

Atmos. Chem. Phys. Discuss., referee comment RC1  
<https://doi.org/10.5194/acp-2021-1099-RC1>, 2022  
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## Comment on acp-2021-1099

Joel Savarino (Referee)

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Referee comment on "Diagnosing the stratospheric proportion in tropospheric ozone using triple oxygen isotopes as tracers" by Hao Xu et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-1099-RC1>, 2022

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This paper follows a first publication in RCMS in 2021 that described a new methodology for ozone isotope analysis. In this new manuscript, the authors implement this technique and document the isotopic composition of ozone at two urban sites in Japan. Documenting the isotopic composition of ozone in time and space is fundamental because it is the source of the propagation during oxidation reactions of  $^{17}\text{O}$ -excess in the atmosphere. Constraining the isotopic composition of ozone allows to establish the oxidation mechanisms and to model them.

There is no doubt that the new data are of very high quality and deserve to be published. However, I have some fundamental criticisms on the interpretation of the data which unfortunately prevents the publication of the article as it is.

At no point in the article is the contradiction brought about by an interpretation involving ozone mixing from two regions of the atmosphere with radically different P and T conditions discussed. Indeed, it is well established that ozone formation and destruction are in dynamic equilibrium and that its isotopic composition is controlled by P and T conditions. Although the lifetime of ozone is a few days to a few weeks, at the molecular scale, ozone is destroyed and then reformed at the half-hour scale (i.e.  $1/J(\text{O1D})$ ). Moreover, the isotopic exchanges resulting from the equilibrium  $\text{O} + \text{O}_2 \rightleftharpoons \text{O}_3^*$  are themselves 50 times faster than the stabilization of  $\text{O}_3^*$  into  $\text{O}_3$ . Therefore, ozone is considered to be permanently in isotopic equilibrium with the environment in which it is found (Vicars 2014, Yeung 2012). As a result, stratospheric ozone entering the troposphere almost instantaneously acquires an isotopic composition corresponding to the P and T conditions of the troposphere. The interpretation of the  $\Delta^{17}\text{O}$  peak observed in spring is therefore in contradiction with what we know about ozone formation and it is never discussed.

On the other hand, since the sampling is not continuous but at the frequency of about one weekly collection per month, it is difficult to measure the natural variability of the isotopic

composition of ozone, especially in spring when the stratospheric contributions are considered as maximum, and thus to see the dynamics of this spring peak and its statistical significance between years.

The interpretation of the diurnal variability based again on air-mass mixing could have been easily tested. I have no doubt that there is a possibility in Japan to install their very simple collection device at an altitude above the boundary layer and to test the hypothesis that the free troposphere has a higher  $\Delta^{17}\text{O}$ . This hypothesis is currently based on modeling work (Lyons, 2001) that has otherwise never been confronted with observation. Here the authors have missed an occasion to improve our understanding of the ozone isotopic composition and check the hypothesis they are using. Could for instance the difference between day and night been the result of the temperature difference alone? All chemical sinks of  $\text{O}_3$  is currently considered as mass-dependent but is it true? For instance we know that the  $\text{CO}+\text{OH}$  sink is not.

There may be some processes other than P & T that influence the ozone  $\Delta^{17}\text{O}$ . There is now a body of evidence (e.g. diurnal variation, seasonal maximum, hemispheric difference) that ozone isotopic composition varies well beyond what PBL P and T range allows but the isotopic equilibrium during ozone formation cannot be ignore in the discussion.

In Vicars 2014, nitrogen isotopes of the nitrate produced by ozone is used as a quality check, and to correct ozone  $\Delta^{17}\text{O}$  variability, why in Xu et al 2021 and in this paper, nitrogen isotopes are not reported? Checking  $\Delta^{17}\text{O}$  versus  $^{15}\text{N}$  may reveals some artefacts.

A revised version where ozone formation is discussed in light of its isotopic equilibrium is definitely required before the paper can be published. Without it, it gives the false impression that interpreting  $\Delta^{17}\text{O}$  of ozone is just a question of air-mass mixing.

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