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Atmospheric Chemistry and Physics Discussions

Interactive comment on "OH reactivity measurements in a coastal location in Southwestern Spain during DOMINO" *by* V. Sinha et al.

V. Sinha et al.

profvsinha@gmail.com

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We thank both reviewers for their careful reading of the manuscript and positive comments recommending that the paper merits publication in ACP due to its novel application of using in-situ OH reactivity measurements to constrain ozone production potentials of air masses.

The reviewers have made several valuable suggestions which have helped us to improve the clarity and focus of the manuscript further.

Below we detail the replies and revisions made in the final manuscript for all the specific comments made by reviewer 1 and reviewer 2. Some of the comments were common

to both reviewers but for completeness sake we have posted the replies and revisions individually as well (at the cost of repetition).

Reply to comments of Reviewer 1:

Comment: Although OH and HO2 measurements were made, these are not used to examine the OH or HO2 budget in any way via comparison with a model, rather to estimate the rate of O3 production using the two methods (OH used in one, HO2 used in the other). Also, due to a lack of detailed VOC measurements, it was not possible to calculate the OH reactivity for comparison with the measurements. Although a lack of VOC data may make it difficult to constrain a box model to calculate OH and HO2 concentrations, the OH reactivity and OH concentrations could be used together to determine the rate of OH production, for comparison with the sum of measured OH sources (HO2+NO, O(1D)+H2O and so on). Will the HOx measurements be looked at in more detail in an accompanying paper?

Reply: Yes. A paper by Andrés Hernández et al. (2012) has just been submitted to the DOMINO special issue in ACPD . Peroxy radical budgets have been analyzed therein making use of the HO2 measurements in detail. A paper by Regelin et al. focusing on the HOx budget has also been planned as a submission to the DOMINO special issue. In view of this, the present manuscript is focused on OH reactivity measurements and ozone production chemistry during DOMINO.

Comment: The title does not reflect the use of OH reactivity measurements particularly well – how the OH reactivity data are used is a little different in this paper, and so perhaps the title could be made more informative.

Reply: Both the reviewers have made this very valid point and we accept their pertinent suggestion concerning revision of the title wholeheartedly. Accordingly the title of the revised manuscript is: "Constraints on Instantaneous Ozone Production Rates and Regimes during DOMINO derived using in-situ OH Reactivity Measurements"

Comment: Page 4980 – line 25 “in the literature”, likewise page 4982, line 15.

Reply: Done Replaced “. . .in literature. . .” by “. . .in the literature. . ..” in both places

Comment: Is there a reason why so few VOCS were measured, i.e. not any of the smaller ones, or CO? This is surprising given this appears to be a fairly large field campaign? Can CO be estimated from historical measurements somewhere else in the region? Certainly methane can be estimate as it is well mixed.

Reply: Due to instrumental failures at the start of the campaign to the proton transfer reaction mass spectrometer (PTR-MS) deployed for VOC measurements and the CO gas phase analyzer, data pertaining to CO and light VOCs and oxygenated VOCs from the PTR-MS instrument are unavailable for interpretation. Song et al. (2011) measured isoprene, acetone, benzene, toluene, xylene, ethylbenzene, alpha pinene, eucalyptol and camphor using a thermal desorption gas chromatography mass selective detector (TD-GC-MSD) but the low temporal resolution of those measurements (sampling time of 1 hour; wind direction dependence gets masked) and lack of coverage when several plumes impacted the site (implying average values are lower since several peak events are missing from the GC data)) limit a meaningful comparison of the OH reactivity and the TD-GC-MS measurements.. For interpreting general OH reactivity levels we do make use of the available VOC data in the manuscript (Page 4991; Lines10-15) to conclude that levels of the measured VOCs were very low (frequently few ppt) for any significant fraction of the measured OH reactivity to be attributed to these VOCs.

Methane was measured using a gas chromatograph equipped with a flame ionization detector (GC-FID). We did not include the methane data in the initial submission because we found its contribution to the measured OH reactivity was only a maximum of 0.3 /s. Acting on the reviewer’s suggestion, we examined the methane data for possible wind sector dependence and found that the average levels of methane followed the same trend as the measured OH reactivity namely, Continental wind sector > Huelva WS > Ocean WS.

This information regarding the methane data has been added as follows: at (Page 4991of ACPD version Line16 onwards; Page 13; Lines 365-370 of revised version)

Methane was measured using a gas chromatograph equipped with a flame ionization detector (GC-FID). Instrumental details can be found in Sinha et al. (2007). The average methane value of 1.87 ppmV for the entire campaign contributed only 0.3 /s of OH reactivity. Thus the contribution of methane, the measured biogenic VOCs and the aromatic VOCs to the OH reactivity was extremely low (< 1.5 /s).

and again at (Page 4993; Line 15 of ACPD version; Page 13 Lines 445-448 of revised version) as:

Indeed, the only measured alkane was methane and average methane levels followed the same trend as observed in the average OH reactivity levels namely: Continental wind sector (WS) (1.88 ppmV) > Huelva WS (1.86 ppmV) > Ocean WS (1.85 ppmV).

