RC1: 'Comment on egusphere-2025-4664', Anonymous Referee #1, 30 Oct 2025

This manuscript by Chen et al. modified the chemical mechanism of the CMAQ model to incorporate 54 VOC species included in PAMS. Furthermore, the anthropogenic VOC emissions in the emission inventory were adjusted under the constraint of PAMS observation data from Taiwan, resulting in modeled VOC concentration results that are close to the observed levels. This study conducts model evaluation for individual PAMS VOC species.

Main comments:

1. The authors appear to frame the inclusion of PAMS species as a key feature of this study. Based on current research in this field, lumped mechanisms are widely recognized as a reliable method for improving model operational efficiency—specifically by grouping species with similar photochemical reaction behaviors. Different gas-phase chemical mechanisms may treat certain species (deemed important) as individual components, whether in the context of emissions or chemical reaction mechanisms. More notably, the explicit Master Chemical Mechanism (MCM) includes no fewer than 6,000 explicit species. Therefore, the novelty of developing the CMAQ-PAMS modeling system needs to be discussed in Introduction and Discussion section.

Reply: We thank the reviewer for this insightful comment. We agree that lumped checmical mechanisms have long been the standard approach for regional and operational air quality modeling due to their computational efficiency and their abaility to represent the aggregate reactivity of VOC groups. However, despite their widespread use, lumped VOC species cannot be directly compared with observational VOC datasets (e.g., NMHC or PAMS measurements), because only a limited subset of modeled surrogates corresponds to measureabe compounds. As a result, validation of VOC simulations has remained an unresolved issue: most previou stidies evaluate model performance for O_3 or NO_x prior to conducting sensitvity or scenario analyses, yet rarely validate VOC simulations due to this incompatibility. This gap maks it difficult to assess whether simulated VOC composition and reactivity are reasonable, even though these precursors critically determine O_3 formation behavior.

Although the explicit mechanisms such as the Master Chemical Mechanism (MCM) can represent thousands of VOC species, their computational cost make them impractical for 3-D regional simulations, especially for regulatory or episodic modeling. Conversely, traditional lumped mechanisms (e.g., CB6, SAPRC, RADM2, etc.) provide only a limited number of explicit VOC species-such as isoprene or

several small carbonyl compounds-that can be compared with observations. However, the vast majority of VOCs are represented as lumped surrogates, preventing species-resolved evaluation against comprehensive PAMS measurements.

The novelty of CMAQ-PAMS lies in bridging this long-standing gas between lumped-mechanism modeling and species-resolved VOC observations. In this study, we introduce 54 PAMS-targeted VOC species into a regional CTM without resorting to a fully explicit mechanism, thereby maintaining the computational efficiency and chemical structure of the CB6 framework. At the same time, the model incorporates species-specific emission mapping and output configurations that allow direct comparison with PAMS measurements. This development establishes a new evaluation framework in which modeled and observed VOCs can be compared at the individual-species level—an outcome that has not been achieve using lumped mechanisms alone. As a result, CMAQ-PAMS substantially improves diagnostic capability for source attribution, emission speciation assessment, and photochemical regime classification (e.g., VOC-limited vs. NO_x-limited conditions), now grounded in PAMS-resolved VOC reactivity rather than aggregated surrogates.

These perspectives are now explicitly discussed in the manuscript (Introduction: lines 43-49, 87-109; Results and Discussion: lines 305-310, 386-393, 436-440, and 551-557). The CMAQ-PAMS does not aim to replace established lumped mechanisms not to emulate a fully explicit mechanism like MCM. Rather, its contribution is an intermediate and operationally feasible system that provides species-resolved VOC simulation specifically aligned with regulatory PAMS observations, improving both model evaluation and chemical diagnosis for regions where speciated VOC data are available.

2. Although Figure 1 is provided to introduce the CMAQ-PAMS modeling system, it only shows where modifications were made to the model. The process of inventory adjustment and model modification are needed. For instance, how to generate emissions of PAMS species into the CB mechanism via SPECIATE. Mabe it is necessary to include at least one table in the appendices that presents the proportion of each PAMS species within lumped species, preferably disaggregated by emission source.

Reply: We appreciate the reviewer's constructive suggestion. In addition to revising Figure 1 to explicitly indicate where CMAQ-PAMS modifies both the emissions processing and the gas-phase chemical mechanism, we have expanded the model Section 2.1.3 to include a detailed explanation of the inventory-adjustment procedure (in lines 161-165). The revised text now describes how anthropogenic VOC emissions were disaggregated into 54 PAMS species using source-specific

SPECIATE profiles and how these PAMS species were subsequently integrated into their CB6 lumped VOC groups for chemical processing (in lines 130-135).

