Novel insights on causes of disproportionate trends between particulate NO_3^- and NO_x emissions in Canadian urban atmospheres

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Abstract. Particulate nitrate (NO_3^-) is a key target for air pollution control; however, its response to NO_x emission reductions remains uncertain, particularly in cold climates. This study assesses long-term trends in fine- and coarse-mode NO_3^- (f-NO_3^- and c-NO_3^-) from 1990 to 2019 across seven Canadian cities, using data from by the National Air Pollution Surveillance (NAPS) network. The analysis reveals disproportionate trends between NO_3^- and NO_x emissions nationwide. In Edmonton, annual mean f-NO_3^- decreased by approximately 60% between 2007 and 2019, while provincial NO_x emissions declined by only 10–20%. Similar patterns were observed in five of the six other cities during the most recent decade. These disproportionate trends are attributed to reductions in primary f-NO_3^- emissions, localized dispersion processes, and wind anomalies modulated by Arctic Oscillation. In contrast, all cities exhibited a temporary increase in f-NO_3^- during 1998–2007, coinciding with early NO_x control measures and consistent with an unintended enhancement of primary f-NO_3^- emissions formed within stationary combustion plumes. c-NO_3^- was largely insensitive to NO_x reduction in most cities (except for Edmonton), with variability governed primarily by neutralization reactions with alkaline aerosols rather than by the availability of gaseous HNO_3. These findings provide insight into the weak or absent response of f-NO_3^- to NO_x emission reductions observed globally, particularly in cold-climate regions.

Keywords: particulate nitrate, primary nitrate emission, decadal trends, NO_x emission reduction

1 Introduction

Particulate nitrate (NO_3^-) has been a central focus of pollution control strategies in the past several decades due to its impact on air quality, climate, and ecosystem health (Balamurugan et al., 2022; Bell et al., 2007; Chan et al., 2021; Cheng et al., 2024; Dabek-Zlotorzynska et al., Dang et al., 2024; 2011; Duce et al., 2008; Font et al., 2024; Harrison et al., 2022; Man et al., 2015; Pullokaran et al., 2024; Squizzato et al., 2018; Sun et al., 2025; Thunis et al., 2021; Wang et al., 2020; Zaveri et al., 2021; Zhai et al., 2021; Zhang et al., 2008; Zhou et al., 2022). NO_3^- impacts air quality because it is a major chemical component of particulate matter, particularly fine particles. Besides, photolysis of NO_3^- produces highly reactive oxidants, such as hydroxyl radicals, HOCl, and Cl_2, thereby enhancing atmospheric oxidation capacity (Chen et al., 2025; Gen et al., 2022; Peng et al., 2022). NO_3^- contributes to climatic effects directly through radiative forcing and indirectly through increasing cloud condensation nuclei (Drugé et al., 2019; Zaveri et al., 2021). For instance, a modeling study showed that nitrate aerosols contributed significantly to shortwave radiative cooling, reaching up to -5 W m^{-2} on a regional scale under clear-sky condition and -0.8 W m^{-2} on global average (Zaveri et al., 2021). NH_4NO_3 formed from condensation of gaseous species of NH_3 and HNO_3 can rapidly grow to the sizes of cloud condensation nuclei in cold atmospheres (Höpfner et al., 2019; Wang et al., 2022; Zhu et al., 2014). Additionally, NO_3^- contributes to atmospheric nitrogen deposition, which has ecosystem implications (Bose et al., 2018; Iizuka et al., 2025), and it can even undergo long-range transport in the atmosphere and eventually deposit into oceans or remote continental regions (Iizuka et al., 2025; Jonson et al., 2022; Qi et al., 2018).

Given the significant reductions of SO_2 emissions worldwide in the past four decades, the impacts of NO_3^- on air quality, climate, and ecosystem health have garnered increasing attention (Aas et al., 2019; Feng et al., 2020; Hand et al., 2024; Sun et al., 2018; Velazquez-Garcia et al., 2023; Wang et al., 2021; Zhai et al., 2021). Unlike sulfate (SO_4^{2-}), which predominantly exists in fine particulate matter ($PM_{2.5}$), NO_3^- exists in both fine- and coarse-mode particles (referred to as f-NO_3^- and c-NO_3^-,

respectively). As a semi-volatile substance, the fine and coarse fractions of NO_3^- vary with season and location (Peng et al., 2024; Yao and Zhang, 2012a, b; Zhang et al., 2008) because its volatility and partitioning with its gaseous precursors are influenced by ambient meteorological and chemical conditions, including temperature (T), relative humidity (RH), and mixing ratios of HNO_3 and NH_3 (Guo et al., 2016; Huo et al., 2025; Seinfeld and Pandis, 2016; Yao et al., 2003). This complicates the response of f-NO_3^- and c-NO_3^- to changes in NO_x emissions (Balamurugan et al., 2022; Chan et al., 2021; Huo et al., 2025; Thunis et al., 2021; Zhai et al., 2021). Additionally, reduced NO_x emissions may enhance the formation of N_2O_5 at nighttime, a product that can form f-NO_3^- through secondary aerosol formation, thereby further influencing the response of f-NO_3^- to emission reductions (Fan et al., 2020; Shah et al., 2018; Wang et al., 2023; Ward et al., 2025; Yan et al., 2023; Zhou et al., 2022). It has been reported that f-NO_3^- can form from condensable species in fresh stationary combustion plumes, followed by dispersion and evaporation under freezing ambient conditions (Shen et al., 2022; USEPA, 2017; Xiao et al., 2025; Yang et al., 2024). This mechanism has been largely overlooked in studies examining the response of NO_3^- to NO_x emission reductions, particularly in regions with prolonged cold seasons.

Canada is a nation experiencing long cold winters. Higher concentrations of f-NO_3^- were predominantly observed during cold winter seasons, except during large-scale wildfire events mostly occurring in warm seasons (Bari and Kindzierski, 2016a, b; Dabek-Zlotorzynska et al., 2011; Edgerton et al., 2020; Jeong et al., 2011; Wang et al., 2021). The contributions of primary and/or secondary sources to the elevated f-NO_3^- concentrations in Canadian cold atmospheres remain poorly understood. The primary emissions of f-NO_3^- likely arise from two major processes: (i) the rapid formation of f-NO_3^- through reactions between HNO_{3gas} and NH_{3gas} within the first few seconds after combustion plumes exit the stack outlet (or vehicle exhaust pipes) and undergo cooling; and (ii) the formation of f-NO_3^- via the reaction $2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$ within droplets produced in fresh cooling combustion plumes, followed by NH_{3gas} neutralization before these droplets evaporate into ambient aerosols. Note that the fresh

plumes contain extremely high concentrations of various air pollutants, enabling the occurrence of the above-mentioned reactions (Seinfeld and Pandis, 2016; Zhang et al., 2021; Zhang et al., 2023).

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.

Additionally, significant decreases in NO_x emissions across Canada mainly occurred between 1998 and 2008, with slight time shifting across different provinces (ECCC, 2021). $PM_{2.5}$ speciation data since 2003 alone may not fully elucidate the response of NO_3^- to reduced NO_x emissions. Fortunately, both f-NO_3^- and c-NO_3^- data are available from the National Air Pollution Surveillance (NAPS) at 12 urban sites (Dabek-Zlotorzynska et al., 2011; Dabek-Zlotorzynska et al., 2019). Seven of these 12 sites have integrated measurements of particulate chemical components spanning 1-3 decades, enabling the examination of long-term trends in f-NO_3^- and c-NO_3^- in Canadian urban atmospheres and their responses to reduced NO_x emissions.

In this study we investigated long-term trends in the annual average mass concentrations of f-NO_3^- and c-NO_3^- in Canadian urban atmospheres, with a particular focus on the responses of f-NO_3^- and c-NO_3^- to NO_x emission reductions since 1990 and the associated mechanisms. The analyses are structured into three major parts: Part 1 examines the long-term trends of f-NO_3^- and c-NO_3^-, firstly in Edmonton (Section 3.1) and then extended the other six cities (Sections 3.2 and 3.3); Part 2 investigates the key factors influencing f-NO_3^- levels in Edmonton (Section 3.4) and the role of primary f-NO_3^- emissions in shaping these trends (Section 3.5); and Part 3 provides a comprehensive assessment of uncertainties associated with f-NO_3^- and their potential impact on the observed trends (Section 3.6). Finally, a summary of the major findings and potential implications are presented in Section 4.

