Response to RC3

We sincerely thank the reviewer for their careful reading of our manuscript and for their constructive comments and suggestions. We fully agree that the core weakness of the original manuscript lies in the disconnection between the computational results and atmospheric physical reality. In the revised manuscript, we have undertaken a systematic re-evaluation and substantial revision of the entire work:

1. The introduction exhibits obvious selective bias and logical leaps in its literature review. In fact, over the past five years, extensive literature has been published on the aqueous-phase ·OH oxidation and photochemical degradation of nitrophenolic compounds. The introduction fails to accurately delineate research progress across the three domains of "pure gas phase," "pure aqueous phase," and "gas-liquid/gas-solid interfaces," resulting in a rough and inaccurate summary of the existing research landscape.

Response: We thank the reviewer for this critical observation. We fully agree that the original introduction failed to accurately delineate research progress across the three domains and that the summary of the existing research landscape was insufficient. In the revised manuscript, we have inserted a concise, integrated summary paragraph that systematically distinguishes gas-phase, aqueous-phase, and interfacial research. First, in the gas phase, we now cite the kinetic studies on OH-initiated oxidation of nitrophenols (Harrison et al., 2005), and acknowledge that photolysis and NO_3-mediated pathways are recognized as important loss processes,

especially at night. In the aqueous phase, we now explicitly summarize the second-order rate constants for 2,4-DNP with OH radicals determined by Albinet et al. (2010) and the aqueous photo-oxidation kinetics reported by Hems and Abbatt (2018) for nitrocatechol, nitroguaiacol, and dinitrophenol. At gas-liquid and gas-solid interfaces, we now reference the interfacial oxidation studies of phenolic compounds by Pillar et al. (2014), Pillar and Guzman (2017), and Rana and Guzman (2020, 2022a,b). This paragraph concludes with a summary statement that molecular-level understanding remains limited, setting the stage for introducing a model system.

The revised content of the manuscript is as follows: "Over the past two decades, extensive studies have addressed the atmospheric chemistry of nitrophenols, yet the research landscape is unevenly distributed across different phases. In the gas phase, kinetic measurements have established the rate constants for OH-initiated oxidation of nitrophenols (Harrison et al., 2005), while photolysis and NO_3-mediated pathways are recognized as important loss processes, especially at night. In the aqueous phase, the reactions of nitrophenols with OH radicals have been systematically quantified; for 2,4-dinitrophenol, the second-order rate constants are $(1.76 \pm 0.05) \times 10^9$ M^{-1} s^{-1} for the neutral form and $(2.33 \pm 0.11) \times 10^9$ M^{-1} s^{-1} for the phenolate (Albinet et al., 2010), and similar kinetic data have been reported for nitrocatechol, nitroguaiacol, and dinitrophenol (Hems and Abbatt, 2018). At gas-liquid and gas-solid interfaces, the oxidation of phenolic compounds has been shown to yield products distinct from those in the bulk phases (Pillar et al., 2014; Pillar and Guzman, 2017; Rana and Guzman, 2020, 2022a,b). These distinct product distributions underscore the

importance of understanding the molecular-level interactions that govern adsorption and reactivity at aerosol surfaces. However, such understanding remains limited for nitrophenols on carbonaceous surfaces."

2. The introduction completely fails to summarize existing literature on the surface adsorption of real atmospheric carbonaceous aerosols (such as black carbon, soot, and amorphous carbon). The introduction does not clarify "what bottlenecks existing studies have encountered in simulating carbonaceous particle surfaces," and instead abruptly introduces C60 without accurately reflecting the actual research progress in the field of multiphase adsorption on atmospheric particles.

Response: We thank the reviewer for this important observation. We agree that the abrupt introduction of C60 without proper context regarding real carbonaceous aerosol surfaces was problematic.