Regarding estimating CO levels from measurements made elsewhere in the region, we have now added information on average CO levels observed at the air quality monitoring station in Mazagon, Huelva (37.1 N – 6.8 W) from 21.11.2008- 09.12.2008, which was about 680 ppb CO. The station is influenced quite frequently by road traffic emissions and therefore may not be representative of El Arenosillo CO mixing ratios. Nonetheless we agree with the reviewer that providing this information is helpful to some extent and have added it in the revised manuscript at Page 11 , Line 315) as follows:

While CO measurements are unavailable at El Arenosillo due to instrumental failure, average CO levels at the nearby air quality station in Mazagon, Huelva (37.1 N – 6.8 W) for the same period as the DOMINO campaign were about 680 ppb CO (J. A. Adame, personal communication 2012). Unfortunately the Mazagon station is influenced by local traffic and industrial emissions and so the CO measurements cannot be considered representative for El Arenosillo. Nevertheless they do suggest the presence of large CO point sources in the Huelva sector.

Comment: Page 4984 – is there a sea-breeze effect affecting local wind direction compared with the back trajectory?

Reply: Land-sea breeze has been identified to slightly bend locally measured wind directions when air is flowing along the coastline (Diesch et al., 2012, Adame et al., 2010a, Adame et al., 2010b). However, its effect seems to be sufficiently small (less than 9 degrees) to prevent significant mixing of marine and continentally influenced air masses in the identified source categories. The DOMINO campaign was held in late autumn-winter between Nov 21 and Dec 8, 2008 during which period the temperature difference between land and sea is not as large as in summer. Indeed the local wind direction changed only on synoptic scales and no diurnal variations driven by sea-land breeze effects were observed in the local wind direction profiles.

Comment: Page 4986 – the uncertainty in the OH reactivity is quoted as 20% - but surely it is larger than this as the DL of 3.5 /s is approached?

Reply: Yes, as noted in Sinha et al.(2008), a paper we cite in the current work for details, the uncertainty is much larger close to the detection limit. We also make this clearer by adding the following clarification in the experimental section of the revised version (Page 9, Lines 247-248) as follows:

Note however that close to the detection limit the overall uncertainty can be larger than 20 % as noted in Sinha et al. (2008).

Comment: It is stated that laboratory tests established an interference for the OH measurement. This is a hot topic at the moment, and some more details are needed on this. What tests exactly, and what sort of interference? Were the follow up measurements of OH mentioned performed at the same site in Spain in 2009? It wasn't clear. If so, these data could also be shown as well as the 2008 data? How was the interference of 60% determined? The reference is a personal communication and so it is difficult for the reader to know exactly what has been done here, and more information is needed. Why is it just 1000-1500 that the interference is seen? Presumably this means that the

O3 production rates calculated later using the first method are also upper limits? Also, if there is an HO2 interference and the values reported are an upper limit, then this would impact on the second method to determine O3 production rates?

Reply: OH and HO2 should be seen in this study as an upper limit. An upcoming paper combining also data from other field studies will describe the results from 2009. The interference of 60% was determined by using a device to remove ambient OH with the method described by Brune et al. (2009).

Adding the 2009 data in this study, which only uses the HOx measurements nominally and as upper limits for interpretation, will not add significant value to the current study because unlike in 2008 except for HOx, no other measurements were performed in 2009. Moreover, as pointed by the reviewers, the current work outlines a novel method for applying in-situ OH reactivity measurements to constrain instantaneous ozone production rates and regimes, and we believe this has been demonstrated well in the current work.

We agree with the reviewer that both methods would provide upper limits due to the HOx interferences. To make this clearer we have added the following lines at Page 21 (Lines 625 – 628; Conclusion section) in the revised manuscript:

However note that due to interferences on both the OH and HO2 measurements which caused the HOx measurements to be higher than the actual ambient levels, the values obtained in this study for the ozone production rates using both methods should also be regarded as upper limits.

Comment: Section 2.3.4. For the PERCA instrument, for what species was the instrument calibrated? HO2? CH3O2? A detection limit is given, does this refer to one of these only and assumed the same for the other species?

Reply: For DOMINO the data were analyzed considering the calibration of the PerCA instrument only for HO2. The detection limit refers to this HO2 calibration. For the radical measurements, this can lead to an underestimation of the total sum of radicals as other peroxy radicals might have less losses before the amplification zone in the reactor. Laboratory experiments using different HO2+RO2 mixtures indicated that for 50% [HO2] in the air mass, [RO2*] is 15% underestimated by the DUALER reactor used for DOMINO.

We have added the above information in the experimental section on Page 12 of the revised manuscript where the peroxy radical measurement method has been described.

Comment: What VOCS were actually measured? What is the reason for the absence of light VOCs or CO?

Reply: The VOCs that were measured are mentioned in the cited reference (Song et al., 2011) and also in the text already. For easy reference we list them here as well: formaldehyde, methane, isoprene, acetone, benzene, toluene, xylene, ethylbenzene, alpha pinene, eucalyptol and camphor.