2 Methodology

2.1 Monitoring sites and data sources

The present study utilized long-term data monitored at two urban sites in Edmonton (S-90132, Latitude: 53.486, Longitude: -113.465; and S-90130, Latitude: 53.544, Longitude: -113.499), as well as one urban site in each of the other six cities, including Winnipeg (49.898, -97.147), Victoria (48.442, -123.363), Vancouver (49.281, -122.849), Montreal (45.543, -75.572), Quebec City (46.821, -71.221), and Hamilton (45.258, -79.862) (Figures S1 and S2). The first four cities are in western Canada with Edmonton in the province of Alberta, Winnipeg in the province of Manitoba, and Victoria and Vancouver in the province of British Columbia. The other three cities are in eastern Canada with Montreal and Quebec City in the province of Quebec and Hamilton in the province of Ontario.

In Edmonton, at the S-90132 site speciation $PM_{2.5}$ samplers have been used since 2007 to measure mass concentrations of $PM_{2.5}$, ionic concentrations in $PM_{2.5}$, and the levels of acidic and alkaline gases, with 24-h integrated sampling occurring one in every three days (Bari and Kindzierski, 2016a, b). At the S-90130 site, ionic species, including

NO_3^-, SO_4^{2-}, NH_4^+, Na^+, and various elements in both $PM_{2.5}$ and $PM_{2.5-10}$ were collected using Dichotomous Air Samplers (Thermo, US), with 24-h integrated sampling occurring one in every six days during 1986-2005. Since no emission data were available before 1990, only the data after 1990 were included in this study. The ionic data were missing in 2006 at both sites. Note that the identical Dichotomous Air Samplers were also used at S-90132 for several years to collect $PM_{2.5}$, though no ionic data, for comparison purpose. Both datasets were included because neither alone covers the primary NO_x mitigation period in Edmonton.

In Hamilton, an identical speciation sampler has been used since 2013 to measure ionic components in $PM_{2.5}$ and gases, with sampling occurring one in every three days. In this city, only elements have been measured in samples collected by the Dichotomous Air Sampler since then. At the other five urban sites selected for this study, speciation $PM_{2.5}$ data were either unavailable (Winnipeg and Quebec City) or collected one in every six days after 2005 (Victoria, Vancouver, and Montreal). $PM_{2.5}$ air samplers (Thermo, US) were used in Victoria and Winnipeg after 2012, and $PM_{2.5}$ samplers (TISCH, US) were used in Vancouver and Montreal after 2016. Corresponding NO_3^- data in $PM_{2.5-10}$ were not available at these sites since then. In this study, NO_3^- in $PM_{2.5}$ collected by speciation samplers was also referred to as f-NO_3^-. The same definition is applied to f-SO_4^{2-} and f-NH_4^+, which were used to facilitate the analysis of f-NO_3^-.

Hourly average mass concentrations of $PM_{2.5}$ and mixing ratios of NO_2 were also routinely measured at each site, except that no NO_2 mixing ratios were reported at S-90132. In this case, the values from S-90130 were used in this study. For certain parts of the year at the sites in Victoria and Quebec City, NO_2 mixing ratios were also unavailable. In these cases, the mixing ratios of NO_2 measured at different sites within a 1-2 km radius in the same city were used to facilitate the analysis. All the data are publicly available through the National Air Pollution Surveillance (NAPS) program network (https://data-donnees.ec.gc.ca/data/air/monitor/national-air-pollution-surveillance-naps-program/?lang=en) and summarized in Table S1.

NO_x, SO_2, and NH_3 emissions data at the provincial level in Canada were obtained from https://www.canada.ca/en/environment-climate-change/services/environmental-indicators/air-pollutant-emissions.html. The monthly average wind fields were downloaded from https://psl.noaa.gov/data/gridded/data.narr.html (Figures 1 and S1), and the Arctic Oscillation (AO) Indexes were obtained from https://www.ncdc.noaa.gov/teleconnections/ao/ (Figure S1d). Ground-level meteorological data from the airports of these cities were also downloaded from https://www.wunderground.com/about/data.

It should be noted that existing techniques for measuring ambient HNO_{3gas} are subject to certain artifacts. Specifically, the Na_2CO_3-coated denuder used in speciation samplers is designed to remove acidic gases upstream of $PM_{2.5}$ collection on a Teflon filter, thereby minimizing positive artifacts in the collected $PM_{2.5}$ (Dabek-Zlotorzynska et al., 2011, 2019). However, measurements obtained using the denuder technique do not exclusively represent HNO_{3gas}. Instead, they include HNO_{3gas}, N_2O_{5gas}, and other acidic gases that react with Na_2CO_3 to form $NaNO_3$. Consequently, the reported concentrations reflect an upper bound of (HNO_{3gas} + N_2O_{5gas}). To avoid ambiguity, the measured values are denoted as HNO_{3gas}* rather than HNO_{3gas} throughout the following discussion. 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_{5gas}.

2.2 Statistical analysis

Annual average mass concentrations of f-NO_3^- and c-NO_3^- were calculated from all available data in each calendar year. However, data loss was common in each city and year despite sampling occurring one in every three or six days. To minimize uncertainty from data loss and ensure sufficient data for trend analysis, data for trend analysis were excluded for any year when measurements for two consecutive months were unavailable. To analyze the time series of the annual average mass concentrations of each species, the Mann-Kendall (M-K) analysis was employed. The qualitative trend results determined by the M-K method include: (i) an increasing/decreasing trend with a P value of <0.05, (ii) a probable increasing/decreasing trend with a P value between 0.05 and 0.1, (iii) a stable trend with a P value >0.1, as well as a ratio of <1.0 between the standard deviation and the mean of the dataset, and (iv) a no trend with a P >0.1 and other conditions (Lin et al., 2022).

To quantify the overall effect of climate anomalies on the annual average f-NO_3^- between a pair of two years, our recently developed identical-percentile regression analysis was used (Lin et al., 2022; Yao and Zhang, 2024). In this method, the data sizes of the paired two-year should be the same (e.g., with the same time resolution and filling up all the missing data). The two sets of data, originally in time series, are sorted separately from the smallest to the largest to generate two percentile-based data arrays, which were then used for regression analysis with the intercept being set to be zero. The regression analysis can also be conducted using data in any particular percentile range for exploring different research targets. If the data sizes of the paired two-year are different, the one with a larger size can be modified to match the one with a smaller size using the method presented by Lin et al. (2022) and Yao and Zhang (2024) before applying the regression analysis described above. Moreover, a Random Forest (RF) model was employed to evaluate the relative importance of meteorological and seasonal timing variables in driving f-NO_3^- formation (Text S2 of SI), and the Flexible 0-D

Atmospheric Model (F0AM) was applied to simulate secondary production of f-NO_3^- (Text S3 of SI).

3 Results and discussion

3.1 Complexity of particulate nitrate trends in urban atmosphere of Edmonton

As mentioned in Section 2.1, two sites (S-90130 and S-90132) in Edmonton were selected for investigation due to the discontinued data coverage at both sites. Annual average mass concentrations of f-NO_3^- at S-90130 from 1990 to 2005 and at S-90132 from 2007 to 2019 were analyzed to illustrate the complexity of particulate nitrate trends in the urban atmosphere (Figure 1a). As mentioned in Section 2.1, data in 2006 were missing at both sites. For comparison, annual average mass concentrations of c-NO_3^- at S-90130 from 1990 to 2005 are also shown in Figure 1a and those of f-NH_4^+ and f-SO_4^{2-} at S-90130 and S-90132 from 1990 to 2019 are shown in Figure S3. To facilitate analysis, annual average mixing ratios of NO_2 at S-90130 from 1995 to 2019 are shown in Figure 1b, and annual provincial total emissions of NO_x, SO_2, and NH_3 in Alberta are also presented (Figures 1b, S3a and S3c, respectively). Correlation analyses between f-NO_3^- (or c-NO_3^-) and provincial total emissions of NO_x in 1990-2005 and between f-SO_4^{2-} and provincial total emissions of SO_2 in 1990-2019 are conducted (Figures 1c and S3b, respectively).

