

The authors thank the two reviewers for their thoughtful comments. A reply to each comment, including changes to the manuscript, is included below with the original comment in *italic* font and the reply in normal font.

**Referee #1:**

*Page 1, lines 25-27: At this point in the abstract, it is not clear what the difference is between prompt and time-delayed conversion of ISOPPOOH to formaldehyde. I suggest adding a brief explanation.*

**Author reply:**

To address this point, the abstract text was modified to read:

“Time-delayed conversion, where previous exposure to ISOPPOOH affects measured HCHO later in flight, was conservatively estimated to be < 10% of observed HCHO and is significant only when high ISOPPOOH sampling periods immediately precede periods of low HCHO.”

*Page 2, lines 10-19: A figure to illustrate the reaction pathways that form MVK, methacrolein and formaldehyde from different ISOPPOOH isomers would be helpful to better understand this part of the paper without going back right away to some of the cited references.*

**Author reply:**

A new figure (Fig. 1) was added to show the two main ISOPPOOH and their hydrocarbon products.

*Page 4, lines 29-30 and page 5, line: Several choices that constrain the fit parameters in Equation (1) are described here, without much explanation. Probably the exact values do not matter much, as long as the data are described well by the fit function? If that is the case, I suggest adding a sentence to that extent.*

**Author reply:**

The reviewer is correct that the exact values do not matter much as long as the data are well described by the function. The resulting time constants, however, are probably close to the actual time constants of the processes controlling the time response. In this case, the system is a laboratory set-up unique to these experiments and does not have a utility beyond these experiments.

To help clarify the thought process in obtaining the correction functional form, the text was modified:

“All fits were constrained to require positive values for all fit parameters, and the data for post-experiment zero data could not be negative after subtraction of the decay fit. These constraints were imposed to prevent the fit from using one term from offsetting a non-physical value for another. The data were then fit using the selected three time constants (100 s, 800 s, 2000 s) to obtain the best pre-exponential terms to describe all of the experiments. The final fit was conducted with the ratio of the first three pre-exponential terms fixed relative to each other:  $A_1 = A_2$  and  $A_3 = 0.25 \times A_1$ . Two variables were optimized:  $A_1$ , and  $c$ . The goal of the preceding steps was to obtain a three term exponential function that would reasonably describe the data from multiple experiments by fitting a single scaling factor (representing [ISOPPOOH] at  $t=0$ ) and a constant (representing a background).”

*Figure 2, top panel: The graph might be clearer if the different conditions that gave rise to these steps in formaldehyde were added. The same applies to Figs. S2-S4.*

**Author reply:**

The steps in HCHO shown in Figure 3 (previously Fig. 2) are due to changes in ISOPPOOH mixing ratio. To clarify this, the figure caption now reads:

“Figure 3: (Top Panel) Time series of dry air conversion experiment E10 with (1,2)-ISOPPOOH at three ISOPPOOH mixing ratios. (Bottom Panel) Linear fits to experiments E1 and E10 individually (red lines) and together (black line).”

For Figs S2-S4, the HCHO time series is accompanied by an ISOPPOOH time series, so the relationship is more readily deduced. The reviewer might have been referring to the shorter-term changes in ISOPPOOH and HCHO apparent in S2 and S4 (Fig. S4 at  $t=18.2$  hrs and Fig. S2 at  $t=22.2$  hrs). These changes are due to instruments not used in this paper starting or stopping their sampling from the chamber sample line. When the total instrument sample flow changes, the flow balance between the dilution flow and the chamber flow changes, affecting the ISOPPOOH mixing ratio in the sample line. The change in ISOPPOOH mixing ratio is also reflected in the HCHO mixing ratio, and effectively provides an additional ISOPPOOH set point.

*Section 3.4: These experiments leave the reader with some questions. Figure 3 shows low conversion fractions for the standard inlet at temperatures between 20-60 C, and higher conversion fractions on a bare stainless inlet at temperatures between 80-160 C. The temperature obviously plays a role in the conversion, but to what extent does inlet material matter? It seems that all the data can be well explained by a single curve that is relatively insensitive to temperature until 60 C and then starts to rise with temperature. If that is the case, then inlet material does not appear to matter. It is an important question, as it tells experimentalists how to minimize the unwanted conversion of ISOPPOOH in their instruments. It seems that a few experiments with a bare stainless inlet at lower temperature would have been helpful.*

**Author reply:**

The reviewer makes a good point. The temperature range explored with the ISAF inlet only covered the range relevant to the operation of the instrument, primarily because ISAF field operation is the focus of the paper, but also due to experimental constraints. The bare stainless tubing experiments were added to provide some guidance on inlet design considerations and weren't intended to be a complete investigation. The guidance definitely would have benefitted from more temperatures. The general point is still robust: investigators designing new instruments will be best served by minimizing uncoated metal surfaces at elevated temperatures in their sample lines.

