: The authors state that " There is not a clear relationship in winter, spring and autumn, probably due to the short variation range of 210Pb values." Do you mean that it is related with the comparison if the 210Pb lifetime versus the atmospheric transport timescale in winter, spring and autumn? Please clarify.

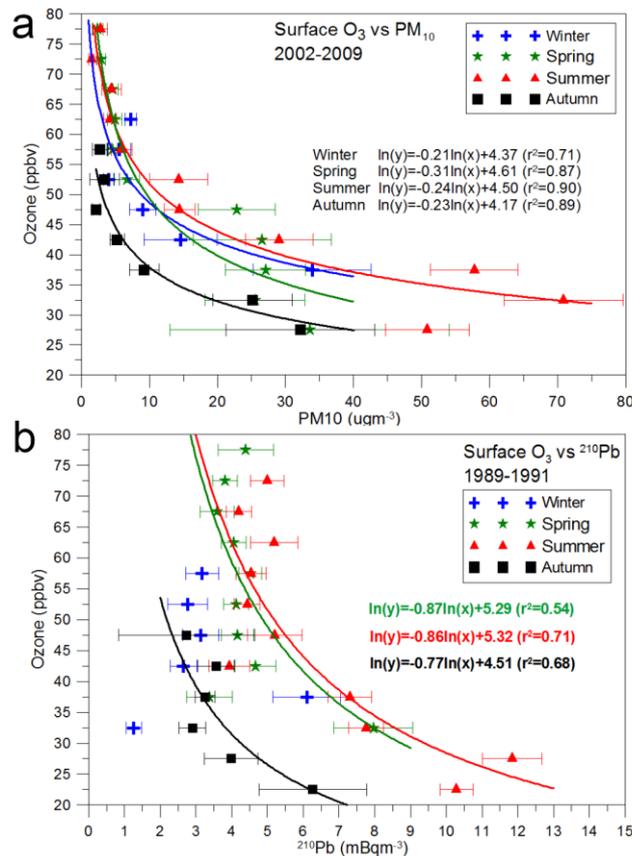
We agree. This sentence is not clear. ^{210}Pb is a good tracer of air masses originating in the continental boundary layer (CBL) or near the ground. Since Izana is mainly impacted by Saharan CBL air masses in summertime, it is only in this season when we expect a significant variation in the range of ^{210}Pb values. In Autumn (mainly December), and Spring (mainly April) the impact of the low-level Saharan outbreaks is very limited. The top of the Saharan Air Layer (SAL) just reaches the level of IZO (around 2400 m asl) during Saharan intrusions. For this reason we can find in spring and autumn signature of the Saharan CBL with relatively high values of ^{210}Pb , but not as clearly as seen in summer, and with smaller variation in ^{210}Pb values than observed in summer.

This comment has helped us to improve Figure 8b adding ^{210}Pb -O₃ fits for spring and autumn in order to clarify this point.

We have rewritten this part as follows:

The relationship between surface O₃ and ^{210}Pb is shown in Fig.8b. In summer we obtain a logarithmic fit with a good correlation which resembles the O₃-PM₁₀ fit in the same season. Prospero et al. (1995) had reported preliminary results of O₃ and ^{210}Pb relationship for summer-time. However, in spring (mainly in April) and autumn (mainly in December), when Saharan low-level intrusions over the Canary Islands occur (Alonso-Pérez et al., 2007), IZO is only slightly impacted by the top of the Saharan Air Layer (SAL). So, we can see Saharan CBL signature with relatively high values of ^{210}Pb , although the O₃- ^{210}Pb relationship is not as clear as that seen in summer. In winter, no correlation between surface O₃ and ^{210}Pb is found.

The new Figure 8b is the following:



7. Page 28403, liens 3-5: The authors state that "So, it is noteworthy that in 10% of days in winter and autumn, backward trajectories have been impacted by uppertroposphere air masses with PVU > 1." A plausible justification could be also downward transport from the stratosphere to the troposphere followed by mixing with tropospheric air which would decrease the PV of the air mass.

We agree. We have rewritten this sentence as follows:

"So, it is noteworthy that in 10% of days in winter and autumn, backward trajectories have been impacted by upper-troposphere air masses with PV>1pvu. Some of them might even be affected by previous stratospheric intrusions mixed with upper-troposphere air masses."

8. Page 28403, lines 15-17: Please provide some references to justify the use of 1 and 1.6 pvu as thresholds to identify the impact of STT transport (see for example Stohl et al., Atmos. Env., 2000; Akritidis et al., Meteor. Atmos. Phys., 2010). A common threshold for dynamical tropopause is the 2 pvu.

Some references were already provided in Section 2.4. ("Potential vorticity") to justify the stratospheric-PV theshods. We have included Stohl et al. (2000) and Akritidis et al. (2010).

Stohl, A., N. Spichtinger-Rakowsky, P. Bonasoni, H. Feldmann, M. Memmesheimer, H.E. Scheel, T. Trickl, S. HuKbener, W. Ringer, M. Mandl, The influence of stratospheric intrusions on alpine ozone concentrations, Atmospheric Environment 34, 1323-1354, 2000.

Akritidis, D., P. Zanis, I. Pytharoulis, A. Mavrakis, Th. Karacostas, A deep stratospheric intrusion event down to the earth's surface of the megacity of Athens, Meteorol. Atmos. Phys., 109:9–18, DOI 10.1007/s00703-010-0096-6, 2010.

The corresponding paragraph in Section 2.4 has been rewritten as follows:

“The dynamical tropopause is typically defined with a PVU value ranging from 1PVU (Shapiro et al., 1987) to 2PVU (Appenzeller et al., 1996; Parrish et al., 2000). The dynamical tropopause is defined by WMO (1957) as the 1.6PVU iso-surface. This value is used by some authors to identify the tropopause and the signature of stratospheric air (Stohl et al., 2000; Cristofanelli et al., 2006), while other authors consider two threshold values for the dynamical tropopause, 2 and 1.5 PVU, for deep stratospheric intrusion analysis, as Akritidis et al. (2010). It is assumed that $PV > 1PVU$ are typical values of tropospheric regions that have been impacted by stratospheric intrusions. Beekman et al. (1994) made use of the positive correlation of PV with O₃ in separating tropospheric O₃ sources on the basis of high and low PV. However, we should note that diabatic heating can reduce the PV values without changing O₃. So, PV must be viewed as a bottom-indicator of air masses with upper troposphere/lower stratosphere (UTLS) signature.”

9. Page 28404, lines 25-27: The threshold value of 8 mBq/m³ for an air mass with stratospheric signature which was suggested by Reiter et al. (1983) and applied also in other studies (see e.g. Stohl et al., Atmos. Env., 2001) is an arbitrary value that was resulted for Central Europe but maybe different from one place to another. Apart from this approach, there have been many studies in which different thresholds of ⁷Be activity were used for identifying air masses of stratospheric origin based on statistical criteria (see e.g. Elbern et al., Atmos. Env. 1997 ; Gerasopoulos et al., Atmos. Env., 2001). I would suggest that some discussion for the threshold value of Be-7 should be added.

We have added the following references in Section 3.6:

Zanis, P., Schuepbach, E., Gäggeler, H. W., Hübener, S., Tobler, L. Factors controlling beryllium-7 at Jungfrauoch in Switzerland, Tellus B, Vol. 51, 4, 789-805, 1999.

Bonasoni, P., F. Evangelisti, U. Bonafe, F. Ravegnani, F. Calzolari, A. Stohl, L. Tositti, O. Tubertini, T. Colombo, Stratospheric ozone intrusion episodes recorded at Mt. Cimone during the VOTALP project: case studies, Atmospheric Environment, Vol. 34, 9, 1355–1365, 2000.

Stohl, A., N. Spichtinger-Rakowsky, P. Bonasoni, H. Feldmann, M. Memmesheimer, H.E. Scheel, T. Trickl, S. Hübener, W. Ringer, M. Mandl, The influence of stratospheric intrusions on alpine ozone concentrations, Atmospheric Environment, Vol. 34, 1323–1354, 2000.

Gerasopoulos, E., P. Zanis, A. Stohl, C.S. Zerefos, C. Papastefanou, W. Ringer, L. Tobler, S. Hübener, H.W. Gäggeler, H.J. Kanter, L. Tositti, S. Sandrini, A climatology of ⁷Be at four high-altitude stations at the Alps and the Northern Apennines, Atmospheric Environment, 35, 6347–6360, 2001.

Cristofanelli, P., P. Bonasoni, L. Tositti, U. Bonafè, F. Calzolari, F. Evangelisti, S. Sandrini, and A. Stohl (2006), A 6-year analysis of stratospheric intrusions and their influence on ozone at Mt. Cimone (2165 m above sea level), J. Geophys. Res., 111, D03306, doi:10.1029/2005JD006553, 2006.

The paragraph concerning the ⁷Be threshold has been rewritten as follows:

“Reiter et al. (1983) suggested a ${}^7\text{Be}$ threshold value of 8 mBq/m^3 , above which an air mass probably has stratospheric signature. This value has been used by several authors to identify stratospheric intrusions in high mountain stations (Zanis et al. 1999; Stohl et al., 2000, Bonasoni et al., 2000; Cristofanelli et al., 2006) although it is not possible to consider ${}^7\text{Be}$ as an unambiguous stratospheric tracer (Zanis et al., 1999; Stohl et al., 2000). Gerasopoulos et al. (2001) found at four high-altitude alpine stations that high ${}^7\text{Be}$ values (above 6 mBq/m^3) correspond to air masses from the north and high altitudes, as it is characteristic for stratospheric intrusions. Reiter et al. (1983) showed that the range of ${}^7\text{Be}$ values $> 7.4 \text{ mBq/m}^3$ corresponds to direct stratospheric intrusions near the station, without a long advection path. The third quartile of ${}^7\text{Be}$ data series at IZO is 8.2 mBq/m^3 , and stratospheric air mass intrusions normally reach the ground after considerable mixing with tropospheric air. Therefore a threshold value of 8 mBq/m^3 is reasonable to estimate the impact of UTLS air masses at IZO.”

10. Page 28407, lines 27-29. The authors state that " The results identify a main contribution from pollution episodes over North America in winter, with backward trajectories heights below 4 km, whereas in spring aged air masses (previously transported from North America) are found over North Atlantic at high altitudes (above 4–5 km)." I understand and I agree with what but the authors should also mention that these height values are median values and there is a large overlap in the altitude range between A3 and B3 in Figure 13.

This paragraph has been rewritten as follows:

“The results identify a main contribution from pollution episodes over North America in winter, with backward trajectories heights below 4 km , whereas in spring aged air masses (previously transported from North America) are found over North Atlantic at slightly higher altitudes (above $4\text{--}5 \text{ km}$), although there must be stated that there is substantial overlap in the ranges of altitude in both seasons (Figures 13 and 13b).”

11. Page 28408, lines 28-29: Shouldn't be 0.58 instead of 0.54 according to Table 5?

No. The ratio 0.54 corresponds to the mean O_3/CO ($0.53 + \text{about } 0.1 \text{ SD}$) value associated to identified long-range transport of air masses from North America in spring with a good correlation of hourly $\text{O}_3\text{-CO}$ (>0.75) and for $\text{O}_3 > \text{P}75\text{th}$ (See new Table 5; Type 3). This represents the upper ratio O_3/CO ratio of aged air masses, while 0.58 is the “climatological” mean O_3/CO ratio for $\text{O}_3 > \text{P}75\text{th}$ in Spring (see Table 4)

12. Section 3.7: The authors should also take into account in their discussion on O3-CO relationship that there is an O3/CO seasonal cycle in the baseline (background) atmosphere. I am not sure if I understood well but if this O3/CO seasonal cycle in background atmosphere is not considered, maybe could lead to speculative conclusions.

Thank you for this comment. Yes, we have taken into account in our discussion of the $\text{O}_3\text{-CO}$ relationship that there is an O_3/CO seasonal cycle. In fact O_3/CO ratios observed during long-range transport events are compared with “climatological” O_3/CO ratios obtained for each season with hourly $\text{O}_3\text{-CO}$ data pairs, which represent the baseline O_3/CO ratios. However, this comment has motivated us to try to further clarify the content of Section 3.7 as a whole. We have reorganized the Section, exchanging Tables 4 and 5, and we have completed the information in the new Table 5. We have refined the discussion and emphasized aspects that were more hidden before, while making the section more readable.

13. Figure 11: Why the authors use a different color scale among the 4 plots? In Figure caption please denote what is the percentage number in red.

Please, see answer to question 14.

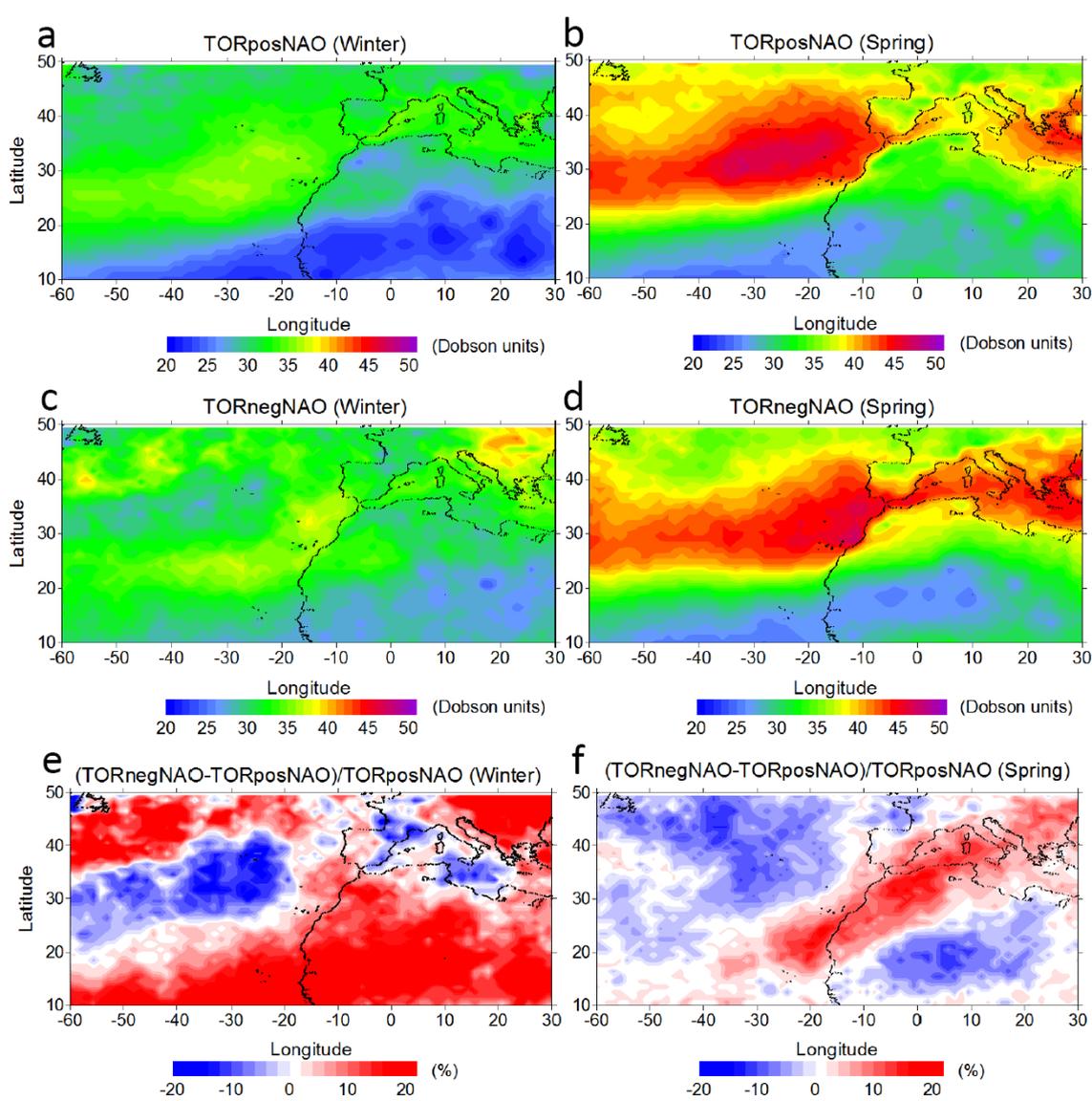
14. Figure 13: Why the authors use a different color scale among the 3 plots? Please also clarify what are the arbitrary units for the residence time.