At S-90130, annual average f-NO_3^- and c-NO_3^- was 0.48 ± 0.25 μg m^{-3} (average ± standard deviation) and 0.15 ± 0.05 μg m^{-3}, respectively, during 1990 - 2005. No trend or stable trend was found for these species ($P > 0.10$), likely due to a bell-shaped change in provincial total NO_x emissions from 1990 to 2005. In fact, a significant correlation was found between annual average c-NO_3^- and provincial total NO_x emissions during 1990-2005 ($P < 0.01$). However, a significant correlation between annual average f-NO_3^- and provincial NO_x emissions was obtained only during 1992-2005 ($P < 0.01$), but not for the entire period during 1990-2005 with the values in 1990-1991 being substantially deviating from the regression curve. Such a deviation is yet to be

252 explained. Notably, f-NO_3^- and c-NO_3^- were not significantly correlated in any
253 individual year during 1990–2005 ($R^2 < 0.1$; $P > 0.05$). The same pattern was observed
254 at the other six sites analyzed in this study. The lack of correlation between f-NO_3^- and
255 c-NO_3^- is discussed in detail in Section 3.2.
256
257 At S-90132, annual average f-NO_3^- was 1.3 ± 0.40 μg m^{-3} during 2007 - 2019. f-NO_3^-
258 exhibited a decreasing trend ($P < 0.01$), with a Sen's Slope of 0.063 μg m^{-3} yr^{-1},
259 resulting in an overall decrease of approximately 60% during this period. In
260 comparison, the monitored NO_2 mixing ratios at a different site (S-90130) decreased by
261 approximately 20%, while provincial total NO_x emissions in Alberta were reduced by
262 only ~10% during the same period. Such disproportionate decreases were also
263 identified for both f-NO_3^- and c-NO_3 at S-90130 in the selected period of 1997-2005,
264 with a ~60% decrease in their annual average concentrations compared to a ~20%
265 decrease in both the NO_2 mixing ratios and provincial NO_x total emissions. Notably,
266 NO_2 mixing ratios at the urban site were significantly correlated with Alberta's total
267 provincial NO_x emissions, with $R^2 = 0.81$ over 1997–2019 ($P < 0.01$) and a slightly
268 weaker correlation ($R^2 = 0.57$) over the shorter period of 2007–2019 ($P < 0.01$). These
269 results indicate broadly consistent NO_x mitigation signals at both the provincial and city
270 scales. Thus, the disproportionate large decrease in the annual average f-NO_3^- at S-
271 90132 relative to the reduction in provincial NO_x emissions is analyzed below by
272 considering major driving factors (Section 3.4), primary and secondary sources
273 (Section 3.5), and potential uncertainties in the data of the generated annual average f-
274 NO_3^- (Sections 3.6). It should be noted that the annual average f-NO_3^- measured at S-
275 90132 in 2007-2019 were significantly higher than those recorded at S-90130 in 1990-
276 2005 (P<0.01), which could be attributed to an unexpected mitigation effect, as
277 analyzed in Section 3.3 below.
278
279 Unlike f-NO_3^-, annual average f-SO_4^{2-} exhibited a relatively smooth decreasing trend
280 ($P < 0.01$), with a Sen's slope of 0.029 μg m^{-3} yr^{-1} if combining data at S-90130 from
281 1990 to 2005 and at S-90132 from 2007 to 2019 together (Figure S3a). This trend was

mostly consistent with a 0.021 μg m^{-3} yr^{-1} decrease in the provincial total SO_2 emissions from 1990 to 2019. Additionally, a moderately strong correlation was found between the annual average f-SO_4^{2-} and the provincial total SO_2 emissions over the three decades ($P < 0.01$, Figure S3b). The f-SO_4^{2-} trend in the urban atmosphere reflects the mitigation effect, as has also been reported for rural atmospheres in Canada (Cheng and Zhang, 2017; Feng et al., 2020). f-SO_4^{2-}, typically formed through in-cloud aqueous reactions and with non-volatile properties, is generally associated with regional sources, and thus tends to be spatially homogeneously distributed in urban scales (Bell et al., 2007; He et al., 2001; Park et al., 2004). This may explain the much smaller gaps in the annual average f-SO_4^{2-} between the two nearby urban sites, as compared to the case of f-NO_3^- .

Annual average f-NH_4^+ exhibited a decreasing trend ($P < 0.05$) if combining data at S-90130 from 1990 to 2005 and at S-90132 from 2007 to 2019 (Figure S3c). However, the trend was stable at both sites during the two separate periods ($P > 0.10$). From 1990 to 2019, the provincial total NH_3 emissions increased by approximately 40% (Figure S3c). The phenomenon of the decoupled trends between f-NH_4^+ and NH_3 emissions widely occurred in Canada and the U.S. in the recent decades, as reported in Yao and Zhang (2019). This is because the level of f-NH_4^+ was mainly controlled by those of SO_4^{2-} and NO_3^- through neutralization reactions, especially under NH_3-rich conditions (Bari and Kindzierski, 2016b; Dabek-Zlotorzynska et al., 2011; Edgerton et al., 2020). The equivalent ratios of NH_4^+ to (SO_4^{2-} + NO_3^-) in two selected years support this hypothesis (Figure S4).

3.2 Trends of f-NO_3^- and c-NO_3^- in urban atmospheres of Winnipeg – an inland city in western Canada

The annual average f-NO_3^- in Winnipeg varied within a range of 0.07-0.70 μg m^{-3}, with a long-term average of 0.32 ± 0.15 μg m^{-3} from 1990 to 2018. A stable trend in annual average f-NO_3^- was identified by the M-K method ($P = 0.51$; Figure 1d). The annual average c-NO_3^- varied within an even smaller range of 0.13-0.29 μg m^{-3}, with a long-

term average of 0.19 ± 0.04 μg m^{-3} during 1990–2012. A probable increasing trend in annual average c-NO_3^- was identified ($P = 0.06$). Over the same period, both the annual average mixing ratio of NO_2 at this site and provincial total NO_x emissions in Manitoba exhibited decreasing trends ($P < 0.01$) (Figure 1e), and they correlated with each other strongly ($R^2 = 0.90$, $P < 0.01$). The absence of a corresponding decrease in f-NO_3^- concentration compared to NO_x emissions is likely attributable to enhanced primary emissions of f-NO_3^--containing aerosols, as discussed in Sections 3.3 and 3.5 below. This is clearly supported by the following evidence: from 1999 to 2004, annual average f-NO_3^- increased by approximately 200%, even as provincial NO_x emissions and NO_2 mixing ratios declined by about 10%. Accordingly, the trend in f-NO_3^- concentrations was analyzed in two separate periods: 1990–2002 and 2003–2018. The year of 2003 is allocated into the second rather than the first period based on the curve of annual variation shown in Figure 1d. In the first period (1990–2002), f-NO_3^- showed a probable decreasing trend, with a Sen's Slope of 0.017 μg m^{-3} $year^{-1}$ and a total decline of about 80%. This sharp decrease cannot be explained by the relatively modest 10–20% reductions in NO_2 and NO_x during the same period, suggesting that highly localized factors and/or uncertainties caused by coarse resolution data (1 in every 6 days) were likely the dominant contributors. The related uncertainty analysis is presented in Section 3.6 below. In the second period (2003–2018), f-NO_3^- exhibited a decreasing trend with a Sen's Slope of 0.018 μg m^{-3} $year^{-1}$, amounting to an overall reduction of approximately 70%, which also exceeded the ~50% reduction in NO_2 mixing ratios at the same site and the ~30% reduction in provincial NO_x emissions. The disproportionate trends between f-NO_3^- and NO_x emissions observed in Winnipeg are similar to the case in Edmonton discussed above.

When the time series of daily concentrations of f-NO_3^- and c-NO_3^- were examined for a low-concentration year (1996) and a high-concentration year (2007) (Figure 1f-g), elevated concentrations of f-NO_3^- were predominantly observed during the cold months. High concentrations of f-NO_3^- were likely from primary sources, as discussed in Section 3.5 below, considering the similar climate in inland western Canada. This,

however, needs to be confirmed using HNO_{3gas}^* data, which are not available at this site. In contrast, elevated concentrations of c-NO_3^- typically occurred during warmer months. 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_{3gas}^* 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. This interpretation is also supported by findings reported in literature at rural sites in Canada (Cheng and Zhang, 2017; Feng et al., 2020) and urban and rural sites in the U.S. (Sickles II and Shadwick, 2015) and U.K. (Tang et al., 2018), where positive correlations between HNO_{3gas}* and NO_2 have been observed, suggesting that a reduction in NO_x would not typically lead to enhanced HNO_{3gas}^* formation.

