Atmos. Chem. Phys. Discuss., 11, C15935–C15959, 2012
www.atmos-chem-phys-discuss.net/11/C15935/2012/

Atmospheric Chemistry and Physics Discussions

ACPD

11, C15935–C15959, 2012

Interactive Comment

Interactive comment on "Iodine monoxide in the north subtropical free troposphere" *by* O. Puentedura et al.

O. Puentedura et al.

puentero@inta.es

Received and published: 9 March 2012

First we all want to thank the referees for their valuable comments and suggestions. In the following, the comments are addressed and discussed. According to referees' suggestions, more effort has been put on measurement sensitivity and interpretation by using a radiative transfer model.

RC: Referee comments – AR: Author Replies Please note that figures are re-numbered by the conversor to journal format. To facilitate the view we have included the figures as a supplement.

Anonymous Referee #1

The manuscript by O. Puentedura et al. reports on the first IO observation in the sub-

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

tropical free troposphere. The relevance of halogen chemistry on e.g. ozone chemistry and oxidation capacity of the atmosphere in combination with the little knowledge on the global distribution of IO renders these findings important and well suited within the scope of ACP. The manuscript describes the measurements of IO column densities by ground based MAX-DOAS. A simple approximation based on O4 observations is used to derive an IO mixing ratio representative for the FT. Radiative transfer calculations and meteorological observations are utilized to analyze instrument sensitivity to IO in the MBL as well as possible transport of IO from the MBL into the FT. The latter part as well as the discussion of the IO diurnal profile needs some further analysis and revisions before final publication in ACP. Also, the paper would benefit if the full information content of the presented measurements was explored with respect to the vertical distribution of IO.

RC: Proof reading of the final manuscript by an English speaking native is advised. AC: Manuscript has been revised by a native English speaker, co-author of this paper.

General comments:

Radiative transfer: RC: At which wavelength were the Box-AMF calculated? AR: At 427 nm, in the mid point of the IO analysis spectral range. This information has been included in the text.

RC: How strong is the sensitivity to SZA? (see also "diurnal cycle" below). AR: Response below.

RC: The radiative transfer inside clouds is very complex and an opaque cloud layer is not realistic (Figure 6, cloud case, looks rather like the result of having a ground height of 1000m with a ground albedo of 0.8). Box-AMFs depend on OD and vertical extension of the cloud. The contribution of MBL IO to the measurements also depends on its vertical distribution and whether it is collocated with the clouds. Further sensitivity studies are needed to better constrain a possible IO MBL signal contribution to the measurements. AR: A radiative transfer subsection has been included under "Re-

ACPD
11, C15935–C15959, 2012

sults and Discussion" dealing specifically with sensitivity of the measurements to the radiation from below. Simulations have been performed for a 6.5° FOV and for conditions taken from the climatology of the area (level and depth of the cloud in summer from ECMWF 24h forecast at 6 hour interval validated by local radiosoundings, AOD from the ISCCP database. This information has been included in section 4 where the description of the radiative transfer model is made. In Figure 5 (Figure 6 in previous manuscript) intensity-weighted box-AMF are shown for a number of instrument elevation angles (IEA), for two SZA (30° and 75°) and for cloud and no-cloud conditions to test the dependence on SZA and cloud. Results are shown in subsection "Radiative transfer calculations" under "Results and discussion". As a summary, only for 0° IEA there is a significant contribution from layers below the observatory. For the rest of IEA the box-AMF are close to zero for any cloud conditions, making the contribution from altitudes below 1000m (upper level of the MBL) insignificant. We understand that the selection of 5° as IEA to look for FT IO is well justified now. Figure 5 is attached to this document.

Diurnal cycle: RC: The case on a u-shaped diurnal profile based on dSCDs cannot be made without proper AMF correction. It is a good first step to correct the IO dSCDs by O4 measurements to explore the variations seen in the lower elevation angles. However, the overall U-shape in e.g. O4 is caused by a change in AMF due to a change in SZA. A simple correction for the SZA dependence should show a more realistic picture of the diurnal profile of IO. Generally, any use of O4 to approximate path length should include a discussion on possible differences in vertical profile shapes of both O4 and IO. AR: AMF computation requires a good knowledge of the vertical distribution of IO, which is not known. The optical path based on O4 measurements assumes that both O4 and IO have the same vertical distribution in the FT. The advantage is that only measurements are used, without any AMF calculations based on assumptions. In the absence of more reliable information, the IO to O4 ratio provides a way to approximately eliminate the contribution of changes in the path. The actual concentration might differ depending on the vertical distribution. We have added in the text

ACPD

11, C15935–C15959, 2012

Interactive Comment

that this relationship is strictly true only if the vertical profile shapes are the same for both species. This method has been used only as complementary information. The same diurnal evolution is obtained by taking differences in the IO DSCD with respect to zenith ones (70° in our case) thus eliminating the SZA dependence. Results are shown in Figure 4 (attached to this document).

