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-NO₃⁻ and c-NO₃⁻) in seven Canadian urban atmospheres using NAPS observations. The authors identify systematic, disproportionate trends between particulate nitrate concentrations and NOₓ emission reductions, particularly in cold-climate cities. Despite modest declines in provincial NOₓ emissions (typically 10–30%), f-NO₃⁻ concentrations decreased by up to ~60–70% in recent decades, while c-NO₃⁻ remained largely insensitive to NOₓ controls.

Primary f-NO₃⁻ 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-NO₃⁻ 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-NO₃⁻ and NOₓ emissions across multiple cities strongly suggest that, during this early control window, NOₓ mitigation measures may have been accompanied by an unintended increase in primary f-NO₃⁻ 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 NOₓ 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. 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-NO₃⁻ 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-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 NO_2. This divergence supports the interpretation that reductions in primary f-NO₃⁻ 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."

HNO₃* measurements: The clarification that denuder-based HNO₃ represents an upper bound (HNO₃ + N₂O₅) 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.