As mentioned in reply to one of the previous comments in this response: Due to instrumental failures at the start of the campaign to the proton transfer reaction mass spectrometer (PTR-MS) deployed for VOC measurements and the CO gas phase analyzer, data pertaining to CO and light VOCs and oxygenated VOCs from the PTR-MS instrument is unavailable for interpretation.

Comment: The levels of isoprene and the aromatics are not that high (< 150 pptv) – and so will not provide a significant OH reactivity, so when the measured reactivity is up to 80 /s (the maximum value observed) – can the authors speculate on what is contributing to the OH reactivity?

Reply: We thank the reviewer for this useful suggestion.

As discussed in the manuscript, the highest measured OH reactivity values for the entire campaign period of 63–83 /s were observed between 12:00 UTC and 14:00 UTC on 22 November 2008. This was also associated with the highest wind speeds of the

campaign, which would have favoured long distance transport. The back trajectory for the air mass which arrived at the measurement site at 12:00 UTC on 22 November 2008, showed that the air masses had passed over Madrid less than 13 h previously. There is a mountain range about 1km high just south of Madrid. Thus, instead of direct advection to El Arenosillo, emissions from Madrid and surrounding areas could have undergone upward and horizontal transport accompanied by photochemical processing during the daytime boundary layer growth, mixing in with emissions from Seville and other upwind areas before arriving at El Arenosillo. As already noted in the paper, the trajectories within the first few hundred metres stayed within the convective boundary layer.

We note that the urban centre of Madrid, its surrounding industrial areas and the industrial region of Seville are arguably amongst the strongest point sources in Spain. In particular the Seville industrial area has high emissions from solvent use and associated products which alone amounted to 2050 Mg/yr of NMVOC emissions in 2007 (Source: EMEP,UNECE 2009). Several reactive anthropogenic alkenes (e.g. 1,3-butadiene, isobutene, , trans-2 butene, pent2-ene, hexenes and heptenes) , multi substituted mono aromatic compounds (e.g. 1,2,4- trimethyl benzene and 2,4,6-trimethyl benzene) and oxygenated VOCs (e.g. acetaldehyde, hydroxyl acetone) and higher alkanes (e.g. methyl pentane , hexane, heptanes), were not measured during DOMINO. We speculate that the highest observed OH reactivities could be due to a mixture of these emissions and their oxidation products. Using sensitive 2-dimensional gas chromatography, Lewis et al. (2000) detected more than 500 volatile organic compounds in urban air, including over 100 multi-substituted monoaromatic and volatile oxygenated hydrocarbons. Even if 300 out of 500 such compounds were present at 100 pptV and had a rate coefficient comparable to isobutene or trimethyl benzene (kX+OH > 5 x 10-11 cm3/molecule/s or half as reactive as isoprene), the total would contribute about 38 /s of OH reactivity.

Following up on the reviewer's suggestion to speculate on the cause of the high OH reactivities of upto 80 /s , we have included the above useful discussion in the revised manuscript at Page 13 Lines 379-396.

Comment:

Page 4992 – the OH reactivity is seen to be higher with a peak probably due to ship emissions – did SO2 correlate with OH reactivity in this sector?

Reply: The peak of the OH reactivity always occurred at the same time as the peak in the SO2 mixing ratio but due to below detection limit OH reactivity values for several hours of the day, a strong correlation was not observed (r = 0.6). This can also be made out from Figures 3b and 4 of the manuscript.

Comment: Page 4993- the highest values of OH reactivity were seen at the highest local wind speeds. Can inlet effects at high wind speeds be ruled out?

Reply: Yes. As noted in the experimental section, out of the large flow sampled through the main inlet (about∼ 60 L/min with inlet residence time of 4 seconds), only a minor amount of 180 ml/min of ambient air was being sampled into the reactor at a constant rate. Therefore wind speed effects on the amount of total air entering the main inlet in turn causing an effect on the ambient air flow into the reactor can be completely ruled out.

Comment: 4994 – line 1, it is noted that HO2 levels are twice as high in air masses with a strong continental influence (Fig 4). Any interference in the HO2 measurement would be expected to be higher in this sector as the concentration of alkene-derived RO2 species would be higher?

Reply: This is difficult to conclude with certainty as the structure of the alkenes is expected to play an equally important role for determining the magnitude of the interference. Both Huelva and continental air are likely to have alkenes. In the absence of the alkene speciation, we think it is reasonable to consider that the interference is not too different for both air masses. But even if the continental air mass HO2 levels

are higher than the Huelva sector HO2 levels due to this alkene interference, we note in Figure 6, that method 2 for calculating the ozone production rate (which uses HO2 values), still shows lower values for continental air masses compared to the Huelva air masses, strengthening our argument about the NOx limited production of ozone in continental air masses.

Comment: Page 4995 lines 15-20 – it should be made clear that CO is included in the OH reactivity due to VOCs (this is mentioned elsewhere but most relevant in the section that defines OH reactivity due to VOCs). Can CO levels can be estimated in some way to calculate the OH reactivity due to CO? CH4 levels can certainly be estimated?