IO analysis and detection limit: RC: Why was a filter applied? Was there a problem with systematic structures in the RMS? The determination of a detection limit based on RMS should also be based on how statistical the RMS is. Applying a filter could easily lead to underestimating a suitable detection limit. Also, have sensitivity studies been performed to check how robust the IO fit is? Changes in fit settings are a good indicator for the real uncertainty of a SCD measurement and are often higher than the WinDOAS fit error output. In my experience the inclusion of CHOCHO in the IO analysis (that does not include the strong CHOCHO band above 440nm) leads to a negative correlation between CHOCHO and IO. Did the author's observe such a correlation? AR: We have re-evaluated the data series without any smoothing to avoid uncertainties on detection limits and errors. As previously, we estimated the detection limit by Platt and Stutz (2008) as (rmse*sqr(Cjj)*param/sqr(n-1)), where Cjj is the covariance matrix IO element, param=number of parameters in the retrieval, and n=number of equations. Prior to the evaluation of IO data series, sensitivity tests to find the optimal configuration for the retrieval of IO were carried out. IO DSCD differences due to changes in the fit parameters such as cross sections, degree of orthogonalization and interpolation polynomials as well as in the spectral interval were within 15%. And as the Referee points out, there is a clear interference of glyoxal in the IO analysis for the selected spectral range. The correlation is negative. To test if the glyoxal was genuine, we extended the evaluation range up to 460 nm (to cover the glyoxal large band at 455 nm) and found no signature of this species in any spectrum. For that reason glyoxal cross-sections were excluded in the analysis now. We have added a sentence in the section 3.2 to account for this particular point. (Platt, U. and Stutz, J.: Differential Optical Absorption Spectroscopy: Principles and Applications, Springer-Verlag, Berlin,

ACPD

11, C15935–C15959, 2012

Germany, 2008).

Vertical distribution of IO: RC: Even though the information content of a ground based instrument is somewhat limited with respect to a full vertical profile inversion, some kind of inversion technique should be explored to retrieve the full information content of the measurements. This information would also allow a more profound basis for the discussion on transport and possible precursors. AR: We agree with the referee that profile inversion would provide extra-information of great interest. However, the large FOV of the instrument combined with the low signal to noise ratio of the measurements during the reported period makes the inversion for a vertical distribution non feasible. Optimal estimation (Rodgers, 2000) was applied to the measurements, but due to the low information content there was a high degree of vertical smoothing in the inversion with only one degree of freedom in the retrieved mixing ratios from the surface up to five km. a.s.l. (Rodgers, R. C.: Inverse methods for atmospheric soundings: Theory and practise. World Scientific Publishing, 2000.)

Discussion on Saharan dust events and Fig. 8: RC: Since EA 70 is used in the argument for enhanced IO during Saharan dust event periods, EA 70 should be explicitly included in the radiance and optical path length calculations presented in Fig.8. A more explicit quantitative treatment of these observations would also allow for a more quantitative discussion on proposed IO background values, on the additional possible contribution of dust and subsequently on possible precursors. AR: Now radiance and optical path length calculations at IEA=70° instead 90° have been included in Figure 8. As expected, little difference has been found and the explanation remains valid. The text has been changed accordingly to take this into account (Figure 8 is attached to this document).

Specific Comments: RC: p. 27838, ln.19: why is the time that the sun needs to move between certain SZAs chosen as measurement time? AR: This is simply the standard measurement scheduling of INTA spectrometers. It was established for comparison purposes at fixed SZA between measurements obtained on different seasons during

ACPD
11, C15935–C15959, 2012

twilight. In practice, we get roughly one measurement every 90s. Since it adds nothing to the paper and can introduce confusion, we have removed the sentence in the "Instrument Description" section (now 3.1.).

RC: p. 27840, ln.9: state e.g. AOD or trace gas threshold for "clear and clean days". AR: Text has been changed. In Section 5 the following sentence has been added: "only clear days, defined as AOD at 500 nm less than 0.05, are considered in the estimation of IO concentrations . . ..".

RC: p. 27840, ln.12: typically zenith references are chosen at the lowest possible SZA, with a SZA of 49 degrees this does not seem to be the case. Why?. AR: The minimum SZA in mid winter time is around 50°. We have used a single reference for evaluating the entire measurement period. Results do not change if the reference is taken at lower angles except at SZA angles lower than 20° when artifacts appear due to reflections inside the telescope.

RC: p. 27840, ln.13: dSCDs are already analyzed against a zenith reference. What is the purpose of subtracting dSCDs of EA 70 from dSCDs of lower EAs? Daily mean differences shown in Fig.3 middle panel are equally affected by differences in EA70. AR: This is equivalent to subtract the corresponding value of the zenith dSCD for every cycle of measurement (one cycle is formed by a scan at different IEAs). The purpose of this calculation is to eliminate the SZA dependence as well as the reference contribution to the IO dSCD. Since many zenith measurements are contaminated by reflections inside the telescope, 70° has been used instead.

Technical corrections: RC: p.27835, ln.21 and 24: replace "Schöenhardt et al.," with "Schönhardt et al.," AR: Done.