The specific additions are as follows: "At gas-liquid and gas-solid interfaces, the oxidation of phenolic compounds has been shown to yield products distinct from those in the bulk phases (Pillar et al., 2014; Pillar and Guzman, 2017; Rana and Guzman, 2020, 2022a,b). These distinct product distributions underscore the importance of understanding the molecular-level interactions that govern adsorption and reactivity at aerosol surfaces. However, such understanding remains limited for nitrophenols on carbonaceous surfaces. Real atmospheric carbonaceous particles, such as black carbon and soot—which are products of incomplete combustion of fossil fuels or biomass—exhibit significant complexity in both chemical composition and physical structure. Their polyaromatic (graphite-like) surfaces can form π-π electron

donor-acceptor complexes with nitroaromatic compounds, yet the adsorptive strength depends greatly on pyrolysis temperature, formation conditions, and subsequent environmental weathering. Moreover, the filling of micropores and mesopores is subject to steric effects due to size exclusion, and the adsorptive capacity becomes attenuated by fouling with natural organic matter that blocks pores and competes for adsorption sites. These factors, together with the chemical heterogeneity (oxygen-containing functional groups, defect sites, metal impurities) and morphological complexity (aggregates, pore structures) of real aerosol particles, make it extremely difficult to decouple adsorption from partitioning contributions or to identify specific non-covalent interaction types at the molecular level. Consequently, a well-defined model system is needed to iso-late the specific interactions from the confounding effects of surface heterogeneity."

3. The introduction merely glosses over this with a single sentence—"traditional experiments are difficult to fully identify"—and fails to clearly summarize the latest progress in computational toxicology (QSAR) for evaluating atmospheric secondary products. This makes the subsequent discussion on toxicity appear abrupt and lacking a solid literature foundation.

Response: We agree that the single sentence regarding experimental limitations was insufficient and that the QSAR discussion lacked proper literature foundation. In the revised manuscript, following the discussion of experimental limitations, we have added a new paragraph summarizing recent progress in computational toxicology for atmospheric secondary products: "In parallel, computational toxicology has emerged

as a complementary approach for evaluating the toxicity of atmospheric transformation products when experimental data are unavailable. Recent studies have demonstrated that for a subset of 104 secondary organic aerosol compounds, reliable in silico predictions were obtained for 82% of the species, whereas experimental data were available for only 13% (Decesari et al., 2018). Importantly, transformation products generated during atmospheric oxidation can exhibit toxicity exceeding that of their parent compounds (Vom Eyser et al., 2013). These findings underscore the necessity of integrating toxicity prediction into the assessment of atmospheric transformation pathways. However, the application of QSAR to nitrophenolic transformation products remains limited, and the uncertainties inherent in such predictions require careful interpretation."

4. The manuscript focuses exclusively on a single compound, 2,4-DNP, yet repeatedly draws overarching conclusions about the atmospheric fate and risk amplification of "nitrophenolic compounds" or "nitroaromatics" as a whole.

Response: We thank the reviewer for this critical observation. We agree that the original manuscript repeatedly drew overarching conclusions about "nitrophenolic compounds" or "nitroaromatics" as a whole, despite focusing exclusively on 2,4-DNP. This overgeneralization was inappropriate and has been corrected. In the revised manuscript, we have systematically revised the language throughout the text to ensure that quantitative conclusions are explicitly attributed to 2,4-DNP rather than generalized to all nitrophenolic or nitroaromatic compounds.

Specifically, in the Abstract, we have revised the concluding sentences to clarify that the quantitative findings apply specifically to 2,4-DNP, while the qualitative framework may provide reference for related systems: "These findings provide mechanistic insights into the atmospheric transformation pathways of this specific dinitrophenol and highlight the importance of evaluating transformation product toxicity in the environmental risk assessment of nitrophenolic compounds". Throughout the Results and Discussion and Conclusions, we have systematically replaced overgeneralized phrases (e.g., "nitrophenolic compounds," "nitroaromatics," "these findings reveal the environmental risk amplification associated with nitroaromatic compounds") with compound-specific phrasing (e.g., "2,4-DNP," "this compound," "the present system") where the statement refers to quantitative results, while retaining broader language only when discussing qualitative mechanistic insights that may be generalizable.

