Response to comments by anonymous Referee #2

General Comments

This manuscript describes a fascinating and impressive study that revisits questions about the germicidal properties of rural air, which has been called the Open-Air Factor (OAF). This term was proposed roughly 50 years ago based on a few studies showing that microbes could be efficiently killed by exposure to rural air, but then subsequently received little attention. It is highly relevant today for obvious reasons. Here, the authors consider possible chemical components that could be responsible for the effect, using a combination of modeling and literature data to interpret the results of the experiments of Dark and Nash (1970), which clearly demonstrated this phenomenon by exposing microbes to ozone and the products of reactions of ozone with various alkenes. The re-analysis is exceptionally thorough, and employs state-of-the-art mechanisms and the latest data on the ozonolysis reactions, as well as careful consideration of factors such as VOC vapor pressure and lipid solubility, which influence the interactions between reaction products and microbes. The authors are able to rule out a number of possible chemical components, and then focus primarily on peroxides, which are known to be formed in alkene ozonolysis and to act as disinfectants. Though the results do not provide a definitive answer as to the chemical identity of the OAF, they provide an excellent starting point for others to explore this important and mysterious phenomenon. I think the manuscript should certainly be published in ACP, after the following few comments are addressed.

Response: We would like to thank this reviewer for the positive assessment of our manuscript.

Specific Comments

Comment 1. I did not see any mention of how much NO might have been present in the experiments of Druett and May (1968) and Dark and Nash (1970), and how this might have impacted the concentrations of peroxides formed through either bimolecular reactions or autoxidation. I can imagine that even in a rural area at this time NO might have been sufficient to quench the peroxide-forming reactions, though the authors probably have information on this.

Response: The Druett and May (1968) experiments sampled night-time ambient air at Porton Down, a rural location in the southern UK. As shown in the examples below in Figure 1, data from air quality monitoring sites in comparable rural locations (https://uk-air.defra.gov.uk/data/) show that annual mean NO_x mixing ratios have generally followed the documented trend in road transport emissions, showing a progressive decline since the early 1990s in response to EU controls of anthropogenic NO_x emissions. Based on the estimated historical trend in UK emissions shown (https://naei.beis.gov.uk/), it can therefore be inferred that the annual mean NO_x mixing at such rural locations was probably about 5-10 ppb at the beginning of the series in 1970. The monitoring data also show that NO accounts for about 20 % of NO_x on average at these NO_x levels, consistent with an annual mean NO mixing ratio of about 1-2 ppb. It should be noted that the partitioning of NO_x into NO and NO_2 shows a strong diurnal variation, with NO suppressed to very low levels at night (when regeneration by NO_2 photolysis cannot occur) by virtue of its reaction with excess ozone.

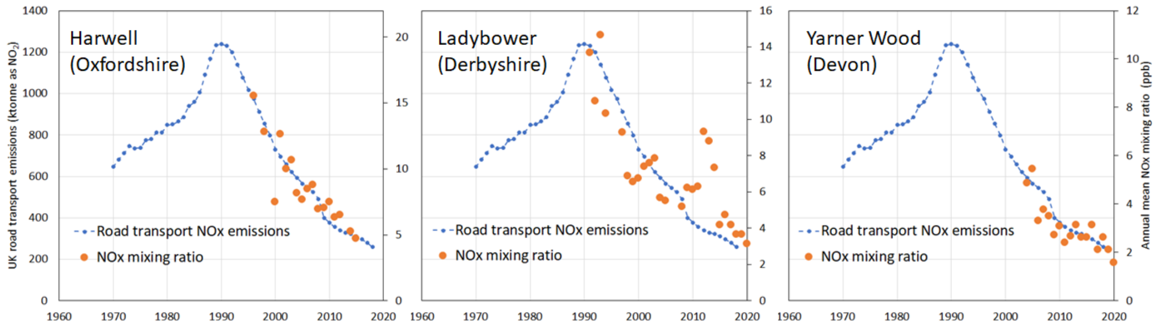

Figure 1: Measured annual mean mixing ratios of NO_x at three rural measurement sites together with their road transport emissions.

