

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 NO_x emissions, explored the disproportionate trends between particulate NO₃⁻ and NO_x emissions in Canadian urban atmospheres. The main reasons were further identified as reduced primary f-NO₃⁻ emissions, localized dispersion, and Arctic Oscillation–modulated wind anomalies for Edmonton, and unintended enhancement of primary emissions of f-NO₃⁻ 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 NO₃⁻ emissions in influencing NO₃⁻ pollution and its long-term trends, based on the following considerations:

(1) The formation of primary f-NO₃⁻ and its effects on NO₃⁻ 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-NO₃⁻, 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 NO₃⁻ will remain substantially constrained.

(3) Given the current state of knowledge and data availability, the importance of primary f-NO₃⁻—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-NO₃⁻ 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-NO₃⁻ 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 NO₃⁻, including its levels, variability, and responses to emission reductions. We therefore included a brief review of particulate NO₃⁻ 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-NO₃⁻ in emission inventories could facilitate future improvements in particulate NO₃⁻ 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 NO₃⁻ 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 NO₃⁻ 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} NO₃⁻ 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.”

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

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., NH₃-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-fired SCR DeNO_x 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, SO₂, and NH₃) 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 NO₃⁻ 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-NO₃⁻ emissions influence the annual-scale response of f-NO₃⁻ to NO_x emission reductions. This gap appears to be global rather than unique to Canada, as indicated by the brief review of particulate NO₃⁻ 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 NO₃⁻ across Canada, including f-NO₃⁻ and total NO₃⁻ (=f-NO₃⁻+c-NO₃⁻) in suspended particles, suggest that long-term changes are neither spatially uniform nor monotonic. (2) The non-linear and sometimes counterintuitive response of particulate NO₃⁻ 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-NO₃⁻ 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 (NO₃⁻) and sulfate (SO₄²⁻) 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 (NH₄⁺) (Jeong et al., 2020). In contrast, in Edmonton (2007–2014), neither PM_{2.5} nor the major inorganic ions (NO₃⁻, SO₄²⁻, NH₄⁺) 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 NO₃⁻ 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 SO₄²⁻ and NO₃⁻ responses becomes clearer at the eastern North American scale. During 1990–2015, SO₂ 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, SO₄²⁻ and NH₄⁺ in TSP decreased substantially (-73.3% and -67.4%), whereas NO₃⁻ decreased by only -29.1% (largely after 2000), indicating that NO₃⁻ responds more weakly and more conditionally to emission controls than SO₄²⁻ and NH₄⁺.

Winter-focused analyses further illustrate why NO₃⁻ 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 SO₂ (-58%) and NO_x (-35%) emissions, winter PM_{2.5} NO₃⁻ showed little change. Similarly, a detailed analysis at paired urban and rural sites in Rhode Island (northeastern U.S.) reported pronounced increases in NO₃⁻ in PM₁₀ (particle < 10 μm) during 2005–2015 (+95% urban; +57% rural) despite substantial SO₂ 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 NO₃⁻ across the eastern U.S. For example, NO₃⁻ 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, NO₃⁻ 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 NH₃ during 2000–2019. Correspondingly, particulate SO₄²⁻ in TSP declined at ~3–4% yr⁻¹, whereas total

nitrate ($\text{HNO}_{3\text{gas}} + \text{particulate NO}_3^-$) decreased more slowly at $\sim 1.5\text{--}2\%$ 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, $\text{PM}_{2.5}$ NO_3^- increased by $\sim 28\%$, accompanied by a $\sim 30\%$ 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-NO₃⁻ 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-NO₃⁻ was much higher than in the other seasons and largely dominated the annual trend. In winter, SO₄²⁻ concentrations in PM_{2.5} were substantially lower than NO₃⁻ concentrations and were therefore less likely to influence the latter. The mass ratios between NO₃⁻ and SO₄²⁻ 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 NH₃ increased across Canada, while the amount consumed to neutralize SO₄²⁻ and NO₃⁻ in PM_{2.5} decreased, strongly suggesting that NH₃ is abundant and unlikely to be the limiting factor for NO₃⁻ 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 NH₃ and f-SO₄²⁻ have been reported to influence long-term trends in f-NO₃ to some extent. However, evidence of increasing atmospheric NH₃ in Canada, together with reduced NH₃ consumption for neutralizing the two major inorganic acids, suggests that NH₃ is generally abundant and unlikely to be the limiting factor for f-NO₃⁻ formation (Yao and Zhang, 2019). Consistent with this interpretation, large f-NO₃⁻/f-SO₄²⁻ mass ratios are frequently observed in high-f-NO₃⁻ samples during the cold season across Canada. For example, in Edmonton in 2010, samples with f-NO₃⁻ > 4 µg m⁻³ exhibited f-NO₃⁻/f-SO₄²⁻ mass ratios ranging from 1.5 to 12, with a median of 5.5. These results indicate that the elevated f-NO₃⁻ concentrations overwhelmingly dominated its long-term trend. In such cases, the slight decrease in f-SO₄²⁻ may exert only a minor influence on the trend in f-NO₃⁻. 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-NO₃⁻), 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 NO₃⁻ 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 NO₃⁻ 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 NO₃⁻ 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 $\text{PM}_{2.5} \text{NO}_3^-$ over the U.S. ($1.89 \mu\text{g m}^{-3}$ vs. $0.70 \mu\text{g m}^{-3}$), 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.”

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 Electricity 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-NO₃⁻ emissions in Canadian cities.

The weaker decrease in f-NO₃⁻ 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-NO₃⁻ relative to NO₂ concentrations over the last decade in Edmonton would suggest one remaining possibility: a decline in primary f-NO₃⁻ 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-NO₃⁻ emissions have likely declined in recent years. At the national scale, Canada’s electricity supply has shifted markedly toward CO₂-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-NO₃⁻ emissions from the transportation sector (Statistics Canada, 2024). Consistent with these broader trends, observations in Edmonton show that the decline in annual mean f-NO₃⁻ concentrations over the past decade has been substantially larger than the corresponding decrease in NO₂. This divergence supports the interpretation that reductions in primary f-NO₃⁻ emissions have likely been an important contributing factor.”