Response to Referee #1

We greatly appreciate the reviewer for providing constructive comments, which have helped us improve the paper quality. We have carefully addressed all comments, as detailed below.

Comments from Anonymous Referee #1:
This manuscript utilizes long-term observational data to investigate the characteristics of fine particulate nitrate (f-NO$_3^-$) variations in Canada under the context of NOx emission reductions. It proposes that primary fine particulate nitrate may play a significant role in annual average concentrations and their trends. The research topic is of practical relevance and attempts to explain the observed nonlinear responses from perspectives of meteorological modulation and chemical mechanisms. However, the current version suffers from several weaknesses and the following concerns are addressed:

Response: The concerns raised by the reviewer have been thoroughly addressed, as outlined in our detailed responses to the specific comments below.

We would like to emphasize that the present study represents an important initial effort to elucidate the role of primary NO$_3^-$ emissions in influencing NO$_3^-$ pollution and its long-term trends, based on the following considerations:

(1) The formation of primary f-NO$_3^-$ and its effects on NO$_3^-$ trends, as well as its responses to NO$_x$ emission reductions, are highly complex. The measurement protocol for condensable particulate matter (CPM), a major component of primary f-NO$_3^-$, was not established by the U.S. EPA until 2017. Moreover, measurements of CPM under sub-zero ambient conditions remain largely unavailable worldwide.

(2) Our analytical results indicate that more comprehensive investigations are urgently needed, particularly systematic measurements of CPM from various stationary sources under a range of sub-zero ambient temperatures. Newly obtained emission data should be incorporated into updated emission inventories for contemporary combustion sources. Until such improvements are made, the performance of three-dimensional (3-D) air quality models in simulating particulate NO$_3^-$ will remain substantially constrained.

(3) Given the current state of knowledge and data availability, the importance of primary f-NO$_3^-$—especially that derived from CPM—prior to 2017, and even for several years thereafter, may need to be assessed largely on the basis of observational evidence (such as the one conducted in the present study). The relative contributions of primary and secondary f-NO$_3^-$ could be re-examined using 3-D air quality modeling once the accuracy of emission inventories (used as model inputs) and the representation of key physical and chemical processes have been substantially improved.

1. *The Introduction provides a general motivation related to NOx reductions and nitrate responses but offers only limited discussion of previous studies that have examined the effects of emission changes, climate or meteorological variability on air pollution in Canada. A more comprehensive and regionally focused literature review is needed to better justify the scientific scope and originality of the work.*

Response: To justify the scientific scope and originality of the work, in the revised manuscript, we have conducted a comprehensive review of the existing literature on long-term trends in particulate nitrate in Canada. Given the limited number of such studies in Canada, we have also included a brief review of trend analyses from the United States, Europe, and China that investigate particulate nitrate responses to NO_x emission reductions. As the manuscript is already lengthy (nearly 800 lines), these review materials are provided in Text S1 of the Supporting Information. The key findings from this review have also been summarized in the revised Introduction.

The revised text in the Introduction reads as follows: "The aforementioned knowledge gap hinders our understanding of how changes in primary $f\text{-}NO_3^-$ emissions influence the annual-scale response of $f\text{-}NO_3^-$ to NO_x emission reductions. This gap appears to be global rather than unique to Canada, as indicated by the brief review of particulate NO_3^- trends and their responses to NO_x emission reductions summarized in Text S1 of the Supporting Information (SI). Two key points emerge. (1) The limited number of trend studies on particulate NO_3^- across Canada, including $f\text{-}NO_3^-$ and total NO_3^- ($=f\text{-}NO_3^-+c\text{-}NO_3^-$) in suspended particles, suggest that long-term changes are neither spatially uniform nor monotonic. (2) The non-linear and sometimes counterintuitive response of particulate NO_3^- to NO_x emission controls has been widely reported in the United States, Europe, and China, yet the underlying drivers remain insufficiently constrained. Together, these cross-regional comparisons motivate a Canada-focused synthesis that explicitly evaluates the non-linear influences of co-evolving precursor emissions, gas–particle partitioning, and meteorological variability in interpreting long-term $f\text{-}NO_3^-$ trends."

