Reviewer 1.

The manuscript "Contributions to OH reactivity from unexplored volatile organic com- pounds measured by PTR-ToF-MS – A case study in a suburban forest of the Seoul Metropolitan Area during KORUS-AQ 2016" by Sanchez et al., present results from OH reactivity measured in spring 2016 in a Research Forest Station of Korean pine located roughly 35km from the centre of Seoul. This site is influenced by both local biogenic emissions and transported anthropogenic emissions. OH reactivity measurement were operated with a CIMS-CRM instrument and Volatile Organic Compounds (VOCs) were monitored with a high resolution Proton-Transfer-Reaction Time-of-Flight Mass Spectrometer (PTR-ToF-MS). The authors found in addition to the most commonly monitored VOCs, 346 unidentified peaks that got assigned in three different categories in order to estimated their potential contribution to the observed missing OH reactivity. The missing reactivity is defined as the difference between measured total OH reactivity and the OH reactivity calculated from the known species quantified in the same air masses. While the addition of previously unexplored VOCs to the analysis decreased the amount of missing OH reactivity, still 42.0% of missing reactivity remained. The authors hypothesis is that this might be due to oxidation products from both biogenic and anthropogenic compounds.
I found the manuscript clear and concise. The introduction places this study in context in a comprehensive fashion. The methods and the results are mostly well explained and are sound. I found a few places, where the manuscript could benefit from further clarifications (see specific comments below), in particular explaining some assumptions taken for the calculations of OH reactivity from unidentified PTR-ToF-MS peaks. Therefore, I would recommend ACP to publish this manuscript after minor corrections have been done.
Specific comments:

- p.3, ll.61-66: Are the authors aware of the more recent publications by Nölscher et al. (2012) and by Praplan et al. (2019) for additional OH reactivity measurements in Hyytiälä? Their findings were similar to the ones of Sinha et al. (2010) in terms of missing reactivity. Nölscher et al. found for instance that the highest missing reactivity values occurred during a period of higher temperature (labelled "stress" period). Praplan et al. also found among other things that including modelled oxidation compounds from the Master Chemical Mechanism only decreased the missing fraction by about7% at most.

In the revision we have included the suggested references. Now it is read:

Nolscher et al. (2012) observed the highest level of missing OH reactivity during a heat wave episode, possibly inducing a stress emission response from the local forest. A comprehensive analysis by Praplan et al. (2019) using a long-term observation dataset and a photochemical model framework with the Master Chemical Mechanism illustrates that the model simulated oxidation compound contribution can only contribute 7 % of missing OH reactivity. (line 71 - 78 in the track change version)

- p.8, ll.180-182: Fuchs et al. (2017) also found that some CRM instrument see an interference with additional O3 introduced from ambient air in the reactor. Has this interference also been investigated in the UCI CIMS-CRM? It would be a good thing to explicitly mention that this effect can be ruled out.

We conduct one experiment by adding standard (propene) when ozone was 60 pppb and 120 ppb during MAPS-Seoul campaign and does not see the statistical difference but we did not follow up more systematic fashion as Fuchs et al. did. This is something we should address in the up-coming lab study. We have included that this discussion in the revised manuscript. Now it is read:

In addition, Fuchs et al. (2017) also described a potential interference from ambient O_3 in some CRM systems. In the 2015 field campaigns conducted in Seoul South Korea (Kim et al., 2016), we conducted a standard addition experiment for the propene standard for additional ~ 30 s^{-1} in two different ozone environment 65 ppb and 123 ppb. The outcome illustrates an agreement between two additions within the analytical uncertainty. (line 263 - 267 in the track change version)

- p.9, ll.189-193: I understand that the detailed calibration procedures are detailed in another publication, but I believe that some additional information regarding the total OH reactivity instruments could be included. For instance there is no indication about what the pyrrole-to-OH ratio is during this campaign (and if it is the same as for the laboratory calibrations). Also from the Supplementary Material in Sanchez et al. (2018), if understand Fig. S1 correctly, the instrument response (without unit, but is it OH reactivity?) is about a quarter of what is expected and this is consistent over a wide spectrum of kOH values. I personally would find value in summarizing this in a couple of sentence in the present manuscript. Consequently, should we understand that the multi-point calibrations performed during the campaign were consistent with the measurements in Sanchez et al. (2018)?

