RC2: 'Comment on egusphere-2025-4664', Anonymous Referee #2, 05 Nov 2025
General Comments

In this study, the authors have incorporated speciated VOC measurements from Taiwan's PAMS network into the CMAQ model, addressing the limitations of conventional lumped-species chemical mechanisms. The revised model is now capable of explicitly simulating 54 PAMS-targeted species, more direct and comparable evaluation against observed VOC data. This work is timely and valuable, however, there exists some issues which need to be addressed before publishing. Therefore, it requires substantial revisions to improve its clarity and presentation. I recommend a major revision. The specific suggestions are as follows:

Reply: We sincerely thank the reviewer for the careful evaluation of our manuscript and for recognizing the significance of integrating Taiwan's PAMS speciated VOC measurements into CMAQ to enable explicit simulation of 54 VOC species. We appreciate the reviewer's constructive feedback and acknowledge the need for substantial revisions to improve clarity, organization, and presentation. In response, we have thoroughly revised the manuscript and addressed all specific comments point-by-point. We believe these revisions have strengthened the scientific rigor and readability of the work. Detailed responses to each comment are provided below.

Specific Comments

1. Lines 25–30: Could the authors clarify which substances are included under the term "most primary pollutants"?

Reply: Thank you for the comment. To avoid ambiguity, we have clarified which substances are included under the term *"most primary pollutants."* In the revised manuscript, we now explicitly state that this refers to pollutants such as NO_x, CO, VOCs, all of which have exhibited long-term declining trends in Taiwan due to regulatory controls. The text has been rephrased as in Line 29: "… most primary pollutants, including NO_x, CO, VOCs, have shown a declining trend (Chen et al., 2021)."

2. Lines 35–40: While "grouping chemically similar VOCs into lumped surrogate species" is a common approach, it is not the only method used. I suggest the authors provide a more comprehensive overview of chemical mechanisms employed in chemical transport models (CTMs).

Reply: Thank you for your constructive suggestion. We agree that the original text overly emphasized lumped-structure mechanisms. In the revised manuscript, we have expanded the overview of chemical mechanisms used in CTMs to provide a more balanced and comprehensive description. Specifically, we now distinguish between lumped surrogate mechanisms (e.g., CB05, CB6, SAPRC) and explicit or semi-explicit mechanisms (e.g., MOZART, RACM2, MCM), noting their respective advantages and computational trade-offs. This broader context helps clarify how different mechanisms represent VOC species in regional air quality modeling.

The text has been rewritten as in Line 37-41: "Many widely used mechanisms, such as the Carbon Bond families (Yarwood et al., 2005) and SAPRC families (Carter, 2010), reduce computational cost by grouping chemically similar VOCs into lumped surrogate species. Other mechanisms, including RACM2 (Goliff et al., 2013), MOZART (Emmons et al., 2010), and the near-explicit Master Chemical Mechanism (MCM) (Metzger et al., 2008), provide more detailed or explicit representations of VOC oxidation pathways, albeit with substantially greater computational demands."

3. Lines 70–75: The Introduction lacks sufficient context regarding the significance and necessity of developing CMAQ-PAMS.

Reply: Thank you for this insightful comment. We agree that additional context is needed to better motivate the development of CMAQ-PAMS. In the revised manuscript, we have expanded the Introduction to clarify the scientific and practical significance of CMAQ-PAMS. Specifically, we now highlight: (1) the lack of speciated VOC representation in conventional CMAQ simulations, (2) the importance of reproducing individual PAMS species for process-level understanding of ozone formation, and (3) the need for improved tools to reconcile discrepancies between model simulations and PAMS observations. These additions provide clearer justification for developing and applying CMAQ-PAMS in this study.