Text S1 of the Supporting Information reads:
"Within Canada, long-term observations indicate that trends in inorganic aerosols are neither spatially uniform nor monotonic. For example, in Toronto, both nitrate (NO_3^-) and sulfate (SO_4^{2-}) in $PM_{2.5}$ (particles < 2.5 µm) declined rapidly during 2004–2017 (-6.9% yr^{-1} and -8.1% yr^{-1}, respectively), accompanied by decreases in ammonium (NH_4^+) (Jeong et al., 2020). In contrast, in Edmonton (2007–2014), neither $PM_{2.5}$ nor the major inorganic ions (NO_3^-, SO_4^{2-}, NH_4^+) exhibited statistically significant trends (Bari and Kindzierski, 2016).
    At a broader rural and non-urban scale, data collected through the Canadian Air and Precipitation Monitoring network (CAPMoN) (1988–2007) revealed distinct non-monotonic annual variations in particulate NO_3^- in total suspended particle (TSP): approximately stable during 1988–1993, increasing during 1993–2002, and declining during 2002–2007. Site-to-site differences suggest strong modulation by meteorology,

long-range transport, and aerosol thermodynamics in addition to precursor emissions (Zbieranowski and Aherne, 2012).

This asymmetry between particulate SO_4^{2-} and NO_3^- responses becomes clearer at the eastern North American scale. During 1990–2015, SO_2 emissions fell sharply (−84% in the eastern U.S.; −66% in eastern Canada), while NO_x reductions were more modest (−54% and −22%, respectively). Corresponding, SO_4^{2-} and NH_4^+ in TSP decreased substantially (−73.3% and −67.4%), whereas NO_3^- decreased by only −29.1% (largely after 2000), indicating that NO_3^- responds more weakly and more conditionally to emission controls than SO_4^{2-} and NH_4^+.

Winter-focused analyses further illustrate why NO_{3-} can resist or even offset expected declines. Shah et al. (2018) compared winter conditions in 2007 and 2015 and found that, despite substantial reductions in winter SO_2 (-58%) and NO_x (−35%) emissions, winter $PM_{2.5}$ NO_3^- showed little change. Similarly, a detailed analysis at paired urban and rural sites in Rhode Island (northeastern U.S.) reported pronounced increases in NO_3^- in PM_{10} (particle < 10 µm) during 2005–2015 (+95% urban; +57% rural) despite substantial SO_2 and NO_x emission reductions, consistent with acidity- and partitioning-driven feedbacks that can partially counteract NO_x controls (Kim et al., 2023).

In line with the findings described above, early NO_x-control phases were sometimes accompanied by rising particulate NO_3^- across the eastern U.S. For example, NO_3^- in TSP increased by 11% from 1990–1994 to 2000–2004 (winter: 31%) even as NO_x emissions declined by 22% (Sickles II and Shadwick, 2015). Similarly, at several CAPMoN sites (ALG, LON, EGB, and KEJ) in Canada, NO_3^- in TSP increased significantly during 1993-2002 followed by declines during 2002-2007 (Zbieranowski and Aherne, 2011). These findings underscore the nonlinear and phase-dependent response of nitrate to precursor controls.

Comparable non-linearities have also been documented in other fast-changing regions. In Europe, EMEP assessments report >80% reductions in SO_x and ~50% reductions in NO_x, but only ~12% reductions in NH_3 during 2000–2019. Correspondingly, particulate SO_4^{2-} in TSP declined at ~3–4% yr^{-1}, whereas total nitrate (HNO_{3gas} + particulate NO_3^-) decreased more slowly at ~1.5–2% yr^{-1} (Aas et al., 2024). Observations in the United Kingdom further illustrate phase-dependent decoupling: at two London sites, NO_3^- in PM_{10} changed only slightly during 2012–2018 and became largely stagnant after 2014, despite continued significant declines in ambient NO_x and NO_2; meanwhile, rural AGANET measurements (2000-2020) show that NO_3^- in TSP decreased at 2.12% yr^{-1}, significantly slower than the decline in NO_x emissions (2.84% yr^{-1}) and rural NO_x concentrations (3.48% yr^{-1}), implying an increasing nitrate-to-precursor ratio over time and highlighting the roles of NH_3 availability, thermodynamic partitioning, and regional transport (Harrison et al., 2022).