RC: p.27837, chapter 3.1. be consistent with using present or past tense. AR: Done. It's now all in the past tense.

RC: p.27838, ln.2: include value of FOV. AR: Done. Now it's included in section 3.1.

ACPD
11, C15935–C15959, 2012

Interactive Comment

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

RC: p.27840, ln.5: 430nm instead of 43nm. AR: Done.

RC: Table 1: Molecule: O3: missing subscript for I zero. AR: Done.

RC: Fig.2: lowest panel: rmse instead of ecm. AR: Figure 2 now shows unsmoothed DOD. Done. (Figure 2 is attached to this document).

RC: Fig.3: top panel, y-axis: DSCD instead of SCD. AR: A new panel has been included. (Figure 3 is attached to this document). Done.

RC: Fig4: y-axis: DSCD instead of SCD. AR: Done. This figure has been slightly changed and there are now four panels instead two ones (Figure 4 is attached to this document). .

RC: Fig.5: both red tones and blue and green(?) are hard to differentiate in a printed copy. AR: Now Figure 4 (c) and (d). Symbols have been changed to be different for each elevation angle (Figure 4 is attached to this document).

Anonymous Referee #2 Received and published: 7 November 2011 The manuscript entitled 'Iodine monoxide in the north subtropical free troposphere' by Puentedura et al. describes the first measurements of the iodine monoxide (IO) radical in the free troposphere. Measurements are performed by MAX-DOAS, and the data are interpreted on the basis of radiative transfer modelling calculations. IO concentrations are estimated on the basis of a simple approach using O4 as an indicator for the atmospheric light path. Previous modelling studies have shown that halogen radicals potentially have a large impact on the chemical balance and the oxidative capacity of the free troposphere, even if they are present in very small amounts. Therefore the novel findings presented in this paper are of very high relevance for our understanding of atmospheric chemistry and the topic fits well in the scope of ACP. However, I have several concerns which are described in the general comments below and which should be addressed before considering a publication in ACP. In particular, the method for determination of the detection limits and the way the data are averaged requires substantial revision.

Furthermore, the way the effect of clouds on the radiative transfer is treated in the model simulations is too simplistic.

General comments: RC: I would appreciate a more detailed presentation of related work and a more detailed discussion of the findings resulting from the measurements. The conclusions section mainly contains technical information, but no discussion on possible sources of IO in the free troposphere and its impact on photochemistry. IO, as well as many of its organic precursors, is a very short- lived substance, and it is believed that the presence of IO is restricted to the boundary layer since its lifetime is too short to reach higher altitudes. Therefore, the question how this reactive species can reach the free troposphere should be discussed on the basis of previously published studies. What are the sources and lifetimes of IO precursors, and is it possible that reactive iodine reaches the free troposphere? What are possible organic or inorganic mechanisms resulting in a production of reactive iodine? The results of Williams et al. are only mentioned briefly, but his findings regarding a possible inorganic release of iodocarbons from Saharan dust are of great relevance here. They strongly support the findings from the MAX-DOAS measurements and should be discussed in much more detail. AC: We appreciate the interest of the referee in having a complete explanation of the reasons why IO is present in the free troposphere at the measured levels, but this will be a subject of future work since it is not possible to reach a conclusion from MAXDOAS measurements only. Further measurements with complementary instrumentation would be required. The main purpose of the paper is to report the observed clear IO signal in measurements carried out in an observatory well above the boundary of the MBL. The following sentence has been added to reinforce the possibility of CH3I as the IO source: “Several aircraft campaigns have reported observations of sub-pptv levels of CH3I in the free troposphere (Bell et al., 2002, and references therein). CH3I emitted from the oceans has a local lifetime of $\sim$ 7 days and thus can reach the free troposphere where its photolysis can provide a source of reactive iodine in this region of the atmosphere”.

ACPD
11, C15935–C15959, 2012

RC: The methods for determination of the errors and detection limits of the spectral analysis of IO appear to be too optimistic. Prior to the analysis, the spectra were smoothed using a 4-pixel boxcar average, and the authors claim that this leads to a reduction in RMS error (P27839, L9ff). Indeed, the apparent reduction in RMS residual is about 55% if a 4 point boxcar average is applied to a normally distributed noise spectrum, while the smoothing leads to a reduction of the optical density of IO of only about 5%. Although the residuals look better, a smoothing neither leads to a reduction of the true spectral noise nor to an improvement of the true signal-to-noise ratio and the fit errors. Usually, the error in retrieved slant column density is determined by DOAS retrieval algorithms under the assumption that the error in intensity is independent for each pixel. This assumption does not hold if the spectra are smoothed prior to the analysis. Consequently, a correction factor needs to be applied to the fit errors and the detection limits in order to provide a realistic estimate of the true error. This is discussed in detail by Stutz and Platt [1996]. This correction needs to be applied to the measurements (alternatively, the spectra can be analysed without smoothing), and their significance needs to be re-assessed on the basis of a realistic estimate of the detection limits. AC: Following Referee's suggestions, we have re-evaluated the data series without any smoothing to avoid uncertainties on detection limits and errors. As previously, we estimated the detection limit by Platt and Stutz (2008) as (rmse*sqr(Cjj)*param/sqr(n-1)), where Cjj is the covariance matrix IO element, param=number of parameters in the retrieval, n=number of equations. In figure 3 IO DSCDs are plotted together with their detection limits.