The Y-axis in the calibration curve, presented in Sanchez et al. (2018), used an arbitrary unit as we were using pyrrole to OH ration of 3:1, which would not warrant the pseudo first order reaction regime. Since the the publication of Sanchez et al. (2018), we have maintained identical configuration and sensitivity has been maintained within 30 %. This description has been included in the revised manuscript.

Now it is read

We consistently kept the pyrrole to OH ratio at 3:1 and so did not achieve a pseudo first order relationship.(line 214 - 215 in the track change version)

- p.9, ll.202-203: Out of curiosity, is there a reason that the authors did attempt CIMS-CRM calibrations with the PTR-ToF-MS calibration mixture? (possibly before or after the measurement campaign, not necessarily during the campaign, as I understand that the instruments were physically located in two different shacks)

This calibration standard mixture is only used for PTR-ToF-MS calibration. We have make it clear in the revised manuscript. We did not use the multi-component mixture for the CIMS-CRM calibration.

Now it is read

. This standard mixture was only used for the PTR-ToF-MS calibration and not the CRM-CIMS calibration. (line 279 -280 in the track change version)

- p.11, ll.236-246: Category I: My main issue here is that, even if I am not familiar with the PTRwid software, I assume that it delivers "calculated molecular formula" (and not chemical structures) as mentioned by the authors. Looking at Table S2 of the Supplementary material I understand that for some of the molecular formula, there is only one sound structure

possible. Could the authors discuss the chances that they found only one match in the NIST database, while other chemical structures, for which the database contain no data, could be possible? I also fail to understand how a SAR-based estimate can be given for compound without any given "Possible ID". I understand that it is a lot of work to compile all these reaction rate coefficients, but the authors definitely ought to explain their assumptions better. Do authors rely on previous studies with the same instrument? Previous studies at the same site? I also could not find where the NIST value for k comes from for C4H4H+, for instance. Is it just in the wrong column? And why were the authors not able to use the SAR method for maleic anhydride? Is it a limitation of the method?

Most of cases, we encountered more than one possible structures. Then we go over the previous publications such as Williams et al. (2001), de Gouw et al. (2003), Jordan et al. (2009), Ruuskanen et al. (2011) Müller et al. (2012), and Koss et al. (2017) to list all the possible compounds, reported in the ambient air before. Then we took a median for the rate constant. The detailed list and process is well described in Sanchez (2019). We have included this discussion in the revised manuscript. For C4H4H+ we categorize it as vinylacetylene (C4H4) with a reported rate constant. We also have included this in the revised manuscript. For that specific case of m/z 75, the reviewer raised, we found that there are five possibilities - hydroxyacetone, propionic acid, unidentified oxidation product fragments of terpenes, methyl acetate, and ethyl formate. Among them, we choose the median reaction constant. The detailed selection process for all masses is thoroughly discussed Dianne Sanchez's Ph.D. dissertation. The embargo period has been over since July 8th of 2020 so we add this to the reference and have included detailed discussion on this.

Now it is read

As the only information we have is the molecular composition, we identified multiple isomers with different functional groups and thus different reactivity. We have extensively reviewed previous publications (Williams et al., 2001;De Gouw et al., 2003;de Gouw and Warneke, 2007a;Jordan et al., 2009a;Ruuskanen et al., 2011;Muller et al., 2012;Koss et al., 2017a) identifying ambient VOCs using PTR-MS with both quadrupole and time-of-flight systems to identify possible compounds. For example, for the m/z of 75.043, there are four possible compounds including hydroxy acetone, propionic acid, methyl acetate, and ethyl formate. We used the median reaction constant for the set of possible compounds. The detailed description of the OH reaction constant determination process for the Category I peaks is described in Sanchez (2019) (line 329 -338 in the track change version).

- p.11-12, ll.252-264: Category II: Should there be a regression adjusted to the m/z of isoprene for m/z 116.036 in Table S3, which is correlating with isoprene? (Also there is no mention of Table S3 and S4 in the main text)

We have added the regression line in Figure S1 for the k_{OH} calculation of the isoprene type compounds in the revised manuscript.