In contrast, under aggressive SO_2 controls in North China (2008–2016), SO_2, NO_x and NH_3 emissions decreased by −60%, −16% and −7%, respectively (Liu et al., 2018). Nevertheless, $PM_{2.5}$ NO_3^- increased by ~28%, accompanied by a ~30% rise in gas-phase NH_3, underscoring how shifts in aerosol acidity and NH_3 availability can

redirect inorganic aerosol composition and even promote nitrate under certain control phases (Liu et al., 2018).

The cross-regional comparisons presented in this section underscore the inherently nonlinear behavior of particulate nitrate trends. This complexity calls for a regionally focused Canadian synthesis that explicitly accounts for the coupled evolution of SO_2, NO_x, and NH_3 emissions, thermodynamic partitioning processes, and meteorological variability when interpreting long-term f-NO_3^- trends."

2. *The manuscript's key conclusion is based primarily on indirect evidence, including trend mismatches between NOx and f-NO$_3^-$ and seasonal behavior. While these analyses are suggestive, they largely rely on exclusion and correlation rather than direct constraints. Without additional lines of evidence (e.g., source apportionment or model-based sensitivity tests), it remains difficult to clearly separate primary nitrate formation from complex secondary or heterogeneous processes. The uncertainty associated with this inference should be more explicitly acknowledged.*

Response: Existing source apportionment studies have typically identified NO_3^- sources in $PM_{2.5}$ across Canada and the United States. Our study presented here suggest that NO_3^- in $PM_{2.5}$ may originate predominantly from primary NO_3^- rather than secondary NO_3^-, or primary and secondary NO_3^- may contribute comparably. We admit these interpretations remain highly uncertain and open to debate, and further investigations are still needed to address this important knowledge gap.

As summarized in the general response above, the relative contributions of primary and secondary f-NO_3^- can be quantitatively assessed through model-based sensitivity analyses only after substantial improvements have been made to the accuracy of emission inventories (used as model inputs) and to the representation of key physical and chemical processes in three-dimensional (3-D) air quality models. At present, existing modeling frameworks for simulating particulate NO_3^- formation are subject to considerable uncertainties. To support this argument, we have conducted a brief review of studies on particulate NO_3^- modeling in Canada and the United States, which is presented in Text S4 of the Supporting Information, with key points generated from this review presented in Section 3.6. This review underscores the substantial challenges in accurately simulating particulate NO_3^- in this region.

Nevertheless, these challenges may be mitigated as primary f-NO_3^- is more clearly recognized, better quantified, and systematically incorporated into updated emission inventories. We are optimistic in this regard and believe that this represents an important implication of the present study.

Additional discussion added in Section 3.6 reads as follows: **"**Existing studies using 3-D chemical transport models (CTMs) simulating particulate NO_3^- over North America are summarized in Text S5 of SI. Several key points can be generated from these studies. (1) CTMs are widely applied and can often reproduce broad spatial patterns and major controlling processes of particulate NO_3^- over the United States

