Reply to Reviewer 1

This study conducted laboratory research on the nucleation mechanisms during the cooling process of motor vehicle exhaust, constructed mechanistic models, and empirically applied them in a chemical transport model. Although the authors have undertaken substantial work, the logical connections among the three parts of the manuscript remain somewhat unclear. Significant revisions are required before reconsideration for publication.

Reply:

Thank you for the constructive comments, which have helped us to improve the manuscript. We agree that the logical connections among the three components of the manuscript can be made more explicit. Accordingly, we have reframed the study as a hierarchical, scale-bridging framework that progresses systematically from controlled laboratory observations to mechanistic insights, and ultimately to atmospheric-scale implications. To improve clarity and highlight this integration, we have revised the final paragraph of Section 1 as follows:

"The study is structured as a hierarchical, scale-bridging framework that progresses from controlled laboratory evidence to mechanistic understanding and, ultimately, to atmospheric-scale implications. The engine-exhaust experiments in Section 2 establish the empirical foundation by demonstrating the critical role of ambient aerosols in new particle formation under realistic combustion conditions. These findings motivate the idealized air-parcel simulations in Section 3, which translate the experimental conditions into a mechanistic framework that explicitly resolves particle evaporation during heating and nucleation during subsequent cooling. The parcel model explains the observed relationship between ambient aerosol loading and the resulting particle number concentration, and further examines the effects of incomplete particle evaporation. Insights gained from both the experiments and parcel simulations are then synthesized into a RIN parameterization implemented in the CMAQ regional air-quality model in Section 4. This final step assesses the atmospheric relevance of RIN by evaluating whether a mechanism identified at the laboratory scale can account for the long-standing underestimation of particle number concentrations in urban simulations without substantially altering $PM_{2.5}$ mass."

Major comments:

(1) In the introduction, the review of research progress on RIN is insufficient. It only briefly outlines various reasons that may lead to underestimation in particle size

spectrum simulations, without introducing the mechanistic research advancements specifically related to RIN, which is the focus of this study.

Reply:

Thank you for pointing this out. We agree that the original introduction did not sufficiently highlight prior mechanistic research related specifically to the RIN mechanism. In fact, progress on this topic has been relatively limited to date, which is a key motivation for the present study. Nevertheless, we have revised the introduction to more explicitly summarize the existing literature that has discussed RIN-related processes. Specifically, we now note that the RIN mechanism has been suggested to contribute to contrail formation from cryoplanes that do not emit combustion aerosols due to the use of liquid hydrogen (Ström and Gierens, 2002; Gierens et al., 2008; Lee et al., 2010), and that it has also been invoked to explain anomalous increases in particle number during dilution tunnel experiments (Lombaert et al., 2006). The relative scarcity of research beyond these specific cases highlights a significant gap in our mechanistic understanding of RIN and its broader air-quality impacts—a gap that the integrated experimental and modeling approach of this study is specifically designed to fill.

(2) In section2, Is the use of SMPS alone sufficient to characterize the number concentration of nucleation-mode particles? Nucleated particles often exist in large quantities below 3 nm, while the detection limit of SMPS starts at approximately 11 nm. This likely leads to an underestimation of particle counts at 11 nm and below.

Reply:

The reviewer raises a valid point regarding the detection limit. While the critical size of nucleation is indeed in the sub-3 nm range, several factors suggest that the SMPS (starting at 11 nm) captured the significant portion of the nucleation mode in this study. First, our measured PSDs consistently show a sharp decrease in number concentration as they approach the 11 nm lower limit. If a substantial population of smaller particles existed, we would expect to see an increasing trend toward the lower detection threshold. Second, the approximately 20-second residence time in the sampling tubing allows for significant particle growth via condensation and coagulation before the exhaust reaches the SMPS. This duration is sufficient for the majority of nucleated particles to grow beyond 11 nm. We have added a discussion of these sampling considerations and their impact on the captured PSDs to the end of Section 2.2.

(3) In section3, the experiments in section2 were conducted using gasoline engines to quantify the nucleation process during exhaust cooling. Is this mechanism

applicable to diesel vehicles? At the very least, this should be discussed. In real-world emissions, non-road mobile machinery, diesel vehicles, and even ships often use fuels with higher sulfur content. If the sulfuric acid-water binary nucleation mechanism can explain particle nucleation during cooling, these sources with higher fuel sulfur content might be more representative than gasoline vehicles. And what about the volatile organic.

