We thank the two anonymous referees for their insightful and helpful comments. These comments are addressed below. Note that the line numbers in the referee comments refer to the line numbers in the document submitted to the referees. The corresponding page and line numbers in the discussion paper are indicated by square brackets for the convenience of those following the open discussion. In the interest of clarity, we present referee comments (exactly as they appear in the open discussion) in italic font, our responses in roman font, and changes to the text in bold italic font.

Referee 1:

Comment: "*line385-387 [p. 6135, lines 15-19]: NO from NO2 (46%) would be significant influence to the results, even in clean ambient air condition (low NO but some NO2). If NO2 convert to NO on surface, does this conversion factor depend on relative humidity (or water content) of the air? The condition of the surface will be influenced by water concentration. Also, does the conversion factor depend on NO2 concentration?*"

Response: For this work, we have not tested the dependence of the NO_2 conversion on relative humidity within the reactor. We did, however, perform these tests after the intercomparison at a relative humidity representative of the relative humidity of ambient air during the intercomparison, i.e. approximately 50%. In addition, Michoud et al. (2015) performed further investigations in the laboratory, as shown in Fig. 4 from their manuscript. The conversion of NO_2 to NO was investigated at three different pyrrole-to-OH ratios (1.6, 2.0 and 3.2). For these tests, the pyrrole-to-OH ratio was adjusted by changing the relative humidity (RH) inside the reactor. The range of pyrrole-to-OH ratios used by Michoud et al. (2015) covers most of the RH conditions observed at the ground level during this study. A close examination of Fig. 4 in Michoud et al. (2015) seems to indicate that there is not a significant dependence of the conversion of NO_2 to NO on RH. This figure also shows that the percentage of conversion of NO_2 to NO in the reactor is, on average, independent of NO_2 concentration.

Comment: "*line 629- [p. 6145, line 4] : Are there O3 scrubbers before trapping the ambient air sample?*"

Response: No O_3 scrubbers were used for the GC instruments during this intercomparison. There are, therefore, legitimate concerns about potential artifacts on the VOC measurements, since O_3 can oxidize unsaturated reactive VOCs. This may lead to the consumption of these VOCs and the formation of secondary OVOCs. We address these concerns below.

For the NMHC measurements, unsaturated species, such as alkenes, may slowly react in the sampling line, leading to a small underestimation of their concentration. The resulting artifact will depend on the reactivity of these compounds with ozone, the ambient ozone mixing ratio, and the residence time in the sampling line. No reaction is expected in the trap due to the low temperature of -30°C.

We estimated the abovementioned artifact based on the following:

-   during the intercomparison campaign, ambient ozone mixing ratios ranged from 0.1–60 ppbv,

- most ozone-alkene reaction rate constants are in the range 10^{-16}-10^{-18} cm^3 molecule^{-1} s^{-1}, with a few exceptions,
- the residence time in the sampling line of the two GCs was approximately 40 seconds.

Using an ozonolysis rate constant of 10^{-15} cm^3 molecule^{-1} s^{-1} (representative of a highly reactive alkene) and an ozone mixing ratio of 60 ppbv (maximum observed during the intercomparison), we calculate an underestimation lower than 6% for unsaturated VOCs. We therefore do not expect any significant artifact on the NMHC measurements.

For OVOC measurements, laboratory tests were performed to estimate the impact of ozone on the measurements since the higher temperature of the trap (12°C) may lead to further oxidation of adsorbed VOCs in the trap itself. Sampling synthetic OVOC mixtures (16 OVOCs, aldehydes, ketones, alcohols, approximately 3 ppbv of each VOC) showed that 50-90 ppb of ozone would lead to artifacts on the order of -7/+30%, with acetaldehyde (+30%), acetone (+15%) and butanal (+12%) being the most impacted VOCs. In addition, tests performed by sampling a mixture of 50 hydrocarbons (alkanes, alkenes and aromatics) free of OVOCs showed that in the presence of 100 ppbv of ozone, several hundreds of pptv of acetaldehyde, acetone and butanal were generated inside the instrument. These results indicate that significant artifacts may have occurred during the intercomparison campaign, especially for acetaldehyde, acetone and butanal. However, these compounds contribute to only 3%, on average, of the total OH reactivity calculated in Fig. 8, and these artifacts, if present, do not impact the conclusions of this study.