and Canada; however, they frequently exhibit systematic biases in magnitude, long-term trends, and sensitivities to emission controls, with a substantial risk of error compensation (Pun et al., 2009; Smyth et al., 2009; Walker et al., 2012; Kim et al., 2014, 2023; ECCC, 2016; Shah et al., 2018; Luo et al., 2019; Russell et al., 2019; Pappin et al., 2024; Semeniuk et al., 2025). (2) The standard GEOS-Chem v12.0.0 simulation substantially overestimated surface $PM_{2.5}$ NO_3^- over the U.S. (1.89 µg m^{-3} vs. 0.70 µg m^{-3}), with pronounced spatial heterogeneity: outside California, the normalized mean bias reached +176%, whereas California exhibited an opposite bias of −62%, implying region-dependent dominant error sources (e.g., meteorology, emissions, and/or thermodynamics) (Walker et al., 2012; Luo et al., 2019). (3) simulated particulate NO_3^- often responds to NO_x controls in a strongly non-linear, and sometimes counterintuitive manner, posing a persistent "acidity–partitioning" challenge for trend attribution. For instance, in the northeastern United States, observations show that PM_{10} nitrate increased by 95% (urban) and 57% (rural) from 2005 to 2015 despite declining NO_x emissions, and this behavior was attributed to changes in aerosol acidity and gas–particle partitioning feedbacks that can offset the expected effect of precursor reductions (Kim et al., 2023). Finally, condensable particulate nitrate, as defined in US EPA Method 202 (US EPA, 2017), as well as its enhanced fraction under sub-freezing conditions, is generally not represented in current emission inventories. Given its potential importance, as suggested by our analysis presented above, incorporating temperature-dependent condensable nitrate into emission inventories is likely necessary to improve the representation and prediction of f-NO_3^- in 3-D air quality modelling."

3.   *The manuscript argues that wintertime stagnant conditions enhance local accumulation of f-NO_3^-, thereby supporting a primary formation pathway. However, stagnant meteorology would also be expected to suppress dispersion and increase coarse nitrate (c-NO_3^-) concentrations. The manuscript does not sufficiently explain why c-NO_3^- responds much more weakly than f-NO_3^- under similar conditions, nor does it quantitatively compare their sensitivities to stagnation. A clearer discussion of the differing source regions, formation rates, and transport characteristics of fine versus coarse nitrate is necessary to strengthen this argument.*

Response: In the revised manuscript, we included a correlation analysis between f-NO_3^- and c-NO_3^- and, as expected, found no significant association between the two. We have added this finding in the revised Section 3.1,which reads "Notably, f-NO_3^- and c-NO_3^- were not significantly correlated in any individual year during 1990–2005 ($R^2 < 0.1$; $P > 0.05$). The same pattern was observed at the other six sites analyzed in this study. The lack of correlation between f-NO_3^- and c-NO_3^- is discussed in detail in Section 3.2".

In principle, c-NO_3^- is governed more strongly by the availability of alkaline species associated with suspended road dust and road-salt particles, as well as by the abundance of total gaseous nitrate ($HNO_3 + N_2O_5$). As demonstrated in this study, stagnant winter meteorological conditions did not result in elevated $HNO_3 + N_2O_5$

levels, likely due to the accompanying freezing temperatures. Moreover, stagnant and freezing conditions are not conducive to the suspension of road dust and road-salt particles during winter. We have added such explanation in Section 3.2,which reads: "Again, no significant correlation was observed between f-NO$_3^-$ and c-NO$_3^-$ in any year (R^2<0.1, P>0.05). Given the probable increasing trend in annual average c-NO$_3^-$ despite decreasing NO$_x$ emissions at both city and provincial scales, and considering the seasonal pattern of elevated levels, it is likely that the trend in c-NO$_3^-$ was governed by the availability of alkali aerosols associated with suspended road dust and road-salt particles capable of neutralizing HNO$_{3gas}$*, rather than by changes in HNO$_{3gas}$* itself. As further illustrated in Section 3.4 below for the case of Edmonton, stagnant winter meteorological conditions did not coincide with elevated HNO$_3$(g)* concentrations, likely due to the accompanying sub-freezing temperatures. Moreover, stagnant and freezing conditions are not conducive to the suspension of road dust and road-salt particles during winter."

