Environment and
Climate Change Canada
Environnement et
Changement climatique Canada

February 26, 2026

Dear Editor of *Atmospheric Physic and Chemistry*,

We are submitting the revised manuscript (egusphere-2025-6080) titled "Novel insights on causes of disproportionate trends between particulate NO3- and NOx emissions in Canadian urban atmospheres" to *Atmospheric Physic and Chemistry* for possible publication.

We have carefully considered the comments provided by the three reviewers cand revised the manuscript accordingly, as explained in the attached *Response to Reviewers* file. Major changes in the revised manuscript are highlighted in yellow.

We hope you and the reviewers will find the paper meets the standard of this reputable journal.

Sincerely,

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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-NO_3^- emissions influence the annual-scale response of f-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-NO_3^- and total NO_3^- (=f-NO_3^-+c-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-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 $\mu g\ m^{-3}$ vs. 0.70 $\mu g\ m^{-3}$), 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 $\mu g\ m^{-3}$ in 2010 to 0.89 $\mu g\ m^{-3}$ 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 reevaluate 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-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-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-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-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-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-NO_3^- were mainly determined by higher concentrations of f-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.

Response to Referee #2

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 #2:

The diverse trends of air quality and emissions are always a big concern of atmospheric chemistry community, as they heavily highlighted the complex formation mechanisms of secondary aerosols, the varying emissions from multiple sources, and the difficulty of evaluating the benefit of emission controls on air quality. This work, relying mainly on long-term observation data of nitrate aerosols and estimation of NOX emissions, explored the disproportionate trends between particulate NO_3^- *and* NO_x *emissions in Canadian urban atmospheres. The main reasons were further identified as reduced primary f-*NO_3^- *emissions, localized dispersion, and Arctic Oscillation–modulated wind anomalies for Edmonton, and unintended enhancement of primary emissions of f-*NO_3^- *formed within stationary-combustion plumes for other cities. Although the analysis presented useful and valuable information, I personally think there remained some unclear issues that were insufficiently explained. I should acknowledge, as well, that the topic the authors wanted to stress is quite complicated and observation alone might not fully interpret the mechanisms.*

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 current work relied largely on or. As presented in figures, the analysis is somehow descriptive, and many judgments or hypothesis could not be validated. Therefore, my biggest concern is that the analysis might be improved with air quality modeling. Some numerical experiments might help better understanding the various responses of air quality to emission change.*

Response: We agree with the Referee that numerical air quality modeling can provide additional process-level constraints beyond an observation-based analysis, and that model experiments (e.g., emissions-perturbation and sensitivity simulations) would be valuable for quantitatively attributing the responses of particulate nitrate to emission changes. However, as emphasized in our response to a similar comment from Reviewer 1, the relative contributions of primary and secondary f-NO_3^- can only be quantitatively assessed through model-based sensitivity analyses after substantial improvements are made in both (i) the accuracy of emission inventories used as model inputs and (ii) the representation of key physical and chemical processes in three-dimensional (3-D) air quality models. Existing 3-D air quality models still show considerable uncertainty in simulating particulate NO_3^-, including its levels, variability, and responses to emission reductions. We therefore included a brief review of particulate NO_3^- modeling studies over Canada and the United States in the Supporting Information (Text S4) and summarized the key points in Section 3.6, which together highlight persistent limitations in current model performance.

Nevertheless, more explicit treatment of primary f-NO_3^- in emission inventories could facilitate future improvements in particulate NO_3^- simulations and associated sensitivity analyses. 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 $\mu g\ m^{-3}$ vs. 0.70 $\mu g\ m^{-3}$), 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."

2. *In abstract, the authors stated that "all cities exhibited a transient f-NO_3^- increase during 1998–2007, coincident with early NOx controls and consistent with unintended enhancement". Why early NOx controls could result in growth of f-$NO3^-$?*

Response: We have conducted a brief literature review to better interpret this phenomenon. Based on this review, the increase in f-NO_3^- during the early NO_x-control period occurred in both Canada and the United States, rather than in Canada alone, within that specific time window. Early NO_x control measures may have contributed to increased emissions of condensable particulate matter (CPM). However, routine measurements of CPM were not available before it was formally defined by the U.S. EPA in 2017 (U.S. EPA, 2017). Recent studies from developing countries may offer insight into this potential increase. For example, selective catalytic reduction of nitrogen oxides (NO_x) with ammonia (NH_3-SCR) has been implemented to comply with NO_x regulations for stationary and mobile sources operating at temperatures above 300 °C. Effective NO_x reduction requires precise ammonia injection, whereas early-stage controls may have suffered from imperfect dosing, as reported in China (Yang et al., 2016). Nevertheless, because routine measurements of condensable particulate emissions from stationary sources in Canada and the United States were largely unavailable prior to 2017, the underlying causes remain difficult to determine definitively.