To further enhance transparency, we have added a new table to the Supplementary Information (Table S3), which presents the proportional contribution of each PAMS species within its respective CB6 lumped group, based on domain-wide anthropogenic emissions. This table documents the final speciation structure used by the CMAQ-PAMS emission processor and provides a clear quantitative link between the SPECIATE-based disaggregation and the implementation of the CB6 mechanism. We believe these additions fully address the reviewer's request for clarification regarding the inventory adjustment process and the model modifications supporting CMAQ-PAMS.

3. There is no doubt that using VOC observation data to constrain emissions is an effective method for improving VOC simulation performance. However, details are needed for the approach used to adjust emissions:

- The manuscript states that VOC observations from 12 sites were used to modify emissions based on the ratio of simulated to observed values. Were the remaining grid points calculated via linear interpolation (Lines 314–316)?
- Was this adjustment applied to the total emissions for the study period or conducted hourly?
- When referring to "the total VOC amount is conserved," does this mean the total VOC emissions in the inventory remained unchanged (and if so, were the proportions of other VOC species reduced?)? Or does it mean emissions of PAMS-corresponding VOCs remained unchanged?
- It is essential to include the calculation formula for this emission adjustment process to clarify these ambiguities.

Reply: We thank the reviewer for pointing this out. The previous wording has been corrected because the total VOC mass is "not" conserved in our adjustment procedure. Consistent with Chen et al. (2014), the PAMS-species emissions were scaled according to the simulated-to-observed ratios, and the resulting increase or decrease in PAMS emissions was directly incorporated into the inventory, thereby modifying the total VOC amount. No compensatory reduction was applied to non-PAMS species. Asa result, the adjusted emissions alter the total VOC mass, rather than redistributing it among existing species. This clarification has been added to the revised manuscript in a new Section 2.1.4.

4. Lines 90–91: Adjustments to PAMS emissions would likely have a significant impact on O_3 formation—insights that could help us better understand the role of VOC emissions in pollutant simulation. What are the results of O3?

Reply: We thank the reviewer for raising this insightful comment. In this study, the adjustment of PAMS emissions serves as a necessary preprocessing step to obtain a chemically consistent VOC inventory that can be directly compared with PAMS observations. Because the revised VOC emissions are used as the baseline configuration for all subsequent simulation, the O_3 results presented in Section 3.5 already reflect the influence of the PAMS-adjusted emissions.

Accordingly, the manuscript does not include a separate comparison of O_3 concentrations before and after the emission adjustment. Instead, all O_3 analyses in the Results and Discussion section correspond to simulations that incorporate the updated PAMS emission speciation. This clarification has been added to the revised manuscript (Lines 394-396).

Minor comments:

1. There are multiple instances of inconsistent subscript formatting for O_3 and NO_x throughout the manuscript, such as in Line 9, Line 29, Line 35, and Line 37. Please standardize subscript formats; as inconsistencies may be interpreted as evidence of AI-generated content.

Reply: Thank you for pointing out the inconsistent subscript formatting in the chemical species (e.g., O_3 and NO_x). We have carefully reviewed the entire manuscript and standardized all chemical formulas to use proper subscript formatting. The inconsistencies now in Lines 10, 30, 32, and 43—as well as elsewhere in the text—have now been corrected. We appreciate this comment, as consistent notation improves readability and avoids any confusion regarding formatting quality.

2. Lines 34–39: This section summarizes the research status of VOCs in air quality models, but every sentence lacks supporting literature citations.

Reply: Thank you for this valuable comment. We agree that the discussion on VOC representation in air quality models should be supported with appropriate literature. In the revised manuscript, we have added citations to foundational and recent studies that describe (1) the chemical diversity of VOCs, (2) challenges in emission estimation and model evaluation, and (3) the use of lumped chemical

mechanisms in regional CTMs. These citations help strengthen the context and grounding of our statements regarding current research status.

3. There are numerous issues with the reference citation format in the manuscript. For example: Line 50: Cardelino and Chameides (Cardelino and Chameides, 1990)→Cardelino and Chameides (1990); Line 87: (Knote et al.) → (Knote et al., 2015). Please standardize all reference citations to comply with the journal's formatting requirements.

Reply: Thank you for this helpful comment. We have thoroughly reviewed all in-text citations throughout the manuscript and corrected inconsistencies to ensure full compliance with the journal's reference formatting requirements. Specifically, issues such as duplicated author names (e.g., "Cardelino and Chameides (Cardelino and Chameides, 1990)") and misleading of citation (e.g., "(Knote et al.)") have been corrected to the appropriate forms (e.g., "Cardelino and Chameides (1990)" and "hydroxyl (OH)"). We also conducted a comprehensive check to ensure that all citations follow a consistent and standardized format.