The text in Lines 80-83 are revised as "… *However, conventional CMAQ configurations do not explicitly resolve the full suite of PAMS species, limiting their ability to diagnose species-specific contributions to ozone formation or to evaluate model performance against detailed observational datasets….*", and in Line 102-109 as "*This gap is critical because individual VOCs exhibit highly variable reactivities, emission sources, and sensitivities to control strategies. Developing CMAQ-PAMS—an enhanced version of CMAQ capable of simulating individual PAMS species—provides a necessary framework for directly linking model outputs with observational constraints, refining VOC emission inventories, and improving mechanistic understanding of ozone formation processes. By enabling species-level comparisons between simulations and PAMS observations, CMAQ-PAMS facilitates a more rigorous assessment of VOC model performance than has been possible with standard lumped-species mechanisms. This capability is particularly important for regions like Taiwan, where ozone episodes are strongly influenced by* *speciated VOC chemistry but where emission inventories and model representations remain uncertain*."

4. Lines 80–85: Please provide detailed information on the 54 PAMS species and their corresponding mappings in the CB05e51 and CB6r3 mechanisms directly.

Reply: We thank the reviewer for this helpful suggestion. To address the comment, we have added a clear description in Lines 82–86 explaining how each of the 54 PAMS species is mapped onto the corresponding lumped VOC species in the CB05e51 and CB6r3 mechanisms. Because the full mapping table is lengthy, the complete list—containing all PAMS species, their chemical structure classification, and their associated CB05e51 and CB6r3 surrogate species—is now included in the Supplementary Information as Table S1. This provides the requested level of detail and allows readers to directly examine how individual PAMS species are treated within both chemical mechanisms.

5. Lines 85–90: The reference to (Knote et al.) appears to be incomplete.

Reply: Thank you for pointing out this issue. The reference "(Knote et al.)" now in Lines 123-126 was indeed incorrect and was intended to denote the hydroxyl radical instead of a literature citation. In the revised manuscript, we have replaced "(Knote et al.)" with "(OH)" in Line 125.

6. line100: The additional chemical reaction pathways should be presented as supplementary.

Reply: We thank the reviewer for this helpful suggestion. Additional reaction pathways associated with the newly introduced PAMS species have now been compiled and included in the Supplementary Information (Table S2), as well as additional text content in Section 2.1.1 (Lines 136-138). Although several reaction concepts were adapted from our earlier PAMS-AQM development (Chen et al., 2010), all pathways have been reformulated to ensure full compatibility with the CB6 chemical mechanism used in CMAQ-PAMS. Only the reactions that were newly added or modified in this study are listed, enabling readers to reproduce the CMAQ-PAMS chemical configuration without redundancy.

7. lines 119-121: The processes of converting VOC concentrations into emission rates and spatially allocating these emissions within a gridded inventory remain unclear.

Reply: We appreciate the reviewer's comment and agree that the description in the manuscript was not sufficiently clear. In this study, VOC concentrations were not converted directly into emission rates. Instead, following the top-down adjustment approach of Chen et al. (2014), the observed-to-simulated PAMS VOC ratios were used to derive hourly species-specific correction factors. These factors were then applied to the original PAMS emissions to scale the emission upward or downward. Thus, the spatial allocation of emission remains identical to the original TEDS inventory, and only the species-level magnitudes are adjusted. The revised manuscript now clarifies this process (in Section 2.1.4) and explicitly states that total VOC mass is not conserved after applying the adjustments.

8. Lines 145–150: The statement “the transboundary influence for the PAMS species is limited” represents a rather bold assumption. What evidence supports this claim? It also appears to be inconsistent with the results discussed in Section 5.3.

Reply: We appreciate the reviewer’s insightful comment. We have clarified the justification for the assumption directly based on the evidence within the manuscript and have revised the text to avoid any ambiguity.