RC: The estimation of IO mixing ratios and the subsequent discussions are mainly based on the daily averaged IO dSCD at 5 elevation angle which are shown in the middle panel of Fig. 3. For the averaging, all data below the detection limit has been excluded (P27842, L21f). This leads to an artificial increase in the average value, and means that the 'average' is automatically above the detection limit. For example, on day 162 all measurement except one at 5 elevation angle appears to be above 1x10 13 molec/cm2, but the 'average' of the DSCD is above 1:5x10 13 molec/cm2. From

ACPD
11, C15935–C15959, 2012

Interactive Comment

visual inspection of the data presented in Fig. 3, it seems that the true daily average is significantly below the reported values, since many hourly values at 5 elevation angle are very close to zero and were therefore omitted. Again, the question arises to which degree the measurements presented here are significant. AC: We fully agree with the referee comment. The use of a single reference for the whole period has the advantage of allowing following the day to day evolution of the column but neglecting low values, which are below the IO detection limit, yields unrealistic averages. We checked the evaluation consistency by proving that the IO DSCD between 5° and 70° was the same within the errors regardless if the 70° was used as reference on every cycle or a single reference for all period was used. Diurnal means are now obtained using all available data.

RC: Radiative transfer modelling: If I understand it right, an opaque cloud cover with an albedo of 0.8 means that no light can penetrate the interior of the cloud and the atmosphere below. As a result, the box AMFs shown in Fig. 6 appear to be zero below the cloud top height. This is an unrealistic scenario, since a significant fraction of the light observed from above comes from inside the cloud, and it is well known that the light paths inside a cloud can become very long, resulting in an enhancement of the airmass factor due to multiple scattering. Useful conclusions on the sensitivity inside and below the cloud can only be drawn if the optical properties of the cloud (optical density, phase function, etc.) are modelled realistically. AC: A radiative transfer section has been included dealing specifically with sensitivity of the measurements to the radiation from below. Simulations have been performed for a 6.5° FOV and for conditions taken from the climatology of the area (level and depth of the cloud in summer from ECMWF 24h forecast at 6 hour intervals validated by local radiosoundings, AOD from the ISCCP database). This information is included in section 4. In figure 5 intensity-weighted box-AMF are shown for a number of instrument elevation angles (IEA), for two SZA (30° and 75°) and for cloud and no-cloud conditions to test the dependence on SZA and cloud. Results are shown in subsection “Radiative transfer calculations” under “Results”. As a summary, only for 0° IEA there is a significant contribution from below. For the rest of the IEA the box-AMF are close to zero for both cloud and clear conditions, making the contribution from altitudes below 1000m (MBL) insignificant. We understand that the selection of 5° as an IEA to look for FT IO is well justified now. (Figure 5 is attached to this document). Specific comments: RC: P27835, L14: Regarding the measurements of Mahajan et al. (2010), it is not clear what is meant with 'local biogenic activity is supposed not to have an important impact'. Iodocarbon measurements show that biogenic emission of iodinated precursors from biogenic activity takes place (although it is insufficient to explain the measured IO concentrations), and it is concluded that other iodine compounds must be emitted from the ocean surface. It is not clear, if this missing source is of biological origin or not. Again, the introduction is too short and sources for iodine radicals and its impact on atmospheric chemistry should be explained in much more detail. AC: We have modified the redaction to: "IO has also been measured under open ocean conditions. Observed concentrations are significantly lower than at coastal locations and with little annual variation (Mahajan et al., 2010). Observations performed during dedicated campaigns at Tenerife (Allan et al., 2000) and Cape Verde (Read et al., 2008) reported concentrations between 0.2 and 4 pptv" since the referred sentence is not really relevant for this paper due an in-depth overview the different sources and its impact on the atmospheric chemistry is beyond the scope of this paper.

RC: P27835, L24ff: The reference for Grossmann et al. (2011) is missing, and I was not able to get hold of this paper. If this should be unpublished data, please remove the paragraph. AC: Reference has been properly addressed.

RC: P27835, L29: Reference for Butz et al. (2008) is missing. AC: Reference has been properly addressed.

RC: Section 2: Specify the measurement period, which is mentioned later on several times in the manuscript. AC: Period of measurement is specified in the introduction.

RC: P27836, L21f: 'A persistent sea of clouds...'; add 'at Tenerife' to the end of the

ACPD

11, C15935–C15959, 2012

Interactive Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

sentence (otherwise one might think that the sea of clouds appears everywhere). AC: Included.

RC: P27837, L4: I cannot see how molecules like CO_2 and H_2O are 'absorbed or destroyed'. CO_2 is a stable molecule. For water vapour, it is obvious that concentrations at higher altitudes are lower since (1) water vapour is removed by condensation in the cloud, and (2) at constant relative humidity, the water vapour concentration strongly depends on temperature. AC: The referee's comment is clear. We apologize for this sentence since obviously it is a wrong statement that was there unwittingly. The sentence has been removed.