Reply: Agreed. In the revised manuscript (Page 17; Line 504-507) we have made this clear by replacing the relevant Lines 15-20 Page 4995 of the discussion manuscript as follows:

Carbon monoxide’s (CO) contribution is included in the VOC OH reactivity term as calculated above. The above approach also assumes that OH reactants other than CO, VOCs and NOx, do not contribute significantly to the directly measured OH reactivity, which is a reasonable assumption since most other abundant inorganic species (e.g. O3, H2O2) react only slowly with OH and SO2 contribution to OH reactivity during DOMINO is negligible.

As mentioned in reply to a previous comment in this response we have already added the information on methane levels and their contribution to the measured OH reactivity and CO levels from an air quality monitoring station in Huelva.

Comment: Page 4996- why is the ratio 0.2 the transition to VOC limited, and why is the ratio 0.01 the threshold for NOx limited, what is special about these actual values? Presumably this was something determined by Kirchner et al? Likewise for the VOC/NOx ratio of 5.5 for the second method. Is this independent of the type of VOC in the air mass?

Reply: Yes, the reviewer is correct in understanding that the ratios for the indicator thresholds were determined by Kirchner et al. (2001) and this has been noted in the manuscript. Regarding what is special about these actual values, two aspects are worth remarking. The robustness of this indicator against several parameters such as temperature, humidity, photolysis, and initial ozone concentrations has been tested in a box model and compared to the robustness of other earlier proposed indicators such as the O3/NOz ratio and H2O2 / HNO3. In contrast to other indicators, this one is not based on photochemically produced long-lived species but describes the instantaneous regime of an air parcel. Furthermore, three-dimensional studies were also performed for Athens and the Swiss plateau to test the behaviour of the indicator under conditions of variable emissions, transport, and dilution, providing additional confidence in the use of this indicator ratio.

The rationale for the VOC/NOx threshold of 5.5 is described in detail in Seinfeld and Pandis (2006) and has been traditionally used to identify tropospheric ozone production regimes. The rationale for using this ratio as sourced from Seinfeld and Pandis (2006) is given below:

At ambient conditions the second-order rate constant for the OH + NO2 reaction is, in mixing ratio units, approximately 1.7 × 10ˆ4 /ppm/min. Considering an average urban mix of VOCs, an average VOC-OH rate constant, expressed on a per carbon atom basis, is about 3.1 × 10ˆ3 /ppmC /min. Using this value for an average VOC-OH rate constant, the ratio of the OH-NO2 to OH-VOC rate constants is about 5.5. Thus, when the VOC:NO2 concentration ratio is approximately 5.5:1, with the VOC concentration expressed on a carbon atom basis, the rates of reaction of VOC and NO2 with OH are equal. If the VOC: NO2 ratio is less than 5.5:1, reaction of OH with NO2 predominates over reaction of OH with VOCs.

It is not independent of the type of VOC mixture in the air mass, as it has been arrived at by assuming an average VOC-OH reaction rate constant that is typical of the urban atmosphere. Method 1 and Method 2 would have been independent approaches to determine the transition between VOC and NOx limited regimes.

However, we agree with Reviewer 2's comments that by replacing the conventional VOC/NOx ratio by the VOC/NOx OH reactivity for the DOMINO data due to absence of comprehensive VOC measurements, and using the threshold of 5.5, we have rendered it only marginally different from Method 1 which uses the same ratio with a value of 5 to mark the distinction between VOC and NOx limited regimes. Hence in the revised manuscript we have decided against using Method 2 for the DOMINO data interpretation but still retain its description, as given above for the benefit of future studies where both VOCs and VOC OH reactivity are measured directly and individually.

We also note that the Method 1 delineates between three ozone production regimes based on the value of the indicator ratio (Θ) as reiterated below, whereas the more traditional Method 2 considers that ozone production regime can fall under only two of the three regimes, namely the NOx limited or VOC limited regimes. It would be a good test in future studies to compare these different approaches for consistency using field data.

$\Theta < 0.01$; NOx limited

$0.01 < \Theta < 0.2$; Both NOx and VOC limited

$\Theta > 0.2$; VOC limited

Accordingly the first paragraph of the discussion manuscript under Section 3.3 (Pages 4994-4995) has been rephrased in the revised manuscript (Page16-17; Lines 485-490) as under:

We assess whether the ozone production regime was limited by NOx or VOCs or both, using a method based on the approach of Kirchner et al. (2001). A second method based on the traditional VOC/NOx ratio method as given in Seinfeld and Pandis (2006) is also given below but could not be applied to the DOMINO dataset due to absence of comprehensive VOC measurements. In studies where comprehensive VOC speciation, NOx measurements and direct OH reactivity measurements are available the two methods can be compared for consistency.

We have also rephrased the text describing Figure 5 accordingly in the revised manuscript.

Comment: Page 4998 – line 22 – It is assumed that all RO2 radicals react only with NO, and not amongst themselves – due to the level of NOx encountered. This needs to be checked via a quick calculation, as there is quite a range of NOx, and in the continental sector the RO2 and HO2 levels are higher and the cross-reaction may compete with reaction with NO?

