Response to Reviewer 1

General comments

Organophosphate esters (OPEs) are emerging contaminants that have attracted significant attention due to their negative impact on the environment and human health. While there are numerous reports of the occurrence of OPEs in the atmospheric environment, studies on the gas-particle partitioning and precipitation scavenging of OPEs are rare. In particular, no previous studies have investigated OPEs in different environmental media (atmospheric gas and particle phases, precipitation, and surface water) simultaneously. Based on the comprehensive filed measurements of OPEs in Southern Canada, this study provides new insights into the seasonal variability, gas-particle partitioning behavior, precipitation scavenging, and air-water equilibrium status of OPEs. Such information would be valuable to understand the atmospheric fate of OPEs. Therefore, I recommend publication of this manuscript after minor revisions, as outlined below.

We appreciate the reviewer's endorsement of our work.

Specific comments

1. Line 326, unlike TCEPi and TPHPi (which are produced in large quantity), the usage and production of TCPPi have not been reported. As a result, the formation of TCPP from TCPPi seems unlikely.

The reviewer is correct that the usage and production of TCPPi have not been reported. We also mentioned this in lines 330 and 331. Nevertheless, the absence of reports does not neccesarily mean that this chemical has not been produced or used. As such production and use at least is possible, we suggested this possibility. More information is needed regarding the possible formation of TCPP from TCPPi.

2. It is known that OPAs can transform to OPEs through atmospheric reactions. However, it is difficult to evaluate the contribution of OPA transformation chemistry to the measured OPEs in air due to the complex atmospheric processes. The ΔH_{AS}-app analysis in Section 4.1 may provide a potential tool to examine this issue. The authors may want to discuss this point in the manuscript.

Thanks for this suggestion. While we agree that the measured $\Delta H_{\text{AS-app}}$ may potentially contain information on the contribution of the transformation of OPAs to the presence of OPEs, it likely would be beset by large uncertainties. The value of $\Delta H_{\text{AS-app}}$ can be influenced by atmospheric advection and by several processes that vary with temperature, such as the OPE source strength to the atmosphere, the exchange between air and surface, and the transformation of OPA to OPEs. If the influence of temperature on OPE source strength is trivial and the value of $\Delta H_{AS\text{-}ap}$ is higher than ΔH_{AW} and ΔH_{AO}, the difference between $\Delta H_{\text{AS-app}}$ and ΔH_{AW} or ΔH_{AO} may contain information on the contribution of the transformation of OPA. However, this can at most be considered semi-quantitative and will incur high uncertainties. We will add the following sentence to section 4.1:

"The value of the measured $\Delta H_{\text{AS-app}}$ may potentially contain information on the contribution of the transformation of OPAs to OPEs in the atmosphere, i.e., the extent to which $\Delta H_{\text{AS-app}}$ exceeds ΔH_{AW} and ΔH_{AO} may indicate the extent of such transformation. However, this would be beset by high uncertainties considering the complex set of factors influencing the $\Delta H_{\text{AS-app}}$"

3. Line 359, It is surprising that the particle-phase fractions of TCPP and EHDPP in Toronto are 56-68% given their low-volatility nature. How about the measurement results in other urban areas?

In our study, Toronto was the only urban area in which we had an active air sampler deployed. The other two active air sampling locations were deployed in remote areas. Wang et al. (2020b) reported particle-bound fractions for TCPP and EHDPP of 40% and 89%, respectively, when conducting active air sampling in an urban area in Dalian, China.

We had referred to the modelling study by Zhao et al. (2021a) to explain why the particle sorption of EHDPP may be lower than expected: "the unexpectedly low fraction observed in the particle phase may suggest that TPhP and EHDPP are emitted at higher temperatures and are not in a state of equilibrium between gas and particle phase (Zhao et al., 2021a)". We now will add another potential explanation: "Alternatively, the fraction of TPhP and EHDPP in the gas phase may have been overestimated if very fine and ultrafine particles containing these OPEs passed through the glass fiber filters (Zhao et al., 2021b)."

4. Line 370, Please provide some details regarding the impact of particle composition, relative humidity, and degradation on the gas-particle partitioning of OPEs, so that readers can better understand the OPEs' behavior.

We thanks the reviewer for the suggestion. However, we do not have empirical data on particle composition, relative humidity and possible degradation reactions to aid in the interpretation of our measurement. We had referenced the work by Li et al. (2017b) and Wu et al. (2020) to indicate that other factors may play a role in the gas-particle partitioning of OPEs. We think it would be too speculative to try to explain our observations based on these factors without empirical data. We will rephrase and expand the sentence as follows: " **While it has been suggested that** the composition of the particles (Li et al., 2017b), relative humidity (Li et al., 2017b; Wu et al., 2020), and degradation of OPEs in gas and particle phases may also influence the gas-particle partitioning of OPEs, **we do not have the empirical data to explore the influence of these factors on our measurements**."

Technical comments

Some typos: Line 201, "We are no comparing…"; Line 407, "regardless of".

We will correct these typos in the manuscript. "no" will be replaced with "not", and "regardless" will be replaced with "regardless of".

All references cited in this response can be found in the submitted preprint of the manuscript.