Our statement that “the transboundary influence for the PAMS species is limited” is based on the chemical characteristics and observations of the 54 PAMS species during the September-October 2021 case. As described in the manuscript:

1. Most PAMS species are short-lived primary NMVOCs: These species-primary C2-C9 alkanes/alkenes/aromatics-react rapidly with OH, O_3, and NO_3 radicals (Section 2.1), and therefore cannot sustain long-range transport across the East Asian continent with lifetimes of only minutes to several hours. This is the reason PAMS species are modeled with loss processes only and do not contribute to boundary conditions (lines 223-228).
2. Even the relatively long-lived PAMS alkanes show minimal contribution during LRT events: As described in Section 2.2.1, a small subset of PAMS species (ethane, propane, butanes) have longer lifetimes and can be detectable in long-range transported air masses (Chang et al., 2022). However, the revised text also clarifies that these long-lived alkanes exhibit only minimal mixing ratios in LRT air compared with local concentrations due to extensive dilution over the ocean. Thus, even for the longest-lived species, the transported signal is negligible relative to local emissions, consistent with our assumption.
3. Observations during the 2021 event show no transboundary enhancement of PAMS species: Synoptic patterns (Fig. S1) show that although East Asian circulation affected O_3, PAMS species did not exhibit coherent large-scale enhancements that are characteristic of long-range pollutant arrival. Also, time series at all PAMS sites (Fig. S3-S4) show strongly localized patterns with site-specific diurnal signals, rather than regional spikes expected from transported plumes. These figures demonstrate that while O_3 and secondary pollutants can

be transported, primary PAMS VOCs do not display a regional transport signature.

4. Section 5.3 (now in Section 3.3) does not discuss O_3 or transboundary influence; therefore, there is no inconsistency: The reviewer raised concern about inconsistency with Section 5.3. However, Section 5.3 ("In-depth diagnosis of ModSIM by CMAQ-PAMS", now in Section 3.3) focuses exclusively on local emission characteristics of toluene and isoprene-including their emission distributions, diurnal cycles, and interactions with local meteorology. This section does not discuss: transboundary transport, regional inflow, or ozone formation. Instead, it strictly evaluates how adjusted emissions improve local VOC simulations.

To improve clarity, we revised the original sentence in Line 223-228: "… *Because the 54 PAMS species are short-lived primary VOCs, their direct long-range transport from outside Taiwan is expected to be minimal. This assumption applies only to PAMS species themselves and does not affect discussions related to ozone or secondary products in later sections*."

9. Line 164, figure S2: Is it showing the O3 vertical profile? What does the left axis stand for? How were the vertical winds observed?

Reply: We thank the reviewer for the question and we clarify that Figure S2 does not show O_3 vertical profiles. The figure shows surface O_3 time series plotted as a function of time and station index, along with surface horizontal wind vectors from Taiwan's air quality monitoring network. To avoid misunderstanding, we revise the caption in Figure S2 as "Fig. S2. Hourly observations of O_3 and horizontal surface wind vectors (10m) at all AQS from north to south of Taiwan (IS→NT→CM→CT→YCN→KP→YHD) for the selected case in 2021 (2021/09/27-10/03). The y-axis indicates station sequence, not altitude."

10. Section 3.3: What is the rationale for comparing the computational times of the new (cb6rpams_ae6) and the old (cb6r3_ae6) chemical mechanisms in this study?

Reply: We thank the reviewer for the question. The comparison of computational times between the original CB6 (cb6r3_ae6) mechanism and the new PAMS-extended mechanism (cb6r3pams_ae6) was included for the following reasons:

1. The PAMS mechanism substantially expands the chemical system, and the added computational burden must be documented, such as the new CMAQ-PAMS mechanism explicitly simulated 54 additional VOC species, increasing the number of model-integrated gas-phase species from 219 species (cb6r3_ae6) to 275 species (cb6r3pams_ae6), as shown in Table 1. Also the

number of chemical reactions, the dimensionality of the ODE system solved by the EBI solver, memory usage and output file sizes.
2. CMAQ-PAMS is intended to be used to operationally and in future research; model users need to know the performance impact: How much additional wall-clock time is required, how CPU usage scales with the enlarged chemical mechanism, and whether the computational overhead remains manageable.
3. Including performance metrics is standard practice when introducing a modified CTM mechanism: when a new chemical mechanism, solver configuration, or model module is introduced, performance benchmarking is commonly reported in the atmospheric modeling literature.