Reply: We could not follow why the reviewer wants us to do those calculations. From the NOx profiles and discussion of ozone production regimes, it is obvious that ozone production is mostly NOx limited at this site. The purpose of using this calculation method based on the directly measured OH reactivity and hydroxyl radical concentration is to calculate the ozone production potential rates for assessing how high the ozone production rates could become in different wind sector air masses arriving at the site , if the conditions were no longer NOx limited. For the actual production rates at the site we use Equation 14:

O3 production potential = kHO2+NO [HO2] [NO] + $\sum kRO2i + NO[RO2i][NO]$

We make this clearer in the revised manuscript by adding the following information (Lines 553-558; Page 18-19 of the revised manuscript) :

The first method helps assess the ozone production potential rate if ozone production at the site is no longer NOx limited while the second method provides the in-situ ozone production potential rate in different air masses based on the levels of NOx and radicals measured during the DOMINO campaign.

Comment: Is n=2 always the case? The carbonyl species produced in R3 will react with OH further or be photoylsed leading eventually to more NO to NO2 conversions? For CO n=1?

Reply: No, clearly n depends on the oxidation mechanism of the VOC. Yes for CO, n=1. We chose n=2, because for all VOCs one would expect at least 2 NO to NO2 conversions during its complete atmospheric oxidation with the hydroxyl radical. n=2 is also the number used for assessing the O3 production potential of a given hydrocarbon (Hewitt, 1999) and to decide on policy for control of VOCs that act as ozone precursors.

Comment: Page 5000, there is a statement that O3 production potentials using the measured VOC-OH reactivity and OH values method in the continental sector air masses are “incredibly high” considering the actual levels of O3 seen at the site. The OH values are considered as upper limits so perhaps the O3 production rates calculated by this method could be lower, particularly in this sector?

Reply: This is good point. However, we observed that the large difference in the ozone production potential rates between the continental air masses and the other air masses calculated using this method, is actually driven by the large differences in the OH reactivity between the different air masses rather than the measured OH concentrations. For example from Figure 4, we note that the OH concentration in the continental air mass at 11 UTC is only 1.38 times higher than the OH concentration in the Huelva air mass at 11 UTC. On the other hand in Figure 6, it can be seen that in the method that employs OH reactivity and OH concentrations for calculating the ozone production potential, at 11 UTC the continental sector air mass has an ozone production potential rate that is 4 times higher than the Huelva sector air mass.

Comment: Figure 5 is quite hard to navigate – the hatched horizontal, diagonal and vertical lines may not be necessary, and the y-axis values have too many significant figures for the top panel (method 1).

Reply: We thank the reviewer for this valuable suggestion. Indeed the Figure could be improved.

We have modified Figure 5 in the revised manuscript in the following manner: Method 2 values have been removed from Figure 5 improving the clarity for Method 1 values. Furthermore, we have removed the hatched horizontal, diagonal and vertical lines and corrected the y axis for significant figures.

Please find the modified Figure 5 at the end of the text in this response.

Reply to comments of Reviewer 2:

Comment: The introduction gives a good overview of the OH reactivity measurements in the world but nothing on previous measurements of pollutants in southern Spain and on the rationale of the campaign, what were the main objectives? As a lot of important parameters for OH reactivity (CO, VOC. . .) were not measured, what was the objective for measuring OH reactivity during this campaign? Except a few sentences (regarding the SO2 specific source), there is almost no reference to the other papers from the DOMINO special section and clearly more links should be made.

Reply: We thank the reviewer for this good suggestion. The main objective of the 2008 DOMINO (Diel Oxidant Mechanisms In relation to Nitrogen Oxides) research campaign was to characterize the tropospheric oxidative capacity at a downwind site impacted by contrasting air masses. The main focus was on the daytime chemistry of the OH, HO2 and ozone , the night time chemistry of nitrate radicals and nitrogen pentoxide as well the day and night time chemistry of organic peroxy radicals (RO2*).

The lack of CO and adequate VOC data is unfortunate as they were very much part of the intended suite of measurements along with the OH reactivity measurements. Due to instrumental failures at the start of the campaign to the proton transfer reaction mass spectrometer (PTR-MS) deployed for VOC measurements and the CO gas phase analyzer, data pertaining to CO and light VOCs and oxygenated VOCs from the PTR-MS instrument are unavailable for interpretation. On the positive side, the OH reactivity instrument worked very well and provided a proxy for the reactive VOC loading of different air masses. Further, the lack of CO and VOC data motivated the authors to

apply the OH reactivity measurements for constraining the ozone production potential of the different air masses that impacted the site. As commended by both reviewers, this approach is both novel and original and we are happy that the current manuscript has been received well as an additional application to the conventional OH reactivity budget analyses.

Following up on the suggestion of the reviewer to include previous studies that were done in the region and also strengthen the link to related papers from the DOMINO campaign, we have added the following information to the Introduction section of the revised manuscript (Lines 80-90; Page 4) and also in the Discussion section, where relevant (please see other replies below),

Previous atmospheric chemistry studies at the site and in surrounding regions include investigations on the variability of surface ozone under a mesoscale circulation and in the cities of Huelva and Seville (Adame et al., 2008; Adame et al., 2010a; Adame et al., 2010b). Alastuey et al. (2006) also performed chemical characterization of particulate matter sources in south west Spain, while more recently, Diesch et al. (2012) studied the variability of aerosol, gaseous pollutants and meteorological characteristics associated with changes in air mass origin during the DOMINO campaign and found significantly higher fraction of aged organics in submicron aerosol particles sampled in air masses from the continental sector, when compared with air masses from other wind sectors.