4. *The manuscript introduces the Arctic Oscillation (AO) as a key climate factor modulating wintertime pollution levels, but the rationale for focusing exclusively on AO is not sufficiently developed. Other climate drivers, such as ENSO, Arctic sea ice variability, or long-term warming trends, can also influence regional meteorology and air quality in Canada. The authors should better justify why AO was selected over other factors, or at least briefly discuss the potential roles of these climate influences and why they were not considered.*

Response: This is because elevated f-NO$_3^-$ concentrations predominantly occurred during the cold winter season. Wintertime f-NO$_3^-$ largely determined the annual f-NO$_3^-$ trends across Canada, as clarified in the revised manuscript. Although climate drivers may influence f-NO$_3^-$ levels during the warmer seasons, their contribution to the annual f-NO$_3^-$ trends across Canada is likely negligible. This point has also been incorporated into the revised manuscript (Section 3.4).

5. *To investigate controls on annual mean f-NO$_3^-$, the analysis focuses on a single site (S-90132) and two representative years (2010 and 2015). The manuscript does not sufficiently justify the representativeness of these years, nor does it demonstrate that the inferred mechanisms are robust across the full observational record.*

Response: The two years, 2010 and 2015, were selected because they represent the highest annual mean f-NO$_3^-$ concentration and a climatologically average year, respectively. Between 2010 and 2015, NO$_2$ mixing ratios in Edmonton and provincial-level NO$_x$ emissions decreased consistently by 11% and 10%, respectively. In contrast, the annual mean f-NO$_3^-$ concentration declined by 58%, from 2.1 µg m^{-3} in 2010 to 0.89 µg m^{-3} in 2015. This point has been clarified in the revised manuscript.

Moreover, the original analysis relied solely on 2010 data to examine the role of HNO$_3$* in f-NO$_3^-$ formation, which may raise concerns regarding representativeness. In the revised manuscript, we therefore combined the 2010 and 2015 datasets to re-

evaluate this issue. This approach substantially increased the sample size and yielded the same conclusion. Accordingly, the proposed mechanism is expected to be applicable to the full observational record, as now clarified in the revised manuscript.

6. *In Section 3.5, the analysis is based on a total of only 58 samples divided into three groups. However, the manuscript does not clearly define what constitutes a "sample," nor does it specify the associated site(s), temporal resolution, observation period, or selection criteria. Given the small sample size and subsequent grouping, the statistical representativeness and robustness of the results are questionable.*

Response: The selection criteria have been clarified in the revised manuscript. Briefly, data collected under ambient temperatures of 0–40 °C and <0 °C were used for comparative analysis. The <0 °C dataset was further subdivided into two groups based on $f\text{-}NO_3^-$ concentrations (>4 µg m^{-3} and ≤4 µg m^{-3}).

To increase the sample size, we expanded the analysis to include daily observations from both 2010 and 2015 at the Edmonton NAPS site (S-90132). The temperature–$f\text{-}NO_3^-$ screening identified a total of 108 days (Group 1: n = 23; Group 2: n = 54; Group 3: n = 31). The mean (± SD) $f\text{-}NO_3^-$ and $HNO_3\_gas^*$ concentrations were 8.7 ± 4.1 µg m^{-3} and 0.16 ± 0.11 µg m^{-3} for Group 1; 1.4 ± 0.95 µg m^{-3} and 0.17 ± 0.16 µg m^{-3} for Group 2; and 0.9 ± 1.1 µg m^{-3} and 0.15 ± 0.10 µg m^{-3} for Group 3, respectively.

Even with this expanded dataset, the mean $HNO_3\_gas^*$ concentrations did not differ significantly among the three groups (Welch's one-way ANOVA, p = 0.74), despite the substantial contrast in $f\text{-}NO_3^-$ levels.