The formation rate of hydroperoxides and peroxy acids from the bimolecular $RO_2 + HO_2$ reactions is determined by the ambient concentrations of the precursor RO_2 and HO_2 radicals. It is well established from modelling studies that these concentrations are relatively insensitive to the NO_x level over a wide range in the background ("methane and CO") atmosphere (e.g., Lightfoot et al., 1992) up to about 1 ppb NO_x. At higher NO_x levels, the presence of co-emitted VOCs allows radical levels to be sustained, because reaction of HO with VOCs continues to compete with radical loss via the $HO + NO_2$ reaction. and the conversion of RO_2 and HO_2 to OH through reaction with NO is approximately balanced by conversion of OH to RO_2 and HO_2 through reaction with VOCs. This has been confirmed by measurements of peroxy radicals at a UK rural site by Fleming et al. (2006), which demonstrated sustained concentrations of peroxy radicals up to about 5-10 ppb NO_x during day and night in both summer and winter. In addition, gaseous H_2O_2 was routinely monitored at several UK rural network sites during the late 1980s and early 1990s (i.e. the period when UK rural NO_x levels were likely at their highest), consistent with its formation (at least partially) through the operation of the $HO_2 + HO_2$ reaction (Dollard and Davies, 1992; PORG, 1993; 1997). We therefore expect hydroperoxides and peroxy acids formed from biomolecular $RO_2 + HO_2$ reactions to have been present, both in the rural air sampled by Druett and May (1968), and more generally over the intervening years.

Regarding the possible inhibition of auto-oxidation mechanisms (and HOM formation) by NO, the pseudo-first order loss rate of peroxy radicals with respect to reaction with 2 ppb NO is about 0.4 s^{-1}. Because peroxy radical isomerization rates are very strongly structure dependent, this can compete with and dominate over some of the possible isomerization reactions. However, the majority applied to peroxy radicals formed from cyclohexene ozonolysis in the present work (see Supplement) can compete with reaction with NO at this level, and all of them will certainly be competitive under the night-time conditions considered by Druett and May (1968), when [NO] is heavily suppressed.

Recognizing that hydroperoxides are also formed from other sources (i.e., the reactions of stabilized Criegee intermediates with H_2O and $(H_2O)_2$) which are independent of NO_x, these considerations therefore support our suggestion that mono-, bi- and multifunctional hydroperoxides might be important contributors to OAF. However, we do not rule out the possibility of other species also contributing to OAF, and recognize that the presence of NO_x in ambient air allows formation of mono- and multifunctional oxidized organic nitrogen species. Systematic studies of the diurnal and seasonal variation of OAF, in conjunction with detailed composition measurements, would clearly be valuable, and we hope our paper will help to stimulate such activities in the future.

In the revised manuscript and SI, we will provide more discussion of the likely characteristics of outside air in the rural southern UK at the time of the Druett and May (1968) work, including some of the above information.

The Dark and Nash (1970) chamber experiments were nominally carried out in the absence of NO and alkene impurities, and they report a systematic procedure for minimizing the impacts of such impurities. Whilst we cannot rule out the possibility of trace levels of NO_x being present in their experiments, their procedure suggests that any NO_x present would be in the form of NO_2 rather than NO. Although peroxy radicals (RO_2) also react with NO_2, the impact of these reactions is limited in the majority of cases because the product peroxy-nitrates (RO_2NO_2) are thermally unstable, decomposing rapidly to regenerate RO_2 and NO_2. Based on the generic rate coefficients recommended by Jenkin et al. (2019), only about 4 % of a typical RO_2 radical is sequestered in the form of RO_2NO_2 at 1 ppb NO_2 (298 K, 760 Torr). In the specific cases of acyl peroxy radicals ($RC(O)O_2$), however, the product peroxy-acyl nitrates (PANs) are effectively stable species on the experimental timescale, and the presence of NO_2 could inhibit the formation of products formed from their alternative reaction pathways (e.g., peroxy acids). For the linear alkene systems considered, acyl peroxy radicals are not formed from the first-generation ozonolysis chemistry and only formed in very small concentrations from the uncompetitive secondary attack of HO on the product aldehydes (see Figure 2 below). Consequently, no significant effect of trace levels of NO_2 would be expected for these systems. In the cases of cyclohexene (at the high end of the germicidal impact range), and to a lesser extent 2-methylbut-2-ene and 2,4,4-trimethylpent-2-ene (at the low end of the germicidal impact range), however, acyl peroxy radicals are formed from the first generation chemistry. Although an impact on some pathways could therefore occur in these systems it is difficult to draw firm conclusions on any effect, because the precursor alkenes are at the opposite ends of the germicidal impact range. Once again, highly-instrumented chamber studies would be valuable to help relate germicidal impacts systematically to particular classes of reaction product formed in simulated atmospheric systems.