To address the reviewer's concern, we have added the following explanation at the beginning of Section 2.3.3: "*Because CMAQ-PAMS introduces 54 additional VOC species and substantially increases the size of the gas-phase chemical system, it is necessary to quantify the computational overhead relative to the original CB6 mechanism. This comparison allows model users and operational centers to assess the feasibility and resource requirements of adopting the expanded mechanism*."

11. It is strongly recommended that Sections 2, 3, and 4 be combined into a single "Materials and Methods" section to enhance the overall readability of the paper.

Reply: We appreciate the reviewer's helpful suggestion. In the revised manuscript, Sections 2, 3, and 4 have been consolidated into a single unified "Materials and Methods" section.

12. Figure 3. Why are only the results for the W-site presented? How do the results from other types of sites compare, and what are the key similarities or differences among them?

Reply: Thank you for the insightful comment. The W-site (Wanhua) was selected as the representative example in Figure 3 because it clearly illustrates the four typical simulation behaviors observed across the PAMS species-namely comparable, overestimated, underestimated, and missing (zero) emissions. Results from all other PAMS stations are already included in the Supporting Information (Figure S4).

As for the key similarities across all PAMS stations, OrigSIM shows substantial species-specific biases (over/underestimation or missing species), reflecting the limitations of U.S.-based VOC speciation profiling. ModSIM significantly improves agreement with observations after top-down calibration, reducing biases and recovering missing species. Diurnal patterns are generally well captured at all stations, indicating that physical transport and photochemistry are adequately represented. Temporal alignment of peaks is consistent across stations, showing that meteorological fields are properly simulated. These similarities demonstrate the CMAQ-PAMS framework is spatially robust across very different environments.

Although the four simulation patterns appear at all sites, some regional characteristics are noted: (1) Urban sites (W, Z1, P1, T3) tend to show stronger signals from traffic and solvent-use VOCs (e.g., toluene, xylenes); ModSIM corrects underestimations for these species. (2) Industrial or mixed sites (T1, P2) often exhibit sharper peaks related to local emission variability; ModSIM still captures the amplitude better than OrigSIM. (3) Southern sites (T3, X, C) show slightly higher nighttime VOC accumulation under weaker boundary-layer mixing; ModSIM also improves the magnitude and pattern. (4) Coastal or rural sites (T2, Z2, Q, D) have lower VOC abundance overall, with diurnal patterns driven by advection and boundary-layer evolution; ModSIM reduces biases while maintaining the correct temporal shape.

Despite these local differences, the overall conclusions remain consistent: ModSIM exhibits major improvements across all conditions, and the W-site example effectively captures the general model behavior.

To improve clarity, we added the following statement in Section 4.1.1 in Line 295-297: "… *The W-site is shown as a representative example because it exhibits all four characteristic modeling behaviors observed across the PAMS stations. Full results for all 12 stations, demonstrating similar patterns, are provided in Figure S4*…."

13. Lines 365–370: What exactly is meant by "local circulation" in this manuscript? In what ways does it affect the spatial distribution of pollutants?

Reply: We thank the reviewer for the opportunity to clarify this term. In the manuscript, "local circulation" refers to the thermally and topographically driven wind patterns within Taiwan, including land-sea breeze circulations, mountain-valley winds and terrain-channeled flows along the western plains. These circulations dominate surface wind fields during the selected 2021 episode, which was characterized by weak synoptic forcing and stagnant conditions (Section 2.2.2; see also Fig. S1).

To avoid ambiguity, we have revised the text in Lines 467-470 as follows: "… *The spatial distribution of toluene is strongly influenced by local circulation, referring to diurnally driven land-sea breezes and terrain-channeled valley winds that dominate surface flow under weak synoptic conditions. These circulations transport emissions downwind and reshape concentration patterns, resulting in spatial maxima that do not always coincide with the emission hotspots*…."

