Comments by anonymous Referee #1

Comment 1. *The Opinion article by Cox et al. is a valuable addition to the atmospheric chemistry scientific literature. I fully support its acceptance to ACP.*

Response: We would like to thank the referee for this positive assessment.

Comment 2. *In particular, the goal of the article is to (re)introduce our community to observations and experiments conducted roughly 50 years ago on the "Open Air Factor" of the atmosphere, which refers to the germicidal properties of ambient air. The motivation for the publication of this Opinion is the ongoing pandemic. However, the article illustrates more broadly the impacts that atmospheric composition has on the viability of biological life forms that are exposed to the air. Although I have worked in the atmospheric chemistry field for roughly 35 years, I had never heard of the "Open Air Factor" and so I very much enjoyed reading the Opinion.*

Response: We fully agree, and we think it is important to remind the wider atmospheric chemistry community of this topic.

Comment 3. *Specifically, this article describes research conducted on the viability of E. coli and Micrococcus albus bacteria when exposed either to ambient air or to controlled exposures of air containing ozone and alkenes. It was known at the time of these experiments that alkene ozonolysis produces oxygenates such as Criegee intermediates, and a suggestion was made then that such species might be the molecular germicide. However, this chemistry has been explored in much more detail in the past few decades, and we now know that many oxygenates can form including peracids, multifunctional molecules containing -OH and –OOH groups, and organic peroxy radicals. The Opinion contends that highly reactive species, such as the Criegees and OH, are unlikely to be the active agents and suggests instead that these other oxygenates are more important. One potential mechanism of action, for example, is the formation of radicals from the decomposition of multifunctional oxygenates.*

I have very few suggestions and corrections to offer. The Opinion is clearly written and topical, and it will likely motivate important follow-up studies. During the pandemic we have learned how hard it has been to fund interdisciplinary research of this type, i.e. which bridges the physical and biological domains. Papers like this will be valuable to encourage funding in this direction.

Response: We fully agree and we hope our opinion article will spur further work, activities and discussions around these effects.

Comment 4. *One suggestion: Secondary ozonides do not easily form in the gas phase, except perhaps from ozonolysis of endocylic alkenes (which apparently have strong germicidal properties). Could secondary ozonides be playing a role? Even if they are not produced in large amounts in the gas phase, they are known to form readily from multiphase ozonolysis of adsorbed alkenes.*

Our simulations of the Dark and Nash (1970) experiments confirm that the gas phase formation of secondary ozonides (SOZs) is unimportant for most of the alkene systems considered. This is because removal of the stabilized Criegee intermediates (sCIs) formed is generally dominated by either thermal decomposition or reaction with H_2O and $(H_2O)_2$, thereby precluding significant formation of SOZs from their secondary reactions with the product aldehydes or ketones. The only exceptions are the 2,4,4-trimethylpent-2-ene and cyclohexene systems, which have the lowest and highest germicidal impacts of the alkene systems considered. In the former case, both thermal decomposition and reaction with H_2O and $(H_2O)_2$ are predicted to be relatively slow for one sCI (Z-pivaldehyde oxide, *Z*-$(CH_3)_3CCHOO$) (Vereecken et al., 2017), allowing its reaction with the product pivaldehyde (in particular) to compete to some extent, forming a C_{10} SOZ (about 150 ppt in the 33 ppb ozone experiment).

In the case of cyclohexene, the small yield (3 %) of the *E*- and *Z*- carbonyl-substituted sCIs is represented to react exclusively by ring-closure to form an SOZ, this being based on the extremely rapid rate coefficients calculated by Long et al. (2019). This results in about 600 ppt SOZ in the 33 ppb ozone experiment. However, it is noted that Berndt et al. (2017) reported detection of the cyclohexene-derived carbonyl-substituted sCI(s), and tentative rate coefficients for the bimolecular reactions with added SO_2, acetone and acetic acid – suggesting that rapid SOZ formation does not occur. However, either way, the trend of gas-phase SOZ formation for the series of alkenes considered cannot explain the variation of germicidal impact observed by Dark and Nash (1970).

In the condensed phase, as the reviewer has mentioned, the formation and stability of secondary ozonides is well established and characterized, e.g., for unsaturated fatty acids or their esters (Pleik et al., 2018; Zahardis and Petrucci, 2007; Zahardis et al., 2005). In contrast to the gas phase, in the condensed phase, typical fates of the sCI are 1,3-dipolar cycloaddition with the carbonyl containing product that was formed from the decomposition of the primary ozonide (Zahardis and Petrucci, 2007). The products of these reactions are SOZ or polymeric ozonides. Cycloaddition with another sCI leads to diperoxides and peroxidic polymers. In presence of protic solvents, hydroperoxides are formed (Bailey, 1958). Thus, the formation of SOZ is strongly depending on the polarity of the condensed-phase matrix. As already mentioned in the submitted manuscript, the germicidal effects of ozonized unsaturated oils were suggested to be related to the presence of SOZ (Travagli et al., 2010).

We will emphasize the difference between gas-phase and condensed-phase routes of SOZ formation better in the revised version and provide the additional information in the supporting information.

Comment 5. *One correction: Line 48. The author name for the 1934 reference on olive oil ozonolysis is missing.*

Response: Thank you for pointing this out; will be fixed.

References

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