The backward trajectories residence times for each season shown in Figures 11 (the four seasons) and 13 (winter and spring) correspond to days that meet some criteria. These criteria are met in a number of days which is different for each season, so that the residence times cannot be compared between different seasons. These residence times only identify the preferred geographic regions over which pass air masses that meet those criteria. Furthermore, the residence times have been corrected by a central convergence effect factor, which is proportional to the distance of the grid cell from receptor. So, the numbers in color scales of Figures 11 and 13 don't strictly correspond to the number of trajectories in each season expressed in percentage (or probability), and this is the reason to use arbitrary units (physically meaningless units). We have to take into account that residence time analysis is only a qualitative method.

15. Figure 15: The fact that a negative phase of NAO results in higher tropospheric ozone amounts in winter over the whole north Atlantic it is not very clear from Figure 15. I would suggest to add in Figure 15 plots of the ozone differences between NAO+ and NAO-.

We have followed this suggestion and included the plots of ozone (TOR) differences between $NAO > +0.5$ and $NAO < -0.5$. At this point we call your attention to the recalculation of TOR in terms of NAO + and NAO- conditions, as was suggested by Referee # 2. Basically we have recalculated the values of TOR for winter and spring using monthly average values of TOR in months of each of the two seasons that meet $NAO > +0.5$ or $NAO < -0.5$.

The new Figure 15 is the following:



We have taken the opportunity to include the following article, recently published, which is very timely to confirm certain aspects of our discussion in Section 3.8.

Pausata, F. S. R., L. Pozzoli, E. Vignati, and F. J. Dentener, North Atlantic Oscillation and tropospheric ozone variability in Europe: model analysis and measurements intercomparison, *Atmos. Chem. Phys.*, 12, 6357–6376, 2012.

16. Table 4. Please denote how many cases are included for each type.

The number of cases has been included in former Table 4 (now Table 5)

Reply to Referee#2

Our responses to all comments are given hereafter. We thank the Referee for his comments, especially that concerning the TOR data in positive and negative NAO

phases. Attached is the draft revised manuscript where added information or rewritten paragraphs have been marked in yellow.

1. My main comment relates to the use of TOMS TOR data to look at the effect of the NAO on ozone, please could you clarify (in the text and the figure 15 caption) which years of TOMS TOR data have been used. In section 2.6.3 you state the data ranges from 1979-2000, whereas in Figure 16 you only plot the NAO index starting in 1988, which is fine since that is when the IZO data starts, but if you have NAO data back to 1979 and have used TOR data from this date then please confirm this. As it stands, comparing what you have plotted in Figure 15 with the NAO index in Figure 16 then you have only 1 year of data for which the NAO < -0.5 (1996), and it is dangerous to draw conclusions based on 1 year of data which could be an anomalous year. The NASA Langley TOR dataset extends up to and including 2005, this data should be included in your analysis and will provide further years for which the criteria NAO < -0.5 is satisfied.

Thank you for this question. Indeed TOR data corresponding to the period 1988-2005 were used in our analysis shown in the ACPD manuscript. Unfortunately no TOR data are available in 1996. So, we had only two winters with NAO<-0.5 (2001 and 2005). However, and in order to improve the representativeness of this statistics, we have changed the strategy for averaging seasonal TOR data by using monthly TOR data corresponding to positive and negative NAO phases on a monthly basis, instead of a seasonal basis. We think we have improved the TOR data representativeness in the negative phase of the NAO, for which less data exist.

We have added the following text explaining the data used in each case:

“The TOR seasonal average value for each phase of the NAO within the period 1988-2005 was obtained by averaging for each season the TOR monthly mean values of those months in which NAO > +0.5 (positive NAO) or NAO < -0.5 (negative NAO). Thus, to calculate the TOR mean value corresponding to winter of positive NAO phase seventeen months of ten years were used, for winter of negative NAO phase, three months of three years, for spring of positive NAO phase, twelve months of nine years, and for spring of negative NAO phase, eleven months of nine years. It should be noted that no TOR data are available in 1994, 1995 and 1996, and in much of the years 1993 and 1997.”

Figure 15 has been re-plotted with the new criteria. TOR differences between positive and negative phases have been included as suggested by Referee#1.

We have taken the opportunity to cite the following article, recently published, which is very timely to confirm certain aspects of our discussion in Section 3.8.

Pausata, F. S. R., L. Pozzoli, E. Vignati, and F. J. Dentener, North Atlantic Oscillation and tropospheric ozone variability in Europe: model analysis and measurements intercomparison, *Atmos. Chem. Phys.*, 12, 6357–6376, 2012.

On the other hand, Figures 15 and 16 cannot be compared now in terms of NAO, since NAO index information in Figure 16 corresponds to seasonal NAO means, while in Figure 15 we have used monthly NAO means.

2. Figures 4, 7, 8, 9 and 13 are referred to in the text by figure part (Figure 4a, Figure 4b etc..), the figures themselves should be updated to include these labels as it is unclear which parts of the figures are being referenced, figure 13 it particularly confusing.

Done

3. Figures 5 and 6. Please use a thicker line for the map as it is very difficult to make out.

Done

4. Figure 11. The quality of the plots in the second column of this figure is very bad. The axes lines need to be thicker, and it is almost impossible to see the line for P25th, please use choose a different color to plot this line.

Done

5. Page 28399, line 28 states '(3) transport from North America, is defined much better in this season.' Should read 'Transport from North America is more well defined in this season'

Done

6. Page 28401, line 13, 'A 67% of the hourly' Remove the 'A'

Done

7. Page 28410, lines 23-24, 'travelling most of them at levels', should read 'most of them travelling at levels ...'

Done

Assessment of atmospheric processes driving ozone variations in the subtropical North Atlantic free troposphere

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Abstract. An analysis of the 22-yr ozone (O₃) series (1988–2009) at the subtropical high mountain Izaña station (IZO; 2373 m a.s.l.), representative of free troposphere (FT) conditions, is presented. Diurnal and seasonal O₃ variations as well as the O₃ trend ($0.19 \pm 0.05 \text{ \% yr}^{-1}$ or $0.09 \text{ ppbv yr}^{-1}$), are assessed. A climatology of O₃ transport pathways using backward trajectories shows that higher O₃ values are associated with air masses traveling above 4 km altitude from North America and North Atlantic Ocean, while low O₃ is transported from the Saharan continental boundary layer (CBL). O₃ data have been compared with PM₁₀, ²¹⁰Pb, ⁷Be, potential vorticity (PV) and carbon monoxide (CO). A clear negative logarithmic relationship was observed between PM₁₀ and surface O₃ for all seasons. A similar relationship was found between O₃ and ²¹⁰Pb. The highest daily O₃ values (90th percentile) are observed in spring and in the first half of summer-time. A positive correlation between O₃ and PV, and between O₃ and ⁷Be is found throughout the year, indicating that relatively high surface O₃ values at IZO originate from the middle and upper troposphere. We find a good correlation between O₃ and CO in winter, supporting the hypothesis of long-range transport of photochemically generated O₃ from North America. Aged air masses, in combination with sporadic inputs from the upper troposphere, are observed in spring, summer and autumn. In summer-time high O₃ values seem to be the result of stratosphere-to-troposphere (STT) exchange processes in regions neighbouring the Canary Islands. Since 1995–1996, the North Atlantic Oscillation has changed from a predominantly high positive phase to alternating between negative, neutral or positive phases. This change results in an increased flow of the westerlies in the mid-latitude and subtropical North Atlantic, thus

favouring the transport of O₃ and its precursors from North America, and a higher frequency of storms over North Atlantic, with a likely higher incidence of STT processes in mid latitudes. These processes lead to an increase of tropospheric O₃ in the subtropical North Atlantic region after 1996 that has been reflected in surface O₃ records at IZO.

1 Introduction

Ozone (O₃) is an important trace gas in the troposphere (Fishman and Crutzen, 1978). It affects the oxidizing capacity of the troposphere (Levy, 1971; Logan, 1985; Thompson, 1992), it is a phytotoxicant that can affect public health (Tiao et al., 1975), and is an important greenhouse gas (Ramanathan et al., 1985; Mitchel, 1989). A portion of the O₃ is downward transported from the stratosphere (Junge, 1962; Danielsen, 1968; Levy et al., 1985), while most of the tropospheric O₃ is believed to be produced in the troposphere itself by photochemical reactions involving nitrogen oxides (NO_x) and carbon monoxide (CO) (Lelieveld and Dentener, 2000; Jonson et al., 2006). Thus, O₃ concentrations may be viewed as the sum of a global/hemispheric background concentration and regionally/locally produced O₃ (Jonson et al., 2006).

Results from Graustein and Turekian (1996) indicate an upper troposphere source for elevated O₃ in summer-time subtropical free troposphere (FT) of the Eastern North Atlantic, and James et al. (2003) found evidence of deep stratospheric intrusions down to the lower FT over the Canaries even in summer. Oltmans et al. (1996) reported evidence of high O₃ concentration ($\sim 100 \text{ ppb}$) layers in the middle and

upper troposphere over the North Atlantic which are invariably associated with transport characteristics that strongly support a stratospheric source for these layers.

However, other authors (e.g. Moody et al., 1996; Creilson et al., 2003; Hegarty et al., 2009) suggest that a substantial amount of photochemically generated tropospheric O₃ is transported from continental source regions over the North Atlantic. Some studies have revealed the great impact of this pollution over the air quality of Europe (e.g. Parrish et al., 1993; Li et al., 2002a; Prather et al., 2003). As pointed out by Stohl (2001) and Stohl et al. (2002) the long-range transport of O₃ from North America to Europe is more efficient in the middle and upper FT because the westerlies are stronger than in the marine boundary layer (MBL), and because of a longer O₃ lifetime. Val Martin et al. (2008) suggest that a substantial amount of additional O₃ formation occurs in the anthropogenic plumes during transport to the Central North Atlantic lower FT.

Assessment of long-term trends in tropospheric O₃ is difficult due to the scarcity of representative observing sites with long records (Solomon et al., 2007). In addition, the long-term tropospheric O₃ trends vary both in terms of sign and magnitude and in the possible causes of the change (Oltmans et al., 2006). Some O₃ trends have been attributed to changes in O₃ precursor emissions (Scheel, 1983). However further studies reveal that O₃ trends cannot be fully explained based on its precursors alone. For example, Staehelin and Poberaj (2008) argue that further increase in background O₃ over Europe and North America since the early 1990s cannot be solely explained by regional O₃ precursor changes because anthropogenic O₃ precursor emissions were drastically reduced in the industrialized countries as a consequence of air quality legislation. Gilge et al. (2010) also state the apparent contradiction between the rather constant O₃ concentrations observed at ground stations during the end of the 1990s to 2007 and the substantial reductions in anthropogenic emissions. The surface O₃ positive trend found at elevated European sites was explained by Ordóñez et al. (2007) in terms of an increased contribution of stratospheric O₃ in the 90s. Conversely, Tarasova et al. (2003) found negative trends in a high mountain in Russia, and Vingarzan (2004) and Tarasova et al. (2009) reported a slower rate of tropospheric O₃ increase or in some cases lack of an increase over the past decade. Logan et al. (2012) found a slow decrease in summer surface ozone in alpine stations, and in the free troposphere over Europe, with an average trend of -0.15ppbyr^{-1} since 1998. Spatial and temporal evolution of atmospheric processes driving O₃ concentrations affect stations located in different regions of the world in different ways, as it has been recently reported by Oltmans et al. (2013). In this regard, Jonson et al. (2006) address the question if the observed O₃ trends can be understood.

Model simulations suggest that the increase of background tropospheric O₃ observed in mountain tops can be only partially explained by changes in emissions of precursors over

continents, and may be affected by changes in the circulation of the troposphere (Jonson et al., 2006). For example, Appenzeller et al. (2000) found a good correlation between the North Atlantic Oscillation (NAO) index and column tropospheric O₃ over Eastern North Atlantic, and Eckhardt et al. (2003) demonstrated how the NAO controls the air pollution transport to the Arctic. Duncan and Bey (2004) explained that the CO burden from Europe tended to be higher over the North Atlantic and lower over the Arctic when the NAO was in the negative phase. So, reductions in O₃ caused by reductions in precursors may be masked by periodical changes in atmospheric circulation. As noted by Jonson et al. (2006), the changes suffered by the stratospheric O₃ in the last decades could alter the circulation patterns, which would affect, in turn, the exchange between the stratosphere and troposphere.

Most of the studies address the origin of tropospheric ozone from only one of the most common approaches: photochemistry or atmospheric dynamics, which is a limited and partial view of the driving forces. So, we propose, firstly, a detailed analysis of a long-term (22 yr) surface O₃ time series (1988–2009) at the Izaña high mountain station (hereafter IZO), which is representative of background conditions of the lower troposphere in the subtropical North Atlantic region, where there is very little information available. Secondly, we present an extensive and multidisciplinary review of the O₃ transport processes into the FT of the North Atlantic subtropical region, incorporating other components such as particulate matter, CO, ⁷Be, ²¹⁰Pb, and additional information from backward trajectories, potential vorticity (PV), and NAO index.

The surface O₃ measurement programme of IZO is run with an independent quality assurance system, within the World Meteorological Organization (WMO) Global Atmospheric Watch (GAW) Programme, which precludes data biases and prevents wrong interpretations in trends analysis. Our paper is structured as follows: data and methods are described in Sect. 2. In Sect. 3 a surface O₃ climatology and transport pathways characterization is presented, and a discussion about surface O₃ observations, their relationships with other atmospheric components (PM₁₀, ²¹⁰Pb, PV, ⁷Be, and CO), and their connections with synoptic scale dynamical processes driven by the NAO is given. In Sect. 4 a summary and main conclusions are provided.

2 Data and methods

2.1 Measurement site

The Izaña GAW Observatory is located at 28.3° N, 16.5° W at an altitude of 2373 m a.s.l. (annual mean pressure of ~770 hPa) on Tenerife Island, (Canary Islands, Spain) on top of a mountain platform on a dorsal ridge which crosses the island from SW to NE. A belt of endemic pine forest (*Pinus Canariensis* CHR, Sm. Ex DC) grows between 600 and

Table 1. Description of O₃ analyzers, associated quality assurance, and data acquisition system, used during the period 1988–2009. Ri = Reference instrument; Bi = Basic instrument; Bp = Backup instrument; MPC = Multipoint calibration.

Period	Instrument	Calibration system/ Quality Assurance	International Reference	Data acquisition
May 87–Jul 95	Dasibi-1008-AH #4283 (Bi)	Dasibi-1008-RS #5797 (Ri) MPC/ 2 months	NIST Traceable	Continuous Record: 10 min ± SD
Jul 95–Jul 96	Dasibi-1008-RS #5797 (Bi)		NIST Traceable	Continuous Record: 10 min ± SD
Jul 96–Feb 99	TEI 49C #55912-305(Bi) Dasibi-1008-RS #5797 (Bp)	EMPA Audit (Nov 96) TEI 49C-PS #56085-306 (Ri) (Apr 97) MPC/ 3 months EMPA Audit (Feb 98)	NIST-EMPA	Continuous Record: 1 min ± SD
Feb 99–Nov 03	TEI 49-C #62900-337(Bi) Dasibi-1008-RS #5797 (Bp)	TEI 49C-PS #56085-306(Ri) MPC/ 3 months EMPA Audit (Jun 00)	NIST-EMPA	Continuous Record: 1 min ± SD
Nov 03–Now	TEI 49-C #62900-337(Bi) TEI 49-C #72491-371(Bp)	TEI 49C-PS #56085-306(Ri) EMPA Audit (Nov 04) EMPA Audit (Nov 09)	NIST-EMPA	Continuous Record: 1 min ± SD

2000 m a.s.l., whereas at higher levels there is only a sparse cover of local species of broom (*Spartocytisus supranubius*) growing on lava terrain. Except for a few scattered residences, Tenerife is uninhabited above the 1000 m level. The horizontal distances from IZO to the northwest and to the southeast coasts (the direction of the prevailing winds) are less than 15 km. The nearest distance to the European continent is 1300 km and about 350 km to Africa.