It is worth noting that O$_3$ scrubbers have been used continuously on our GC instruments since 2013 to avoid the above-mentioned artifacts.

Comment: "*line667-[p. 6146, line 16], 927 [p. 6156, line 23]- Fig.8 : It is regret that CO concentration is not available and is assumed to be constant. The contribution of CO seems to be 10- 25 % (Fig. 8) of the total OH reactivity and CO concentration change will not be negligible. Usually CO and anthropogenic VOCs will change similarly. If some of CO and VOCs are available near this observation site, CO concentration change can be estimated by VOC concentration change.*"

Response: It is indeed unfortunate that ambient CO concentrations were not measured during the intercomparison. Additionally, no concomitant measurements of both CO and VOCs are available in the vicinity of the site, which will make it difficult to establish a suitable surrogate for CO. In Fig. 8, the contribution shown for CO + CH$_4$ ranges from 15–25%. CO alone exhibits a contribution lower than 20%. A relative uncertainty of 50% was associated with the constant concentration of CO used in this study and was factored into the error bars shown in Fig. 8. We do think that this level of uncertainty is large enough based on recent CO measurements made at this site showing variations between 50 and 400 ppbv.

Comment: "*line847-857 [p. 6153, line 21 – p. 6154, line 3]: Underestimate of CRM in Fig.S8 is 45%. In ambient air measurement, is it possible to assume that concentration of VOCs which absorb UV is similar proportion of the VOC standard gas?*"

Response: Similar VOCs are present in the standard mixture and in ambient air, and we do expect a similar behavior for the CRM measurements, i.e. an underestimation of the ambient OH reactivity. The assumption made that 45% of the OH reactivity due to VOCs is not seen by the CRM instrument

during ambient measurements is a crude assumption, since this value will depend on the composition of the sampled air masses. However, this assumption was only made to show that the fraction of OH reactivity that is not seen by the CRM is similar to the potential offset of 2 s^{-1} in the zero for the pump-probe instrument.

Comment: "*line 855 [p. 6154, line 1]: Fig.5 -> Fig. 6*"

Response: We have corrected this.

Changes:

(Section 3.2.2: p. 6153, line 29 – p. 6153, line 30): "…total OH reactivity (bottom panels of Fig. **6**, black trace)…"

Comment: "*Fig. 8 : CRM is larger than FAGE in most time. This is not consistent with Fig. 7. Is this mistake of making figure legend? Or did CRM show higher value during the week (relatively clean condition) ?*"

Response: The legend in Fig. 8 is correct, and the CRM measurements were higher than the pump-probe measurements during this time period of low OH reactivity. This figure is counterintuitive, because both the offset and the slope of the regression line shown in Fig. 7 have to be taken into account to compare the CRM and Pump-Probe measurements. As indicated in lines 20–22 on p. 6154, this linear relationship indicates that for ambient OH reactivity values lower than 10 s^{-1}, the CRM measurements will be higher than the Pump-Probe measurements, while the opposite is expected for ambient OH reactivity values higher than 10 s^{-1}. In Fig. 8, most of the measurements are close to or lower than 10 s^{-1}, leading to CRM measurements being higher than Pump-Probe measurements. We have clarified this point in the last paragraph of Section 3.3 by adding the following sentence.