- pp.12-13, ll. 278-281: Does this assumption rely on the fact that light hydrocarbons are not emitted locally? Can the authors be sure that there is no strong vertical gradient for these compounds regardless of the evolution of the boundary layer height?

We assumed the homogeneous distribution of small alkanes and alkenes in the boundary layer because they have relatively long chemical lifetime in comparison with the mixing time scale of the convective boundary layer. As the referee suggested, certainly, no

known strong emission sources of those compounds is the important factor. We have included this discussion in the revised manuscript.

Not it is read

In this suburban forest, we do not think there is any substantial emission sources of these relatively long-lived VOCs. (line 411-412 in the track change version)

Technical corrections:
p.27, Table 1, 3rd row: "Scientific" instead of "Scien8fic"

We have corrected this in the revised manuscript.

pp. 21-27: Check the format of the references. Sometimes "Doi" is used, sometimes "DOI", sometimes nothing; one link appears, "–" (l. 699) should probably be fixed, etc. Supplementary material, Tables S3 and S4: I would use "peaks" instead of "compounds" in the tables' captions.

We have corrected this in the revised manuscript.

Reviewer 2.

This paper shows the results of the measurements of the total OH reactivity in the Taehwa Research Forest, southeast from the center of Seoul, South Korea. The authors indicate the existence of the missing OH sink and its sources. Due to the elucidation of the formation of the tropospheric ozone and SOA, this research is very important. In addition, this paper shows the detail results and discussions. Therefore, I recommend that this paper should be published if the minor revisions shows below is done.

«Comment» L.146-148: The mini tunable infrared laser direct absorption spectroscopy instrument (TILDAS) has applied to the measurements of HCHO, methane and so on. Is the TILDAS commercially available, or home-made? If the authors have already explain the detail of the TILDAS in some paper, the author should add a reference.

We added a reference and manufacturer information about the instrument (Table 1).

2.4. OH reactivity Calculation The authors grouped the 346 unidentified measured mass peaks into three categories. The authors should show the number of the unidentified peaks for each categories.

We have included the information about the number of peaks for each category (Line number 327, 353, and 368 in the track change version).

Figure 5(A) In general, anti-correlation between NO and O3 have been observed due to the reaction of NO with O3. In addition, ozone is formed secondary, which is similar with some OVOCs. Therefore, I recommend that the diurnal variation of the OH reactivity for O3 were distinguished with other pollutants.

As shown in Figure 2 and Figure 3, the OH reactivity contribution of ozone is very minor. Most of the OH reactivity contribution in this category comes from NOX (mostly NO2). We clarify this point in the revised manuscript.

Now it is read

Furthermore, no significant variance of the different classes of reactive gases such as criteria air pollutants (CO, NO_x, O_3, and SO_2), mostly contributed by NO_X, OVOCs (acetone, acetaldehyde, formaldehyde, methylglyoxal, methanol, methyl ethyl ketone), aromatics (benzene, toluene, xylenes, styrene, benzaldehyde, trimethylbenzenes), and BVOCs (isoprene, monoterpenes, sesquiterpenes, MVK+MACR) was observed during the different periods (Figure 5). (Line number 460 - 464 in the track change version)

(very) Minor: Font of the subscript of NO"x" is not unified. The authors should check it. In addition, the font of "k_OH" and "r^2" are not unified.

We double-checked throughout the manuscript to make the notation consistent in the revised manuscript.

Reviewer 3.
This manuscript reports a comparison of OH reactivity measurements performed dur- ing the KORUS-AQ 2016 field campaign to OH reactivity values derived from the mea- surement of trace gases. In this study, the authors observed a large amount of missing OH reactivity, similar to that observed in previous campaigns focusing on areas impacted by biogenic emissions. The authors propose a procedure to assess the contribution of unidentified species detected by a high resolution PTRMS to the missing OH reactivity. This reviewer thinks that this work is of interest for the scientific community and de- serves publication. However, several aspects of this publication need to be straighten, especially the measurement quality of the CIMS-CRM instrument. I therefore recommend publication in ACP after the authors address the following comments:
Major comments:

L183-185: "This included a laboratory-built catalytic converter (Pt-wool at 350 ∘C) that minimized the interferences due to changes in air to prevent the interference from the difference in humidity for the zero air characterizations." – Heated Pt-wool will not remove NOx and may even lead to a higher NOx concentration at the output of the catalytic converter due to the oxidation of organic nitrate species present in ambient air. This has been reported in Hansen et al. (2015) where the authors used filters made of Purafil and activated charcoal upstream the catalytic converter to remove NOx. If NOx is not removed from the VOC-free air provided by the catalytic converter, the CRM measurements will be biased low. How did the authors remove NOx from the VOC-free air generated by their catalytic converter?