RC: Section 3.1: Specify the FOV of the instrument here. If I understand it right, there is no real entrance optics but only a tube that leads to a very large FOV. Why isn't a lens used as entrance optics, which should limit to FOV to less than 1 degree as for most DOAS instruments? AC: FOV =6.5° is included in 3.1. The "light entrance device", not strictly a telescope, was a heritage of the former zenith NDACC spectrometer on site since 1998. In 2011 a new FOV=1° "telescope" was installed.

RC: P27837, L24: Specify where the dry nitrogen was pumped through (I guess the detector housing). AC: Dry nitrogen is pumped into the isolating box containing the detector to prevent condensation on the detector. It has been added in section 3.1.

RC: P27838, L19: Is there a practical reason why spectra are accumulated for the time required for the Sun to move from 90° to 90.2° AC: This is simply the standard measurement scheduling of INTA spectrometers. It was established for comparison purposes at fixed SZA between measurements obtained on different seasons on twilight measurements. In practice, we get roughly one measurement every 90s. Since it adds nothing to the paper and can introduce confusion, we have removed the sentence in the "Instrument Description" section (now 3.1.).

RC: Section 5: The authors use a simple approach to determine IO concentrations from slant column density measurements of IO and O_4. I believe that this method is very

ACPD
11, C15935–C15959, 2012

Interactive Comment

useful, but its restrictions should be discussed: Equation (1) is strictly fulfilled only if the dSCDs of O4 and IO are proportional to each other, which means that the vertical profiles IO and O4 need to have the same shape (and thus the same total airmass factor). AC: AMF computation requires a good knowledge of the vertical distribution of IO, which is not known. The optical path based on O4 measurements assumes that both O4 and IO have the same vertical distribution in the FT. The advantage is that only measurements are used without any AMF calculations based on assumptions. In the absence of more reliable information, the IO to O4 ratio provides a way to approximately eliminate the contribution of changes in the path. The actual concentration might differ depending on the vertical distribution. We have added in the text that this relationship is strictly true only if the vertical profile shapes are the same for both species. This method has been used only as complementary information. The same shape of the diurnal evolution is obtained by taking IO differences with respect to zenith ones (70° in our case), thus eliminating the SZA dependence. Results are shown in figure 4(b).

RC: P27842, L27: What is meant by 'extra absorption'? AC: The part showing the IO concentration calculation using O4 has been removed. Concentration has now been estimated only from the radiative transfer model. See "Radiative transfer calculations" under "Result and discussion"

RC: P27843, L7ff: The definition of the MBLPI is difficult to understand. Please clarify. Is this a common meteorological quantity, and if so, can you provide references? AC: To our knowledge this index has not been previously published. We have changed the sentence and we hope it is now more understandable: "The Daily Marine Boundary Layer Penetration Index (MBLPI) can be defined as the area contained between the H2O partial pressure diurnal variation curve and the straight line joining the minima of the preceding and subsequent nights." We previously stated that H2O increases during the day having the maximum around noon.

RC: P27843, L21ff: This paragraph presents important conclusions and should therefore be moved to the Conclusions section. AC: This part has been also added to

ACPD

11, C15935–C15959, 2012

Interactive Comment

conclusions.

RC: P27843, L17ff: Again, IO concentrations can only be inferred from the comparison of O4 and IO dSCDs if the IO vertical profile has the same shape as the O4 profile. The conclusion that 'observed increases in the DSCDs must be due to larger IO concentrations' (L22) is therefore not necessarily true. AC: The sentence has been reformulated as follows: "Calculations show that very little increase in the O4 zenith AMF occurs when a dense aerosol layer is included. If we assume a background of IO in the FT (see subsection "Radiative transfer calculations"), then vertical IO/O4 ratio would remain nearly constant and observed DSCD increases can be explained if larger IO concentrations at the level and above the station are present."

RC: The Conclusions section is too short and far too technical. I would appreciate a discussion of possible sources of IO, its possible impact on the chemistry of the free troposphere and the question whether IO might be of importance in the FT on a global scale. AC: Conclusions have been re-written accordingly to new RT calculations but a complete explanation on the IO chemistry is out of the scope of this paper.

RC: The last sentence of the conclusions is unclear. What is the 'previously proposed explanation of the existence of a mechanism that introduces significant amounts of IO precursors during such events'? AC: The word 'explanation' here is referred to Williams et al. explanation about the production of CH3I inside the dust cloud. This has been changed in the text.

Technical corrections: RC: P28839, L25: Remove 'photon'. AC: Done

RC: P27840, L9, and P27841 L3: The measurement period is not mentioned anywhere in the manuscript. Specify, e.g., in Section 2. AC: Now it's included in the introduction.

RC: P27840, L14: Replace 'in successive' with 'in the following denoted as'. AC: Done.

RC: P27840, L19: '... up to 6-7 km with an AOD(500 nm) of up to 1...' AC: Done.