2.2 In situ surface O₃ instrumentation

The surface O₃ monitoring programme at IZO started in May 1987 using UV-absorption technique. The analyzers used in different periods from then to now, as well as the reference instruments and the quality assurance programmes are specified in Table 1. The terminology used in Table 1 is the following:

- Basic instrument: analyzer from which the final data result.
- Backup instrument: instrument that is monitoring in parallel to the basic analyzer.
- Reference instrument: analyser for independent comparisons and calibrations (not used for ambient air measurements).

O₃ has been measured continuously recording 10-min averages with the corresponding standard deviation from May 1987 to July 1996. After this date, and up to now, 1-min average O₃ values with corresponding standard deviations are recorded for both the basic and the backup instruments. Zero-checks with an activated-carbon absorber

were performed on a daily basis to detect instrumental offset drifts. Surface O₃ data at IZO have been also calibrated against references that are traceable to NIST (US National Institute for Standards and Technology) reference O₃ photometer (Gaithersburg-Maryland, USA). The Izaña surface O₃ programme has been audited by the World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane (WCC-Ozone-CO-CH₄-EMPA) in 1996, 1998, 2000, 2004 and 2009. EMPA's audit reports are available at http://www.empa.ch/gaw/audits/IZO_yyyy.pdf, where yyyy is the year. The audits were performed according to the “Standard Operating Procedure (SOP) for performance auditing O₃ analyzers at global and regional WMO-GAW sites”, WMO-GAW Report No. 97. All audited field instruments (basic and backup instruments) fulfilled the assessment criteria as “good” over the tested range up to 100 ppbv.

2.3 Backward trajectories, O₃ MCAR plots, residence times, and BTMH plots

Five-day HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) version 4.0 dispersion model backward trajectories (Draxler and Rolph, 2003; Rolph, 1983), with a time resolution of 1h were calculated using the FNL (Final Analysis Data) meteorological data-set (from May 1987 to December 2004) and the GDAS (Global Data Assimilation System) meteorological data-set (from January 2004 to December 2009), both from the National Centres for Environmental Prediction. The vertical component of the backward trajectories was computed using the vertical model velocity. The end-point was set at Tenerife (28.3° N, 16.5° W)

at 2400 m a.s.l. (IZO height) for each day of the study period (1 January 1988–31 December 2009) at 00:00 UTC.

The transport paths of the air masses reaching Tenerife (00:00 UTC) have been characterized using the permanence indexes for the predefined source geographic sectors described in Alonso-Pérez et al. (2007) and summarized in Table 2. Permanence indexes were calculated as the fraction of time that an air mass trajectory calculated for 120 h resides in a pre-defined particular geographic sector and also in a predefined altitude range. We consider “low” an altitude range between surface level and 1.5 km, “medium” an altitude range between 1.5 and 3 km, and “high” > 3 km (normally with a top-height at 6 km). Permanence indexes were obtained using 5-day HYSPLIT backward trajectories.

Table 2. Geographical sectors used in the backward trajectory classification (function of the continental source regions and oceanic sectors, latitude and longitude ranges).

Sector	Latitude Range	Longitude range
North America	30° N–90° N	50° W–135° W
North Atlantic	30° N–90° N	10.5° W–70° W
North Europe	50° N–90° N	10.5° W–50° E
South Europe	36° N–50° N	10.5° W–50° E
Sahara	20° N–36° N	18° W–50° E
Sahel	0° N–20° N	18° W–50° E
Subtropical North Atlantic	0° N–30° N	18° W–135° W
Canary Islands	24.7° N–31.9° N	12.4° W–20.6° W

Source-receptor relationships of atmospheric composition can be investigated with backward trajectory techniques, tracing forward from a defined geographical origin to arrive at measurement sites where the composition may have altered during transport (Fleming et al., 2012). One of these techniques is the so called as Mean Concentrations At Receptor (MCAR). For each pixel of our geographical domain, we select the backward trajectories which arrive to IZO and pass over that pixel. The daily mean O₃ concentrations of the corresponding days are averaged for that pixel. MCAR plots allowed the identification of pathway regions with high and low O₃. The methodology has been described by Rodríguez et al. (2011). Monthly MCAR plots of surface O₃ were determined using daily 5-day backward trajectories calculated at 00:00 UTC and daily (nocturnal) surface O₃ data at IZO for the period 1988–2009.

The identification of the transport corridors and source regions of O₃ was complemented by using the residence time analysis technique (Poirot and Wishinski, 1986). For this issue, the geophysical region covered by the trajectories was divided into 408 grid cells of 5° × 5° (latitude/longitude). The problem with this method is that all of the backward trajectories begin at the receptor site and thus, the residence time is maximum in the cells surrounding the sampling location (Hopke et al., 2005). We refer to this effect as “central convergence”. We have used a modification proposed by Poirot

and Wishinski (1986) to avoid the geometrical “central convergence” effect and highlight the distant O₃ sources.

Backward trajectories have been also used to compute backward trajectory mean height (BTMH) plots. In this case BTMH plots represent the mean height of the air parcel when air masses passed above each 1° × 1° cell.

2.4 Potential vorticity

Potential vorticity (PV; 1 PVU = 10⁻⁶ m² s⁻¹ K kg⁻¹) analysis is a widely used tool to understand the STT exchange (e.g. Danielsen, 1968) since PV, the product of absolute vorticity and thermodynamic stability, is greater in the stratosphere than in the troposphere (Hoskins et al., 1985). The dynamical tropopause is typically defined with a PVU value ranging from 1 PVU (Shapiro et al., 1987) to 2 PVU (Appenzeller et al., 1996; Parrish et al., 2000). The dynamical tropopause is defined by (WMO) as the 1.6 PVU isosurface. This value is used by some authors to identify the signature of stratospheric air (e.g. Stohl et al., 2000; Cristofanelli et al., 2006), while other authors consider two threshold values for the dynamical tropopause, 2 and 1.5 PVU, for deep stratospheric intrusion analysis, as (Akritidis et al., 2010). It is assumed that PV > 1 PVU are typical values of tropospheric regions that have been impacted by stratospheric intrusions. Beekman et al. (1994) made use of the positive correlation of PV with O₃ in separating tropospheric O₃ sources on the basis of high and low PV. However, we should note that diabatic heating can reduce the PV values without changing O₃. So, PV must be viewed as a bottom-indicator of air masses with upper troposphere/lower stratosphere (UTLS) signature.

PV was obtained from ERA-Interim ECMWF (European Centre for Medium-Range Weather Forecasts) reanalysis. Daily reanalysis at 00:00, 06:00, 12:00 and 18:00 UTC were retrieved at 300, 400, 500, 600, 700, 775, 850 and 925 hPa levels from January 1988 to December 2009 in a regular grid with a spatial resolution of 0.5° latitude/longitude, within the geographical domain 20° N–50° W/70° N–30° E.

Maximum PV (PV_{max}) intercepted by daily 5-day backward trajectories for IZO was computed as follows: for each one of the 120 h of the backward trajectory the PV is calculated by performing a 3D nearest-neighbour interpolation with the 8-isobaric PV levels of the ECMWF reanalysis. PV was stored for each 1h point back of the back-trajectory. In this work we have used the PV_{max} found along each backward trajectory together with its latitude and longitude.

2.5 ⁷Be and ²¹⁰Pb radiotracers

The ²¹⁰Pb radiotracer (half-life 22 yr) is the decay daughter of ²²²Rn (half-life 3.8 days) which is emitted from soils (Turekian et al., 1977). So, ²¹⁰Pb is a tracer of air masses with continental boundary layer (CBL) signature (Balkanski et al., 1993). The ⁷Be radiotracer (half-life 53.3 days) is pro-

duced by cosmic ray spallation reactions with nitrogen and oxygen in the stratosphere and upper troposphere (Viezee and Singh, 1980).

The ⁷Be and ²¹⁰Pb radionuclides were measured at IZO on a daily basis within the AEROCE (AEROSol Ocean chemistry Experiment) project (Prospero et al., 1995), in the period 1989–1991, as tracers for UTLS and CBL air, respectively.

2.6 Carbon monoxide (CO)

Carbon monoxide (CO) is a good tracer of anthropogenic pollution because it has a relatively long lifetime in the FT, which permits the study of long range transport. Daily and hourly night-time CO averaged concentrations at IZO, corresponding to the period 2008–2011, have been used for the analysis of long-range transport of photochemical O₃ from polluted regions. CO concentrations have been obtained using an automated TEI 48C-TL (Thermo Electron Corporation) NDIR instrument. The NDIR system was calibrated every 3 months using a 10-ppm CO in N₂ standard from Air Liquide. Automatic zero checks and ambient air measurements are alternated in 15 min intervals to account for short-term drift. A Sofnocat 423 CO scrubber is used for the zero checks. The inlet filter is exchanged every 3 months. One-minute averages including additional instrument status information are stored. The NDIR system has been audited by the WCC-Ozone-CO-CH₄-EMPA in 2009. This audit confirmed the stability and linearity of the instrument, and showed an error of about 10 % when compared to EMPA reference. However, continuous NDIR data have been corrected using discrete NOAA measurements of weekly samples collected in flasks. So, we expect an error lower than 10 %. CO data is used in this work to assess pollution long range transport by analyzing averaged daily O₃/CO ratios. So, the error associated to CO measurements is acceptable for our purposes.

2.6.1 PM₁₀

Daily nocturnal PM₁₀ (particles less than 10 microns in diameter) concentrations at IZO in the period 2002–2009 have been used for assessing the impact of dust laden Saharan air masses on O₃ records. The PM₁₀ measurement programme was described by Rodríguez et al. (2011).

2.6.2 North Atlantic Oscillation (NAO) index

The NAO is one of the major tele-connection patterns of the winter Northern Hemisphere (Wallace and Gutzler, 1981), and represents a measure of the strength of the westerlies across the North Atlantic. Monthly mean values of the NAO index have been obtained from NOAA Climate Prediction Center ftp://ftp.cpc.ncep.noaa.gov/wd52dg/data/indices/nao_index.tim. Indices are normalized using the 1981–2010 base period monthly means and standard deviations.

2.6.3 Tropospheric Ozone Residual (TOR)

Tropospheric Ozone Residual (TOR) data are measurements of tropospheric O₃ obtained by subtracting the stratospheric component of O₃ (in the stratospheric aerosol and gas experiment) from the total atmospheric column of O₃ (by use of the Total Ozone Measurement Spectrometer (TOMS) and Solar Backscattered Ultraviolet (SBUV) instruments).

Data over the North Atlantic, Northern Africa and Europe, within the geographical domain 10° N–30° E/50° N–60° W, have been computed from the database available at NASA site: <http://asd-www.larc.nasa.gov/TOR/data.html>. A description of the technique can be found in Fishman and Balok (1999) and Fishman et al. (2003).

The TOR seasonal average value for each phase of the NAO within the period 1988–2005 was obtained by averaging for each season the TOR monthly mean values of those months in which NAO > +0.5 (positive NAO) or NAO < -0.5 (negative NAO). Thus, to calculate the TOR mean value corresponding to winter of positive NAO phase seventeen months of ten years were used, for winter of negative NAO phase, three months of three years, for spring of positive NAO phase, twelve months of nine years, and for spring of negative NAO phase, eleven months of nine years. It should be noted that no TOR data are available in 1994, 1995 and 1996, and in much of the years 1993 and 1997.

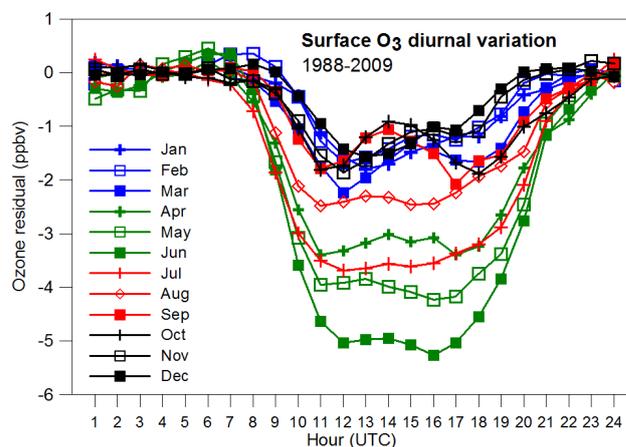


Fig. 1. Diurnal variation of surface O₃ residuals for each month of the year in the period 1988–2009. The O₃ residuals have been calculated on daily basis as the differences of surface O₃ for every hour over the night background level.

3 Results

3.1 Surface O₃ diurnal cycle

Large-scale subsidence, associated to the descending branch of the Hadley cell, is an important meteorological feature of

the subtropical North Atlantic region. The quasi-permanent NNE trade winds flow over a relatively cold ocean surface that inhibits the development of convection in the MBL and enhances subsidence. A temperature inversion layer (TIL) separates two well differentiated air masses: the MBL and the FT (Font, 1956). The TIL is characterized by a layer of stratocumulus formed by condensation of water vapour onto the available pre-existing particles. The top of the TIL is generally located around 1200 m a.s.l. in summer and around 1800 m a.s.l. in winter. IZO normally lies above the TIL that traps local island pollutant emissions. However, under certain synoptic conditions, normally in winter, the TIL reaches the station level or, simply, the TIL is not observed. The effectiveness of the inversion in separating the MBL from the FT at IZO is reflected in the relative humidity typically > 60% below the TIL and ~ 20% above it. Diurnal variations in the altitudes of the bottom (1200 m during daylight and 900 m at night) and the top (1700 m during daylight and 1300 m at night) of the TIL are observed. The influence of buoyant airflows caused by the heating of the air located just above the terrain of the island is observed at IZO. This upslope effect is reflected in the daily cycle of CO₂ concentrations that shows lower values and higher standard deviations during daylight, due to uptake by vegetation growing at lower elevations on the slopes (Cuevas et al., 1992). During the night a catabatic air flow regime is well established over the station favouring the arrival of very clean air masses from higher levels.

The diurnal cycles of O₃ (Fig. 1) were obtained from the differences of O₃ for every hour compared with the night background level. The reference background level has been computed as follows. Firstly, the averages of the pre (00:00–07:00 h UTC) and post (21:00–00:00 h UTC) nights were computed. Then, the linear drift in time passing through both averages is used as the reference background level. The use of a linear drift allows for a background trend. Diurnal cycles of surface O₃ have been averaged for each month using hourly data for the entire period 1988–2009.

Surface O₃ diurnal variations show the lowest values during the afternoon due to an efficient dry deposition on very rough and dark volcanic mountain slopes covered with scattered bushes. This diurnal cycle is the opposite to that recorded in continental regions where a maximum during daylight is observed due to the photochemical production (e.g. Millán et al., 1997). The annual mean difference between the daily upslope and the nocturnal downslope surface O₃ values is within 2 ppbv in winter and autumn. However, in summer and spring day-night differences are normally above 2 ppbv, being somewhat greater than 5 ppbv in June, and reaching up to 25 ppbv in some days. The amplitude and width of the diurnal O₃ “valley” is basically modulated by two factors: the solar radiation, and the consequent heating of the slopes surrounding the observatory, and the strength of the synoptic wind. In wintertime the heating of the slopes is minimal, and the strong synoptic winds dilute air masses from lower levels. By contrast, in spring and summer there

is: (1) a strong warming of the soil (facilitating the mountain breeze); (2) the TIL associated to trade winds is recorded at its lowest level (around 800–1100 m a.s.l.), so the air flows from lower levels, where O₃ concentration is lower, and with a longer path available for dry deposition; and (3) the synoptic winds are usually very weak, resulting in a lower dilution of upslope air. The “ozone valley” in the daytime is a feature also observed in other high mountain stations: Mauna-Loa (Oltmans and Levy II, 1994), and Jungfrauoch Schuepbach et al. (2001).

