Response to Review Comments by Anonymous Referee #2 on "Measurement report: Characterization and source apportionment of coarse particulate matter in Hong Kong: Insights into the constituents of unidentified mass and source origins in a coastal city in southern China" by Yee Ka Wong et al.

General Comments by Anonymous Referee #2:

This study performed chemical speciation for $PM_{2.5}$ and PM_{10} samples collected in Hong Kong during 2020/01-2021/02. The results showed that the annual average concentration of PM_{coarse} (PM_{10}-$PM_{2.5}$ mass) accounted for ~50% of PM_{10}. Unlike $PM_{2.5}$, only ~75% of PM_{coarse} mass was explained by identified chemical components. The authors supposed that the unidentified part was dominated by geological components and aerosol liquid water. Moreover, several tools were utilized to apportion PM_{coarse} to specific sources and areas, particularly for the unidentified fraction. In general, this manuscript is well organized and written. But two major issues should be addressed before the consideration for publication.

Response to General Comments:

We thank the reviewer for the comments and appreciating our work. Our response to the comments is given in the following. The response text is marked in blue. References cited in this response document are placed at the end.

1. In this work, the thermodynamic equilibrium model (ISORROPIA II) was adopted to estimate aerosol liquid water (ALW) in PM_{coarse}. After mass closure and PMF analysis, the authors concluded that the unidentified PM_{coarse} (4.1 µg m^{-3}, ~25%) was substantially contributed by ALW (1.2 µg m^{-3}).

   Have the authors performed mass closure for $PM_{2.5}$ or PM_{fine}? Because the fine particles are more enriched with water soluble components (e.g., secondary inorganic ions), ALW should contribute more fractions to $PM_{2.5}$. According to section 3.1.1 (lines 158-160), it seems that $PM_{2.5}$ is mainly composed of NH_4^+, NO_3^-, SO_4^{2-}, OC, and EC (~80%).

   If ALW contributes a significant fraction of PM_{coarse} based on filter sampling, there's no reason that it contributes less to PM_{fine}.

   In fact, ALW is not stable on filters, and is subject to loss during long-term sampling and transportation.

   So, the contribution of ALW to unidentified PM_{coarse} might not be estimated appropriately with the current study design.

   Response: The reviewer might misunderstand the nature of LWC in the discussion, confusing LWC as existing under ambient condition vs. residue LWC held tightly onto particles under the dry weighing conditions, as stated in Line 331–333 of the updated manuscript file:

   "The thermodynamic equilibrium model ISORROPIA II (http://nenes.eas.gatech.edu/ISORROPIA) is applied to estimate the aerosol LWC under the RH and temperature conditions of gravimetric measurement in the balance laboratory (i.e., temperature = 22 °C, RH = 35 %) (Fountoukis and Nenes, 2007)."

   Still, we applied the ISORROPIA model with the same setting to the $PM_{2.5}$ composition data to estimate residue LWC bound to $PM_{2.5}$ under the dry weighing conditions (Fountoukis and Nenes, 2007). The amount of LWC was calculated to be negligible (average = 0.01 µg m^{-3}), suggesting the inorganic ions in $PM_{2.5}$ do not retain LWC as effective as sea salt in PM_{coarse} under the dry weighing conditions.

   The lower residue LWC in $PM_{2.5}$ is supported by the better mass closure in $PM_{2.5}$ compared with PM_{coarse}. The average reconstructed-to-measured mass ratio for $PM_{2.5}$ is 0.90±0.08, better than the ratio of 0.72±0.10 for PM_{coarse}. The results align with the theoretical residue LWC in $PM_{2.5}$ being lower than that in PM_{coarse}.

2. When input PM_{coarse} mass for PMF analysis, it was presumed that the unidentified PM_{coarse} fraction have the same sources as identified components.

   In this work, four factors linked with soil dust, copper-rich dust, fresh sea salt, and aged sea salt were identified using measured species data. Since understanding the sources and formation pathways of PM largely depends on how well they are identified, the sources of un-speciated coarse PM are unknown and might not be the same as measured species. If the unknown fraction of coarse PM was apportioned to the four identified factors, some factors contributions would be over-estimated. Because PMF may over-attributed PM_{coarse} to certain factors as it fits measured species (Shrivastava et al., 2007). This will occur if makers for unknown PM_{coarse} are not included in the PMF model (Shrivastava et al., 2007).

   Therefore, the source apportionment method for unidentified PM_{coarse} mass is not appropriate. The authors should focus on sources of identified PM_{coarse} components.

   Response: We thank the reviewer for sharing his/her critique on this, which we agree in some sense. But here we would like to raise an opinion that the issue of over-attributing a species in PMF modeling arises when the model is set to fit the species explicitly, and this typically applies to source marker species, and in some occasions to the bulk species being apportioned, such as OC in the study of Shrivastava et al. (2007). However, we took a different approach to apportion PM_{coarse} in our PMF modeling. Specifically, the PM_{coarse} concentration was set to be a total variable with the concentration uncertainties tripled to decrease their weight in the model fit. This would allow the PM_{coarse} to be apportioned based on its temporal covariance with other input species, in other words, not being forced to fit to the apportioned factors, avoiding the issue of over-attribution.

   To examine whether the PM_{coarse} was apportioned in this specified way, the PMF solutions with and without considering PM_{coarse} were compared, as documented in Sect. 3.3 of the revised manuscript. The two solutions are identical in multiple aspects including the chemical composition of the factor profiles resolved and the modeling performance of all individual species. The test demonstrated that the PM_{coarse} was apportioned purely based on its covariance with other species without affecting the apportioning of other species. It is because if a source significant enough to affect the PM_{coarse} variation is missing, and the model attempted to fit the PM_{coarse}, some of the included species would be compromised. The absence of influence by PM_{coarse} and the excellent agreement between the apportioned and measured masses ($R^2 = 0.98$; slope = 1.04) are two important signs to indicate the temporal variation of PM_{coarse} in its entirety, including the unidentified fraction, can be well captured by the resolved sources.

References

Fountoukis, C. and Nenes, A.: ISORROPIA II: A computationally efficient thermodynamic equilibrium model for $K^+–Ca^{2+}–Mg^{2+}–NH_4^+–Na^+–SO_4^{2-}–NO_3^-–Cl^-–H_2O$ aerosols, Atmos. Chem. Phys., 7, 4639–4659, https://doi.org/10.5194/acp-7-4639-2007, 2007.

Shrivastava, M. K., Subramanian, R., Rogge, W. F., and Robinson, A. L.: Sources of organic aerosol: Positive matrix factorization of molecular marker data and comparison of results from different source apportionment models, Atmos. Environ., 41, 9353–9369, https:// doi.org/10.1016/j.atmosenv.2007.09.016, 2007.