We have summarized the above information and added into Section 3.3, which reads "These widespread, disproportionate trends between f-NO_3^- and NO_x emissions across multiple cities strongly suggest that, during this early control window, NO_x mitigation measures may have been accompanied by an unintended increase in primary f-NO_3^- emissions, potentially associated with condensable particulate matter (CPM) and/or byproducts of emission control technologies. However, no direct facility measurement data were made 20-year ago to verify this hypothesis. In fact, the USEPA only issued the method protocol for determining condensable particulate matter in 2017. Evidence from recent studies in developing countries further indicates that early-stage NO_x controls (e.g., NH_3-SCR operated at >300 °C) can be susceptible to imperfect ammonia dosing and the formation of associated byproducts (Yang et al., 2016). This provides a plausible mechanistic explanation, although the specific causes in Canada and the United States cannot be definitively determined in the absence of historical CPM measurements."

Reference mentioned above:

US EPA: Method 202—dry impinger method for determining condensable particulate emissions from stationary sources, Emission Measurement Center, Research Triangle Park, NC, USA, 2017.

Yang, L., Shi, Y., and Luo, L.: Review of emission characteristics of fine particles during coal-fred SCR DeNOx process, Proc. Chin. Soc. Electr. Eng., 36, 4342-4348, 2016.

3. *I suggest a more comprehensive review on the diverse trends of emissions and nitrate aerosol concentration, for both Canada and other countries with fast changing emissions. The topic is interesting and important but not clearly explored. Comparison between Canada and other countries might provide some useful information for interpreting the diverse trends.*

Response: To address this comment, we have expanded the literature review in the revised manuscript to more comprehensively examine the diverse trends in precursor emissions (e.g., NO_x, SO_2, and NH_3) and particulate nitrate concentrations, both in Canada and in other regions undergoing rapid emission changes. Specifically, we added a cross-regional comparison synthesizing evidence from North America (Canada and the United States), Europe, and China to highlight the frequently non-linear and region-specific responses of particulate NO_3^- to emission control measures.

The revised text in the Introduction reads as follows: "The aforementioned knowledge gap hinders our understanding of how changes in primary f-NO_3^- emissions influence the annual-scale response of f-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-NO_3^- and total NO_3^- (=f-NO_3^-+c-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-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."

4. *For Edmonton, the comparison was conducted for observation at individual sites and provincial-level emissions. Could the two urban sites be representative for the regional emission trends? In general, the urban air quality can be more strongly affected by the local emissions while provincial-level emissions are more regional representative. I guess some discussions should be added*

Response: To address this limitation, we further examined the correlations between NO_2 mixing ratios measured at an urban site in each city and provincial-level NO_x emissions to assess the consistency of their temporal trends. In Edmonton, the significant correlation between these variables, together with the more pronounced decline in NO_2 mixing ratios, suggests that NO_x mitigation within the city is aligned with, and potentially more stringent than, measures implemented at the provincial level. Given that mitigation policies are often enforced more rigorously in urban areas than across an entire province, we incorporated both NO_2 mixing ratio and NO_x emission trends in our comparisons with f-NO_3^-.

These clarifications have been incorporated into Section 3.1 and Section 3.4. The newly added text in Section 3.1 reads: "Notably, NO_2 mixing ratios at the urban site were significantly correlated with Alberta's total provincial NO_x emissions, with $R^2 = 0.81$ over 1997–2019 ($P < 0.01$) and a slightly weaker correlation ($R^2 = 0.57$) over the shorter period of 2007–2019 ($P < 0.01$). These results indicate broadly consistent NO_x mitigation signals at both the provincial and city scales." The revised text in Section 3.4 reads: "From 2010 to 2015, the decrease in NO_2 mixing ratios in Edmonton (11%) was consistent with the decline in Alberta's provincial NO_x emissions (10%). In contrast, the annual mean concentration of f-NO_3^- decreased much more sharply (by 58%), falling from 2.1 μg m^{-3} in 2010 to 0.89 μg m^{-3} in 2015."