Changes:

(Section 3.3, p. 6157, lines 25–26): "…in this environment. **It is interesting to note that, in Fig. 8, the OH reactivity values measured by the CRM instrument are higher than those measured by the pump-probe instrument. Indeed, as mentioned in Sect. 3.2.2, this behavior is expected from the linear relationship shown in Fig. 7 for OH reactivity values lower than 10 s^{-1}.**"

Referee 2:

Comment: "*1) Although significant instrument detail is provided, more information on the instrument set up during the experiments would be useful (sections 3.1 and 3.2). The inclusive nature of OH reactivity observations means that inlet losses need to be considered. Hence, differences in instrument inlets and sampling in both the synthetic VOC and ambient comparisons should be discussed. The short lifetimes of many components of total OH reactivity also means that the proximity of all the observations (OH reactivity and ancillary) during the comparison should be provided.*"

Response: As indicated on line 26 of p. 6127-line 2 of p. 6128, a common inlet system was used for all instruments. The different inlets, including those of the two OH reactivity instruments, were located together inside a neck-shaped funnel outside the laboratory to ensure that the same air mass was sampled by the different instruments. For the synthetic VOC comparison, all the inlets were overflowed with the same synthetic mixture. Therefore, there were no changes in inlet configuration between ambient measurements and synthetic VOC tests. This has been clarified in Section 3.1 of the manuscript. We have also provided additional detail on the inlets and sampling flows in sections 2.2.1 and 2.3 for the OH reactivity instruments and in Table 3 for the ancillary measurements. Information about the sampling inlet and sampling flow rate for the pump-probe instrument is mentioned on the paragraph bridging pp. 6137-6138 (line 27, p. 6137 – line 3, p. 6138). We have also clarified in Section 3.1 that the same inlets were used for the ambient and standard measurements.

Changes:

(Section 2.1, line 26, p. 6127): "…detail in Sect. 2.4. *Inlets for all instruments were gathered into a funnel (approximately 7 cm in diameter) located approximately 50 cm away from the PC2A laboratory building to ensure that all instruments sampled the same air masses.*

(Section 2.2.1, line 16, p. 6129): "…pulled through a *3-m long* sampling inlet…(0.64-cm *o.d.*) *at a rate of 415 cm^{-3} min^{-1} (Fig. 1b)*.

(Section 3.1, lines 2-3, p. 6147): "These synthetic mixtures *were overflowed into all the sampling inlets. This ensured that the synthetic mixtures* were sampled simultaneously…GC instruments *under the same inlet conditions as ambient measurements* to investigate the accuracy…"

We have also revised Table 3, adding columns for inlet diameter, inlet length, sampling flow, and residence time.

Comment: "*2) Lines 226 – 236 [p. 6129, lines 9-20] describe the use of platinum wool heated to 350 °C to remove volatile organic compounds (VOCs) from a humid airflow. As OH reactions often show significant temperature dependencies, the authors should note any effect of this approach on the gas temperature within the reactor and a calculated effect on the OH + pyrrole rate constant if non-negligible.*"

Response: The role of platinum wool has been clarified in the manuscript as suggested by the reviewer. The air exiting the catalytic converter passes through 2.6 m of tubing (1.4 m of stainless steel tubing and 1.2 m of Teflon tubing) before entering the CRM reactor. Although this should give the air from the catalytic converter time to thermalize, there is the possibility of a slight temperature increase in the reactor during C2 compared to C3. However, the reactor temperature is buffered by the mercury lamp, which releases some heat through arm 1 (OH injector) as mentioned on lines 16–20 of p. 6156. This increase in temperature is captured by measurements of temperature at the exit of arm 3 on the CRM reactor (Fig. 1). The maximum temperature in the reactor, according to the temperature probe on arm 3, was approximately 30 °C. This is approximately 5–10 °C higher than the ambient temperature in the lab. Using the temperature and pressure dependences for k(OH+pyrrole) recommended by Dillon et al. (2012), a difference of 10 degrees in temperature

would translate to a 5% difference in the rate constant for k(OH+pyrrole); this is within the measurement uncertainty of the OH reactivity measurements. We have added this discussion to the manuscript.