3.3 Time window for unintended effects of NO_x mitigation on f-NO_3^- aerosols in Canadian urban atmospheres and associated shaped trends of f-NO_3^- and c-NO_3^-

Long-term trends of f-NO_3^- could be distorted by unintentionally increased f-NO_3^- primary emissions resulted from certain NO_x mitigation measures. Such phenomena were repeatedly observed in urban atmospheres across Canada during a consistent time window from approximately 1998 to 2007, as illustrated in Figures 1, and S5 as well as those aforementioned in Edmonton and Winnipeg. During this period, similar NO_x mitigation actions were taken in both Canada and the U.S., regulated by the Canada - U.S. Air Quality Agreement signed in 1991 and further expanded in 2000. Although mitigation policies were likely implemented independently in each province in Canada, and the exact timing may have varied slightly, a consistent pattern emerged. For

example, in the province of Quebec, the annual average f-NO_3^- increased by approximately 150% in Quebec City from 1998 to 2003 and by around 300% in Montreal from 1998 to 2002. During the same period, annual average mixing ratio of NO_2 decreased by approximately 10% in both cities, while provincial total NO_x emissions remained nearly unchanged. In the province of Ontario, annual average f-NO_3^- in Hamilton remained relatively low at 0.69 ± 0.09 μg m^{-3} during 1995–1999, but rose sharply to 1.6 μg m^{-3} in 2001, with a notable dip to 0.85 μg m^{-3} in 2002 possibly due to climate anomaly, bounced back to 1.7 μg m^{-3} in 2004 and stabilized at 1.6 μg m^{-3} in 2005. During the period from 1999 - 2005, both observed NO_2 mixing ratios in Hamilton and provincial NO_x emissions in Ontario began to decline by 20–30%. A similar pattern was also found in western coastal urban areas such as Victoria and Vancouver, both located in British Columbia, between 1998 and 2002 (Figure 2), where annual average f-NO_3^- increased by approximately 100% while NO_2 mixing ratios and provincial NO_x emissions declined by 10–30%. 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 by-products 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 by-products (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-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.

Setting the demarcation line at 2003 in Quebec City (noting the substantial data loss in 2002 for this city) and at 2002 in Montreal, the annual average f-NO_3^- decreased by more than 70% over the subsequent 16- or 17-year period, largely agree with the 40-60% reductions in NO_2 mixing ratios and provincial NO_x emissions during the same period. The slight differences in their decreasing rates could be attributed to unintended changes in primary emissions of f-NO_3 aerosols as discussed above, non-linear atmospheric chemistry process involving other chemical species, and data uncertainties, etc. Notably, the annual average c-NO_3^- showed no significant trend during these periods in either city, suggesting that c-NO_3^- levels may have been more strongly influenced by the presence of alkali aerosols capable of neutralizing HNO_{3gas}^* rather than by the availability of HNO_{3gas}^* itself. Data prior to 2002 (Montreal) or 2003 (Quebec City) were insufficient in duration to support robust trend analysis; nevertheless, the influence of unintended mitigation effects during this period was still evident. In comparison, if removing the demarcation line and considering the whole data record together, annual average f-NO_3^- would show no clear trend from 1995 to 2018 in Quebec City and a stable trend from 1997 to 2018 in Montreal. Over the full

period, annual average f-NO_3^- and c-NO_3^- were 0.41 ± 0.19 μg m^{-3} and 0.19 ± 0.05 μg m^{-3}, respectively, in Quebec City and 0.57 ± 0.38 μg m^{-3} and 0.28 ± 0.06 μg m^{-3}, respectively, in Montreal.

Similarly, if setting a demarcation line at the year of 2002 for Victoria and Vancouver, f-NO_3^- would show either a significant decreasing trend or a probable decreasing trend, with a total decrease of around 40% in both cities from 2002 to 2018. These declines were broadly consistent with the 30–40% decreases in both NO_2 mixing ratios and provincial NO_x emissions during the same period. From 1990 to 2002, f-NO_3^- showed either no trend or a stable trend, which was consistent with the trend in the provincial NO_x emissions, but inconsistent with the observed decreasing trend in NO_2 mixing ratio during this period. If looking at the full data record of c-NO_3^- together (from 1990 to 2012 in Victoria or 2015 in Vancouver), either no trend or a stable trend was identified in either city, regardless of using the full data record or just data after the year 2002. The absence of a clear decreasing trend in c-NO_3^- concentration, despite significant NO_x emissions, appears to be a common feature across Canadian urban environments. Unlike the other cities aforementioned where annual average concentrations of f-NO_3^- were much higher than those of c-NO_3^-, in Victoria, annual average concentrations of f-NO_3^- and c-NO_3^- were similar, oscillating around 0.23 ± 0.06 μg m^{-3} (1990 to 2018) and 0.25 ± 0.05 μg m^{-3} (1990 to 2012), respectively. In contrast, annual average concentrations of f-NO_3^- (0.16 ± 0.05 μg m^{-3} in 1990 - 2018) were significantly smaller than that of c-NO_3^- (0.31 ± 0.05 μg m^{-3} in 1990 - 2015) (P<0.01) in Vancouver, and the same conclusion can be generated if only using data in 1990-2015.

In Hamilton, no statistically significant trends were identified for f-NO_3^- and c-NO_3^-, whether considering the full time series or just the period post-2005. This is somewhat different than the cases in the other cities discussed above, suggesting potentially strong impact of local sources, besides the other main factors discussed above, considering that Hamilton is an industrial city with heavy density of industries. Annual average f-

NO_3^- and c-NO_3^- in this city were 0.88 ± 0.35 μg m^{-3} and 0.46 ± 0.12 μg m^{-3}, respectively, during the period of 1995 to 2019.

3.4 Key factors influencing annual average f-NO_3^- and its trends in Edmonton

To explore key factors influencing the annual average f-NO_3^- and its trends in Edmonton, we selected data from two representative years (2010 and 2015) at site S-90132 for comparative analysis. The year 2010 was chosen because in this year abnormally high annual average f-NO_3^- was observed compared to all the other years during the period of 2007-2019, suggesting possible impact by climate anomaly in this year. The year 2015 was chosen because in this year annual average f-NO_3^- represents the median value of a five-year period of 2015-2019, likely reflecting the average climatic conditions, knowing that the annual average NO_2 mixing ratio observed at a nearby site (S-90130) and the provincial total NO_x emissions were nearly constant during 2015-2019. 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.

Through the comparative analysis, seasonal variations of f-NO_3^-, various single-factor effects on f-NO_3^-, and the impact of climate anomalies on f-NO_3^- were explored. As shown in Figures 3a and 3b, higher concentrations of f-NO_3^- were predominantly observed during cold months, including January to March and November to December, in both 2010 and 2015. 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. Based on wind fields shown in Figures S1 and S2, air masses reaching to this site in the cold winter should come from the remote northern areas with low pollution levels due to the strong northwest wind, which should have lowered concentrations of f-NO_3^- in the urban atmosphere. Thus, the high concentrations of f-NO_3^- observed at this site should be caused by local accumulation

under stagnant weather conditions. Therefore, the emissions of f-NO_3^--contained aerosols related to mitigation measures, the precursors and formation pathways of f-NO_3^-, and meteorological conditions during the winter period should be considered as key factors determining the annual average f-NO_3^-.

We then correlated the 24-hr integrated daily concentrations of f-NO_3^- with ambient T, wind speed (WS), RH, and HNO_{3gas}* to explore various single-factor effects on f-NO_3^- (Figure 3). A demarcation line was observed at -3°C in 2010 and 0.5°C in 2015, with substantially lower f-NO_3^- concentration at T on the right than left side of the line (Figures 3a and 3e). Lower ambient T favored the gas-aerosol partitioning of NH_4NO_3 in $PM_{2.5}$ (Seinfeld and Pandis, 2016; Shah et al., 2018). However, lower ambient T also weakened photochemical reactions due to reduced amounts of intermediate volatility organic compounds or semi-volatile organic compounds in the gas phase (McDonald et al., 2018; Wernis et al., 2022). This reduction in photochemical activity subsequently lowered the concentration of HNO_{3gas}^* to some extent, e.g., the concentrations of HNO_{3gas}^* observed at T > 20°C increased by over a factor of four relative to those at T < -10°C in 2015 as shown in Figures 3e. The sources of f-NO_3^- and its formation pathways during the winter period will be revisited in Section 3.5. The causes for the different T values of the demarcation line between 2010 and 2015 are not clear. The concentrations of f-NO_3^- decreased with increasing WS due to the dispersion effect, and no elevated concentrations were observed once WS is stronger than 5 m/s (Figures 3b and 3f). The concentrations of f-NO_3^- had little dependence on ambient RH (Figure 3c and 3g), e.g., the highest concentrations in both years occurred at RH of 70-80% instead of >80%. The lowest concentrations of f-NO_3^- appearing at RH < 60% is because RH < 60% typically occurred at ambient T greater than 0°C in Edmonton. In addition, the relative importance of 15 major variables on f-NO_3^- concentration was examined using a Random Forest model, as detailed in Text S2 of SI. The ambient T ranked as the dominant factor, followed by $PM_{2.5}$ mass concentration, NO_2 mixing ratio, boundary layer height, etc.