RC: P27840, L21: '... increase in multiple scattering...' AC: Done.

ACPD

11, C15935–C15959, 2012

Interactive Comment

RC: P27842, L9: insert 'height' after 'observatory'. AC: Done

RC: P27842, L19: insert 'that' after 'ensure'. AC: Done.

RC: P27842, L20: replace 'calculations of' with 'estimates of the'. AC: Done.

RC: P27844, L4: O4 is considered not to be an O2 dimer, but rather an O2 collision complex. AC: Done. This sentence has been changed.

RC: P27843, L15, and P27844, L17: replace 'Saharan events' with 'Saharan dust events' or 'Saharan dust outbreaks'. AC: Done.

RC: Figure 3: Use the same colour for the 0 and 5 elevation angle in upper and middle panel. AC: Done. The same code of colours for IEAs is now used for all figures. (Figure 3 is attached to this document).

RC: Figure 4: Please add error bars to the IO dSCDs. AC: Error bars have been added to figure 4. Please note that this figure has been changed and has four panels instead 2. (Figure 4 is attached to this document).

References: Stutz, J., and U. Platt, Numerical analysis and estimation of the statistical error of differential optical absorption spectroscopy measurements with least-squares methods, Appl. Opt., 35, 6041-6053, 1996.

Anonymous Referee #3 Received and published: 8 November 2011 This paper reports on first measurement of iodine monoxide in the tropical free troposphere using multi-axis DOAS instrument. It is well suited for a journal as Atmos. Chem. Phys. but requires more work to be ready for publication. In my opinion, more radiative transfer calculations should be done to convince the reader that the observations are in fact consistent with a FT IO layer. The paper would benefit it the author try to infer consistent information on the IO vertical distribution. It would also be good if an English native could read and correct the text. Several parts are rather difficult to read.

Major comments: RC: -I think the discussion of page 8 - related Figs 5 & 6 – is incor-

ACPD
11, C15935–C15959, 2012

rect or at least incomplete. The author explains the IO minimum around noon by the formation of HOI. I think that before speculating on a photochemical diurnal variation of IO, it would be good to further relate the observations to the box AMFs used by the author. In fact, there is one fact contradicting the photochemical diurnal variation: the U-shape of the IO slant columns at low elevations angles is not observed for high elevation angles (70 and 90). In the text, the discussion on a IO vertical distribution that could eventually be compatible with the observations is far too weak. The arguments given based on the IO/O4 ratio are not sufficient as both species have likely different vertical profile shapes (note this is also the hypothesis made to estimate the IO mixing ratio of 0.18 pptv based on equation 2). I think the author should at least try to infer at which altitude the bulk of IO is. A similar figure as Fig. 5 but showing the box-AMFs could help and convince the reader that the observations are due to a FT IO layer. It is a pity that from the box-AMFs shown in Fig. 7, I can not find any altitude for a presumable IO layer that could reproduce the IO SCD values of Fig. 5. AC: a) U-shape and box-amf (Bulk of IO). Unfortunately AMF computation requires a good knowledge of the vertical distribution of IO, which is not known. The optical path based on O4 measurements assumes that both O4 and IO have the same vertical distribution in the FT. The advantage is that only measurements are used without any AMF calculations based on assumptions. In the absence of more reliable information, the IO to O4 ratio provides a way to approximately eliminate the contribution of changes in the path. The actual concentration might differ depending on the vertical distribution. We have added in the text that this relationship is strictly true only if the vertical profile shapes are the same for both species. This method has been used only as complementary information. The U-shape is also observed if IO SZA dependence is eliminated by using differences with respect to zenith (70° in our case). Results are shown in figure 4. Additionally, the differential intensity-weighted box-AMF (the contribution of IO at each height to the total slant column, not to be confused with the trace gas AMF) shows almost no dependence on the SZA. b) Altitude of the bulk of IO. The radiative transfer model has been run for a number of IO profiles and for cloud below the station and no-cloud conditions to test if the observed amounts could fit any of the model outputs. Results are discussed in the “Radiative transfer section” and in figure 6 (see attached figure 6). (Figures 4, 5 and 6 are attached to this document).

RC: - Are the box-AMFs shown accounts for the large FOV of 6.5? If yes, how are they calculated? This is an essential point to interpret the data. AC: Differential intensity-weighted box-AMFs are computed using a 6.5 FOV in the NIMO full spherical Monte Carlo radiative transfer model. Details are explained in the text (section 4)

RC: I found the explanation of the enhancement of IO inside the dust cloud rather fancy. Again, the discussion might be more interesting knowing the IO vertical distribution. AC: Results show that the model can reproduce the observations if profiles of 0.2 to 0.4 pptv in the FT are considered.

Minor comments: Abstract: RC: -Please avoid acronyms in the abstract, unless it is absolutely necessary. - The author should refer to the Network for the Detection of Atmospheric Composition Change and not to the Network for the Detection of Stratospheric Change. AC: Done.

RC: -I don’t understand the meaning of acronym IEA of elevation angle. AC: Instrument Elevation Angle. Explained.