Changes:

(Section 2.2.1; p. 6129, line 11): "…heated to a temperature of 350 °C. ***The platinum wool leads to the complete oxidation of ambient VOCs to water and carbon dioxide.*** The zero air humidity is therefore close to ambient relative humidity (RH). ***The air passes through 2.6 m of tubing before entering the CRM reactor; this should ensure that the air going through the catalytic converter has been thermalized. While there is the possibility of a slight temperature change between the C2 and C3 conditions (see Sect. 2.2.2), the mercury lamp used to generate OH also releases some heat through arm 1 and tends to buffer the reactor temperature between the C2 and C3 conditions. Measurements of temperature within the CRM reactor (ranging from 24–30 °C) suggest that any increase in temperature compared to ambient is lower than 10 °C. Over this range of temperatures, the rate constant for OH + pyrrole differs by less than 5% based on the temperature-dependent relationship derived by Dillon et al. (2012); this is within the measurement uncertainty for the CRM instrument.*** The catalytic converter…"

Comment: "*3) Possible impurities in the air used for measuring zeros on the pump- probe instrument are highlighted as the likely cause of a 2 s-1 discrepancy between the two instruments during the ambient observations period (section 3.2.2). Similar impurities in the air used to measure the zero on the comparative reactivity instrument (step C2, Fig. S3), however, are not discussed or quantified. In order to minimise humidity effects in the comparative reactivity instrument the air used for step C2 is ambient air that has been passed through a Purafil media and activated charcoal trap to remove VOCs and NOx. The effectiveness of this process needs to be evidenced and discussed, as it seems likely that it is not 100% and if so the possible impact on the reported numbers needs to be quantified. Also, if this process is more effective at providing a clean air supply than the cylinder supply used for the pump-probe instrument, was a Purafil media and activated charcoal trap tested on the zero air supply for the pump-probe instrument also?*"

Response: The Purafil/charcoal trap was added on the setup to remove NO_x from the zero air. This trap was used in conjunction with the catalytic converter. Ambient air was first passed through the Purafil/charcoal trap and then through the catalytic converter. It is possible, though unlikely, that the Purafil/charcoal trap may add a small amount of VOCs into the air sample. However, these VOCs would be subsequently oxidized inside the catalytic converter. As described in Sect. 2.2.1, the catalytic converter was tested with the GC instruments described in Sect. 2.4; it was found that the concentration of VOCs at the exit of the catalytic converter was below the detection limit of the GC instruments ($\approx$ 5 pptv) when synthetic mixtures made of tens of VOCs (a few ppbv of each) were passed through the catalytic converter. To test the effectiveness of the Purafil/charcoal trap, a NO_x analyzer was placed at the exit of the Purafil/charcoal trap-catalytic converter system to measure NO_x species when ambient air was passed through it. It was found that more than 85% of ambient NO_x was removed. We have noted this in the manuscript. During the intercomparison, a Purafil/charcoal trap was not used on the zero air supply for the pump-probe instrument.

Changes:

(Section 2.2.3, p. 6133, line 19): "…remove NO_x species. ***To test the effectiveness of this setup to remove NO_x species, a NO_x analyzer was placed at the exit of the Purafil/charcoal trap-catalytic converter system to measure NO_x species when ambient air was passed through this system. It was found that more than 85% of ambient NO_x was removed.***"

Comment: "*4) It is apparent that possible uncertainties in the zero obtained for both instruments could impact the comparison, but the evidence provided for a 2 s-1 error in the pump-probe instrument is not compelling. The diel average data in fig. 8 does suggest that increasing the pump-probe OH reactivity observations by 2 s-1 would improve agreement with the comparative reactivity observations and the calculated OH reactivity. However, the same conclusion is not as obvious from the data shown in figs. 5 and 6. Would an error of 2 s-1 in the pump-probe instrument zero not also be expected to be visible in the measurements of the synthetic VOC mixtures, which currently agree well with calculations (fig. S8)? It appears to the reader that a zero offset has been suggested to reconcile the two instruments, but that direct evidence that this can be attributed to the pump-probe zero is lacking. The authors should provide evidence that this is the likely cause of the 2 s-1 offset, or make it obvious to the reader that it is a speculative explanation, especially in the conclusions section.*"