It should be noted that gas–particle equilibrium between HNO_3–NH_3 and submicron NH_4NO_3 is unlikely to be achieved at temperatures below -10 °C, given the relatively long equilibration timescales. Based on the results of characteristic timescales analysed by Wexler and Seinfeld (1990, 1992) and dynamically simulated by Meng and Seinfeld (1996), particles with diameters of approximately 0.5–0.7 μm generally require hours to approach equilibrium – typically on the order of ~1–6 h with a more conservative upper bound of ~6–20 h. Under such low-temperature conditions, the assumption of instantaneous thermodynamic equilibrium becomes questionable; therefore, equilibrium thermodynamic modelling was not applied here. At even lower temperatures, the equilibration timescale would extend to tens of hours for highly viscous or glassy particles, as suggested by Li and Shiraiwa (2019).

Correlation analysis between simultaneously measured f-NO_3^- and HNO_{3gas}^* showed that f-NO_3^- concentrations higher than 4 μg m^{-3} occurred when HNO_{3gas}^* concentrations were lower than 0.4 μg m^{-3} in both years (Figures 3d and 3h). Thus, the high f-NO_3 concentrations were not likely caused from the secondary formation of f-NO_3^- from HNO_{3gas}^* in ambient air, as further discussed in Section 3.5 below. Considering that the concentrations of NH_{3gas} (data not shown here) were generally more than one order of magnitude higher than those of HNO_{3gas}^*, NH_{3gas} should not be the limiting factor for f-NO_3^- formation, and was therefore excluded from further analysis below.

Climate anomaly can have significant impacts on air pollution (Andersson et al., 2007; Wetherbee and Mast, 2016; Yao and Zhang, 2020). One of the factors related to climate anomaly in winter Canadian urban atmospheres is AO (Burakowski et al., 2008; Higgins et al., 2002; Yao and Zhang, 2020). Other climate drivers, such as ENSO, Arctic sea-ice variability, and long-term warming, may influence f-NO_3^- during the warming season. However, their impact on the annual trend is likely negligible, as it is dominated by wintertime f-NO_3^-. As shown in Figures S1 and S2, the mean wind speed from January to March across Alberta decreased significantly in 2010 compared to the other years. The AO index during the winter period in 2010 was in the most negative

phase observed in the last four decades (Figure S1d). Typically, the belt of strong winds circulating around 55°N latitude weakens during such a phase, which allows colder Arctic air masses to penetrate further south into the mid-latitudes (Higgins et al., 2002). The substantial decrease in WS during the winter period of 2010 likely contributed to the higher annual average f-NO_3^- in this year. It is noticed that the recorded ambient T in Edmonton in this winter was similar to the climatic mean value (https://www.wunderground.com/about/data), further supporting the hypothesis that it is the weaken WS caused by AO anomaly, rather than changes in T, that enhanced the accumulation of f-NO_3^-.

To further examine the effects of the AO anomaly on f-NO_3^- accumulation in 2010 relative to that in 2015, we conducted the identical-percentile regression analysis between the two years (Figures 4c-e). With the intercept being forced to zero, similar to the approach commonly used in chemical experiments for establishing the standard curve (Yao et al., 2011), the slope of the regression equation was 2.74 if using all the data (0^{th} to 100^{th} percentiles), 1.56 if using the central 50% data (25^{th} to 75^{th} percentiles), and 1.41 if only using the lower 50% data (0^{th} to 50^{th} percentiles). The differences in f-NO_3^- concentration between the two years were clearly enlarged when higher concentrations were included, due to the AO anomaly effect in the winter of 2010. Assuming a log-normal distribution of the data, the lower percentiles and higher percentiles data, i.e., 0^{th} to 2.5^{th} percentiles and 97.5^{th} to 100^{th} percentiles, are normally excluded from 95% confidence level. This is because these data points have lower probability densities and their corresponding values are more vulnerable to climate anomaly impact such as AO with negative and positive phases. The highest probability density should always occur at the 50^{th} percentile, where the corresponding value should be least affected by AO. To minimize potential error from using a single value, we used the average values of the 47.5^{th}-52.5^{th} percentiles, which were 0.63 μg m^{-3} in 2010 and 0.45 μg m^{-3} in 2015. The ratio of these two values (=1.4) was nearly identical to the slope of the regression equation using data from the 0^{th} to 50^{th} percentiles presented above. Thus, the annual average f-NO_3^- in 2010 was recalculated by the

corresponding value in 2015 being multiplying by a factor of 1.4 in order to deduct the AO anomaly effect. The recalculated annual average f-NO_3^- in 2010 would decrease from the original value of 2.1 μg m^{-3} to 1.2 μg m^{-3}. Interestingly, removing the AO effect in 2010 would only have a minor impact on the decadal trends from 2007 to 2019, e.g., the Sen's Slope only showed small changes: which was 0.063 μg m^{-3} $year^{-1}$ using the original annual average values including the year 2010, 0.060 μg m^{-3} $year^{-1}$ if excluding the year 2010, and 0.057 μg m^{-3} $year^{-1}$ if replacing the year 2010 value with 1.2 μg m^{-3}.

Overall, the AO largely affected the annual average f-NO_3^- in 2010. Nevertheless, such an impact only has marginal effects on the decadal trends of f-NO_3^-, as the AO typically oscillates between negative and positive phases within 2-3 years (Figure S1d). The enhanced or weakened effects of AO in 2-3 years can be largely canceled out in extracting the decadal trend of f-NO_3^-. The overall effect appeared to be too small to explain the above-mentioned disproportionate responses of the annual average f-NO_3^- to the reduced NO_x emissions, and more exploration on this issue is presented in Sections 3.5 and 3.6 below.

3.5 Rethinking the role of primary emissions of NH_4NO_3 during the cold season in Canadian urban atmospheres

From the analysis presented in the previous section we concluded that the high concentrations of f-NO_3^- in the winter were mainly due to local accumulation under stagnant meteorological conditions, rather than long-range transport driven by north-westerly winds. This raised the fundamental question: what is the role of primary emissions in combustion plumes or secondary formation of NH_4NO_3 in ambient air in contributing to f-NO_3^- in Canadian urban atmospheres during the cold season? To answer this question, we proposed a hypothesis, i.e., whether HNO_{3gas*} concentrations significantly increased under conditions with low f-NO_3^- concentrations compared to cases with high f-NO_3^- concentrations, and then examined the hypothesis below.

