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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.

Anonymous Referee #1

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This paper presents OH reactivity measurements in southern Spain as part of the DOMINO campaign. OH reactivity measurements are becoming more common and are a very useful way to quantify the loss portion of the OH budget. Usually the OH reactivity measurements are compared with the calculated reactivity using detailed measurements of VOCs and the known rate constants for reaction with OH – to see if there are missing sinks not captured by a box model (this is often the case). These missing sinks could either be unmeasured emitted VOCs, or secondary products. Also, if OH reactivity measurements are combined with OH concentration, using the steady-state allows the rate of production of OH to be found, which can be compared with measured OH sources to see if OH sources are missing in the model.

The focus of this paper though is, however, different. The OH reactivity data are analysed in terms of the air-masses reaching the site, which are of three main types, with the OH reactivity interpreted in terms of the history of the air masses from back trajectories. The "reactive air pollutant loading" is determined from the OH reactivity for each type of air mass. More aged and processed air masses originating from Madrid (600 km distant) have higher OH reactivities compared to fresh emissions from more local sources.

An interesting and novel use of OH reactivity data in this paper is to use the OH reactivity due to VOCs, multiplied by the measured OH concentration, and assuming that reaction of OH with VOCs is the rate limiting rate in the chemistry that leads to ozone production (i.e. NOx limited, but this is an assumption that may not be true) and an assumed number of NO to NO2 conversions per VOC oxidised (2 was used) – to estimate the rate of O3 production. The OH reactivity due to VOCs (CO included) could not be determined directly, but was obtained by subtracting the OH reactivity due to NOx (NO and NO2 were measured) from the total OH reactivity. So from OH reactivity, NO and NO2 alone ozone production potentials could be estimated for different airmasses. This rate of O3 production was compared with the more widely used O3 production rate using measured HO2 and also RO2 (measured from PERCA derived HO2+RO2 and subtracted HO2 measured by FAGE). The two methods are not quite the same though, as for the first the O3 production is for a given airmass, rather than the in situ local rate of O3 production. Indeed the values obtained from the analyses are quite different, with one giving a more regional view on O3 production rather than in situ.

The use of field measurements of OH reactivity, NO and NO2 together to estimate the O3 production potential of a given air mass is a novel use of these data, and hence the paper does merit publication in ACP. The absence of detailed VOC measurements does limit the interpretation of the observed OH reactivity, and it is difficult to rationalise the changes that are observed between the various air masses in detail without these

measurements. The following points should be addressed by the authors.

Comments:

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?

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.

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

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.

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

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-1 is approached?

Page 4988 line 1 – Sorgel et al. gives no details on HO2 measurements in DOMINO, rather just for OH (and only very briefly).

Section 2.3.2. 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?

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?

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

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-1 (the maximum value observed) – can the authors speculate on what is contributing to the OH reactivity?

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?

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?

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?

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?

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?

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?

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?

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? Also, this method relies on the assumption of the NOx limited regime, which as noted by the authors, if not true, could help to explain the "apparently irreconcilable trends" for the different air masses using the 2 methods.

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).

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