Response: It is not straightforward to see this 2 s^{-1} offset in the pump-probe instrument on the time series shown in Figs. 5 and 6, since the CRM instrument also underestimates the OH reactivity due to VOC photolysis. The absolute underestimation of the pump-probe instrument is constant at 2 s^{-1}, while the absolute underestimation of the CRM instrument is not and depends on ambient OH reactivity. It is easier to see the 2 s^{-1} offset in the pump-probe instrument in Fig. 7, since it appears as a significant intercept, while the underestimation due to VOC photolysis in the CRM instrument only impacts the slope.

The 2 s^{-1} offset in the zero for the pump-probe instrument is not visible for the synthetic VOC tests, because the zero air used to generate the VOC mixtures is the same air used to measure the zero of the pump-probe instrument. This zero has therefore been subtracted for the pump-probe measurements to derive the OH reactivity due to the added VOCs. While having some residual reactivity in zero air is not an issue for these tests, it is, however, an issue for ambient measurements.

The zero for the pump-probe instrument measured using this zero air was 5.6 s^{-1}, as mentioned on lines 18–19 of p. 6140. It is also mentioned on lines 21–23 of p. 6140 that zeroes for the pump-probe instrument measured after the intercomparison campaign using ultra high purity air was 4.5 s^{-1}, i.e. lower by 1.1 s^{-1}, which is consistent with an offset in the zero for the pump-probe instrument during the intercomparison study.

It is also interesting to note that if the regression line shown in Fig. S8 (Synthetic VOC tests) for the CRM measurements (bottom panel, red squares) is not constrained to zero, an intercept of 1.4 ± 1.0 s^{-1} (1σ) is observed. While this offset is only barely significant, it is consistent with an OH reactivity of 2 s^{-1} in the zero air.

While we cannot rule out another issue that led to the observed discrepancy between the CRM and pump-probe measurements at low ambient OH reactivity, an offset of 2 s^{-1} in the Pump-Probe zero is very likely. However, as suggested by the referee, we have acknowledged that we cannot provide

compelling evidence and that this conclusion is speculative. We have also incorporated the discussion presented here into the relevant sections of the manuscript.

Changes:

Section 3.1.2 (p.6149, line 26): "…OVOC mixtures. *It is interesting to note that if the regression line for the CRM measurements in Fig. S8b (red squares) is not constrained to zero, there is an intercept of 1.4 ± 1.0 s^{-1}. While the uncertainty on the offset is large, this offset would be consistent with an OH reactivity of 2 s^{-1} in the zero air. However, it must be noted that any discrepancy in the determination of k$_{losses}$ (discussed in Sect. 2.3.2) should not affect the OH reactivity measured by the pump-probe instrument during these tests. This is because the same zero air that was used to measure k$_{losses}$ was also used to dilute the standard mixtures. Furthermore, the OH reactivity from the zero air was subtracted from all measurements.*

Section 3.2.2 (p. 6153, line 25): "…due to a zeroing issue, *as discussed in Sects. 2.3.2 and 3.1.2*, …"

Section 3.2.2 (p. 6154, line 3): "…measurements were increased by 2 s^{-1}. *Due to the nature of the underestimation for each instrument, the effects on the OH reactivity measurements are not apparent in Figs. 5 and 6. While the underestimation by the pump-probe instrument is essentially constant, the underestimation by the CRM instrument varies with the measured ambient OH reactivity.*"

Section 3.2.2 (p. 6154, line 18): "…determination of klosses for the pump-probe instrument. *Since the bias in k$_{losses}$ for the pump-probe instrument is independent of the measured ambient OH reactivity, this bias will be reflected in the intercept. Similarly, as the underestimation of OH reactivity by the CRM instrument is relative to the measured OH reactivity, this underestimation will be reflected in the slope.*"