We have included more details on our approach to handle NOX. Basically, we did a laboratory calibration experiments with different NOX. Our goal was to discern a threshold level that disrupts the calibration curve by increasing NO concentration. The threshold was empirically determined as 5 ppb. In this level, the slope of the calibration curve is statistically deviated from the slope that is observed in the standard matrix with 5 ppb or lower NO levels. We did not add any scrubber except a catalytic converter.

Now it is read:

Hansen et al. (2015) illustrated that NO_X may be generated from the catalytic converter. To prevent potential NO_X interferences, they used a scrubber with Purafil and activated

L186-189: "Additionally, interference from the OH recycling reaction of HO2 with NO in the glass chamber was prevented by removing OH reactivity data points that corre- sponded with ambient NO levels that exceeded 5 ppb to reflect results from a laboratory characterization study (Sanchez et al., 2018)." – The reviewer checked in Sanchez et al. (2018) but did not find the laboratory characterization mentioned in the above sentence. The authors should provide some information about the tests performed on the UCI CIMS-CRM instrument to characterize OH recycling. It is stated that OH reactivity measurements performed when NO was larger than 5 ppb were discarded. However, OH recycling does not stop below 5 ppb NO and still impacts the OH reactivity mea- surements. The impact will be instrument dependent and it is important to assess it on the UCI CIMS-CRM. Fuchs et al. (2017) report corrections of 10-20 s-1 at 10 ppb NO for 3 CRM instruments. Assuming that the correction scales with NO on this small range of concentrations, 5 ppb of NO would lead to a correction ranging from 5-10 s-1 for the instruments used in Fuchs et al., which is significant compared to the range of OH reactivity observed in the present study (20-50 s-1). In addition, NO2 was observed to generate measurement artifacts on some CRM instruments (Michoud et al., 2015; Fuchs et al. 2017), requiring corrections of 1.6-3 s-1 at a NO2 mixing ratio of 10 ppb. For the present study, Figure S2 reports mixing ratios ranging from 2-60 ppb for NO2. Was this issue investigated on the UCI CIMS-CRM?

L189-193: The authors refer the reader to Sanchez et al. (2018) for details on calibration procedures. The reviewer agree with the comments from the first reviewer that additional information on calibration procedures is needed in the present publication. What was the pyrrole-to-OH ratio in the CRM reactor during calibration experiments reported in Sanchez et al. (2018)? Why is there a significant intercept of 3.9 s-1 on the calibration curve (Sanchez et al., 2018)? What was the range of pyrrole-to-OH ratios during the field measurements reported in the present publication? Previous studies have shown that the CRM response can depend on the pyrrole-to-OH ratio (Michoud et al., 2015; Zannoni et al., 2015) and calibrations have to be performed over the range of pyrrole-to-OH ratios observed during field measurements. Can the authors comment on this aspect for the UCI CIMS-CRM?

L236-246: When a molecular formula was determined by PTRwid, how did the authors choose between the different possibilities for isomers? The reviewer checked how the OH rate constant would change between different isomers for C3H6O2 detected at the nominal m/z 75 (methyl acetate 3,5E-13 cm3/molecule/s; propanoic acid 1.2E-12; hydroxyacetone 3E-12; hydroxypropanal 3.5-5.5E-11; and others). The OH rate constant can span 2 orders of magnitude for these isomers. Could the authors comment about the choice made in Table S2 to use a kOH value of 1.2E-12 cm3/molecule/s for this molecular formula? This issue is even worse for ions detected at higher masses since more isomers have to be taken into account. What methodology did the authors used to select the rate constants reported in Table S2? Minor comments:

L57-59: "Di Carlo et al. (2004) conducted a study in a mixed forest near Pellston, Michigan where they reported missing OH reactivity larger than observational uncertainty." – Please be quantitative. How much larger?