5. *The authors made analysis between NO_X emission change and nitrate aerosols. The diverse trends, could also be affected by the changing emissions of other species like SO2 and NH3. I think this issue should also be more carefully analyzed given the interactions between different species. Again, models might be involved to provide more insights.*

Response: Wintertime f-NO_3^- was much higher than in the other seasons and largely dominated the annual trend. In winter, SO_4^{2-} concentrations in $PM_{2.5}$ were substantially lower than NO_3^- concentrations and were therefore less likely to influence the latter. The mass ratios between NO_3^- and SO_4^{2-} in $PM_{2.5}$ ranged from 1.5 to 12, with a median value of 5.5. As shown in our previous study (Yao and Zhang, 2019), atmospheric NH_3 increased across Canada, while the amount consumed to neutralize SO_4^{2-} and NO_3^- in $PM_{2.5}$ decreased, strongly suggesting that NH_3 is abundant and unlikely to be the limiting factor for NO_3^- in $PM_{2.5}$. This information has been added into Section 3.6, which reads: "In the literature (Text S1 of SI), changes in atmospheric NH_3 and f-SO_4^{2-} have been reported to influence long-term trends in f-NO_3 to some extent. However, evidence of increasing atmospheric NH_3 in Canada, together with reduced NH_3 consumption for neutralizing the two major inorganic acids, suggests that NH_3 is generally abundant and unlikely to be the limiting factor for f-NO_3^- formation (Yao and Zhang, 2019). Consistent with this interpretation, large f-NO_3^-/f-SO_4^{2-} mass ratios are frequently observed in high-f-NO_3^- samples during the cold season across Canada. For example, in Edmonton in 2010, samples with f-NO_3^- > 4 μg m^{-3} exhibited f-NO_3^-/f-SO_4^{2-} mass ratios ranging from 1.5 to 12, with a median of 5.5. These results indicate that the elevated f-NO_3^- concentrations overwhelmingly dominated its long-term trend. In such cases, the slight decrease in f-SO_4^{2-} may exert only a minor influence on the trend in f-NO_3^-. Nevertheless, these complex interactions warrant further investigation using three-dimensional (3-D) air quality modelling; however, such efforts remain challenging, as illustrated below."

We agree that 3-D CTM modeling remains necessary to rigorously quantify this issue. Such efforts should incorporate updated emission inventories that explicitly account for primary particulate nitrate (f-NO_3^-), and be supported by additional measurements of condensable particulate matter from diverse combustion plumes across a range of sub-zero ambient temperatures. To provide broader context, we conducted a literature review of particulate NO_3^- modeling studies in Canada and the United States. This review, included in the Supporting Information (Text S5), underscores the substantial challenges associated with accurately predicting particulate NO_3^- concentrations in this region. The key points from this review are summarized in the revised manuscript (Section 3.6), which reads: "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."

We believe this issue may be alleviated as primary f-NO_3^- becomes better recognized, quantified, and incorporated into updated emission inventories.

Reference mentioned above:

Yao, X. and Zhang, L.: Causes of large increases in atmospheric ammonia in the last decade across North America, ACS omega, 4, 22133-22142, 2019.

6. *Is there any strong evidence that primary f-NO_3^- emissions were declining for Edmonton?*

Response: For this issue, two statistics may serve as strong evidence across Canadian cities, i.e., the use of alternative energy in electricity supply and the percentage of electric vehicles in all registered vehicles. 1) Over 2000–2020, increasing use of alternative energy contributed to an approximately 60% decline in CO_2 emissions from Canada's electricity sector. At present, more than 80% of Canada's electricity supply is from CO_2-emission-free sources (Canada Electricty Advisory Council, 2024). This CO_2-emission-free electricity should also be NO_x-emission-free and, accordingly, should reduce primary f-NO_3^- emissions. 2) According to Statistics Canada data (https://www.statcan.gc.ca/en/start), more than 184,000 new electric vehicles were registered in 2023, accounting for ~10.8% of all new motor-vehicle registrations that year—substantially higher than in 2017 (19,696 electric vehicles) and 2019 (56,165). The expanding population of zero-emission vehicles should reduce primary f-NO_3^- emissions in Canadian cities.

The weaker decrease in f-NO_3^- relative to NO_x emissions has been widely reported in the literature. If the explanations previously used to interpret those weak decreases are correct, then the stronger decrease in f-NO_3^- relative to NO_2 concentrations over the last decade in Edmonton would suggest one remaining possibility: a decline in primary f-NO_3^- emissions there.