4. Sections 2–4 can be merged into a single chapter titled "Materials and Methods".

Reply: Thank you for the suggestion. We agree that merging Sections 2–4 into a single chapter titled "Materials and Methods" improves clarity and aligns with common journal structures. In the revised manuscript, we have combined these sections accordingly and reorganized the subsections to ensure a logical flow and avoid redundancy. This restructuring enhances readability and better reflects the methodological framework of the study.

5. Lines 142–144: For the 2021 simulation, the 2010 emission inventory used in the manuscript appears outdated. Although the simulation performance of NO_x and O_3 shown in Figure S3 seems acceptable, statistical parameters (e.g., R^2, NMB, NME) should be added to verify the simulation accuracy.

Reply: Thank you for the comment. The description of the emission inventory has now been clarified to avoid the misunderstanding that a 2010 inventory was directly applied to the 2021 simulation. In our modeling system, The East Asia boundary/parent domain (D1) uses the MICS-Asia 2010 inventory with the officially recommended projections of China's anthropogenic emissions to the year 2017, following Li et al. (2017) and Zheng et al. (2018), which is the most recent large-scale dataset available for regional boundary conditions.

For the Taiwan domain (D2), we use the Taiwan Emission Database System (TEDS) version 11.0, whose baseline year is 2019, and which is the official national

emissions inventory adopted by Taiwan's Ministry of Environment. TEDS11 is considered representative for the 2021 baseline scenario, given the absence of major structural emission changes between 2019 and 2021.

Additionally, we agree that quantitative model evaluation is important. Therefore, R^2, NMB, and NME values for NO_x, and O_3 have been added (Table S4), confirming that the model performance meets widely used regional documents.

6. Improve the standardization of figures and tables. This encompasses, but is not limited to, Figure 3, Table 3, Figure 5, Figure 6, Figure 8, and most figures in the supplementary information. Specifically: Use a consistent Arial font across all figures; Standardize axis scales and labels; Ensure no single figure spans multiple pages. These adjustments are necessary to meet the journal's formatting standards.

Reply: Thank you for the valuable suggestions regarding figure and table standardization. We have carefully revised all figures and tables in both the main manuscript and the supplementary information to comply with the journal's formatting requirements. Specially for the consistent font usage (using Arial), standardized axis scales and labels (harmonized across comparable figures), and figure layout adjustments (prevent any single figure from spanning multiple pages).

7. Lines 350–356: Does Table 2 present the average values of adjustment coefficients? If so, this should be clearly indicated in the table title to avoid ambiguity for readers.

Reply: Thank you for the helpful suggestion. Yes, Table 2 presents the average adjustment coefficients derived for each PAMS species. To ensure clarity for readers, we have revised the table title to explicitly state that the values shown represent average emission adjustment factors.

8. Line 375: The manuscript mentions that the improved simulation includes explicit ISOP compared to previous mechanisms. However, many current research already considered and analyzed ISOP as an individual species. The authors should clarify: What distinguishes your results from these prior studies?

Reply: Thank you for this important comment. We agree that isoprene has been explicitly represented in many contemporary chemical mechanisms and has been extensively analyzed in prior literature (e.g., Guenther et al., 2012; Palmer et al., 2006; Steiner & Goldstein, 2007; Curci et al., 2010). In our study, the key distinction is that isoprene emissions are overwhelmingly dominated by biogenic sources, and therefore no anthropogenic emission adjustment factors were applied to ISOP. Instead, ISOP emissions were directly taken from the MEGAN biogenic emission model without modification.

The contribution of our work is tha**t it represents the first island-wide, station-resolved temporal comparison of simulated and observed isoprene concentrations in Taiwan.** While previous studies have discussed isoprene chemistry or biogenic emission modeling more broadly, detailed **time-series evaluation against in situ PAMS observations across multiple stations in Taiwan has not been documented in prior research**. Therefore, our analysis fills a critical gap by providing the first comprehensive observational evaluation of isoprene simulation performance in a Taiwan-focused CMAQ-PAMS modeling framework.

To address your concern, we have clarified the novelty of our work by adding explanatory text in Lines 480–484. The revised manuscript now includes the following sentence: *"Although isoprene has been explicitly represented and analyzed in many prior studies (e.g., Guenther et al., 2012; Palmer et al., 2006), in Taiwan its emissions are overwhelmingly biogenic. Therefore, no emission adjustment factors were applied to ISOP in this study. Instead, our contribution lies in providing the first island-wide temporal comparison between simulated and observed isoprene concentrations across PAMS stations, offering new insight into the model's ability to capture biogenic emission-driven variability."*