Di Carlo et al. (2004) conducted a study in a mixed forest near Pellston, Michigan where they reported missing OH reactivity (~ 30 %) larger than observational uncertainty. (Line 61 - 63 in the track change version.)

L115: The authors reviewed part of the OH reactivity literature for forested areas showing that variable agreements were observed between measured and calculated OH reactivity (from trace gas measurements or constrained O-D modeling), the disagreement being sometime attributed to (i) unknown emissions of VOC, (ii) oxidation products of primary VOC, or (iii) both. The reviewer would have liked to see a short discussion on the current limits in the identification of the missing OH reactivity. How can additional studies help improving our understanding of the missing OH coreactants? This will help motivating the present work.

We added a sentence read as "This *status quo* urges us to take a convergent approach by effectively integrating observational results from novel instrumentations and model outcomes." In the revised manuscript (the track change version line 126 - 128).

L149-L151: "The OH reactivity and NOx analyzers were located in another nearby air-conditioned shack (3 m apart) and sampled air through an extended Teflon inlet line of 4 m (14" OD) from the ground with a flow rate of 4 sLpm resulting in a 0.5 second residence time." – Please indicate the height of the sampling inlet for the OH reactivity instrument and the NOx analyzers.

We have included the information (3.5 m AGL) in the revised manuscript (track change version line166-167).

L161-162: The authors indicate a pyrrole+OH rate constant of 1.45E-10 cm3/molecule/s at 298 K. The rate constant recommended by Dillon et al. (2012) and Atkinson et al. (1984) is 1.2E-10 cm3/molecule/s at the same temperature. Why did the authors use a different rate constant?

We have corrected the rate constant accordingly in the revised manuscript (178-179).

Not it is read

The CRM method measures total OH reactivity by quantifying the relative loss of pyrrole, a highly reactive gas ($k_{OH+ pyrrole}$ = 1.07 × 10^{-10} cm^3 molecule^{-1} s^{-1} at 298 K (Dillon et al., 2012)) that is rarely found in the atmosphere (Sinha et al., 2008b). (Line 178 - 179 in the track change version)

L212-213: "we determined the VOC sensitivities using equation 1 (Eq 1)" – Equation 1 is not used to derive the VOC sensitivity but to calculate the concentration of uncalibrated species. Please rephrase.

We actually used the relationship not necessarily used the equation for the mixing ratio assessment. We have revised the manuscript to minimize any confusion (296-301).

The application of this equation can be justified since PTRwid provides the mass discrimination corrected counts as a final computational product.

$$ppb_{VOC} = ncps_{VOC} \times k_{benzene}/k_{VOC} \times 1/11.94 \ ncps \ ppb^{-1} \ Eq1$$
where, 11.94 ncps ppb^{-1} is the assessed sensitivity of benzene.

(line 296 - 301 in the track change version)

L219: Equation 1 is confusing. Is "ncps(benzene)/ppb" the normalized signal (corrected for mass discrimination) generated by 1 ppb of benzene? What is the factor of 11.94? Please clarify this equation. How was the ion transmission curve characterized on the PTRMS to correct the normalized VOC signals for mass discrimination?

Mass discrimination has been corrected while we process the raw data as a part of the data mining process. We have clarified the point and the equation in the revised manuscript as shown in the previous response.

L247-251: Please indicate the range of R2 factors for the correlations. Also indicate R2 factors in Table S3.

We have included the information in the revised manuscript (Table S3 in the revised manuscript).

Now it is read

Nonetheless, this group of compounds illustrated a positive correlation (R^2 = 0.19 to 0.88) with either anthropogenic (benzene, toluene) or biogenic (MVK+MACR and monoterpenes) VOCs.

L253-255: "The compounds were grouped into 5 m/z bins and the average kOH of each bin was calculated. The green triangles represent 5 m/z binned averages from these compounds plotted with their respective average kOH." – The reviewer does not understand what was done here. Please clarify this section. Also provide additional information on what is shown in Figure S2. What is the purpose of the different regression lines?

We have further described in this section for clarifications in the revised manuscript.