5. The authors convert the aqueous rate constants to cm^3 $molecule^{-1}$ s^{-1} and directly plot them alongside gas-phase constants in Figure 3. In the actual atmosphere, the overall contribution of a multi-phase pathway depends on the partitioning of the pollutant (Henry's law) and the Liquid Water Content (LWC) of the aerosol. Merely comparing converted rate constants fails to establish whether the aqueous-phase reactions actually matter to the total atmospheric fate of 2,4-DNP.

Response: The overall contribution of a multiphase reaction indeed depends on the phase partitioning of the pollutant, governed by Henry's law and effective

solubility, the aerosol liquid water content, and the availability of oxidants in each phase.

In the revised manuscript, we have systematically addressed this concern through the following modifications: In the revised manuscript, we have systematically addressed this concern through the following modifications: In Section 3.1.2, we have added a new paragraph explicitly clarifying that the converted rate constants represent intrinsic reactivities in each phase rather than actual atmospheric importance: “It should be emphasized that the second-order rate constants presented in Figure 3d–e, even after unit conversion, represent intrinsic reactivities in each phase rather than the actual atmospheric importance of each pathway. The overall contribution of aqueous-phase reactions to the atmospheric fate of 2,4-DNP depends critically on the fraction of the compound that partitions into the aqueous phase. For 2,4-dinitrophenol, the Henry’s law constant has been determined as 5.70×10^{-8} atm·m^3/mol at 5 °C (Lüttke and Levsen, 1997), indicating a strong tendency to partition into the aqueous phase. The partitioning is further modulated by its acid dissociation constant (pKa ≈ 4.09 at 25 °C), as the deprotonated phenolate form is substantially more water-soluble than the neutral phenol. In addition, the aerosol liquid water content—which varies widely depending on relative humidity, particle composition, and atmospheric conditions—determines the available aqueous volume for multiphase reactions. Without quantitative information on these partitioning parameters under specific atmospheric conditions, the aqueous-phase rate constants should be interpreted as intrinsic reactivity indicators rather than direct measures of atmospheric importance.

we have also revised the title and caption of Figure 3 to clearly indicate that the comparison is of intrinsic rate constants: "(d–e) Intrinsic temperature-dependent reaction rate constants for the major channels."

6. The ecotoxicity profiling relies completely on the US EPA's software. QSAR screening is excellent for high-throughput hazard prioritization, but drawing definitive conclusions about environmental risk amplification ("toxicity amplification") purely from in silico endpoints is speculative.

Response: We thank the reviewer for raising this important point. In the original manuscript, we had already included a limitations paragraph in Section 3.3 acknowledging that the QSAR models are constrained by the chemical space of the training sets, that predictions for structurally distinct species such as 2,4-DNP and its nitro-containing derivatives may have diminished confidence, and that the findings should be interpreted as hypothesis-generating rather than definitive:

"The toxicity predictions presented in this section are screening-level assessments based on QSAR models. They are intended for hazard prioritization and hypothesis generation, and should not be interpreted as definitive toxicological conclusions without experimental validation. The predictive performance is fundamentally constrained by the chemical space of the training sets and the defined applicability domains. For structurally distinct species such as 2,4-DNP and its various derivatives, the confidence levels of the predictions may be diminished because these models cannot fully elucidate specific toxicological modes of action. As highlighted by the Ames/QSAR International Challenge Projects, even the