Comment: The experimental section of OH reactivity should be a bit more precise. The authors refer to previous papers, which is convenient for the method itself but more details about the measurements during this specific campaign are needed. For example, it is stated that “frequent tests with air samples of known OH reactivity were performed and excellent accountability for OH reactivity of the test samples was obtained”. Excellent is a nice word but rather vague. What was the range of reactivity investigated? What was the slope of the measured reactivity versus theoretical reactivity? What was the reproducibility of the measurements?...Regarding the role of relative humidity, how was the variation of the humidity in the air taken into account? How was determined the 5% attributed to the "error in matching the humidity of the ambient air exactly"?

Reply: We have now addressed these concerns in the revised manuscript by adding the following details in the experimental section (Lines 204-228; Page 8-9):

A propane gas standard (Westfalen A.G.; 33μmol/mol; stated uncertainty 4%) was used to introduce test samples of different OH reactivities through the same reactor arm that is used to introduce ambient air into the glass reactor.

The range of OH reactivities investigated using the propane test samples during DOMINO was 6.9 /s to 32.1 /s. The slope of the measured reactivity versus theoretical reactivity for all the tests (n=9) was 0.88 ± 0.07 with an offset of 0.01 ± 1.18. The precision error (index of reproducibility) determined using twice the standard deviation (2 sigma) of the slopes obtained on 22/08/2008 and 09/11/2008 was 3.2 %.

The humidity of the air in the reactor is tracked for every data point that is measured, using the m/z =55 signal corresponding to the (H2O)2H3O+ ion in the PTR-MS (e.g. Sinha et al., 2008 and Amman et al., 2006). Thus for every zero air measurement (corresponding to C2 signal of pyrrole) and ambient air measurement (corresponding to C3 signal of pyrrole) in the reactor, the values of m/z=55 are known. If the humidity of the introduced ambient air / zero air is the same, the m/z=55 signal while measuring C2 and C3 is also the same. On the other hand if the humidity of the introduced zero air and ambient air are different, the m/z=55 signal will also be different. During DOMINO we found that the maximum observed difference in the m/z=55 signal between ambient and zero air due to humidity differences, would cause an uncertainty of ~5% in the measured OH reactivity. This in turn was determined by measuring the change in the pyrrole signal as a result of just changing the humidity of the zero air (a direct measure of the changing OH concentration due to the changing humidity). This effect has already been described in detail in Sinha et al. (2008). The humidification of the zero air flow was adjusted (using a commercial humidifier from Bronkhorst, Germany)

to match the ambient air flow, by using the m/z=55 signal as the humidity proxy.

In more recent studies involving the CRM method (e.g. Noelscher et al., 2012a, Nolescher et al., 2012 b), instead of introducing zero air from a gas cylinder for measuring the C2 signal of pyrrole, we generate the zero air from ambient air by passing it over a Pt catalyst VOC scrubber, thereby ensuring that the humidity in the reactor tracks the ambient air humidity without the need for an external humidifier.

Comment: The section presenting and discussing results is divided in three parts, a first section on general trends of OH reactivity, a second one on diurnal variations and finally a section on the ozone chemical regimes. The first section introduces the results of OH reactivity through figure 2. Some co-variations with formaldehyde are noted but not discussed. Why OH reactivity and HCHO co-variate on these specific periods and not on the others? In addition there seems to be some events with higher OH reactivity (for example from 24 to 27/11) but there are not commented. Are they only due to air mass origin changes? Rather than discussing further these influences, the authors prefer to examine diurnal variations of the OH reactivity and then of radical species, formaldehyde and sulfur dioxide. This whole section on diurnal profile is not very informative. Except the fact that usually all compounds follow the scheme that continental sector values > Huelva sector values > ocean sector values, there is no other conclusion. I'm not sure this is the best way to examine dependency of air mass origins and I'm wondering why the authors have chosen these specific compounds to compare with? (why not using in addition or instead the few VOCs which were measured during the campaign?). The following sections are focused on VOC and NOx regimes and these species could be presented as well in the first section. As a conclusion for this section, it could be either shortened if no additional information is available or discussed in more details if more results are presented.

Reply: In the revised version (Page 12; Lines 339-349) we now state the reason for the co-variation of HCHO and OH reactivity time series as under:

As shown in Figure 2, formaldehyde (HCHO) an oxidation product formed during the hydroxyl radical initiated oxidation of many VOCs (Atkinson, 2003), appeared to correlate with the profile of the measured OH reactivity for extended periods on certain days of the campaign such as: 21.11.2008 - 23.11.2008; 30.11.2008 - 01.12.2008; 04.12.2008-06.12.2008 and 07.12.2008-08.12.2008. We note that during most of these periods of co variations, OH reactivity and formaldehyde profiles have a plume like character, rising and falling concomitantly. The most frequent wind direction in all these periods is the continental wind sector and sometimes air masses close to the continental sector but falling in the Huelva urban area (see for e.g. Fig 4 in Diesch et al., 2012). If formaldehyde be regarded as a proxy for oxidation products, it is expected to be present at higher levels in photochemically aged air masses. Moreover, the likelihood of other reactive oxidation products being present at elevated levels just like formaldehyde in air masses arriving in plume like fashion is a likely explanation for the observed co-variations of HCHO with the measured OH reactivity.