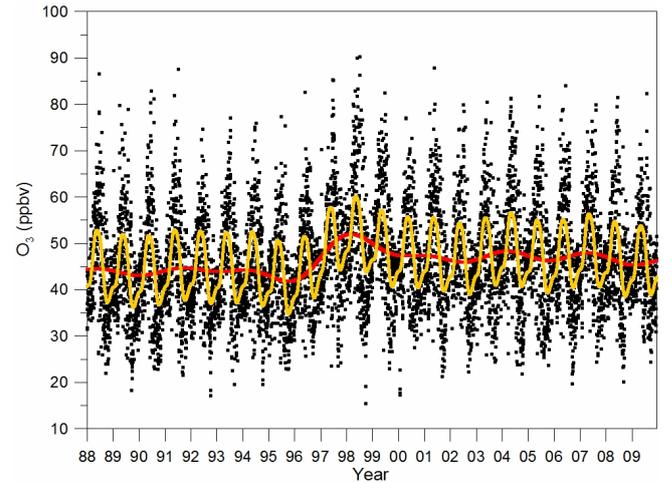


Fig. 2. Surface O₃ daily night means (black dots), inter-annual trend (red line) and inter-annual trend plus annual cycle at IZO from 1988 to 2009.

3.2 Annual and seasonal variations of surface O₃

Daily nocturnal (22:00–06:00 UTC) O₃ values, representative of subtropical FT conditions, have been analyzed for the entire record (1988–2009) using decomposition in three terms: inter-annual trend, annual cycle, and residual. A least squares fit of the daily data to the function:

$$f(t) = a_1 + a_2 t + a_3 t^2 + \sum_{i=1}^p [b_i \cos(w_i t) + c_i \sin(w_i t)] + \sum_{j=1}^4 [d_j \cos(k_j t) + e_j \sin(k_j t)]$$

has been performed, where: t is the time in days ($t = 1$ for 1 January 1988); a_1 , a_2 , a_3 , b_i and c_i are the parameters of the inter-annual trend to be determined; $p = 7$; d_j and e_j are the parameters of the annual cycle (which is assumed constant) to be determined; $w_i = 2\pi i/N$ with N equal to the number of days in the period 1988–2009 ($N = 8036$, number of valid data = 7790); $k_j = 2\pi j/T$ with $T = 365.25$ days. See Gómez-Peláez et al. (2006) for a detailed interpretation of this function. Note that in this work we have

added a quadratic term in time, following Gómez-Peláez et al. (2012), in order to allow a non-periodic growth rate.

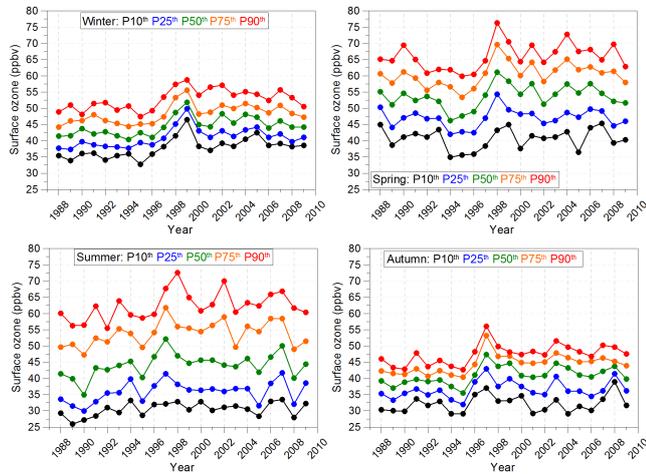


Fig. 3. Long-term (1988–2009) surface O₃ concentrations (night values: 22:00–06:00 UTC) for percentiles 10th, 25th, 50th, 75th, and 90th at IZO for winter (JFM), spring (AMJ), summer (JAS) and autumn (OND).

Figure 2 shows the inter-annual trend and the inter-annual trend + annual cycle. The average yearly mean O₃ value at IZO for the 22 yr period is 46.1 ppbv. The corresponding standard deviation of the mean is 0.12 ppbv. The root mean square of the residuals is 8.9 ppbv, and the peak-to-peak annual cycle amplitude is 15.4 ppbv. It is striking the O₃ increase observed between 1996 and 1998. There is a slight positive trend in the annual mean (0.09 ± 0.02 ppbv yr⁻¹ or 0.19 ± 0.05 % yr⁻¹), that is slightly lower than at Mauna-Loa (0.37 ± 0.26 % yr⁻¹, Oltmans and Levy II, 1992). In European Alpine stations such as Sonnblick, Jungfraujoch, Hohenpeissenberg and Zugspitze trends are observed in the 0.1–0.4 % yr⁻¹ range (Gilge et al., 2010). Over some European stations (Hohenpeissenberg, Zugspitze and Mace Head) small trends or reductions during summer are observed, while there is an increase during winter (Oltmans et al., 2006). Mace Head, a site that is representative of O₃ changes in the air advected from the North Atlantic to Europe in the MBL, has shown a positive trend of 0.16 ± 0.04 ppbv yr⁻¹ over the entire period 1988–2007 but this positive trend has reduced during recent years (Tripathi et al., 2010). So, tropospheric O₃ trends over Europe do not show a homogeneous behaviour.

Long-term O₃ series should be analyzed by seasons since the processes of transport/production of surface O₃ and its precursors can be very different in each season. In Fig. 3 we have plotted the long-term surface O₃ P10th, P25th, P50th, P75th and P90th (1988–2009) for winter, spring, summer and autumn. P_nth is the *n*-percentile. In winter, a change (increase) in all percentiles is observed in 1997 with a maximum in 1999. A similar behavior is found in spring, but only in

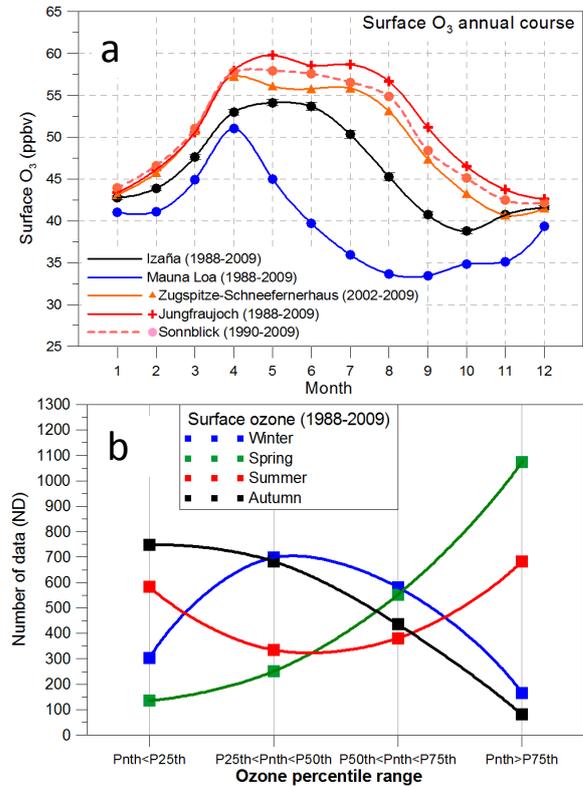


Fig. 4. (a) annual course of surface O₃ at IZO, Mauna-Loa, Zugspitze-Schneefernerhaus, Jungfraujoch, and Sonnblick. Bars associated to monthly mean values at IZO are the standard deviation of the mean. (b) the seasonal distribution of number of surface O₃ daily data (ND) at IZO within the following percentile ranges: P_nth ≤ P10th, P10th < P_nth ≤ P25th, P25th < P_nth ≤ P50th, P50th < P_nth ≤ P75th, P75th < P_nth ≤ P90th and P_nth > P90th.

P50th, P75th and P90th with maximum values in 1998. The lower percentiles do not show significant changes. In summer the increase is smoothed, being only evident in higher percentiles (P75th and P90th). In autumn the change is observable from 1996 in percentiles ≥ P50th. Changes in percentile data series observed in the period 1996–1998 will be discussed in Sect. 4.

Figure 4a shows non detrended monthly means for surface O₃ at IZO, Mauna-Loa (Oltmans and Levy II, 1994), Zugspitze-Schneefernerhaus (Nienerowski, 2004), Jungfraujoch (Logan et al., 2012), and Sonnblick (Federal Environment Agency Austria). Data from Mauna-Loa and the alpine stations have downloaded from the World Data Centre for Greenhouse Gases (WDCGG; <http://ds.data.jma.go.jp/gmd/wdcgg/>). IZO shows characteristics intermediate to those recorded at Mauna-Loa and the alpine stations. Rodríguez et al. (2004) compared the O₃ annual course at IZO with that observed at Mauna-Loa, noting that in summer O₃ monthly

means sharply decrease in the latter, while high O₃ events (daily mean values of 60–70 ppbv) are recorded at IZO. However, the typical continental annual cycle, with a broad spring/summer maximum observed in the alpine stations, is not seen at IZO where the annual cycle peaks in late spring (May–June). This is an indication that IZO is not affected by photochemical production from regional emissions in summer.

The annual course is shifted towards high values (> P75th) in spring, mid values (P25th < P_nth < P50th) in winter, and low values (< P25th) in autumn time, while summer contributes significantly in both low and high values (Fig. 4b). ND is the number of daily mean surface O₃ data in each percentile range for the total period 1988–2009. O₃ data above P90th are found in spring and summer whereas O₃ levels below P10th are found in late summer and autumn.

3.3 Synoptic climatology of surface O₃: transport pathways

A previous analysis of transport pathways of O₃ at IZO was performed by Rodríguez et al. (2004). In the present work we have incorporated a longer data series and followed a different approach, using the MCAR plots for each month for the entire surface O₃ data-set (Fig. 5). This methodology does not assume a priori geographical areas, and allows us to visualize the regions from which air masses reaching IZO come with different O₃ concentrations. Since at higher altitudes in the troposphere are expected higher concentrations of O₃, we have calculated the corresponding BTMH plots for each month of the year for the same period (Fig. 6).

Figure 5 shows in winter (January–March) a well-defined pattern with air masses coming from the North Atlantic and North America with a top-latitude located at about 60° N. It is also noticeable a latitudinal gradient with higher O₃ values in northern regions. Concerning the height of the backward trajectories (Fig. 6), a similar latitudinal distribution to the O₃ is observed, with higher altitudes to the north. The highest trajectory altitudes describe an arc-shape corridor from Western Europe to Northeast North America. Air masses with low O₃ coming from the Sahara are also recorded associated to very low height trajectories. In spring (April–June) we observe a similar O₃ pattern to winter, but with the following characteristics: (1) the latitudinal gradient is much higher, registering very high values at the northern edge of the cloud trajectories and Western Europe, describing an arch-shape pathway; (2) contributions from Sahara and southern part of the North Atlantic are lower; and (3) transport from North America is more well defined in this season. The heights of backward trajectories (Fig. 6) show a similar pattern than in winter, although the lowest trajectories from Africa travel at higher altitudes. In summer months (July–September) there is a sharp change because basically only two geographical sectors of air mass pathways are identified: from North America, with associated medium and high O₃ values, and

from the Sahara and Northern Sahel, with a lower latitude edge set at 10°–15° N, with low and very low O₃ values (Fig. 5). Air masses from North America and North Atlantic travel at relatively high altitude, whereas air masses from Sahara come from low levels (Fig. 6). It is noticeable that in July and August low-level trajectories originate from Western Sahara, while trajectories from the Sahel, and those originated over Western North African countries and the Mediterranean Basin travel at mid-high altitudes. In summertime the contribution from Western Europe is at its minimum, and the highest O₃ values describe an arc-shape pathway over the North Atlantic similar to that found in spring (Fig. 5). The O₃ and trajectory height patterns of autumn rapidly evolve to resemble those found in winter (Figs. 5 and 6), but with significantly lower O₃ values in the southern part of the trajectories cloud.

3.4 Low surface O₃ concentrations

The frequency distribution of trajectories by geographical sectors for low O₃ values (< P25th) registered at IZO is shown in Fig. 7a. Air masses that most often contribute to low levels of O₃ throughout the year are those from the subtropical North Atlantic (below 30° N). However, in summer, especially in July and August the Saharan air masses (with 60 % frequency) are the largest contributor to O₃ levels < P25th. There is a secondary maximum of African air masses in March, when dust layers occurring at low levels (usually within the MBL) impact IZO on their upper edge, although to a much lesser extent than in summer.

In winter, very low O₃ values are recorded also under fog conditions at IZO when the TIL is very high or simply it does not exist (normally with North Atlantic air masses). Hourly O₃ data shows a strong negative correlation with water vapour pressure (not shown here). In summer and autumn low O₃ levels are associated with the arrival of North African air masses that originate from Southern Morocco, Western Sahara and Sahelian regions (25–35 % of occurrence frequency of values < P10th). These trajectories show low-level (< 1500 m) “start-points”, which are usually associated with dust storms driven by surface local thermal lows over the Sahara (Prospero and Carlson, 1981).

There is a clear negative logarithmic relationship between PM₁₀ and surface O₃ in all seasons for the period 2002–2009 (Fig. 8a). Surface O₃ daily nocturnal data have been grouped in 10 ppbv bin ranges from the minimum to maximum value. Each point of the plot represents the median value of surface O₃ concentrations associated to the mean value (and corresponding standard deviation of the mean) of PM₁₀ in a determined bin range.

Most of the Saharan air masses have traveled within the African CBL and a high percentage of them correspond to lower levels (< 1500 m a.s.l.). 67 % of the hourly PM₁₀ records at IZO are lower than 10 µg m⁻³ and monthly means of PM₁₀ P75th are below 10 µg m⁻³ through the year, ex-

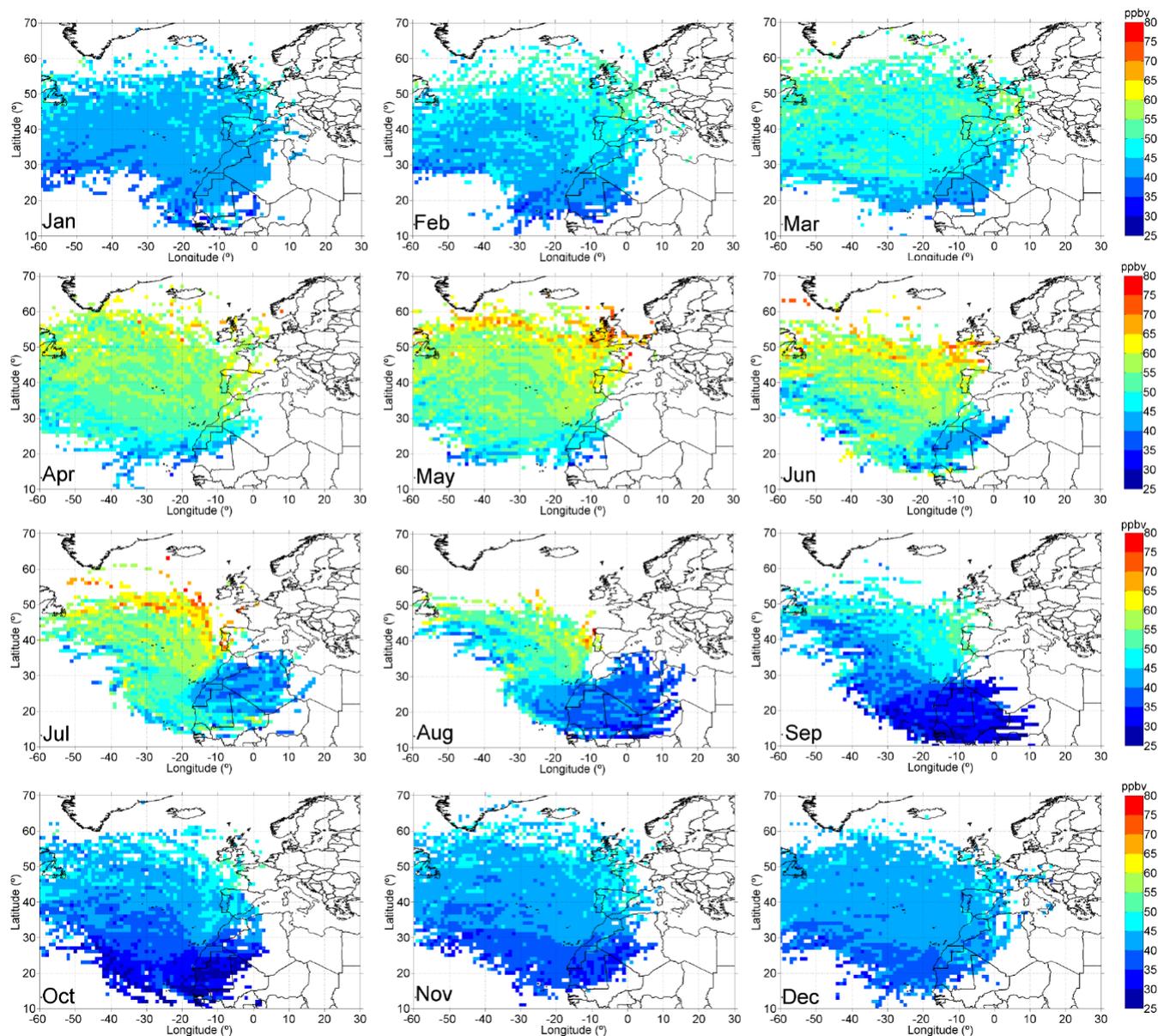


Fig. 5. Surface O₃ MCAR plots for each month of the year for the period 1988–2009. Color bars indicate O₃ concentration in ppbv.

cept in summertime when significant PM₁₀ concentrations are observed above P80th ($26 \mu\text{g m}^{-3}$).