606 Theoretical analysis and implications of the hypothesis were provided in supplementary
607 information (Text S4 of SI).
608
609 To examine the weaker hypothesis outlined above, we first divided the 2010
610 observations into two temperature regimes: $T < 0°C$ and $0°C < T \leq 4°C$. Observations
611 with $T < 0°C$ were further divided into two subsets based on f-NO_3^- concentrations,
612 using the thresholds of > 4 μg m^{-3} and ≤ 4 μg m^{-3}. These three groups were then
613 compared, i.e., Group 1: $T < 0°C$ and f-$NO_3^- > 4$ μg m^{-3}, in which case there were 19
614 samples with average HNO_{3gas}^* and f-NO_3^- concentrations being 0.15 ± 0.09 μg m^{-3} and
615 8.8 ± 4.4 μg m^{-3}, respectively; Group 2: $T < 0°C$ and f-$NO_3^- < 4$ μg m^{-3}, in which case
616 there were 26 samples with average HNO_{3gas}^* and f-NO_3^- concentrations being $0.15 \pm$
617 0.12 μg m^{-3} and 1.3 ± 0.7 μg m^{-3}, respectively; and Group 3: $0°C < T \leq 4°C$, in which
618 case there were 13 samples with average HNO_{3gas}^* and f-NO_3^- concentrations being
619 0.15 ± 0.11 μg m^{-3} and 1.3 ± 1.7 μg m^{-3}, respectively. Apparently, the average HNO_{3gas}^*
620 concentrations did not differ between the three Groups ($P < 0.01$); thus, the initial
621 hypothesis has to be rejected. This suggests that the process of secondary formation of
622 NH_4NO_3 from HNO_{3gas}^* was not the main contributor to the observed high
623 concentrations of f-NO_3^-, leaving the process of primary emissions as the only major
624 contributor. In addition, the markedly reduced f-NO_3^- concentrations at $T > 0°C$ were
625 likely due to volatilization of a portion of primarily emitted f-NO_3^-.
626
627 To further test the robustness of the above analysis, we expanded the dataset to include
628 measurements at $T \leq 4°$ from both 2010 and 2015, yielding a total of 108 f-NO_3^-
629 samples (Group 1: n = 23; Group 2: n = 54; Group 3: n = 31). The mean (± SD)
630 concentrations of f-NO_3^- and HNO_{3gas*} were 8.7 ± 4.1 μg m^{-3} and 0.16 ± 0.11 μg m^{-3}
631 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 the expanded dataset,
633 mean HNO_{3gas*} did not differ significantly among the three groups (Welch one-way
634 ANOVA, $P = 0.74$), despite the intentionally large contrast in f-NO_3^- imposed by the
635 group definitions.

The above analysis results suggest that the trend of f-NO_3^- in Edmonton was likely governed by the primary emissions of f-NO_3^- aerosols, as well as the extents of their volatilization and dispersion during the cold season. The dependence of volatilization of f-NO_3^- on ambient T and dispersion on WS has been recently confirmed in observational and modeling studies (Huo et al., 2025; Peng et al., 2024; Shen et al., 2022). As mentioned in the Introduction, the primary emissions of f-NO_3^- likely have two major sources (or processes). The first source is also conventionally defined as condensable particulate emission and associated with the combustion of (N_2 + O_2), which produces various oxidized nitrogen species, including HNO_{3gas}^*, NO_x, etc. (USEPA, 2017). The amount of primary NH_4NO_3 formed from HNO_{3gas*} in cooling plumes theoretically depends on the combustion technology, the use of catalytic reduction systems employing NH_3, and the ambient T (Palash et al., 2013; Tayyeb Javed et al., 2007; Zhang et al., 2021), which may not be controlled by NO_x emission levels. In some reported cases, mitigation measures reduced NO_x emissions, but simultaneously increased primary emissions of f-NO_3^- (Feng et al., 2020; Palash et al., 2013; Tayyeb Javed et al., 2007; Yang et al., 2024; Zhao et al., 2020). As evidences presented in Sections 3.3, this phenomenon likely occurred across various Canadian urban atmospheres. In contrast, the second source in fresh cooling plumes is directly linked to NO_x emissions through the chemical conversion of NO_2 in cooling plume droplets, although it is highly sensitive to the lifetime of these droplets (Shen et al., 2022; Wang et al., 2016; Wang et al., 2020). In addition, primary nitrate aerosols from traffic emissions were reportedly unimportant in urban atmospheres across Canada and U.S. (Chalbot et al., 2013; Jeong et al., 2020), leaving only one possibility that primary nitrate aerosols were mainly derived from stationary combustion sources.

Although secondary f-NO_3^- formation should always occur to some extent in ambient air, the relative contribution from this process to the total f-NO_3^- is very small during the periods with high f-NO_3^- concentrations. As shown in Text S3 of SI, the modeled maximum potential contribution from secondary formation can only account for a small

fraction of the observed f-NO_3^- (<15% in the baseline runs, and <45% even in the empirical-estimate runs known to have overpredictions in general). These results support the hypothesis presented above that primary f-NO_3^- was the dominant contributor to the high f-NO_3^- concentration in winter. Moreover, higher f-NO_3^- concentrations were generally observed under low wind speeds (WS <1-2 m s^{-1}). Given that the sampling site is about 17 km from the farthest urban edge, the transport time for both primary and secondary f-NO_3^- to reach the site was therefore estimated to be approximately 2–4 h. This timescale is far too short for substantial secondary formation of f-NO_3^- in such cold ambient air (T < −10 °C), unless in-source processes dominated (Shen et al., 2022; USEPA, 2017; Zhang et al., 2023). Within this 2–4 h transport window, the amount of HNO_{3gas}* dry deposition should also be minimum, especially under low-temperature conditions.

3.6 Uncertainties affecting f-NO_3^- trends in Edmonton

Three categories of uncertainties that may affect the observed trends of f-NO_3^- in Edmonton were analyzed: (i) differences in observational results between the speciation sampler and the Dichotomous sampler, (ii) spatial inhomogeneity due to highly localized factors, and (iii) artifacts introduced by the sampling frequency (e.g., every third or sixth day), which may influence the calculation of annual averages. For category (i) uncertainty, $PM_{2.5}$ mass concentrations measured by the two different instruments at site S-90132 in 2010 showed strong agreement for most samples, with occasional discrepancies at lower concentration levels (Figure S6). Specifically, when the regression intercept was forced to zero, the resulting equation was $y = 1.02*x$ (R^2 = 0.94), and the difference in annual average concentrations was less than 10% (10.3 μg m^{-3} from the Dichotomous sampler vs. 11.1 μg m^{-3} from the speciation sampler).

For category (ii) uncertainty, Figure S7 compares real-time $PM_{2.5}$ mass concentrations measured simultaneously at two sites 7 km apart (S-90132 and S-90130) from 2011 to 2014. Other years were excluded due to significant data loss at one or both sites.

Regression slopes between the two sites (with intercepts forced to zero) are 0.86, 0.82, 0.58, and 0.67, with corresponding differences in annual average concentrations of 21%, 15%, 40%, and 39% in 2011, 2012, 2013, and 2014, respectively. The significant year-to-year differences between the two sites are unlikely caused by mitigation policies, climate variability, or changes in the atmospheric formation pathways of $PM_{2.5}$, but rather by spatial inhomogeneity driven by highly localized factors that varied from year to year (Yeganeh et al., 2025). The influence of such localized effects appears to be substantial and may represent an important, yet often overlooked, contributor to the disproportionately large decreases in the annual average f-NO_3^- relative to reductions in provincial total NO_x emissions over decadal timescales. 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.

It is noted that while the annual average $PM_{2.5}$ mass concentrations were significantly higher at S-90130 than S-90132 ($P < 0.01$) during 2010-2014, the opposite trend was observed for the annual average f-NO_3^-, e.g., higher at S-90132 during 2007–2019 compared to those at S-90130 during 1990–2005. The highest annual average f-NO_3^- concentration at S-90130 appeared in 2000 and that at S-90132 appeared in 2010 (Figure 1a). The mass fractions of f-NO_3^- in $PM_{2.5}$ were 0.050 ± 0.065 in 2000 and 0.13 ± 0.13 in 2010 (Figure S4), indicating that $PM_{2.5}$ at S-90132 contained more f-NO_3^- aerosols during 2007-2019 than at S-90130 during 1990-2005, strongly supporting the hypothesis that mitigation measures reduced NO_x emissions in Edmonton, while

simultaneously increased primary f-NO_3^- emissions from the first source (see Section 3.3) after 2005.

Concerning category (iii) uncertainty, no continuous measurements of f-NO_3^- were available to assess its magnitude. We thus used continuous measurements of $PM_{2.5}$ data at S-90130 as a proxy for this evaluation. Given that the annual average $PM_{2.5}$ mass concentration in 2010 was approximately 50% larger than in 2011, the analysis was conducted using data from 2011 to 2020 instead of 2010 to 2020. Daily average $PM_{2.5}$ mass concentrations were first calculated for every day of the year. Then for each year, annual average $PM_{2.5}$ mass concentrations were calculated from daily average concentrations using (i) full dataset, (ii) one in every three days data (three subsets), and (iii) one in every six days data (six subsets). Thus, a total of 10 sets of annual average $PM_{2.5}$ data series was created for the period of 2011-2020, which was then used for decadal trend analysis. The trend derived from the full dataset showed a decreasing trend with a Sen's Slope of 0.43 μg m^{-3} $year^{-1}$. Consistent decreasing trends were also obtained from using the one in every three days subset data series, with Sen's Slope values of 0.46, 0.46, and 0.42 μg m^{-3} $year^{-1}$, respectively, indicating an error of less than 8%. When using the one in every six days subset data series, five out of six data subsets also showed a decreasing trend, with Sen's Slope values of 0.47, 0.50, 0.45, 0.45, and 0.44 μg m^{-3} $year^{-1}$, respectively, indicating an error of less than 10% in most cases. However, one subset data series showed a probable decreasing trend, with a Sen's Slope of 0.38 μg m^{-3} $year^{-1}$.