Regarding the high values observed between 24 to 27/11, we did not comment earlier because for much of this period even the formaldehyde data was not available.

Some high values were observed between 24.11.2008 and 27.11.2008. After checking for the prevalent wind direction for this period we find that on 24.11.2008, continental air masses were sampled for a short while before the air masses started coming from the Huelva wind sector for much of 25.11 and 26.11. This was also the period when several spikes in SO2 and NOx were observed (e.g. see Figure 4 of Diesch et al., 2012).

The above paragraph has also been added to the discussion section in the revised manuscript (Page 13; Lines 350-354).

As already explained earlier in this response and the response to reviewer 1, the lack of supporting CO and VOC measurements prevents us from focusing on individual events.

Regarding the diel description of profiles, we respectfully disagree with the reviewer's point of view.

The diel profiles shown in Figure 4 help to place the discussion on the ozone production chemistry presented in subsequent sections in the right perspective. Note that all the radical species concentrations shown in this Figure 4 are used later on for calculation of instantaneous ozone production rates.

Figure 4 also clearly shows that for all the measured radical species, values in the continental sector air masses are frequently 2-3 times higher than values observed in the other wind sectors. This is a very important confirmation independent of the OH reactivity measurements that the continental sector air masses were clearly chemically very different from the other air masses, and likely richer in oxygenated VOC loadings than the other air masses.

The reviewer states that other than the general scheme that continental sector values > Huelva sector values > ocean sector values, Figure 4 does not convey much information.

We note that this is not true because for SO2, the trend is completely reversed. SO2 is present at several ppb in air masses from the Huelva and ocean sector, but is almost zero in continental sector air masses. This again independently suggests that the source characteristics for Huelva and ocean sector air masses are quite different from the continental sector air masses.

We emphasize this point more strongly in the revised manuscript (Page 17; Lines 48-471) by the following lines:

Yet they do suggest strongly and independently from the OH reactivity measurements, that the continental air masses were very different from the other air masses in terms of chemical composition and likely richer in oxygenated VOCs which can contribute significantly to the OH reactivity of air masses (e.g. Lewis et al., 2000).

Song et al. (2011) measured isoprene, acetone, benzene, toluene, xylene, ethylbenzene, alpha pinene, eucalyptol and camphor using a thermal desorption gas chromatography mass selective detector (TD-GC-MSD) but the low temporal resolution of those measurements (sampling time of 1 hour; so wind direction dependence gets masked) and lack of coverage when several plumes impacted the site (implying measured average values are lower since several peak events are missing from the GC data) limit a meaningful comparison of the OH reactivity and the TD-GC-MS measurements. For interpreting general OH reactivity levels we do make use of the available VOC data in the manuscript (Page 4991; Lines10-15 of ACPD version) to conclude that levels of the measured VOCs was very low (frequently few ppt) for any significant fraction of the measured OH reactivity to be attributed to these VOCs.

Comment: The approach to determine the ozone production regime based on OH reactivity measurements is original and interesting as it gives a direct accessibility on the whole “reactive compounds loading” without knowing the contribution from individual VOCs. Nevertheless, I do not see the point to compare the two methods as at the end it brings a comparison between (almost) identical ratios (once with a threshold at 5 and another at 5.5).

Reply: Agreed.

The rationale for the VOC/NOx threshold of 5.5 is described in detail in Seinfeld and Pandis (2006) and has been traditionally used to identify tropospheric ozone production regimes. The rationale for using this ratio as sourced from Seinfeld and Pandis (2006) is given below:

At ambient conditions the second-order rate constant for the OH + NO2 reaction is, in mixing ratio units, approximately 1.7 × 10ˆ4 /ppm / min. Considering an average urban mix of VOCs, an average VOC-OH rate constant, expressed on a per carbon atom basis, is about 3.1 × 10ˆ3 /ppmC /min. Using this value for an average VOC-OH rate constant, the ratio of the OH-NO2 to OH-VOC rate constants is about 5.5. Thus, when

the VOC:NO2 concentration ratio is approximately 5.5:1, with the VOC concentration expressed on a carbon atom basis, the rates of reaction of VOC and NO2 with OH are equal. If the VOC: NO2 ratio is less than 5.5:1, reaction of OH with NO2 predominates over reaction of OH with VOCs.

It is not independent of the type of VOC mixture in the air mass, as it has been arrived at by assuming an average VOC-OH reaction rate constant that is typical of the urban atmosphere. Method 1 and Method 2 would have been independent approaches to determine the transition between VOC and NOx limited regimes.