Section 4 (p. 6158, lines 14–15): "…has been highlighted. *Based on measured values of the zero for the pump-probe instrument and the results of linear regressions from ambient and standard measurements, we speculate that* this issue could lead to an underestimation…"

Comment: "*5) Further analysis of the agreement between the observed total OH reactivity and that calculated using the ancillary observations would be a nice addition to the paper. Although a detailed analysis is likely outside the scope of this work, the authors should at least comment on how the calculated vs. observed OH reactivity compares to previous studies in similar environments, and on the potential sources of disagreement. Comparison with previous studies will provide a context with which to asses the relevance of the work presented.*"

Response: We agree that it would be helpful to place these measurements in context with other OH reactivity measurements conducted in similar environments (i.e., urban areas where NO$_x$ makes large contributions to total OH reactivity). The limited coverage of ancillary measurements makes a detailed analysis and definitive interpretation difficult. However, we can discuss the measurements that we do have from this intercomparison and compare them to those from previous urban field campaigns. We have included paragraphs in sections 3.3 and 4 to this effect and have added the value for the missing OH reactivity for this intercomparison in Table 1.

Changes:

Section 3.3 (p. 6157, lines 25-26): "…missing OH reactivity in this environment….

*As shown in Table 1, **good agreement between calculated and measured OH reactivity has also been seen in other urban environments. One example is the 2001 PMTACS-NY (PM2.5 Technology Assessment and Characterization Study – New York) field campaign (Ren et al., 2003; Mao et al., 2010), in which the average contribution of NO_x to the total OH reactivity is 50% (Mao et al., 2010). Agreements within 30% between measured and calculated OH reactivity were also seen in other urban areas within regimes where NO_x makes large contributions to the total OH reactivity. This includes a time period dominated by local emissions in Paris (referred to as "period II") during the MEGAPOLI campaign (Dolgorouky et al., 2012) and winter in Tokyo (Yoshino et al., 2006); during both these time periods, NO_x contributed more than 50% to the total OH reactivity. In addition, agreement between measured and calculated OH reactivity was seen for sites in Houston where OH reactivity was dominated by VOCs, which were generally emitted locally at these sites (Mao et al., 2010).***

However, missing OH reactivity was observed during spring, summer, and autumn in Tokyo (Yoshino et al., 2010) and for some periods during the MEGAPOLI campaign in Paris (Dolgorouky et al., 2012). It must be noted that the missing OH reactivity observed during these periods was attributed, albeit indirectly, to products of photochemical oxidation of VOCs. As the PC2A site is adjacent to several major highways (Fig. S1) and this campaign was conducted during autumn, it is likely that primary emissions of NO_x and VOCs from vehicle traffic dominate, especially during times of peak traffic."

(Section 4, p. 6159, line 3): "…humidity correction. **A comparison of the measured OH reactivity to that calculated from measurements of trace gas concentrations during time periods where the full suite of trace species was available show reasonable agreement. This is consistent with previous measurements in sites where the OH reactivity is dominated by NO_x and local VOC emissions.**"

A missing OH reactivity fraction of approximately 1 has been inserted into Table 1.

REFERENCES

Dillon, T. J., Tucceri, M. E., Dulitz, K., Horowitz, A., Vereecken, L., and Crowley, J. N.: Reaction of Hydroxyl Radicals with C_4H_5N (Pyrrole): Temperature and Pressure Dependent Rate Coefficients, J. Phys. Chem. A, 24, 6051–6058, 2012.

Michoud, V., Hansen, R. F., Locoge, N., Stevens, P. S., and Dusanter, S.: Detailed characterizations of the new Mines Douai comparative reactivity method instrument via laboratory experiments and modeling, Atmos. Meas. Tech, 8, 3537–3553, 2015.