Bonasoni et al. (2004) found also negative correlation between surface O₃ and coarse dust particles from North Africa at the high altitude Mt. Cimone station (North Italy). Andrey et al. (2010) found decreases of tropospheric O₃ up to 30% in some layers, between 2 and 6 km altitude, during dust-laden Saharan air mass intrusions over Tenerife, compared to situations of non-Sahara air masses. This result agrees with the relationship between surface O₃ and PM₁₀ found in this work.

The relationship between surface O₃ and ²¹⁰Pb is shown in Fig. 8b. In summer we obtain a logarithmic fit with a good

correlation which resembles the O₃-PM₁₀ fit in the same season. Prospero et al. (1995) had reported preliminary results of O₃-²¹⁰Pb relationship for summer-time. However, in spring (mainly in April) and autumn (mainly in December), when Saharan low-level intrusions over the Canary Islands occur (Alonso-Pérez et al., 2007), IZO is only slightly impacted by the top of the Saharan Air Layer (SAL). So we can see Saharan CBL signature with relatively high values of ²¹⁰Pb, although the O₃-²¹⁰Pb relationship is not as clear as that seen in summer. In winter, no correlation between surface O₃ and ²¹⁰Pb is found.

The low O₃ values associated with African trajectories which, in turn, cause a systematic rise in relative humidity

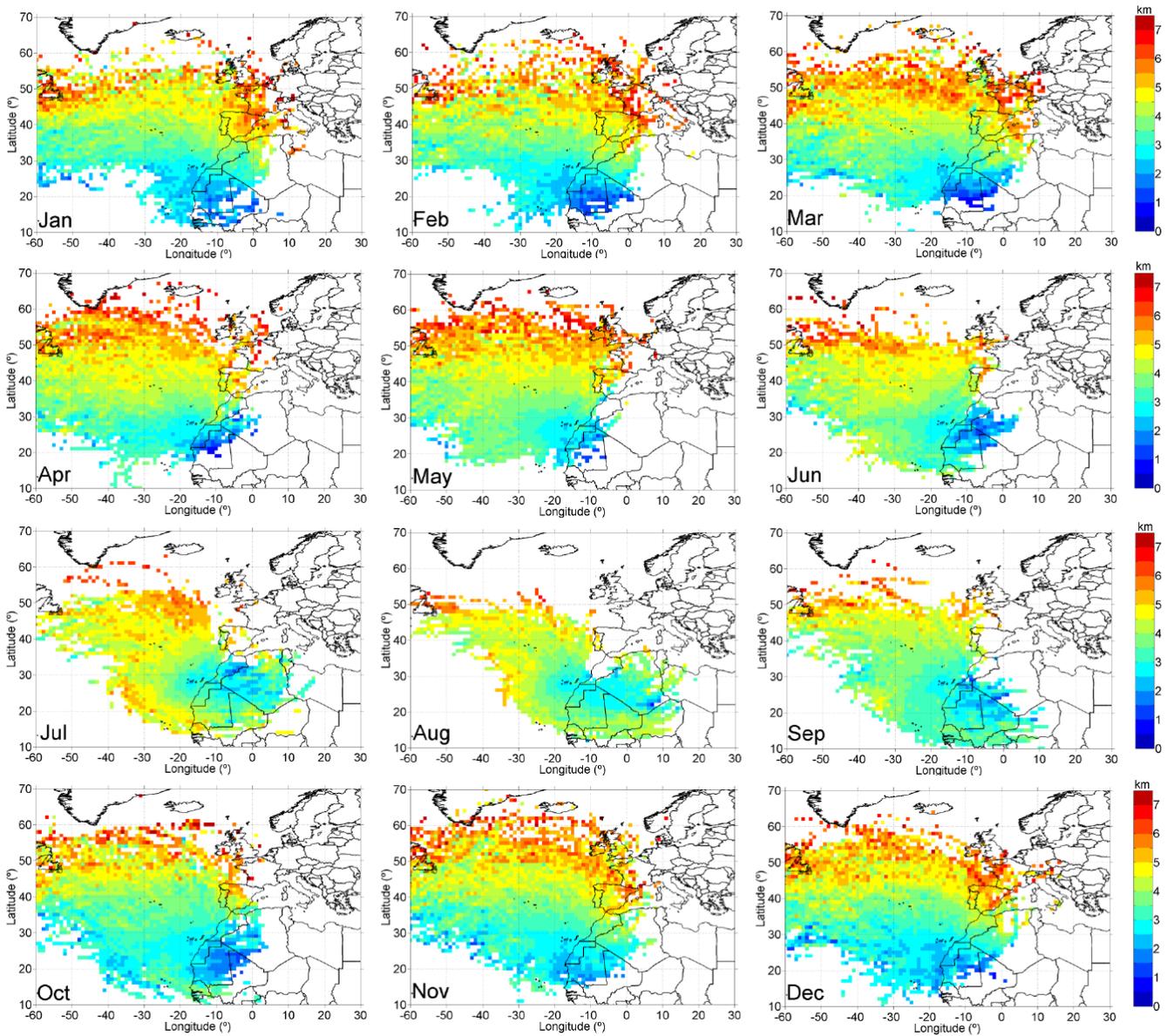


Fig. 6. Backward trajectory mean height plots for each month of the year for the period 1988–2009. Color bars indicate height in kilometers.

records at IZO (Cuevas, 1995), might be due to a sum of all or some of the following causes: (1) air masses come from lower levels within the Saharan CBL where O₃ concentrations are generally low (Güsten et al., 1996); (2) air masses originate from similar or lower latitudes which are not enriched with the latitudinal O₃ gradient existing in spring and summer in the Northern Hemisphere (London and Liu, 1992); (3) O₃ might be destroyed by dry deposition by suspended dust particles because of a larger surface area to dry deposition (Güsten et al., 1996); and (4) heterogeneous removal processes on dust aerosol by nitric acid (de Reus et al., 2000).

3.5 High surface O₃ concentrations

Figure 7b shows the monthly frequency of air masses that contribute most to O₃ values > P75th. Air masses from North America and oceanic sectors that have traveled over the North Atlantic are the largest contributors, by far, to high concentrations of O₃ at IZO. The highest daily O₃ values (> P90th) are observed in May and June, and in the first half of summer time (July and early August). Air mass residence times associated to O₃ concentrations between P75th and P90th (not shown here) show maximum values over Eastern United States (US) and North Atlantic between 30° and 55° N in winter, over the North Atlantic, from 25° to 55° N in spring, and near the Canary Islands and over North Western

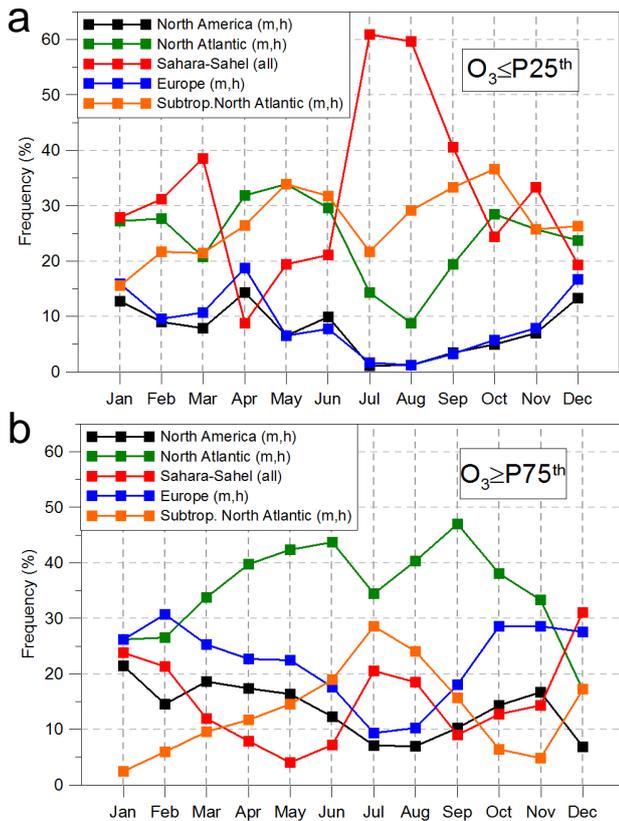


Fig. 7. (a) monthly mean percentage of air mass types arriving to IZO for $O_3 < P25^{th}$ for the period 1988–2009. (b) monthly mean percentage of air mass types arriving to IZO for $O_3 > P75^{th}$ for the period 1988–2009 (bottom panel).

Africa in summer. In autumn the maximum residence times are much shorter and located to the northernmost position.

Summer-time is very interesting since O_3 records differ markedly from other seasons because the O_3 concentration undergoes large and rapid changes (Cuevas, 1995; Rodríguez et al., 2004), often from day-to-day. The alternation of dust transport from the Saharan CBL, lasting 3–7 days, with the arrival of air masses from high levels over the North Atlantic, modulated by the Azores anticyclone, account for these sudden changes in O_3 concentration.

3.6 Upper troposphere contribution

We have computed PV_{max} found by daily 5-day backward trajectories when intercepting ECMWF PV-reanalysis fields for each day of the period 1988–2009. We have observed that mean values of PV_{max} in all seasons are slightly higher than 0.6 PVU. The average PV ranges approximately from 0.3 to 0.5 PVU in the low and middle troposphere (e.g. Rao et al., 2003), while 1 PVU is a typical value of the upper troposphere. So, it is noteworthy that in 10 % of days in win-

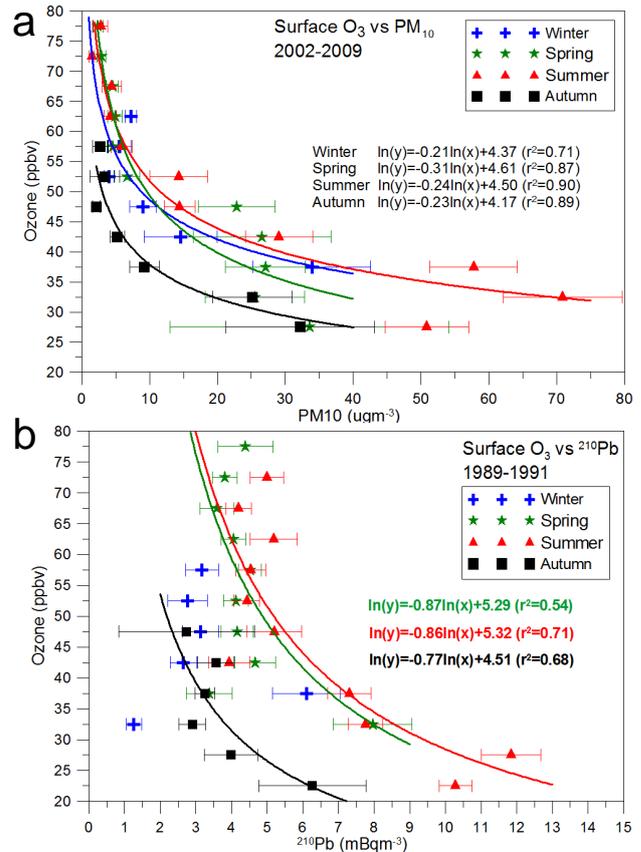


Fig. 8. (a) PM_{10} (μm^{-3}) vs surface O_3 (ppbv) at IZO for winter (JFM), spring (AMJ), summer (JAS) and autumn (OND) in the period 2002–2009. (b) ^{210}Pb ($mBq m^{-3}$) vs. surface O_3 (ppbv) for the same seasons in the period 1988–1991. Surface O_3 daily nocturnal data have been grouped in 10 ppbv bin ranges from the minimum to maximum value. Each point of the plot represents the median value of surface O_3 concentrations associated to the mean values of PM_{10} or ^{210}Pb in a determined bin range. The standard deviation of the mean (SDOM) associated to PM_{10} and ^{210}Pb mean values is represented by horizontal bars.

ter and autumn, backward trajectories have been impacted by upper-troposphere air masses with $PV > 1$ PVU. Some of them might even have been affected by stratospheric intrusions mixed with upper-troposphere air masses.

Seasonal averages of PV_{max} values have been plotted for several surface O_3 bins (Fig. 9a), for winter, spring, summer and autumn. A fair O_3 - PV_{max} correlation is found in all seasons with an O_3 - PV_{max} slope ~ 100 ppbv PVU⁻¹ for winter, spring and summer, and a slope slightly lower ~ 53 ppbv PVU⁻¹, for autumn. These results emphasize the importance of air masses subsidence regardless of the origin of O_3 measured at IZO. Cooper et al. (2002) found over Western North Atlantic an O_3 / PV ratio of ~ 72 ppbv PVU⁻¹ in springtime and ~ 42 ppbv PVU⁻¹ in late summer/early autumn. O_3 / PV ratios found by Rao et al. (2003) at 500 hPa in Northern Europe range from 60

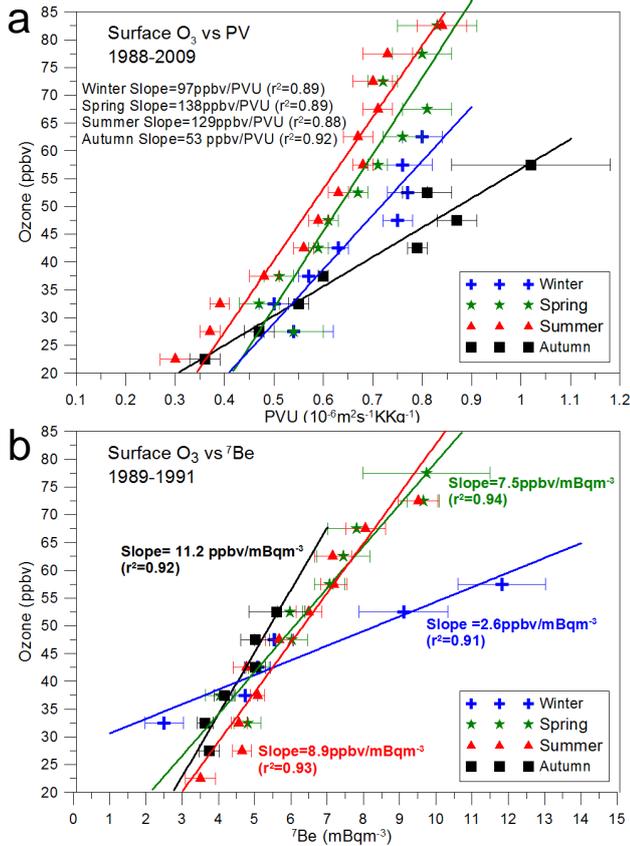


Fig. 9. (a) PV_{\max} ($1 \text{ PVU} = 10^{-6} \text{ m}^2 \text{ s}^{-1} \text{ K Kg}^{-1}$) vs. surface O₃ (ppbv) at IZO for winter (JFM), spring (AMJ), summer (JAS) and autumn (OND) in the period 1988–2009. (b) ⁷Be (mBqm^{-3}) vs. O₃ ozone (ppbv) at IZO for the same seasons in the period 1989–1991. Data have been grouped and depicted as for Fig. 8.

to $120 \text{ ppbv PVU}^{-1}$, which are of the same order as the O₃/ PV_{\max} ratios found at IZO.