Introduction: RC: - P2, l3: UV-Vis-> UV-visible. AC: Corrected already in ACPD.

RC: - P2, l4: does “active DOAS technique” refer to DOAS using an artificial light source? If not simply write “DOAS technique” AC: Corrected already in ACPD.

RC: - P2, l10: “has a synergetic effect..” could be replaced by “ reinforces the ozone depletion capacity of other..” AC: Corrected already in ACPD.

RC: - P2, l24: “is supposed to have a small impact”. Pleas also give a range of values for the IO mixing ratios (pptv) AC: Corrected already in ACPD.

RC: - P3, l4: avoid double parenthesis. AC: Corrected already in ACPD.

ACPD

11, C15935–C15959, 2012

RC: - At the end of the introduction, a sentence is missing, like: ‘In this paper, we report on the first observation of IO in the FT using MAXDOAS measurement at Izana subptropical station. Descriptions of the.” AC: Corrected already in ACPD.

Station description and meteorology: RC: Although I think the description of the meteorological conditions is interesting, it is not clear whether it will help the reader to interpret the IO measurements later in the paper. If it is the case, it is probably worth to mention it in section 2. AC: A description of the orography and wind regime is required for the interpretation of IO in terms of forced penetration of MBL air to the free troposphere and behaviour during Saharan events.

Instrument description: RC: - P4, l17: “diffuse radiation”! “scattered radiation”. AC: Corrected already in ACPD.

RC: - One would expect to have details on the viewing geometry in this section: viewing angles sequence, integration time, etc. AC: Corrected already in ACPD. RC: - The lines 10-12, 26-30 of page 5 and 1-4 of page 6 should belong to section 3.1 in my opinion. AC: Corrected already in ACPD.

RC: - IO retrieval: it is not explained why the spectra are smoothed by a boxcar filter. Is this filter also applied to the cross-sections. AC: Data have been re-evaluated without any smoothing

RC: - Figure 2: what is “ecm”? AC: Corrected already in ACPD.

RC: Box-AMF calculations: for non-specialist readers, it would be good to explain why we need to calcule box-AMFs. Few sentences should be enough. AC: This has been added at section 4.

Results and discussion: RC: - P7, l1: It is a strange statement. From Fig 3, I found the day-to-day variability quite high although it is likely smaller than for the other elevation angles results displayed. AC: This part of the text has been reformulated.

RC: - Figure 4: The author should probably remind that – under Saharan dust events

–the increase of zenith sky radiances is due to multiple scattering while the decrease of 0 elevation radiances is due to a decrease in visibility. AC: This is exactly what we observed and tried to explain. However, the point we want to make here is that the observed changes in the path do not match the observed IO DSCD unless an increase in the Iodine monoxide column within the Saharan layer takes place.

RC: - Figure 5: I suggest to add another x-axis with solar zenith angle; arguably more instructive than DOY - It would be easier for the reader to have “elevation angles colors” harmonized for all figures throughout the paper. AC: Corrected already in ACPD (please, note that figure is now figure 4 and it’s attached to this document).

RC: - The Marine Boundary Layer Penetration Index is a concept difficult to understand. Please explain or add a reference. AC: To our knowledge this index has not been previously published. We have changed the sentence and we hope it is now more understandable: “The Daily Marine Boundary Layer Penetration Index (MBLPI) can be defined as the area contained between the H2O partial pressure diurnal variation curve and the straight line joining the minima of the preceding and subsequent nights.” We previously stated that H2O increase during the day having the maximum around noon.

RC: - P 10, l 17: I guess the author means measurements at 70 (almost zenith measurements). Please clarify. AC: Corrected.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/11/C15935/2012/acpd-11-C15935-2012-supplement.pdf

---

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 27833, 2011.

ACPD

11, C15935–C15959, 2012

Interactive Comment

ACPD

11, C15935–C15959, 2012

Interactive Comment

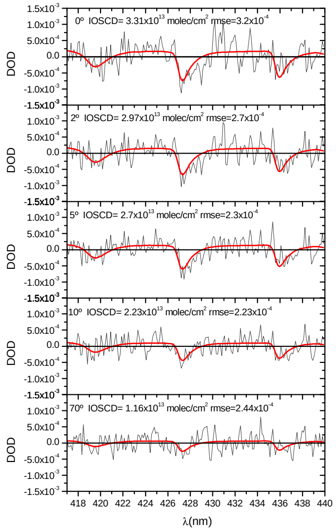

Figure 2. Detected IO absorption structure for a number of elevation angles on day 180 at aprox. SZA= 70º pm.