Using the same approach described above, we also compared the decadal trends obtained from using one in every three days data, which are readily available, with those from using one in every six days data, which are arbitrarily split from the former data set into two subsets. One of the two subsets for f-NO_3^- showed a decreasing trend with a Sen's Slope of 0.055 μg m^{-3} $year^{-1}$, which is close to the original value of 0.063 μg m^{-3} $year^{-1}$; however, the other subset exhibited a stable trend. For f-SO_4^{2-}, both subsets showed decreasing trends, with Sen's Slope values of 0.033 and 0.018 μg m^{-3} $year^{-1}$,

755 respectively, although deviating to some extent from the original estimate of 0.022 μg
756 m^{-3} $year^{-1}$. For f-NH_4^+, both subsets showed stable trends, consistent with the results
757 derived from the original dataset. Overall, using one in every three or six days data can
758 generate decadal trends with reasonable accuracy, although the obtained trends need to
759 be interpreted carefully when the trends are not significant or the changing rates are
760 very small.
761
762 In the literature (Text S1 of SI), changes in atmospheric NH_3 and f-SO_4^{2-} have been
763 reported to influence long-term trends in f-NO_3 to some extent. However, evidence of
764 increasing atmospheric NH_3 in Canada, together with reduced NH_3 consumption for
765 neutralizing the two major inorganic acids, suggests that NH_3 is generally abundant and
766 unlikely to be the limiting factor for f-NO_3^- formation (Yao and Zhang, 2019).
767 Consistent with this interpretation, large f-NO_3^-/f-SO_4^{2-} mass ratios are frequently
768 observed in high-f-NO_3^- samples during the cold season across Canada. For example,
769 in Edmonton in 2010, samples with f-NO_3^- > 4 μg m^{-3} exhibited f-NO_3^-/f-SO_4^{2-} mass
770 ratios ranging from 1.5 to 12, with a median of 5.5. These results indicate that the
771 elevated f-NO_3^- concentrations overwhelmingly dominated its long-term trend. In such
772 cases, the slight decrease in f-SO_4^{2-} may exert only a minor influence on the trend in f-
773 NO_3^-. Nevertheless, these complex interactions warrant further investigation using
774 three-dimensional (3-D) air quality modelling; however, such efforts remain
775 challenging, as illustrated below.
776
777 Existing studies using 3-D chemical transport models (CTMs) simulating particulate
778 NO_3^- over North America are summarized in Text S5 of SI. Several key points can be
779 generated from these studies. (1) CTMs are widely applied and can often reproduce
780 broad spatial patterns and major controlling processes of particulate NO_3^- over the
781 United States and Canada; however, they frequently exhibit systematic biases in
782 magnitude, long-term trends, and sensitivities to emission controls, with a substantial
783 risk of error compensation (ECCC, 2016; Kim et al., 2014, 2023; Luo et al., 2019;
784 Pappin et al., 2024; Pun et al., 2009; Russell et al., 2019; Semeniuk et al., 2025; Shah

et al., 2018; Smyth et al., 2009; Walker et al., 2012). (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) (Luo et al., 2019; Walker et al., 2012). (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.

4 Findings and implications

The in-depth analysis results presented in this study demonstrate that the dynamics of particulate nitrate in Canadian urban atmospheres are governed by complex interactions among emission reductions, primary sources, and cold-climate meteorology. Three key insights emerge:

(i) Non-linear responses of f-NO_3^- to NO_x emission reductions in all the cities: Early phase implementation of NO_x control measures paradoxically increased f-NO_3^- during

1998–2007, likely due to altered combustion plume chemistry favoring rapid f-NO_3^- formation in cold-climate conditions. Significant declines in f-NO_3^- (e.g., 60% in Edmonton) outpaced NO_x reductions in the most recent decade, driven by diminishing primary emissions, highly localized factors, and AO induced dispersion effects.

(ii) Decoupled c-NO_3^- and NO_x reductions in all the cities except Edmonton: c-NO_3^- remained stable or increased slightly while NO_x emissions were reduced. c-NO_3^- trends were likely controlled by the abundance of alkali aerosols, highlighting the limited efficacy of NO_x-focused policies for controlling c-NO_3^-.

(iii) Critical role of primary f-NO_3^- emissions in winter in all the cities: Over 80% of the annual f-NO_3^- burden was originated from cold-season primary emissions, with minimal contribution from secondary formation process, emphasizing the need for season-specific mitigation strategies. However, confirmation of this role requires three-dimensional air quality modeling with updated emission inventories that explicitly incorporate condensable particulate matter under subzero ambient temperatures.

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 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.

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Data availability. The access of the data used in this study is described in Section 2 above.

Author Contributions. QF, XY and LZ designed the research, conducted the data analysis and wrote the manuscript.

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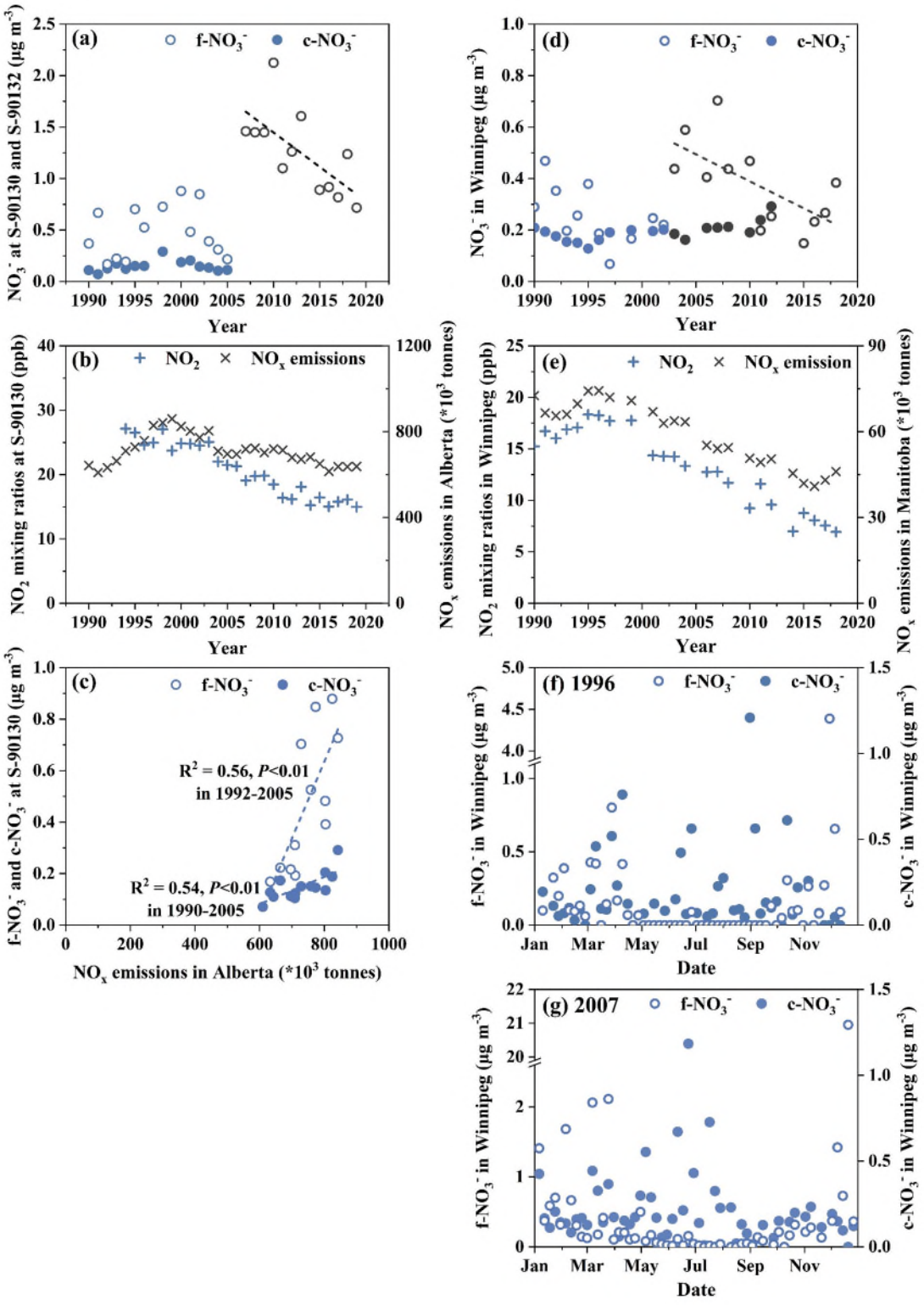