Figure 10 shows the spatial distribution of averaged PV_{\max} recorded by daily 5-day backward trajectories when they are crossed with the ECMWF PV-reanalysis fields for each season. Thresholds of 1 and 1.6 PVU are marked with black lines. PV_{\max} maps provide an estimation of geographical regions of potential STT transport. PV_{\max} might work as a meridional-height coordinate: the highest and most northerly the air mass travels, the more PV_{\max} is associated. In Fig. 10 a latitudinal distribution, with much higher values of PV_{\max} in the north, is clearly appreciated. In mid latitudes there is a belt with relatively high values between 45° N and 55° N that crosses the North Atlantic. This is consistent with the distribution of backward trajectory heights pattern (Fig. 6). In winter and spring this high PV_{\max} belt coincides with the corridor where anthropogenic pollution is exported from North America to the North Atlantic (Cooper et al., 2002; Hegarty et al., 2009), as will be discussed later on. In summer PV_{\max} values are substantially reduced. However,

it is noticeable the relatively high PV_{\max} values found in the vicinity of the Canary Islands over North Africa. This result is also consistent with the high altitudes of backward trajectories observed over North Africa and the Mediterranean basin in July and August (Fig. 6).

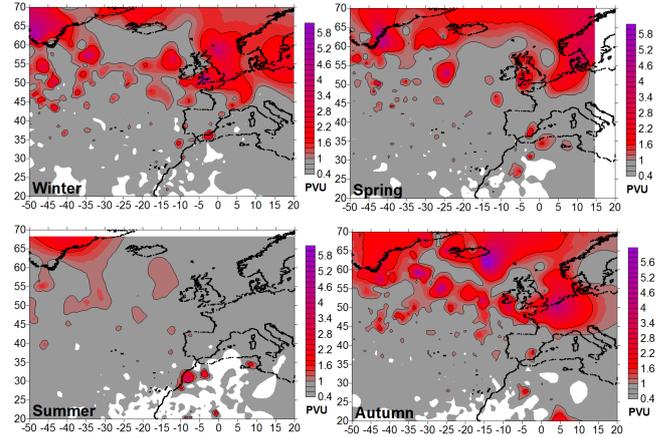


Fig. 10. PV_{\max} maps for winter (JFM), spring (AMJ), summer (JAS) and autumn (OND) in the period 1988–2009. They have been constructed from the coordinates of PV_{\max} values found by 5-day backward trajectories arriving at IZO every day at 00:00 UTC in ECMWF PV-reanalysis fields. Thresholds of 1 and 1.6 PVU are marked with black lines.

The relationships between surface O₃ and ⁷Be are shown in Fig. 9b for winter, spring, summer and autumn. The slope of O₃-⁷Be best fit corresponding to winter is similar to the slope of O₃-⁷Be best fit found by Dibb et al. (unpublished manuscript, 2006; www.espo.nasa.gov/docs/intex-na/Dibb_et.al_INTEXA.pdf) in mid and upper troposphere over North America during INTEX A flight experiment ($1 \text{ mBqm}^{-3} = 0.037 \times \text{fCi m}^{-3}$).

Li et al. (2002b) simulated ⁷Be and ²¹⁰Pb concentrations at Tenerife for summer-time and suggested that the positive O₃-⁷Be and negative O₃-²¹⁰Pb correlation simply reflect the respective common vertical trends. However, Cuevas (1995) and Cuevas et al. (2000) reported some case analysis of high O₃ and high ⁷Be data associated with air mass transport from the western part of cut-off lows (COLs) developed to the west of the Iberian Peninsula in spring and summer. Rodríguez et al. (2004) have also shown that episodes of O₃ > P90th at IZO are associated with strong subsidence in the FT at the western side of COLs located between the Canary Islands and the Iberian Peninsula. The STT processes are frequently associated to COL developments in the subtropical North Atlantic (Kentarchos et al., 2000). Cuevas and Rodríguez (2002), with an 11-yr climatology of ECMWF isentropic potential vorticity fields, concluded that the frequency of COLs and deep lows over the North Atlantic reach a maximum in May–July, in areas surrounding the Iberian Peninsula where

these lows are more frequent. James et al. (2003), with a 15-yr climatology of STT exchange found similar results, concluding that the corridor parallel to the Atlantic coast of the Iberian Peninsula over the ocean down to the Canaries frequently receives stratospheric air.

Reiter et al. (1983) suggested a ⁷Be threshold value of 8 mBq m⁻³, above which an air mass probably has stratospheric signature. This value has been used by several authors to identify stratospheric intrusions in high mountain stations (Zanis et al., 1999; Stohl et al., 2000; Bonasoni et al., 2000; Cristofanelli et al., 2006), although it is not possible to consider ⁷Be as an unambiguous stratospheric tracer (Zanis et al., 1999; Stohl et al., 2000). Gerasopoulos et al. (2001) found at four high-altitude alpine stations that high ⁷Be values (above 6 mBq m⁻³) correspond to air masses from the north and high altitudes, as it is characteristic for stratospheric intrusions. Reiter et al. (1983) showed that the range of ⁷Be values > 7.4 mBq m⁻³ corresponds to direct stratospheric intrusions near the station, without a long advection path. The third quartile of ⁷Be data series at IZO is 8.2 mBq m⁻³, and stratospheric air mass intrusions normally reach the ground after considerable mixing with tropospheric air. Therefore a threshold value of 8 mBq m⁻³ is reasonable to estimate the impact of UTLS air masses at IZO.

We have estimated the impact on O₃ at IZO of air masses with daily mean values of ⁷Be > 8 mBq m⁻³. Results are summarized in Table 3. The percentage of cases per season with ⁷Be > 8 mBq m⁻³ is significant in spring and summer (14.6 % and 8.9 % of cases/season, respectively), while in winter and autumn the percentage of cases/season is much lower (3.8 % and 1.4 %, respectively). The impact of high ⁷Be events on O₃ values at IZO is considerable, recording in these events O₃ averages that are 7 ppbv and 11 ppbv above O₃ climatological values (considering all days independently of ⁷Be values) for spring and summer, respectively.

We have plotted the residence time of air masses with daily ⁷Be > 8 mBq m⁻³, for each season of the year, in Fig. 11. Higher residence times are observed in mid latitudes over northeast US extending over the North Atlantic in winter. In spring several maximum residence-times are observed over North Atlantic, but it is striking a maximum which extends along a north-south corridor over the Eastern North Atlantic

Table 3. Basic statistics of surface O₃ at IZO for days with daily ⁷Be > 8 mBq m⁻³. The term “climat.” refers to the O₃ mean when considering all the ozone values within the indicated period independently of the ⁷Be value.

O ₃ (ppbv)	Winter	Spring	Summer	Autumn
%cases	3.8	14.6	8.9	1.4
Mean	47.8 ± 1.9	60.3 ± 1.4	56.8 ± 2.2	46.3 ± 4.1
Median	45.0	59.4	56.8	42.3
Climat.	44.7 ± 0.3	53.6 ± 0.4	45.5 ± 0.5	40.4 ± 0.3

stretching from Great Britain to the Canary Islands. Similar results were obtained by Rodríguez et al. (2004) for O₃ values within P50th–P100th in spring. In summer, the corridor is strengthened to the vicinity of the Canary Islands, and a secondary maximum is found in North Eastern North America extending over North Atlantic. In autumn this maximum is also identified, and some secondary high residence times near the Canary Islands are observed. In relation to the height at which air masses were travelling, it is noteworthy that in the spring and summer, they come from altitudes above 5 km. Summarizing, the source regions of high ⁷Be air masses with maximum impact on O₃ at IZO are registered in a region around the Canaries extending to the north over North Atlantic in spring and summer. This region coincides with areas where COL developments and STT processes have been reported in previous studies (e.g. Cuevas and Rodríguez, 2002; James et al., 2003; Rodríguez et al., 2004). Nieto et al. (2005), from a 41-yr climatology of COLs in the Northern Hemisphere, reported three preferred areas of COLs occurrence, one of them being the Southern Europe and the Eastern Atlantic coast, in agreement with our results.

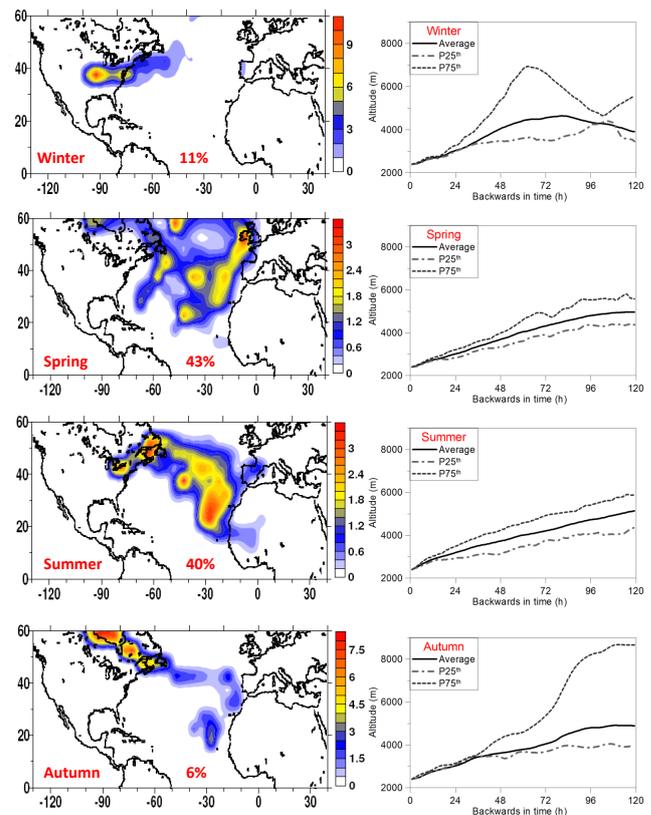


Fig. 11. Residence times and transport pathways of air masses with daily ⁷Be > 8 mBq m⁻³ and corresponding averaged backward trajectories heights for each season of the year. Color bars indicate the residence time in arbitrary units. In backward trajectory heights the mean value, P25th and P75th are plotted.

Recently, Hegarty et al. (2009) revealed that O₃ observations from TES (Tropospheric Emission Spectrometer) also evidence stratospheric intrusions associated with the cyclones over the North Atlantic. According to Wernli and Bourqui (2002), “deep exchange” denotes events where air parcels are rapidly transported from the stratosphere down to levels below 700 hPa level (deep-STT). The STT climatology from Sprenger and Wernli (2003) shows that deep-STT is particularly strong in the 40°–65° N latitude band over the North Atlantic storm track region in winter, just in the high PV_{max} passageway we have found in this season (Fig. 10).

3.7 Relationship between O₃ and CO

Hegarty et al. (2009) reported that composites of O₃ and CO retrievals from TES sensor showed the main pollution export from North America extended in a band from 30° N to 45° N. Strong positive correlations between CO and surface O₃ are found in maritime stations off the coast of Canada (Kasibhatla et al., 1996). These positive correlations are attributed to the transport of photochemically generated O₃ from North America out over the North Atlantic (Parrish et al., 1993).

The concentration of CO at IZO shows a general increase during autumn and winter until the maximum is reached in late March, while the minimum is observed in middle August (Gómez-Peláez et al., 2012). The relationships between surface O₃ and CO at IZO, for each season of the year, are shown in Fig. 12. The good correlation between O₃ and CO at IZO in winter (with an O₃/CO slope of 0.84 ppbv ppbv⁻¹), in spring when surface O₃ is within 30–50 ppbv and CO within 85–115 ppbv (with an O₃/CO slope of 0.91 ppbv ppbv⁻¹), and in Autumn with an O₃/CO slope of 0.81 ppbv ppbv⁻¹ for surface O₃ values below 35 ppbv, supports the hypothesis of long-range transport of photochemically generated O₃ to IZO in these seasons, likely from North America according to the paths of the trajectories (Fig. 5). However, the lack of correlation between surface O₃ and CO found in summer suggests that significant O₃ enhancements are not directly caused by long-range transport of anthropogenic pollution in this season. These results agree with Li et al. (2002b) who found the strongest export of anthropogenic CO from North America in winter, and the weakest in summer.

Chin et al. (1994) found an O₃/CO slope ~ 0.3 ppbv ppbv⁻¹ in aged air masses at rural sites in Eastern North America. Hegarty et al. (2009) found that, under some meteorological conditions, some cyclones near the east coast of the US produced the greatest export to the lower FT with O₃ > 65 ppbv and a well-defined O₃-CO correlation with an O₃/CO slope ~ 0.20 ppbv ppbv⁻¹, indicative of the overall impact of photochemical processes in North American continental export. However, Honrath et al. (2004) reported for the high mountain station of Pico in Azores, in the middle of the North Atlantic, that O₃ and CO were correlated during North American outflow

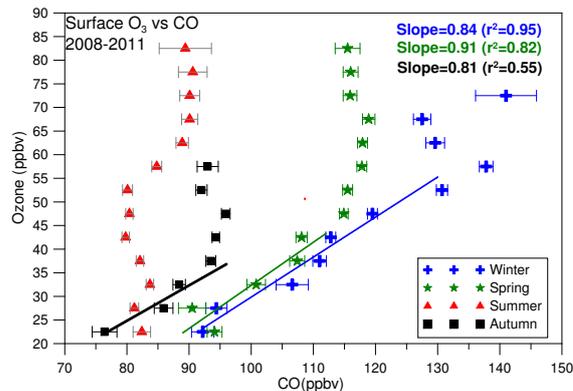


Fig. 12. CO (ppbv) vs. surface O₃ (ppbv) at IZO for winter (JFM), spring (AMJ), summer (JAS) and autumn (OND) in the period 2008–2011. Data have been grouped and depicted as for Fig. 8.

events, with a slope averaging 1.0 ppbv ppbv⁻¹, more than 80 % larger than O₃/CO ratios observed in the Eastern US and near-shore outflow region. Honrath et al. (2004) explained these high ratios by the fact that air masses from North America outflow events have undergone days of photochemical processing, increasing the O₃/CO ratio.

Table 4. Averaged O₃/CO ratios (ppbv ppbv⁻¹) at IZO for winter, spring, summer and autumn (all cases and those with O₃ > P75th), and estimated type of air mass (FP = Fresh Pollution; A = Aged air mass; UT = Upper Troposphere). Types of air masses have been labelled according to the O₃/CO range values.

	Mean ± SD	Median	P25th	P75th	Type
Winter	0.39 ± 0.07	0.38	0.34	0.44	FP
O ₃ > P75th	0.42 ± 0.06	0.40	0.37	0.45	FP
Spring	0.47 ± 0.10	0.46	0.40	0.53	A
O ₃ > P75th	0.58 ± 0.10	0.56	0.51	0.62	A + UT
Summer	0.56 ± 0.15	0.55	0.44	0.65	A + UT
O ₃ > P75th	0.71 ± 0.13	0.70	0.61	0.78	A + UT
Autumn	0.47 ± 0.10	0.47	0.41	0.54	A
O ₃ > P75th	0.54 ± 0.08	0.54	0.49	0.60	A + UT

A 3-yr “climatology” of daily O₃/CO ratios is shown in Table 4. Mean (± standard deviation), median, P25th and P75th of O₃/CO ratios have been calculated for each season. The highest concentrations of CO at IZO (> 133 ppbv, above the P90th) are observed in winter and spring, mostly coming from North America (not shown here). In order to determine the impact of long-range transport of American pollution, and the origin of the fairly good O₃-CO correlation, we have analyzed the events in which, at least during five consecutive

Table 5. O₃/CO ratios at IZO for events with hourly O₃-CO data correlation $r > 0.75$.