14. Figure 6: The title, figure number, content, and caption should remain together rather than separated. Furthermore, to enable a more straightforward comparison, the units (kg/hr and ppbC) should be converted and the time zones harmonized.

Reply: We thank the reviewer for the helpful suggestions. Both formatting and scientific clarity have been improved in the revised manuscript: In the revised version, Figure 6, its panels, and its caption are placed together on the same page. Units are intentionally different because the figure compared emissions vs. concentrations, but we have clarified this in the revised caption. Time zones have now been harmonized.

We have revised the caption to explicitly state: "Figure 6: … Panels (a) and (c) show emission fluxes (kg/hr), whereas panels (b) and (d) show simulated ambient mixing ratios (ppbC). These quantities represent different physical variables and are therefore not directly convertible. All times are shown in CST (UTC+8), consistent with PAMS and TAQMN observations."

15. It is recommended to provide relevant evidence to demonstrate that Taiwan is in a "VOC-limited regime".

Reply: We thank the reviewer for raising this important statement. The manuscript has been revised to provide clearer evidence that the study period and major urban areas in western Taiwan are predominantly VOC-limited. The supporting evidence is based on citations, consistent with established ozone chemistry diagnostics.

We added the following explanatory sentence in Section 3.5 (in Lines 551-557): "*Numerous field and modeling studies have demonstrated that major urban and industrial regions in western Taiwan frequently operate under VOC-limited ozone formation regimes. Early observational analyses showed that ozone formation in Taipei and northern Taiwan is constrained by VOC availability (Chang and Lee, 2006; Wu et al., 2006). Similar VOC-sensitive behaviour has been reported in central Taiwan (Shiu et al., 2007). More recent analyses further confirm this pattern: long-term NOx reductions have led to higher ozone levels across Taiwan (Chen et al., 2021), and scenario-based modeling shows that NOx-only reductions increase ozone in northern Taiwan, consistent with a VOC-limited regime (Chuang et al., 2022). Collectively, these independent studies strongly support the VOC-limited interpretation applied in this study*."

Technical Corrections

1. The citations in the manuscript are not properly formatted. For example, in lines 50-60, "Yang et al. (Yang et al., 2005) analyzed …" should be "Yang et al. (2005) analyzed …". In lines 70-75, "(Chen et al., 2010; Ying and Li, 2011; Chen et al., 2014a; Chen et al.,

2015; Su et al., 2016). (Ge et al., 2024; Rowlinson et al., 2024)" should be "(Chen et al., 2010, 2014a, 2015; Ge et al., 2024; Rowlinson et al., 2024; Su et al., 2016; Ying and Li, 2011)".

Reply: We thank the reviewer for pointing out the inconsistences in the citation formatting. All in-text citations have now been carefully checked and corrected throughout the entire manuscript to follow a consistent and journal-compliant style.

2. The manuscript uses both "ozone" and "O3" in different places; it is recommended to use a consistent notation throughout.

Reply: We appreciate the reviewer's helpful suggestion. In the reviewed manuscript, we have standardized the terminology by using "O_3" consistently throughout the text, figures, tables, and captions. The term "ozone" is now only used when referring to aerosol or gas species in a general narrative context (e.g., "ozone pollution," "ozone episodes"), while all scientific or quantitative references (e.g., concentrations, production rates, chemical mechanisms) use the symbol "O_3" for clarity and consistency.

3. Lines 95: Change to "Figure 1. The CMAQ modeling framework revised for CMAQ-PAMS (red parts)."

Reply: We thank the reviewer for the suggestion. The caption for Figure 1 has been revised accordingly.

4. A few spelling and grammatical errors in the manuscript need to be corrected.

Reply: Thank you for pointing this out. The entire manuscript has been carefully proofread, and all spelling and grammatical errors have been corrected. In addition to standard corrections, we also improved sentence flow and consistency, especially in the Introduction, Methods, and Discussion sections. We appreciate the reviewer's suggestion, which has helped enhance the readability and clarity of the manuscript.