Reply:

In principle, the RIN mechanism is applicable to all combustion processes that ingest ambient air containing pre-existing aerosols. However, the relative importance of RIN depends on the presence and strength of other nucleation pathways associated with fuel-derived combustion products. For on-road diesel vehicles, fuel sulfur content is generally comparable to that of gasoline in most developed regions, as both fuel types are regulated under ultra-low sulfur fuel standards (e.g., ≤10 ppm by mass in the European Union and Taiwan). Under such conditions, fuel-sulfur-driven nucleation in diesel engines is expected to be similar in magnitude to that in gasoline engines, suggesting that the RIN mechanism should operate in a broadly comparable manner for both vehicle types. In contrast, fuels used in marine shipping and some aviation applications may contain sulfur at levels of several thousand ppm, which can lead to strong sulfuric-acid-driven nucleation during exhaust cooling. In such cases, fuel-derived sulfate production may be comparable to or exceed that associated with RIN, and both sources would need to be considered jointly when estimating new particle formation. These combustion sources, however, are not the focus of the present study, which is centered on urban environments dominated by on-road traffic. We have added relevant discussion of these issues in Section 5.4 of the revised manuscript.

(4) Does the current mechanistic model lack consideration of the role of volatile organic compounds and semi-volatile organic compounds in nucleation during the condensation process? What impact would this have on the established mechanistic module and application of air quality model?

Reply:

Nucleation involving volatile organic compounds (VOCs) is another possible pathway. Although sulfuric acid has long been regarded as the primary driver of nucleation, recent studies show that highly oxygenated organic molecules can act as important contributors or even dominant agents in some environments. Nevertheless, our purified-air experiments indicate that particle production from fuel-only combustion—including VOC emissions from gasoline combustion—is much weaker than that associated with the RIN mechanism under our experimental conditions. We

note, however, that this conclusion is based on gasoline-engine experiments only. The potential significance of VOC-induced nucleation in diesel engines or other combustion sources remains uncertain and warrants further investigation.
We have added relevant discussion of these issues in Sections 5.4 of the revised manuscript.

(5) The validation of the numerical simulation is limited. Firstly, the validation of meteorological simulation is missing, making it difficult to confirm whether the underestimation of simulated concentrations is due to biases in the meteorological simulation.

Reply:

We appreciate this comment. To address the concern regarding meteorological validation, we have added new material to the Supplementary Information (Figs. S2 and S3), which compare simulated and observed synoptic-scale weather patterns as well as time series of key local meteorological variables. These comparisons indicate that the meteorological simulations exhibit some biases; however, their magnitudes are comparable to those typically reported in routine weather forecasts by our meteorological agency.
We note that one of the most influential meteorological factors for air-quality simulations in the study region is the planetary boundary layer height (PBLH), which strongly controls pollutant dilution and near-surface concentrations. Unfortunately, direct observational data for PBLH were not available during the study period, preventing a quantitative evaluation of this variable.

(6) Validation for gaseous precursors of PM2.5 such as SO2, NO2 and O3 is absent. Additionally, validation for related components is lacking, making it challenging to quantify the bias in simulated PM2.5 mass. This should be supplemented.

Reply:

Thank you for the suggestion to include validation of gaseous precursors and $PM_{2.5}$. In response, we have added comparisons between simulated and observed SO_2, NO_2, O_3, and $PM_{2.5}$ concentrations in the revised Supplementary Information (Fig. S4), along with brief discussions of the associated biases as follows:
Overall, simulated SO_2 and NO_2 concentrations are lower than those observed at the Xitun station. In addition to uncertainties in the meteorological fields, a likely contributing factor is the treatment of emissions in CMAQ, which spatially distributes point and line sources over the 2 × 2 km grid, thereby smoothing sharp near-road concentration gradients. This effect is particularly pronounced at Xitun, which is located in a dense urban setting adjacent to major roads and highway interchanges.

In contrast, biases in simulated SO_2 and NO_2 are smaller at the Fengyuan station, which lies in a transitional zone between the urban core of Taichung and the more rural northeastern region and is therefore less directly influenced by intense traffic emissions.
Simulated O_3 concentrations show better overall agreement with observations, but exhibit notable nighttime overestimation, especially at Xitun. This bias is likely related to insufficient NO titration when NO emissions are instantaneously diluted over a model grid cell. Unfortunately, routine observations of $PM_{2.5}$ chemical composition were not available during the study period, preventing a more detailed evaluation of individual $PM_{2.5}$ components.

(7) It is recommended to supplement the time-series simulation of particle number concentration and particle size distribution. Presenting only statistical average results lacks persuasiveness.
Reply: Thank you for the suggestion. To strengthen the evaluation, we have added time-series simulations of particle number concentration and particle size distribution for the whole simulation period, which provide a more detailed comparison beyond the statistical averages presented in the main text. Because the time series exhibit substantial day-to-day and diurnal variability, the resulting patterns are highly fluctuating and not easily summarized concisely in the main text. We therefore present these results in the Supplementary Information (Figs. S5 and S6).

Specific editorial issues:

- Line 276: "can be" is repeated.
Reply:
The duplicate phrase has been removed.

- Line 310: The abbreviation PNC and its full form appears redundantly; similar issues occur with PSD and RIN.
Reply:
We thank the reviewer and have standardized the use of acronyms throughout the manuscript to eliminate redundancy.