best-performing models for Ames mutagenicity prediction achieve a balanced accuracy of approximately 76.9% at 100% coverage (Uesawa, 2024), indicating that inherent uncertainties remain. In addition, categorical predictions with probability scores close to threshold are inherently unstable; as shown in Table S4, the "not detected" Ames mutagenicity signals for intermediates such as IM17, IM25, IM44, and IM54 fall within this near-threshold regime. This suggests that these signals may reflect model limitations rather than a definitive absence of toxicity. These compounds should therefore be regarded as high-priority targets for experimental validation. Furthermore, these computational frameworks necessarily simplify complex biological endpoints such as developmental toxicity. A quantitative weight-of-evidence (qWoE) approach, which combines predictions from multiple QSAR models, has been shown to achieve accuracy similar to that of the experimental Ames test (Tintó-Moliner et al., 2020); however, such approaches are beyond the scope of the present screening-level assessment. Therefore, the present findings should be interpreted as hypothesis-generating rather than definitive (Vom Eyser et al., 2013), and we recommend experimental validation through in vitro Ames tests and zebrafish embryo development assays for the high-priority compounds identified".

7. The authors claim that the direct transformation initiated by $\cdot NO_2$ is completely negligible under ambient conditions because its barrier is much higher than OH pathways. This is an unbalance in atmospheric interpretation. During heavily polluted night events, ·OH radical concentrations drop close, whereas $\cdot NO_2$ accumulates significantly. Discarding a daytime-uncompetitive pathway without

conducting a true diurnal chemical box-model or sensitivity analysis under varying pollution regimes is scientifically weak.

Response: The reviewer is correct that the conclusion regarding $\bullet NO_2$ reactivity must be evaluated in the context of diurnal variations in oxidant concentrations. To address this, we have conducted a quantitative analysis using literature-reported field measurements and added the following discussion to Section 3.1.2: "The literature review indicates that •OH concentrations typically reach $1 \times 10^6 \sim 3 \times 10^6$ molecules cm^{-3}, while $\bullet NO_2$ levels are lower due to rapid photolysis under daytime conditions. During heavily polluted nighttime conditions, however, •OH concentrations drop substantially. Geyer et al. (2003) reported a nocturnal OH concentration of $(1.85 \pm 0.82) \times 10^5$ cm^{-3} during the BERLIOZ campaign, and in UK urban surface environments, night-time OH levels were determined to be in the range of $10^5 \sim 10^6$ molecules cm^{-3} (Khan et al., 2011). Meanwhile, $\bullet NO_2$ can accumulate significantly at night, with nocturnal maxima reaching 8.43 ± 0.4 ppb in Guangzhou (Qin et al., 2009). Using these literature-reported concentrations, the pseudo-first-order rate constants under nighttime conditions can be estimated. For the •OH pathway, with kOH = 3.18×10^{-15} cm^3 $molecule^{-1}$ s^{-1} and [OH] ≈ $10^5 \sim 10^6$ molecules cm^{-3}, k'OH ≈ $10^{-10} \sim 10^{-9}$ s^{-1}. For the direct $\bullet NO_2$ pathway, with $k NO_2 \approx 10^{-28}$ cm^3 $molecule^{-1}$ s^{-1} and $[NO_2] \approx 10^{10} \sim 10^{11}$ molecules cm^{-3} (corresponding to ~0.4–4 ppb at 298 K and 1 atm), k'NO_2 ≈ $10^{-18} \sim 10^{-17}$ s^{-1}. Even under the most favorable nighttime conditions (lowest •OH, highest $\bullet NO_2$), the direct $\bullet NO_2$ pathway remains more than 7 orders of magnitude slower than the •OH pathway, corresponding to a lifetime of $>10^{10}$ s, which is

negligible on atmospheric timescales. Therefore, while a full diurnal box model simulation would be required to quantify all pathways under varying pollution regimes, the quantitative analysis above confirms that the direct reaction of $\bullet NO_2$ with parent 2,4-DNP is negligible even under nighttime conditions. The possible involvement of $\bullet NO_2$ in subsequent reactions with primary oxidation intermediates will be discussed separately to provide a complete mechanistic picture of its environmental fate. In summary, the atmospheric degradation of 2,4-DNP is kinetically dominated by •OH, with O_3 playing a significant role in the aqueous phase, while the direct transformation contribution of $\bullet NO_2$ can be neglected in environmental assessments.

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