Now it is read:

More specifically, we assume that k_{OH} is linearly correlated with m/z. To apply this linear relationship, the compounds with known k_{OH} were grouped into 5 *m/z* bins and the average k_{OH} of each bin was calculated. (Line 359 - 362 in the track change version)

L371-374: The authors are discussing the potential species detected at m/z 83.085. This mass is not shown in Figure 6 and the authors may want to add it.

We have included the trace in the revised manuscript (Figure 6 in the revised manuscript).

L417-420: "As NOx illustrates a conspicuous temporal variation that appears to correlate with the fraction of missing OH reactivity, while observed OH reactivity and calculated OH reactivity from VOCs indicate a less pronounced diurnal difference. " - The reviewer does not understand what is meant here. Please clarify/rephrase this sentence.

We have clarify it in the revised manuscript.

Now it is read:
    This leads us to speculate that there is a consistent presence of unquantified trace gases, likely oxidation products of both anthropogenic and biogenic VOCs as we explored the origin of the unexplored peaks causing missing OH reactivity. In other words, NO_x is relatively well measured with a highly pronounced temporal variation that determines the percentage of missing OH reactivity. (line 550 - 553 in the track change version)

L428-430: "Moreover, due to the different inlet configurations for OH reactivity and VOC observations, their contributions towards observed and calculated OH reactivity may not have been consistently evaluated." – This sentence also need to be clarified. Are the authors discussing the impact of the inlet on the measured trace gases and OH reactivity?

 We have added a relevant reference in the revised manuscript.

Now it is read:

Moreover, due to the different inlet configurations for OH reactivity and VOC observations, their contributions towards observed and calculated OH reactivity may not have been consistently evaluated (e.g. Sanchez et al. (2018)). (line 561 - 563 in the track change version)

Table 1: Please include detection limit and time resolution for each instrument. Brand and model of PTRMS?

 We have included the information in the revised manuscript (Table 1 in the revised manuscript).

Figure 2: How did the authors assess the uncertainty associated to the calculated OH reactivity? What were the sources of errors factored in the calculations? What uncertainty did the authors consider on the OH reactivity from categories I-III?

    We have included a discussion about uncertainty associated with calculated OH reactivity in the revised manuscript.

Now it reads

    There are two components that need to be considered for the assessment of uncertainty associated with calculated OH reactivity: the concentration and the reaction constants with OH. The uncertainty of the observed trace gases is in the range of 5 % to 20 % as shown in Table 1 and is associated with the rate constants from laboratory experiments (Atkinson et al., 2006). Combining 15 % uncertainty from reaction constants and 13.5 % from trace gas observations results in 20 % of uncertainty in calculated OH reactivity. This should be considered as a conservative estimate as most VOC concentrations and associated rate constants are empirically estimated. (line 376 - 383 in the track change manuscript)

Figure 3: The authors indicate an uncertainty of 20.1% for the missing OH reactivity? Since the uncertainty stated for the OH reactivity measurements is 16.7%, a quadratic propagation of errors allows calculating that the authors considered an uncertainty of approximately 11% (1 sigma) on the calculated OH reactivity. This seems a bit low since this uncertainty should account for errors associated to measured trace gases and tabulated reaction rate constants, the latter being already in the range 10-25% at 1 sigma. For the measured trace gases, it is stated that the error on NOx, which account for a large fraction of the OH reactivity, is 20% at 1 sigma. While the uncertainty associated to PTRMS measurements of calibrated compounds is within 5-10%, the uncertainty on mixing ratios derived from masses where a default proton transfer rate constant of 3E-9 cm3/s was used will not be better than 25% (1 sigma). How was the uncertainty on the calculated OH reactivity derived?

We acknowledge that it was not entirely clear about the error bars in the figure. We have clarified the confusion by revising the figure caption as

Diurnal averages of OH reactivity during the stagnation period (A) from May 17th – May 22nd in 2016 and the transport period (B) from 28 May – 1 June 2016. The measured and calculated OH reactivity are on the left. The blue shading represents an uncertainty of 16.7% at 1σ. The black bars represent the propagated uncertainty of 20.1% at 1σ from calculated missing OH reactivity. The percent missing OH reactivity is on the right axis (the figure caption in the revised manuscript)