1

Fig. 1. Figure 2 in the text. Please see supplement.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

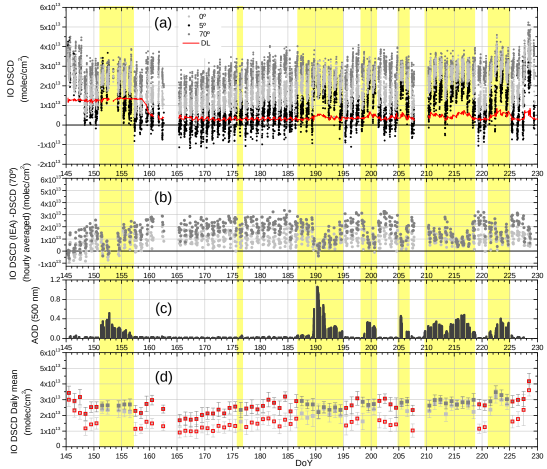

Figure 3. (a) IO DSCD for 0º, 5º and 70º instrument elevation angles elevation evaluated with a single reference taken on the morning of day 180 (June 29th) at 49º SZA. Red line is the most unfavourable detection limit between 0º and 5º IEAs. (b) 0º and 5º differences with respect to 70º for the same measurement cycle (see text). (c) Aerosol optical depths above the station. (d) Daily means and standard deviations. Red encircled squares are pristine days. Yellow shadowed areas corresponding to Saharan events.

.

1

Fig. 2. Figure 3 in the text. Please see supplement.

ACPD

11, C15935–C15959, 2012

Interactive Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

ACPD
11, C15935–C15959, 2012

Interactive Comment

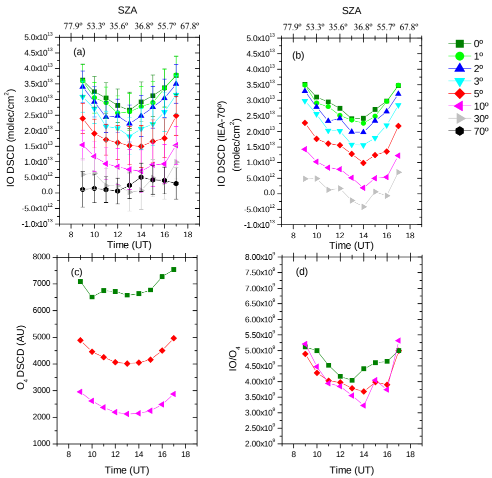

Figure 4. (a) Diurnal evolution of IO DSCD for elevation angles from 0º to 70º during day 278 (October 5th). (b) Differences for each elevation in (a) respect to elevation 70º. (c) O_4 diurnal variation on day 278 for a set of elevation angles. (d) IO/O_4 ratio for the same day.

1

Fig. 3. Figure 4 in the text. Please see supplement.

ACPD

11, C15935–C15959, 2012

Interactive Comment

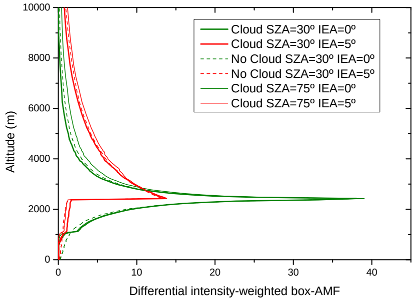

Figure 5. Differential intensity-weighted box-AMF for different conditions, elevation angles of observation and solar zenith angles.

1

Fig. 4. Figure 5 in the text. Please see supplement.

ACPD
11, C15935–C15959, 2012

Interactive Comment

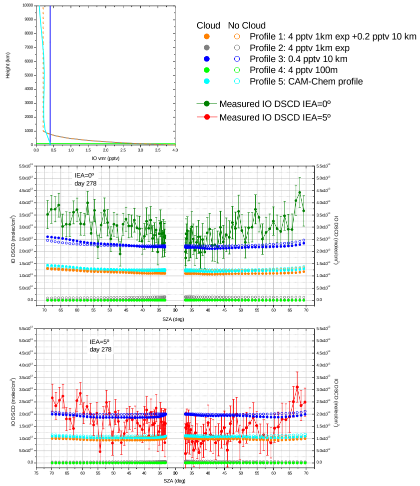

Figure 6. Top panel, different set of IO profiles used to simulate IO DSCD at the level of the observatory for IEA 0º and 5º. Middle panel, simulated IO DSCD using different profiles of IO and comparison with measurements for IEA=0º. Bottom panel, same for IEA=5º.

1

Fig. 5. Figure 6 in the text. Please see supplement.

ACPD

11, C15935–C15959, 2012

Interactive Comment

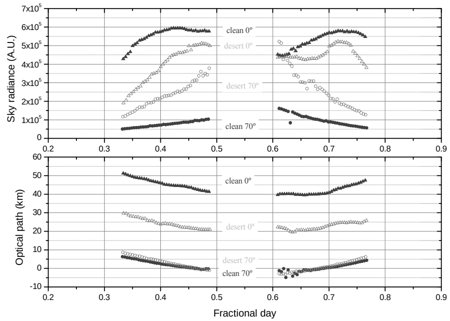

Figure 8. Upper panel, sky radiance at zenith (circles) and horizon (triangles) for a clean (black) and desert (grey) days. Bottom panel, differential optical path for the same cases as upper panel. Clean is day 181/2010 (June 30th). Desert is day 190/2010 (July 9th).

1

Fig. 6. Figure 8 in the text. Please see supplement.