7. *The trend analyses presented in the manuscript appear to be based on annual mean concentrations. Given the pronounced seasonal variability of air pollutants, it remains unclear whether the reported trends remain significant when the data are analyzed on a seasonal basis. Seasonal trend analysis would help determine whether the inferred long-term changes are robust or dominated by specific seasons. In addition, the time period used for pollutant trend analysis does not appear to be fully aligned with the period of major NOx emission reductions. This temporal mismatch complicates causal interpretation and weakens the linkage between observed concentration trends and emission control measures. Clarification and additional analyses addressing these issues would strengthen the trend attribution.*

Response: To avoid potential confusion, we have clarified that wintertime $f\text{-}NO_3^-$ overwhelmingly dominated the annual trend. The revised text reads (Section 3.4): "These higher concentrations during the five cold months contributed to 81% and 88% of the annual averages in 2015 and 2010, respectively. Thus, the annual trends in $f\text{-}NO_3^-$ were mainly determined by higher concentrations of $f\text{-}NO_3^-$ in cold months in Edmonton."

The PM$_{2.5}$ speciation data in Edmonton do not cover the period of major NO$_x$ emission reductions. To address this limitation, we incorporated dichotomous data from another monitoring site in Edmonton for additional analysis. However, these data do not include simultaneous HNO$_3$* measurements and therefore cannot support the mechanistic analysis. These points have been clarified in the revised manuscript.

8. *The random forest (RF) model identifies temperature, PM$_{2.5}$, and NO$_2$ as key drivers of daily f-NO$_3^-$ variability. However, the use of approximately 3,000 trees raises potential concerns about overfitting, which should be discussed. In addition, the inclusion of interaction analyses or partial dependence plots for major predictors (e.g., temperature and NO$_2$) would substantially enhance the interpretability and physical relevance of the RF results.*

Response: We appreciate this insightful comment and agree that the selection of the number of trees should be justified and that additional interpretability diagnostics can strengthen the robustness of the Random Forest (RF) analysis.

To address the potential concern of overfitting, we performed a sensitivity analysis in which the RF model was retrained using the same fixed 70/30 train–test split and identical model configurations (including the feature set, maximum depth, minimum node size, and other hyperparameters), varying only the number of trees. Test-set performance exhibited a clear plateau once the ensemble size exceeded several hundred trees. Specifically, the RMSE/MAE/R^2 values were 1.19/0.421/0.674 (500 trees), 1.18/0.421/0.676 (1000 trees), 1.18/0.420/0.675 (2000 trees), and 1.18/0.421/0.676 (3000 trees). These results demonstrate that increasing the number of trees beyond approximately 1000–2000 produces negligible changes in generalization performance and provides no evidence of degraded test performance attributable to ensemble size. Based on this stability, we revised the manuscript to adopt 1000 trees in the final RF model as a conservative, near-converged configuration.

In addition, partial dependence plots (PDPs) reveal a pronounced nonlinear relationship between predicted f-NO$_3^-$ and temperature, characterized by a sharp decline around 0 °C. In contrast, PM$_{2.5}$ and NO$_2$ exhibit threshold-like increases followed by saturation behavior, suggesting that cold conditions strongly favor particulate nitrate persistence, whereas the effects of overall pollution intensity and NO$_x$-related indicators are modulated and ultimately constrained by other limiting processes. These additional analyses and interpretations have been incorporated into the revised Text S2.

9. *Figures 1-4 share very similar structures and differ mainly by site, resulting in a degree of redundancy that reduces information density and visual clarity. The authors are encouraged to consider alternative visualization strategies, such as multi-panel figures, combined plots, or summary representations, to improve readability and overall presentation quality.*

Response: We have combined the original Figs. 1 and 2 into a new Fig. 1 and the original Figs. 3 and 4 into a new Fig. 2 in the revised manuscript.

10. *The meanings of the open circles and filled circles are inconsistent between Figures 1a and 1c, which may cause confusion for readers. The slanted lines shown in the figures appear to represent regression lines; however, this is not specified in the figure captions. The authors should explicitly clarify this in the captions to avoid ambiguity.*

Response: These Figures have been revised accordingly to ensure consistency.