*Figures 4 and 5, top panel: The color for the formaldehyde from ISOPPOH conversion data is not easy to see.*

**Author reply:**

The color schemes of Figures 4 and 5 have been updated to improve clarity.

*Page 8, lines 24-26: Is this sentence really supported by the results of this study? Again, some measurements on different inlet materials at the same temperature would have been helpful.*

**Author reply:**

We believe it is supported by the study results, even with the parameter space of possible inlet temperatures and materials not fully explored. To address the reviewer's concern, we modified the sentence to read:

“These experiments suggest that instruments with any amount of metal surface uncoated with a fluoropolymer, particularly if the surface is heated, are likely susceptible to conversion of organic peroxides such as ISOPPOH.”

We agree that there would be a benefit to the community from a technical paper that thoroughly explores organic peroxide transmission through a number of tubing materials with different coatings, separate from this paper with its focus on the ISAF instrument.

**Referee #2:**

*Page 4, lines 19 – 20 and figure S1: A possible ISOPPOH to HCHO conversion up-stream of the instrument is inferred and corrected for. Figure S1: Shows an example of such a possible ISOPPOH to HCHO conversion and the respective corrected time series. The difference of the pre-corrected and post-corrected values of ISOPPOH and HCHO*

*should reflect the conversion factor of ISOPPOOH to HCHO. At t=0 the initial difference of ISOPPOOH is approximately (10 – 8) ppb = 2 ppb (Figure S1 states pptv!!!) whereas the respective HCHO difference is (2.2 – 0.8) ppb = 1.5 ppb. How can this conversion factor (1.5 ppb/2 ppb) 0.75 be explained? Is this conversion factor dependent on the residence time within the sampling tube?*

**Author reply:**

The similarity of both the magnitude and the time constant of the change in ISOPPOOH and HCHO is what suggested to us that they are the same phenomenon. While the cause of this apparent conversion is not clear, the fact that it appears in both the ISOPPOOH and HCHO data implies that it occurs upstream of all the instruments and therefore not relevant to conversion within the ISAF instrument.

*Page 5, line 30 and table 2: Uncertainties are provided for the conversion fraction. Please explain what this estimate is based on (Error of the fit parameter?).*

**Author reply:**

The error of the fit parameter was actually an order of magnitude+ smaller than the uncertainty provided in Table 2. The Table 2 uncertainty was intended as a conservative estimate that would encompass the potential error in the pre-instrument decay correction and background subtraction, as well as the fit error. We have formalized the uncertainty approach to make it easier to describe in the paper, updated the values in Table 2, and have added a note at Table 2 referring to the following text now in the supplementary material:

“The uncertainty was conservatively estimated using data without applying the pre-instrument conversion correction. The ratio of the HCHO data / ISOPPOOH data, both background-subtracted, was plotted for each experiment. The highest value of the ratio, taken as a mean for each data section selected for the conversion fits (red dots in Fig. 3), was determined for each experiment and was averaged if there were two of that experiment type. For the dry experiments, the uncertainty in Table 2 was set to the difference between the highest value and the fit value. For the humid experiments, the uncertainty was taken as twice the difference.”

*Page 6, paragraph 3.4 and figure 3: More data is required for the conversion fraction with stainless steel at temperatures below 80 C to determine the applicability of stainless steel tubing for HCHO sampling under high ISOPPOOH concentrations.*

**Author reply:**

Referee #1 made a similar point, and our response is above.

*Page 7, last paragraph and figure 5: A long term HCHO from ISOPPOOH conversion has been estimated for sampling conditions as observed during a flight campaign. The data used for that model has been measured during ascents and descents of the*

*airplane over several kilometers altitude. Which influence on the long term ISOPOOH to HCHO conversion is expected from the respective pressure change in the sampling line?*

**Author reply:**

The effect of inlet pressure is an interesting question, and not one that was investigated in these experiments. The long-term/delayed conversion of ISOPOOH to HCHO may only be a consequence of the very high ISOPOOH used in these lab experiments. If it is relevant to the instrument performance in the real atmosphere, a number of factors compete to determine how ambient pressure affects the instrument recovery time: location of the conversion surfaces, inlet mass flow, and sample line pressure. If the inlet is configured to provide a high flow bypass that the instrument subsamples, the mass flow through the inlet will decrease at lower pressure and less efficiently clear the surfaces. Mass flow through the instrument is constant. In ISAF, the likely surface conversion location is the pressure controller, which is separate from the high flow bypass line. Lower sample line pressure, mass flow aside, would presumably clear ISOPOOH/HCHO out faster and shorten the instrument recovery time.

*Supplement page 1, figure S1, bottom panel; the title of the y-axis states ISOPOOH (pptv); Change to ppbv.*

**Author reply:**

We thank the reviewer for pointing out this error. It has been corrected.