However, we agree with Reviewer 2’s comments that by replacing the conventional VOC/NOx ratio by the VOC/NOx OH reactivity for the DOMINO data due to absence of comprehensive VOC measurements, and using the threshold of 5.5, we have rendered it only marginally different from Method 1 which uses the same ratio with a value of 5 to mark the distinction between VOC and NOx limited regimes. Hence in the revised manuscript we have decided against using Method 2 for the DOMINO data interpretation but still retain its description, as given above for the benefit of future studies where both VOCs and VOC OH reactivity are measured directly and independently.

We also note that the Method 1 delineates between three ozone production regimes based on the value of the indicator ratio (Θ) as reiterated below, whereas the more traditional Method 2 considers that ozone production regime can fall under only two of the three regimes, namely the NOx limited or VOC limited regimes. It would be a good test in future studies to compare these different approaches for consistency using field data.

$\Theta < 0.01$; NOx limited

$0.01 < \Theta < 0.2$; Both NOx and VOC limited

$\Theta > 0.2$; VOC limited

Accordingly the first paragraph of the discussion manuscript under Section 3.3 (Pages

4994-4995) has been rephrased in the revised manuscript (Page16-17; Lines 485-490) as under:

We assess whether the ozone production regime was limited by NOx or VOCs or both, using a method based on the approach of Kirchner et al. (2001). A second method based on the traditional VOC/NOx ratio method as given in Seinfeld and Pandis (2006) is also given below but could not be applied to the DOMINO dataset due to absence of comprehensive VOC measurements. In studies where comprehensive VOC speciation, NOx measurements and direct OH reactivity measurements are available the two methods can be compared for consistency.

We have also rephrased the text describing Figure 5 and modified Figure 5 accordingly in the revised manuscript.

Comment: Finally the last part compares two complementary methods for estimating the ozone production potential. The second method (based on measured HO2, RO2, NO) seems relevant here, although presenting a higher limit. It is questionable if the first method can be used for this dataset as it is “valid only for air masses where NOx is not the limiting reactant”. In the previous section, the authors have shown that all continental air masses were NOx limited and therefore, if it is decided to keep the simulation of the ozone production with this method in Figure 6, the corresponding discussion and conclusion should be more justified (especially for continental air masses).

Reply: Perhaps the text in the ACPD version was not very clear.

From the NOx profiles and discussion of ozone production regimes, it is clear that ozone production is mostly NOx limited at this site. Nevertheless, the purpose of using the calculation method based on the directly measured OH reactivity and hydroxyl radical concentration is to calculate the ozone production potential rates for assessing how high the ozone production rates could become in different wind sector air masses arriving at the site, if the conditions were no longer NOx limited. For the actual production rates at the site we use Equation 14:

O3 production potential = kHO2+NO [HO2] [NO] + $\sum kRO2i + NO[RO2i][NO]$

We have made this clearer in the revised manuscript by adding the following lines (Lines 553-558; Page 18-19 of the revised manuscript) :

The first method helps assess the ozone production potential rate if ozone production at the site is no longer NOx limited while the second method provides the in-situ ozone production potential rate in different air masses based on the levels of NOx and radicals measured during the DOMINO campaign.

Minor comments:

The current title is a bit vague and it is suggested to make it more precise.

Reply: Both the reviewers have made this very valid point and we accept their pertinent suggestion concerning revision of the title wholeheartedly. Accordingly the title of the revised manuscript is:

“Constraints on Instantaneous Ozone Production Rates and Regimes during DOMINO derived using in-situ OH Reactivity Measurements”

Technical comments On page 11, Song et al. 2011 and 2012 but it seems to be the same paper.

Reply: Yes. It is Song et al., 2011 and corrections have been made to the revised manuscript.

To summarize the final response, we believe we have comprehensively addressed all the concerns of the reviewers and hope that the revised manuscript will be acceptable for publication in ACP. We also thank the Editor and the ACP office for the kind extension in filing this response.

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Other references can be found in the ACPD version

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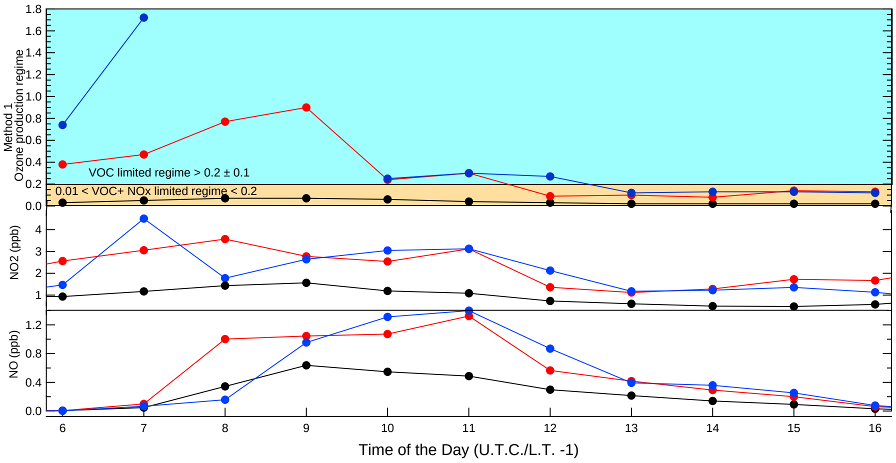

Fig. 1. Modified_Fig5