These clarifications have been added into Section 3.3, which reads: "In contrast to this early-phase behavior, several lines of evidence suggest that primary f-NO_3^- emissions have likely declined in recent years. At the national scale, Canada's electricity supply has shifted markedly toward CO_2-emission-free sources (now exceeding 80%), which are also largely free of NO_x emissions. This transition should reduce primary nitrate-related emissions from the power sector (Canada Electricity Advisory Council, 2024). In addition, the rapidly increasing share of zero-emission vehicles, accounting for 10.8% of new vehicle registrations in 2023, is expected to further decrease primary f-NO_3^- emissions from the transportation sector (Statistics Canada, 2024). Consistent with these broader trends, observations in Edmonton show that the decline in annual mean f-NO_3^- concentrations over the past decade has been substantially larger than the corresponding decrease in NO_2. This divergence supports the interpretation that reductions in primary f-NO_3^- emissions have likely been an important contributing factor."

Response to Nima Zafarmomen

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

Comments from Nima Zafarmomen:
This study presents a comprehensive long-term (1990–2019) analysis of fine- and coarse-mode particulate nitrate (f-NO_3^- and c-NO_3^-) in seven Canadian urban atmospheres using NAPS observations. The authors identify systematic, disproportionate trends between particulate nitrate concentrations and NO_x emission reductions, particularly in cold-climate cities. Despite modest declines in provincial NO_x emissions (typically 10–30%), f-NO_3^- concentrations decreased by up to ~60–70% in recent decades, while c-NO_3^- remained largely insensitive to NO_x controls.

Primary f-NO_3^- emissions hypothesis: The explanation is physically plausible and well-argued, but remains indirect. The manuscript would benefit from clearer discussion of how future studies (e.g., near-source plume measurements or isotopic constraints) could directly validate this mechanism.

Response: We acknowledge that our primary f-NO_3^- hypothesis is presently supported largely by indirect evidence. To address this limitation, we have strengthened the revised manuscript by (i) explicitly recognizing the absence of historical facility-level measurements of condensable particulate matter (CPM) prior to the implementation of the U.S. EPA Method 202 protocol (2017), and (ii) incorporating a forward-looking discussion outlining how future studies could directly test and potentially validate or falsify the proposed mechanism.

The discussion of indirect evidence has been incorporated into Section 3.3 and reads as follows: "These widespread, disproportionate trends between f-NO_3^- and NO_x emissions across multiple cities strongly suggest that, during this early control window, NO_x mitigation measures may have been accompanied by an unintended increase in primary f-NO_3^- emissions, potentially associated with condensable particulate matter (CPM) and/or byproducts of emission control technologies. However, no direct facility measurement data were made 20-year ago to verify this hypothesis. In fact, the USEPA only issued the method protocol for determining condensable particulate matter in 2017. Evidence from recent studies in developing countries further indicates that early-stage NO_x controls (e.g., NH_3-SCR operated at >300 °C) can be susceptible to imperfect ammonia dosing and the formation of associated byproducts (Yang et al., 2016). This provides a plausible mechanistic explanation, although the specific causes in Canada and the United States cannot be definitively determined in the absence of historical CPM measurements. Accordingly, trend analysis of particulate nitrate should treat this period separately, with a demarcation line drawn at approximately 2002 or later.

In contrast to this early-phase behavior, several lines of evidence suggest that primary

$f\text{-}NO_3^-$ emissions have likely declined in recent years. At the national scale, Canada's electricity supply has shifted markedly toward CO_2-emission-free sources (now exceeding 80%), which are also largely free of NO_x emissions. This transition should reduce primary nitrate-related emissions from the power sector (Canada Electricity Advisory Council, 2024). In addition, the rapidly increasing share of zero-emission vehicles, accounting for 10.8% of new vehicle registrations in 2023, is expected to further decrease primary $f\text{-}NO_3^-$ emissions from the transportation sector (Statistics Canada, 2024). Consistent with these broader trends, observations in Edmonton show that the decline in annual mean $f\text{-}NO_3^-$ concentrations over the past decade has been substantially larger than the corresponding decrease in NO_2. This divergence supports the interpretation that reductions in primary $f\text{-}NO_3^-$ emissions have likely been an important contributing factor."