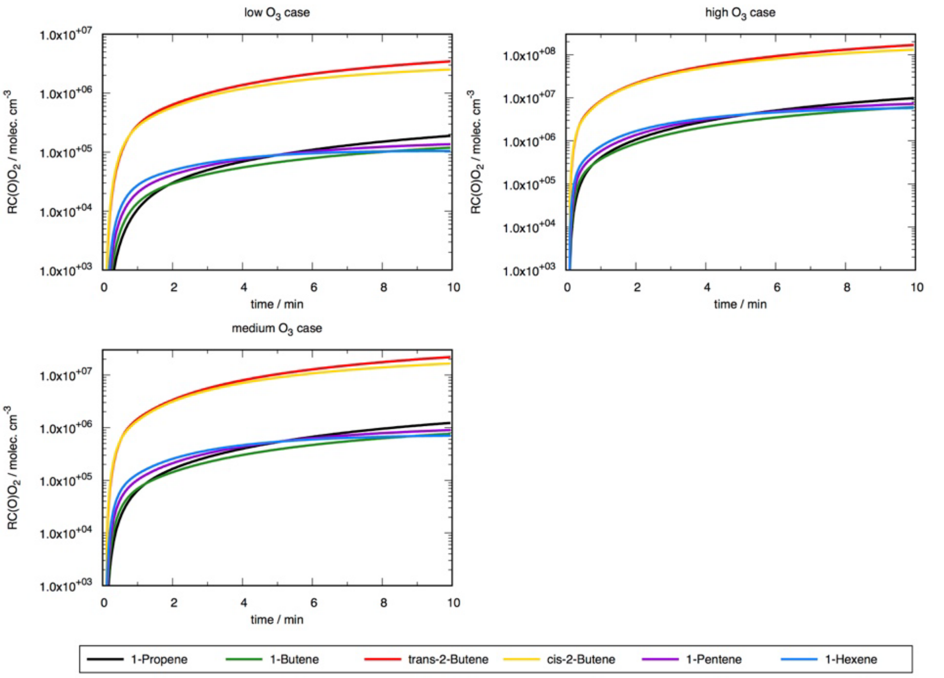

Figure 2: Modelled concentration profiles of acyl peroxy radicals ($RC(O)O_2$) for six different alkene-ozone experiments conducted by Dark and Nash (1970) under low, medium and high ozone conditions.

In the revised manuscript and SI, we will provide more discussion of the possible effects of the presence of NO_x in the Dark and Nash (1970) work, and how this might influence the interpretation of the results.

Comment 2: The uptake of VOCs to the brass tube walls in the Dark and Nash (1970) experiments is likely to have been more complicated than the treatment used in the modeling. I suggest the authors read the paper by Deming et al., AMT, 2019, which shows that VOC adsorption to metal tubing walls is highly dependent on the composition and concentrations of VOCs in the mixture and the RH. Depending on the experimental conditions, this could possibly have resulted in complete removal of oxygenated VOCs of the type discussed here for periods on the order of an hour or more before surfaces became passivated.

Response

In our analysis, we have assumed that the alkene precursors do not significantly partition to the brass tube wall of the Druett and May experiment. In turn, we suggested that oxygenated products, and especially the peroxidic products that might be among those species exhibiting germicidal activity are indeed strongly partitioning to the brass tube. Thus, the brass tube would essentially act not only as a temporary reservoir (as in the Deming et al. study) but even as a permanent sink for these. This has been mentioned in the form of the walls ‘acting as denuder’ for these species. In this sense, the Deming et al. study is supporting our hypothesis. We will extend this discussion and cite the Deming et al. study to make this aspect clearer.

References

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Executive summary available at: https://uk-air.defra.gov.uk/assets/documents/reports/empire/porg/fourth1.html.