	O ₃ range (ppbv)	O ₃ /CO (ppbv/ppbv)	Cases (2008–2011)
Type 1	P50th–P75th	0.41 ± 0.03	8 in winter
Type 2	P75th–P100th	0.43 ± 0.07	5 in winter
Type 3	P75th–P100th	0.53 ± 0.07	58 in spring
Type 4	P75th–P100th	0.67 ± 0.14	7 in summer
Type 5	P75th–P100th	0.45 ± 0.04	7 in autumn

days, a good correlation ($r > 0.75$) between hourly concentrations of O₃ and CO is observed within the period 2008–2011. We have separated the events in five groups, according to O₃ ranges and seasons. The O₃/CO ratios are summarized in Table 5. In winter, the events Type-1 and Type-2 show O₃/CO ratios of 0.41 and 0.43 ppbv ppbv⁻¹, respectively, which lie within the climatological median-P100th O₃/CO range for this season (Table 4). The events with the highest O₃/CO values (0.53 ± 0.07 ppbv ppbv⁻¹) were recorded in spring, all of them for O₃ > P75th (Type-3), being within the climatological P25th–P75th O₃/CO range for O₃ > P75th (Table 4). In summer, the only 7-day event recorded (type-4), showed a mean O₃/CO ratio of 0.67 ppbv ppbv⁻¹, which is lower than the climatological mean for O₃ > P75th (Table 4). In autumn, events of high O₃-CO correlation, associated to long-range transport, were also recorded (Type-5), but the averaged O₃/CO ratio (0.45 ± 0.04 ppbv ppbv⁻¹) is lower than the climatological mean for this season.

As demonstrated in Table 5, most of the events showing a good correlation between O₃ and CO, and so, unambiguous transport of likely anthropogenic O₃, are observed in spring and winter. Thus, a residence time analysis of air masses with an O₃-CO correlation > 0.75 has been performed for these two seasons (Fig. 13a). The results identify a main contribution from pollution episodes over North America in winter, with backward trajectories heights below 4 km, whereas in spring aged air masses (previously transported from North America) are found over North Atlantic at slightly higher altitudes (above 4–5 km), although there must be stated that there is substantial overlap in the ranges of altitude of both seasons (Figures 13 and 13b). In both cases maximum residence times are observed over Eastern US and Western North Atlantic, on a corridor bounded by the parallels 20° and 50° N. High trajectories suggest that pollution was injected previously over the US east coast, into the FT. These results agree with previous studies in which the warm conveyor belt associated with cyclonic pressure systems lift O₃ produced photochemically in the CBL up into the FT over eastern continental US and then the O₃ is transported by the westerlies across the North Atlantic onto Europe (Berkowitz et al., 1996; Stohl and Trickl, 1999; Cooper and Parrish, 2004).

In winter the O₃/CO ratios found during long-range transport events (~ 0.42 ppbv ppbv⁻¹) agree quite well with the

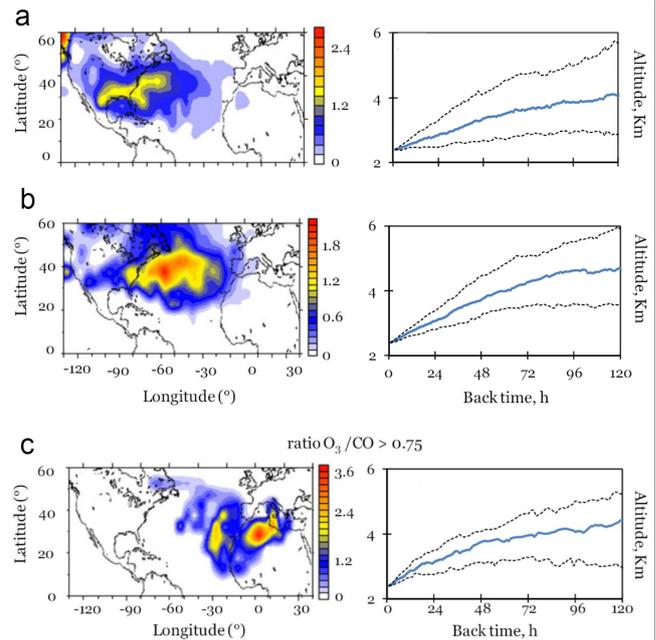


Fig. 13. Residence time of air masses (corrected by central convergence) that show an O₃-CO hourly correlation $r > 0.75$ for winter and spring (a,b). Color bars indicate residence time in arbitrary units. Mean, P25th and P75th of 5-day backward air masses travelling altitude for these events in winter and spring are depicted. (c) residence time of air masses that show an O₃/CO hourly ratio > 0.75 ppbv ppbv⁻¹, and corresponding averaged backward trajectories height.

climatological ratio for this season. The ratios do not differ substantially from those calculated for high O₃ values (> P75th) and from those obtained for all values of O₃ for the study period. So, in winter, when the westerlies blow with their maximum intensity, O₃ measured at IZO might have a large contribution of pollution long-range transport from North America. The O₃/CO ratios reported near the pollution sources range from 0.2 to 0.3 ppbv ppbv⁻¹ (e.g. Chin et al., 1994; Dickerson et al., 1995; Li et al., 2002b; Hegarty et al., 2009). The higher ratios found at IZO imply an additional O₃ amount and/or CO reduction which may arise, in part, from photochemical processing during transporting. In these conditions we could consider that the transport events labelled Type-1 and Type-2 (Table 5) correspond to a fresh pollution that is transported rapidly from North America to the subtropical FT. In spring, the climatological O₃/CO ratios differ notably if we consider O₃ values > P75th (~ 0.58 ppbv ppbv⁻¹) or all O₃ values (~ 0.47 ppbv ppbv⁻¹). The average ratio found in pollution transport events labelled Type-3 (~ 0.53 ppbv ppbv⁻¹) is between these two values. This may be due to the fact that in spring a higher insolation speeds up in-situ photochemistry in the FT (Yienger et al., 1999), and also to large-scale downward transport of O₃ rich air from the upper troposphere. So, O₃/CO ra-

tios between 0.47 and 0.54 ppbv ppbv⁻¹ might be typical of aged air masses originating in North America, while ratios above 0.54 ppbv/ppbv might be explained by a mix of aged air masses and upper troposphere O₃ rich air masses. These assumptions are consistent with the analysis of residence times and heights of air masses characterized by high O₃-CO correlation (Fig. 13a). In spring, air masses come normally from higher altitudes than in winter, and the maximum of air masses residence-times is located northeast of the maximum found in winter, over western and central North Atlantic, further from pollution sources. On the other hand the seasonal averaged O₃/CO slopes (0.84 ppbv ppbv⁻¹ for winter and 0.91 ppbv ppbv⁻¹ for spring; see Fig. 12), which include all kinds of O₃ production and transport processes are higher than the O₃/CO ratios found in well identified long-range pollution transport (0.42–0.53 ppbv ppbv⁻¹), suggesting the contribution of a second source of O₃. The corridor of North American pollution events (Cooper et al., 2002; Hegarty et al., 2009) overlaps to a large extent the belt with relatively high PV_{max} values found in winter and spring between 45° and 55° N, crossing the North Atlantic (Fig. 10). Differences found between the O₃/CO ratios at IZO and seasonal O₃/CO slopes, on one hand, and between the latter with O₃/CO ratios near the pollution sources, on the other hand, could be explained with the following conceptual model based on two processes: (1) O₃ continued to be produced in the plume during transporting in the FT (Honrath et al., 2004; Mao et al., 2006); and (2) contribution from the upper-level air transported downward in the descending dry airstream of cyclones over the North Atlantic, that may have enhanced the lower tropospheric O₃ keeping levels high (Hegarty et al., 2009). Bearing in mind that high O₃ values at IZO are normally associated to high altitude backward trajectories, high PV and high ⁷Be values, this conceptual model might conciliate the apparently contradictory results of finding simultaneous positive O₃-CO correlation (Fig. 12), on the one hand, and positive O₃-PV (Fig. 9a) and O₃-⁷Be (Fig. 9b) correlations, on the other hand, in winter and spring. So, a mixture of photochemical O₃ produced as a result of pollution export from North America and O₃ from stratospheric intrusions over the North Atlantic into the FT seems to be a likely process. This result agrees with Hegarty et al. (2009) who highlighted that some frequent meteorological patterns could produce a well-stirred region of the atmosphere over the North Atlantic that continuously interleaves air masses originating from the lower mid- and upper troposphere, so favouring the mixing of polluted air masses with stratospheric O₃-rich air masses.

Concerning high O₃ values recorded at IZO in summertime some authors (e.g. Schmitt and Carretero, 1992; Raes et al., 1997; Li et al., 2002b) hypothesized that, under some conditions during the summer, pollutants and photochemically-produced O₃ can be transported to the Canary Islands from the Iberian Peninsula and adjacent regions in Europe. Such conditions would be favoured by a coupled

system consisting of the Iberian thermal low at ground level and anticyclonic subsidence aloft (Millán et al., 1997). However, this transport is most likely to occur within the MBL and not in the FT, as stated by Stohl et al. (2002) who analyzed the southward flow of European pollution in summer over the Mediterranean Basin and North Africa. The MCAR plots of O₃ pathways (Fig. 5) do not show significant transport of O₃ from Europe, and there is no relationship between O₃ and CO (Fig. 12). These results suggest a low probability of occurrence of pollution transport from Europe within the subtropical FT over the North Atlantic. These results agree with Duncan and Bey (2004) who concluded that there was no evidence of a summertime CO maximum at IZO in either the observations or the model simulations they performed for IZO. Concerning potential pollution from North America, we have found a single 7-day long-range transport pollution event at Izana in this season. Owen et al. (2006) documented that, on average, 38 % of the North American CO export occurs below 3 km altitude, and that advection of pollution layers at low levels, but decoupled from the BML, is responsible for the majority of transport to Central North Atlantic during summer-time. However, in summer, air masses arriving to IZO from the North Atlantic show a strong subsidence (see Fig. 6), most of them travelling at levels higher than 3 km. Moreover, aged air masses from North America that recirculate, turning around the Azores high anticyclonically (Auvray and Bey, 2005), are decoupled from the air mass pathways to IZO for the same reason. This may be the explanation for finding lower O₃/CO ratios at IZO than at the Azores Pico station.

The climatological O₃/CO ratios at IZO in summertime are significantly higher, 0.56 ppbv ppbv⁻¹ if we consider the whole dataset, and 0.71 ppbv ppbv⁻¹ for O₃ > P75th (P75th O₃/CO ratio ~ 0.78 ppbv ppbv⁻¹). We have analyzed all the episodes in which O₃/CO ratio > 0.75 ppbv ppbv⁻¹. In these cases O₃ does not correlate with CO (O₃-CO correlation < 0.1). We have identified 41 cases in the period 2008–2011, 10 % of them in spring and 90 % in summer. The median value of the relative humidity associated to these events was 12 %, so very dry air suggesting a mid-upper-troposphere origin. The residence time analysis show two predominant origin of the air masses arriving at IZO (Fig. 13b): one located over North Africa and Central Mediterranean Basin, and the other one in a corridor stretching from the Canary Islands to the west of the Iberian Peninsula. These air masses come from altitudes higher than 4 km showing a strong subsidence. All these events are associated with COL or deep lows developments which indicates they come from upper troposphere and likely could be influenced by STT processes. The geographical origin of these events agree with the PV_{max} distribution over North Africa (Fig. 10), and the maximum residence time distribution of air masses with ⁷Be > 8 mBq m⁻³ (Fig. 11). These results also agree with Nieto et al. (2005) who identified North Africa and the Mediterranean Basin (centred over the Italian Penin-

sula), and the corridor between the Canary Islands and the west of the Iberian Peninsula as main areas of occurrence of COLs in summer-time in the Northern Hemisphere.

3.8 The role of the NAO in tropospheric O₃ budget over the subtropical North Atlantic

The large swing in the phase of the NAO between 1995 and 1996 brought international attention to the physical connection between the NAO and e.g. availability of water in Scandinavia for hydropower generation (Hurrell et al., 2003). Indeed, changes in time series pattern have also been observed in surface O₃ records at IZO between 1996 and 1998 (Fig. 3). Logan et al. (2012) show a significant change in monthly mean times series of surface ozone at the alpine stations in 1997. These changes cannot be attributed to changes in O₃ precursors, but to dynamical processes.

Positive phases of NAO indicate stronger Azores high and stronger Icelandic low and thus more active westerlies over the North Atlantic above 50° N. However, in lower mid latitudes and in the subtropical North Atlantic, winter positive phases of NAO mean less zonal west-to-east transport. Positive NAO also implies drier conditions than average over Northern Africa and a strong subtropical high pressure over the North Atlantic resulting in an increase of dust mobilization through strengthening of trade winds over the Sahara (Chiapello et al., 2005; Evan et al., 2006), and higher frequency of dust intrusions over the subtropical North Atlantic, and specifically over the Canaries (Alonso-Pérez et al., 2011). As we have shown in previous sections Saharan air masses loaded with mineral dust are associated with low concentrations of surface O₃ at IZO. The negative phase of NAO results in a higher flow of westerlies in the range 30°–45° N, as can be derived from the Dickson's scheme www.ices.dk/globec/data/bf4/naomap.htm.

Figure 14 shows the correlation between NAO and the zonal component of the wind (u) at 700 hPa (NCEP reanalysis) in winter, spring, summer and autumn for the entire period 1988–2009. A strong negative correlation is found in winter and autumn within the 20°–40° N belt, with a weaker correlation in spring. These results indicate a more effective air mass transport from North America to the Canaries within the low mid- and subtropical latitudes belt (between 20° and 40° N) with negative phase of NAO. So, this “transport belt” appears to be more active over the subtropical North Atlantic during negative phases of NAO in winter and spring. The effect of inter-continental transport is expected to be weaker in summer (Li et al., 2002a).

Hurrell et al. (2003) concluded that, generally, positive NAO phase winters are associated with a northeastward shift in the Atlantic storm activity. These results agree with findings of Andrade et al. (2008) who reported that the inter-annual correlation between the enlarged winter (October to March) NAO index and the total number of storms observed in the Azores Islands is negative and statistically significant.

Sprenger and Wernli (2003) found that there is a strong relationship between the negative phase of NAO and cyclone frequency across the North Atlantic, and specifically that during the negative phase of NAO the low tropospheric destination of the deep-STT extends over a large region of the North Atlantic, below the 40° N parallel, covering the Canary Islands. Nieto et al. (2000) reported that during positive NAO years, a high occurrence of COLs is detected for all the longitudes from 70° N to about 44° N, while during negative NAO years this high density of COLs is detected on a band from 60° N to 35° N over North Atlantic, so shifted southwards, and consequently, most likely to influence the subtropical region of the North Atlantic.

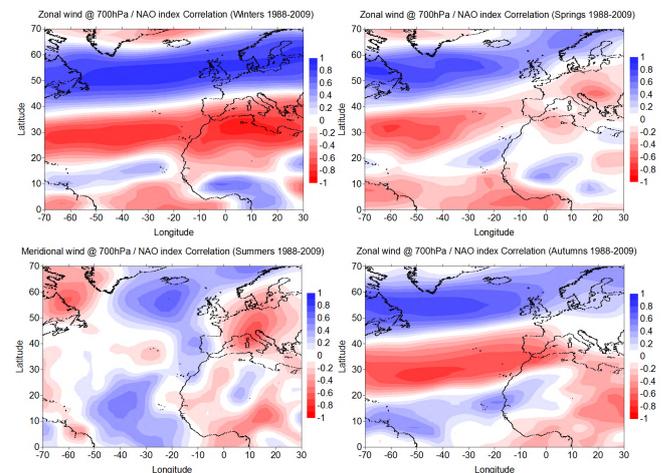


Fig. 14. Correlation between zonal wind component (u) at 700 hPa and NAO-index in winter (JFM), spring (AMJ), summer (JAS) and autumn (OND) for the period 1988–2009.