The revised forward-looking text has been added to Section 4 and reads as follows: "Collectively, these findings call for a paradigm shift in air quality management. Effective mitigation strategies must explicitly address primary particulate nitrate sources, incorporate gas–particle partitioning dynamics under cold-climate conditions, and account for interactions with alkali-containing aerosols. Policy frameworks should further prioritize enhanced real-time measurements of $PM_{2.5}$ chemical composition to better resolve localized and seasonal variability, particularly in regions experiencing prolonged winter conditions. In parallel, coordinated unmanned aerial vehicle (UAV) and ground-based observations of CPM under contrasting temperature and atmospheric dispersion regimes are essential to provide direct observational evidence of its role and contributions."

HNO_3 measurements: The clarification that denuder-based HNO_3 represents an upper bound (HNO_3 + N_2O_5) is important and appropriately handled. Consider briefly discussing how this uncertainty might bias wintertime interpretations (even qualitatively).*

Response: We agree that denuder-based HNO_{3gas}* measurements should be interpreted as an upper bound of total gaseous nitrate ($HNO_3 + N_2O_5$), and we have added a brief clarification regarding the potential qualitative bias under winter conditions. Importantly, this uncertainty does not materially affect our analysis as HNO_{3gas}* concentrations are consistently much lower than the corresponding particulate nitrate levels during the high-nitrate winter periods examined here. Thus, our principal conclusions do not depend on precise gas–particle partitioning of total nitrate. Nevertheless, the upper-bound nature of HNO_{3gas}* may bias any gas–particle equilibrium inference, particularly during winter nighttime high-concentration episodes, when the true HNO_3 mixing ratio may be substantially lower than HNO_{3gas}* due to a potentially significant N_2O_5 contribution. For this reason, we did not conduct a quantitative gas–particle partitioning (equilibrium) analysis based on HNO_{3gas}* and explicitly acknowledged this limitation in the revised Section 2.1, as follow: "Importantly, this measurement uncertainty does not materially affect the conclusions of the present study, as HNO_{3gas}* concentrations remain substantially lower than the corresponding particulate nitrate levels during the high-nitrate winter periods examined here (see Section 3.4). Nevertheless, the upper-bound nature of HNO_{3gas}* may introduce bias in gas–particle equilibrium analyses, particularly during winter nighttime high-concentration episodes, when the true HNO_{3gas} mixing ratio may be considerably lower than HNO_{3gas}* due to a potentially substantial contribution from N_2O_5(g)."

Given the study's emphasis on spatial inhomogeneity and the impact of localized urban sources (as discussed in Category ii uncertainties, Section 3.6), it is essential to contextualize these findings within the broader framework of high-resolution urban monitoring.

Response: In fact, pronounced intra-urban heterogeneity has been widely documented for most ionic aerosol components: not only nitrate, but also many other major ions, whereas sulfate typically exhibits a more regional character. Long-term, high-resolution measurements of PM chemical composition within urban cores would therefore be highly valuable, where resources permit, to better resolve localized sources, seasonal contrasts, and representativeness limitations that may not be fully captured by fixed monitoring sites. At the same time, we acknowledge an important practical constraint: compared with routine PM mass monitoring, chemical speciation measurements entail substantially higher capital and operational costs, including instrumentation, consumables, and maintenance. These requirements make sustained, high-resolution, long-term deployment considerably more challenging.

We have added this contextual discussion to Section 3.6 to clarify both the scientific motivation and practical feasibility, which reads: "More broadly, pronounced intra-urban spatial heterogeneity has been documented for many ionic aerosol components (with sulfate generally exhibiting a more regional character), underscoring the importance of high-resolution urban monitoring for interpreting long-term trends. At the same time, compared with routine PM mass measurements, sustained long-term, high-resolution chemical speciation monitoring requires substantially greater investment in instrumentation, maintenance, and operational resources, making such measurements more challenging to maintain over multi-year periods. This practical limitation highlights the need to carefully consider site representativeness and spatial heterogeneity when interpreting long-term nitrate trends derived from fixed-site observations."

I strongly suggest citing the following paper to bolster the discussion on how localized traffic and industrial emissions create complex urban aerosol patterns that traditional stationary sites might struggle to represent: Comprehensive spatiotemporal analysis of long-term mobile monitoring for traffic-related particles in a complex urban environment. > DOI: 10.1016/j.apr.2025.102870

Response: The recommended reference (Yeganeh et al., 2025) has been added in Section 3.6 in the revised manuscript.