Creilson et al. (2003), using TOR data, found that the latitude band of greatest tropospheric O₃ was in the central mid latitudes (35°–40° N) and not the upper latitudes (40°–45° N). In Fig. 15 we have plotted the averaged TOR in winter (January–March) and spring (April–June) for years with NAO $\geq +0.5$ and for years with NAO ≤ -0.5 , as well as the corresponding ozone relative differences between negative and positive NAO phases for each season. It is noteworthy that in winter, a negative phase of NAO results in higher tropospheric O₃ amounts over most of the geographical domain of our study, and clearly over the Eastern North Atlantic. These results agree with Pausata et al. (2012) who found an increase of few ppbv of surface O₃ concentrations in stations of the western part of the Iberian peninsula in winter under negative phase of NAO, corresponding to the increase of TOR as can be seen in Figure 15e. In spring, with a negative phase of NAO, there is a significant increment in tropospheric O₃ ($\sim 10\%$; 5 Dobson Units) in a band that stretches across the eastern North Atlantic (over the Canaries), North Africa, the western Mediterranean basin, and southern countries of Eastern Europe. The relationship between TOR and

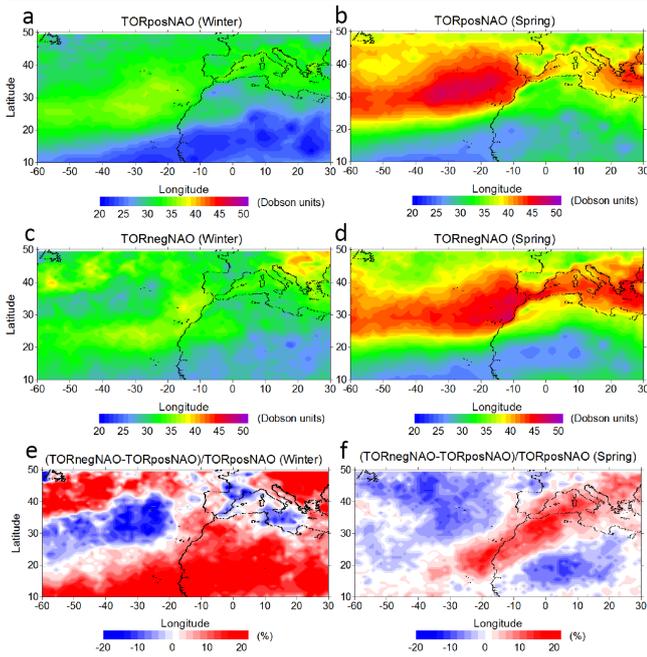


Fig. 15. Averaged Tropospheric Ozone Residual (TOR) data (in Dobson units) in winter (JFM) and spring (AMJ) for years with NAO $> +0.5$ (a,b) and for years with NAO < -0.5 (c,d). Percentage differences between TOR with negative NAO, and TOR with positive NAO in winter and spring, respectively (e,f).

NAO breaks down in summer and autumn when the westerlies are not so strong (Creilson et al., 2003).

Table 6. Mean surface O₃ for NAO $> +0.5$ and NAO < -0.5 for each season in the period 1988–2009 with the corresponding standard deviation of the mean. The third column shows the confidence level for the difference between the means.

	A NAO $> +0.5$	B NAO < -0.5	Confidence Level
Winter	42.9 \pm 0.3 (<i>n</i> = 605)	45.2 \pm 0.3 (<i>n</i> = 349)	100.0 %
Spring	51.4 \pm 0.5 (<i>n</i> = 440)	53.9 \pm 0.6 (<i>n</i> = 362)	99.9 %
Summer	44 \pm 0.7 (<i>n</i> = 366)	46.3 \pm 0.6 (<i>n</i> = 456)	98.8 %
Autumn	40.3 \pm 0.3 (<i>n</i> = 368)	40.8 \pm 0.3 (<i>n</i> = 537)	76.2 %

These results are confirmed by our analysis using surface O₃ at IZO (Table 6). In years with NAO < -0.5 surface O₃ is systematically higher than in years with NAO $> +0.5$ in all seasons. However, the highest differences between the two phases of NAO are observed in spring (~ 3 ppbv), and the lowest in autumn (~ 1 ppbv). The confidence level of O₃ differences is higher than 99 % for winter and spring. We can see in Fig. 16 that a significant change in air mass fre-

quencies after 1996 is observed. For example, a considerable reduction in frequency of African air masses associated with O₃ $< P25^{\text{th}}$, and a significant increase in frequency of air masses associated with O₃ $> P75^{\text{th}}$ from North America and North Atlantic are registered in winter at IZO. In winters with negative phases of NAO a more active jet stream and a higher frequency of storms over the North Atlantic, within the 30°–45° N belt, are observed, resulting in a stronger transport west-to-east of potentially polluted air masses from US and major impact of storms over this belt. This is a probable explanation to the sharp increase observed in the O₃ record between 1996 and 1998 (Fig. 3). This is in agreement with the flattening in surface O₃ series observed at European stations since the late 1990s (e.g. Ordóñez et al., 2007; Gilge et al., 2010; Logan et al., 2012).

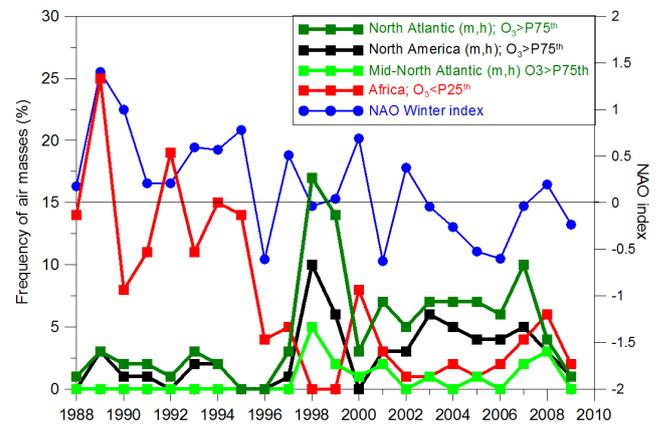


Fig. 16. Long term frequency of air masses arriving to IZO from Africa sector associated with O₃ $< P25^{\text{th}}$, and from North Atlantic and North America associated with O₃ $> P75^{\text{th}}$ in winter. NAO index for winter is also shown.

4 Summary/conclusions

A detailed analysis of a high quality long-term (22-yr) surface O₃ time series (1988–2009) at the subtropical high mountain IZO station has been conducted. Diurnal and seasonal O₃ variations have been assessed. Surface O₃ diurnal variations show the lowest values during the afternoon mainly due to an efficient dry deposition on the mountain slopes. The annual mean difference between the daily up-slope and the down-slope surface O₃ values ranges from 2 to 5 ppbv. The amplitude and width of the diurnal O₃ “valley” is basically modulated by two factors: the solar radiation, and the consequent heating of the slopes surrounding the Observatory, and the synoptic wind strength.

Daily nocturnal (22:00–06:00 UTC) O₃ values have been analyzed for the entire record. The average yearly mean O₃

value at IZO for the 22 yr period is 46.1 ppbv and the peak-to-peak annual cycle amplitude is 15.4 ppbv. There is a slight positive trend in the annual mean ($0.19 \pm 0.05 \% \text{ yr}^{-1}$ or $0.09 \text{ ppbv yr}^{-1}$). There is a notable increase in O₃ observed between 1996 and 1998. Seasonal O₃ cycles show a broad maximum beginning in late spring (May), with frequent daily means of 60–70 ppbv. The annual minimum is found in October with O₃ values often falling in the range 30–45 ppbv.

An analysis of the climatology of O₃ pathways using backward trajectories showed that higher O₃ values are associated with air masses travelling above 4 km altitude from North America and the North Atlantic Ocean, while low O₃ is transported from the Saharan CBL, largely corresponding to transport at lower altitudes (< 1500 m a.s.l.).

An extensive review of the potential O₃ production and transport processes into the FT of the North Atlantic subtropical region has been presented, incorporating other measurements from the IZO station such as PM₁₀, CO, ⁷Be, ²¹⁰Pb, and additional information from backward trajectories and PV. A clear negative logarithmic relationship was observed between PM₁₀ and surface O₃ for all seasons. A similar relationship was found between O₃ and ²¹⁰Pb.

A positive correlation between O₃ and PV_{max}, and between O₃ and ⁷Be is found throughout the year, indicating that relatively high surface O₃ values at IZO originate from the middle troposphere and in some cases from the upper troposphere. Spatial analysis of PV_{max} show a belt with relatively high values between 45° and 55° N crossing the North Atlantic. In winter and spring this high PV_{max} belt coincides with the corridor where anthropogenic pollution is exported from North America to the North Atlantic. In summer the relatively high PV_{max} values found in the vicinity of the Canary Islands over North Africa are notable. The impact of high ⁷Be events on O₃ values at IZO is considerable; O₃ averages recorded during these events are 7 ppbv and 11 ppbv above climatological values for spring and summer, respectively. Residence time analysis of air masses with daily ⁷Be > 8 mBq m⁻³ (threshold value above which an air mass has stratospheric signature) showed a region around the Canaries extending to the north over North Atlantic in spring and summer. This region coincides with areas where COL developments and STT processes have been reported in previous studies.

The influence of pollution long-range transport events on O₃ levels has been studied using CO data. At IZO a good correlation between O₃ and CO in winter (with an O₃/CO slope of 0.84 ppbv ppbv⁻¹) and in spring, when surface O₃ is within 30–50 ppbv and CO within 85–115 ppbv (with an O₃/CO slope of 0.91 ppbv ppbv⁻¹), is observed. This supports the hypothesis of long-range transport of photochemically generated O₃ from North America. In order to determine the impact of long-range transport of American pollution events, those days in which, at least during five consecutive days, a good correlation ($r > 0.75$) between hourly concentrations of O₃ and CO is observed within the pe-

riod 2008–2011 were analyzed. These events presented the highest O₃/CO ratios ($0.53 \pm 0.09 \text{ ppbv ppbv}^{-1}$) in spring. In winter this ratio was lower ($\sim 0.42 \text{ ppbv ppbv}^{-1}$), and agrees quite well with the climatological ratio for this season. The time residence analysis highlights a main contribution from pollution episodes over North America in winter, whereas in spring the origin of the air masses are identified over North America as well over North Atlantic at high altitudes. So, in winter, when the westerlies blow with their maximum intensity, and to a lesser extent in spring, O₃ measured at IZO might be affected by pollution long-range transport from North America.

Differences found between the daily O₃/CO ratios at IZO and seasonal O₃/CO slopes and between the latter with O₃/CO ratios near the pollution sources could be explained with the following conceptual model based on two processes: (1) O₃ continued to be produced in the plume during its transport in the FT; and (2) contribution from the upper-level air transported downward in the descending dry airstream of cyclones over the North Atlantic, that may have enhanced the lower tropospheric O₃ keeping levels high. This conceptual model conciliates the apparently contradictory results of finding simultaneous positive O₃-CO correlation and positive O₃-PV_{max} and O₃-⁷Be correlations in winter and spring. So, a mixture of photochemical O₃ produced as a result of pollution export from North America and “natural” O₃ from stratospheric intrusions over the North Atlantic into the FT seems to be a likely process. In summer the MCAR plots of O₃ pathways do not show significant transport of O₃ from Europe, and no relationship between O₃ and CO is also found. These results suggest a low probability of occurrence of pollution transport from Europe within the subtropical FT over the North Atlantic. We have analyzed all the episodes in which O₃/CO ratio > 0.75 ppbv ppbv⁻¹. In these cases, 10 % of them in spring and 90 % in summer, O₃ does not correlate with CO (O₃-CO correlation < 0.1).

The residence time analysis of air masses with O₃ > P75th show two main origins: one located over North Africa and Central Mediterranean Basin, and the other one in a corridor stretching from the Canary Islands to the west of the Iberian Peninsula. These air masses come from altitudes higher than 4 km and show a strong subsidence. All these events are associated with COL or deep lows developments which indicates they are caused by STT processes. The geographical origin of these events agree with the PV_{max} distribution over North Africa and the maximum residence time distribution of air masses with ⁷Be > 8 mBq m⁻³.

Taking into account all O₃-CO relationships found at IZO and in other studies, we propose the following approach concerning the origin of O₃ at IZO. Fresh Pollution O₃ from North America, mainly observed in winter, might be associated with O₃/CO ratios between ~ 0.34 and $\sim 0.4 \text{ ppbv ppbv}^{-1}$. O₃/CO ratios within ~ 0.40 – $0.55 \text{ ppbv ppbv}^{-1}$ range likely correspond to aged air masses originated in North America and North Atlantic,

in winter, spring and autumn. Aged air masses in combination with inputs from the upper troposphere observed in spring, summer and autumn might be identified by O₃/CO ratios from ~ 0.55 to 0.62 ppbv ppbv⁻¹. In summertime high O₃ values are associated with O₃/CO ratios > 0.65 ppbv ppbv⁻¹, normally the result of STT processes in regions neighbouring the Canary Islands (North Africa, and the corridor extending from Great Britain to the Canaries).

Summarizing, tropospheric O₃ recorded in the subtropical North Atlantic is the result of the interaction between transport of photochemical produced O₃ within the North American CBL, the in-situ photochemical O₃ produced within the FT during its transport over the North Atlantic, and the “natural” O₃ intrusions from the lower stratosphere over the North Atlantic and North Africa. However, we cannot discern the relative contribution of each main source quantitatively. For this, further studies are needed which might be supported with photochemical model simulations.

Finally, the role played by the NAO in the O₃ content over the North Atlantic, and specifically at IZO has been analyzed. The predominant high positive phase of NAO changes appreciably from 1995–1996. Since this date the NAO alternates between negative or neutral phases and positive phases. This change in the pattern of atmospheric circulation over the North Atlantic results in an increased flow of the westerlies in the mid-latitude and subtropical North Atlantic, thus favouring the transport of O₃ and its precursors from North America, and a higher frequency of storms over North Atlantic, with a likely higher incidence of STT exchange processes in mid latitudes. This resulted in an increase of tropospheric O₃ in the subtropical North Atlantic region after 1996 that has been reflected in surface O₃ records at IZO.

Averaged TOR data in winter for years with NAO < -0.5 shows higher tropospheric O₃ amounts on most of our study region, and clearly in the Eastern North Atlantic compared to years with NAO $> +0.5$. In spring there is a significant increase in tropospheric O₃ in a band that stretches across the eastern North Atlantic (over the Canaries), North Africa, the western Mediterranean basin, and southern countries of Eastern Europe in years with negative phase of NAO. These results are confirmed by surface O₃ at IZO. Years with NAO < -0.5 show surface O₃ values systematically higher than those for years with NAO $> +0.5$. The highest differences between the two phases of NAO are observed in spring (~ 3 ppbv), and the lowest in autumn (~ 1 ppbv). This is an important issue in O₃ trend analysis since changes in the phase of the NAO could mask changes in emission of O₃ precursors that have occurred in the last twenty years. O₃ trends over the subtropical North Atlantic region must be properly interpreted taking into consideration phases of NAO. There is still considerable uncertainty in the prediction of NAO, but some studies suggest an intensification of the positive phase of NAO in a scenario of global warming (Gillett et al., 2003), which would impact on the content of tropospheric O₃ over

the North Atlantic through the atmospheric mechanisms analyzed in this work.

Acknowledgements. This study has been developed within the GAW Programme at the Izaña Atmospheric Research Center, financed by AEMET. We are particularly grateful to the Izaña Observatory staff (www.aemet.izana.org) for carrying out carefully essential routine operations. We appreciate the accurate audits performed by the World Calibration Centre (WCC-Empa) for Surface Ozone, Carbon Monoxide, Methane and Carbon Dioxide, for providing a trustful and creditable O₃ and CO data quality assurance system at the Izaña Observatory. Data of radiotracers were obtained from the AEROCE project (Prof. Joseph Prospero as Principal Investigator). The authors would also like to express their gratitude to NOAA-ARL for the provision of the HYSPLIT transport and dispersion model (www.arl.noaa.gov/ready.html) used in this publication. PV data has been obtained from ERA-Interim ECMWF reanalysis. Monthly NAO index data have been obtained from NOAA/CPC. Zonal wind data-sets were retrieved from NCEP/NCAR reanalysis. TOR data have been computed from the database available at the NASA site <http://asd-www.larc.nasa.gov/TOR/data.html>. Data from Mauna-Loa, Zugspitze-Schneefernerhaus, Jungfraujoch, and Sonnblick stations have downloaded from the World Data Centre for Greenhouse Gases (<http://ds.data.jma.go.jp/gmd/wdogg/>).

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