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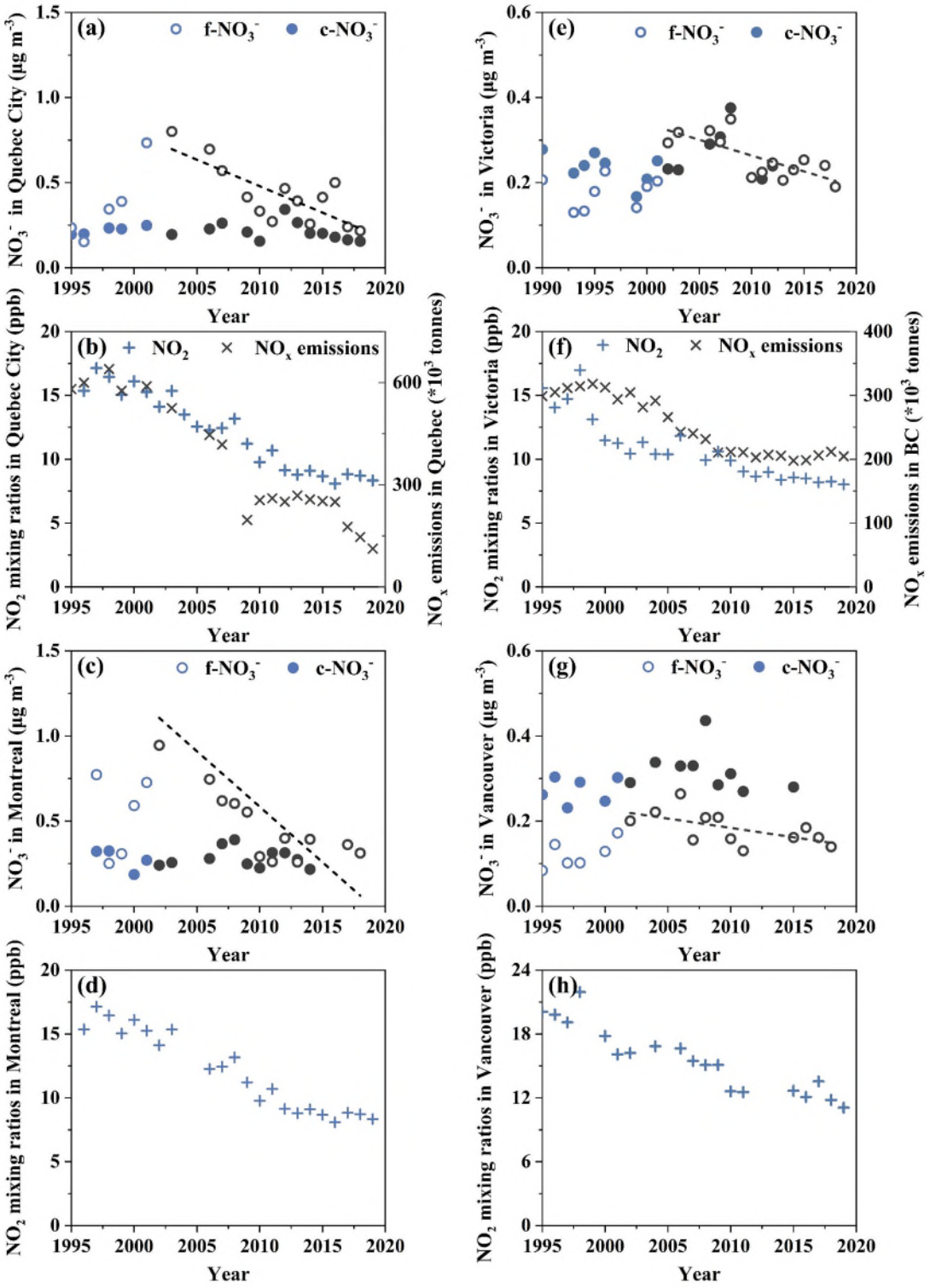

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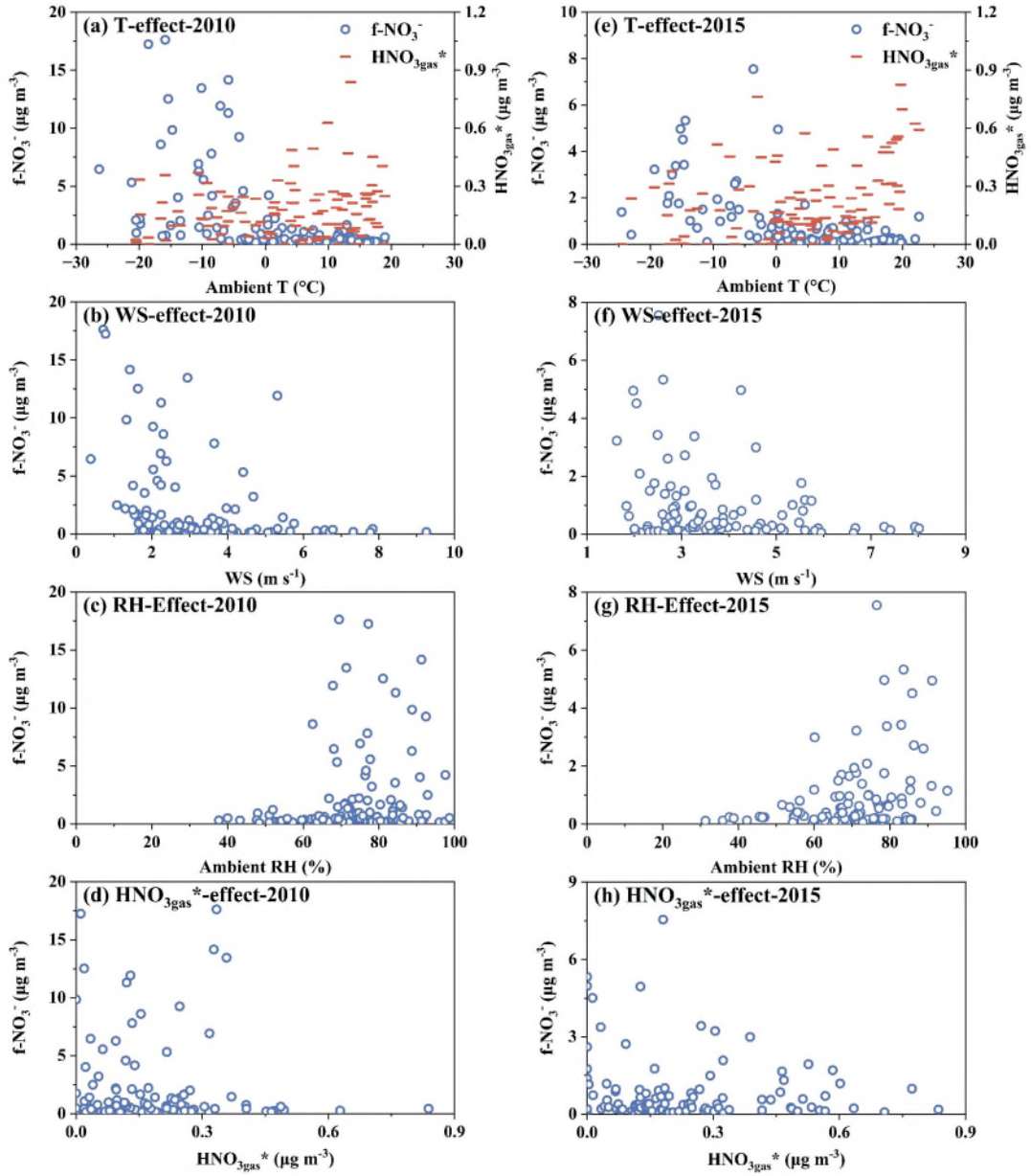

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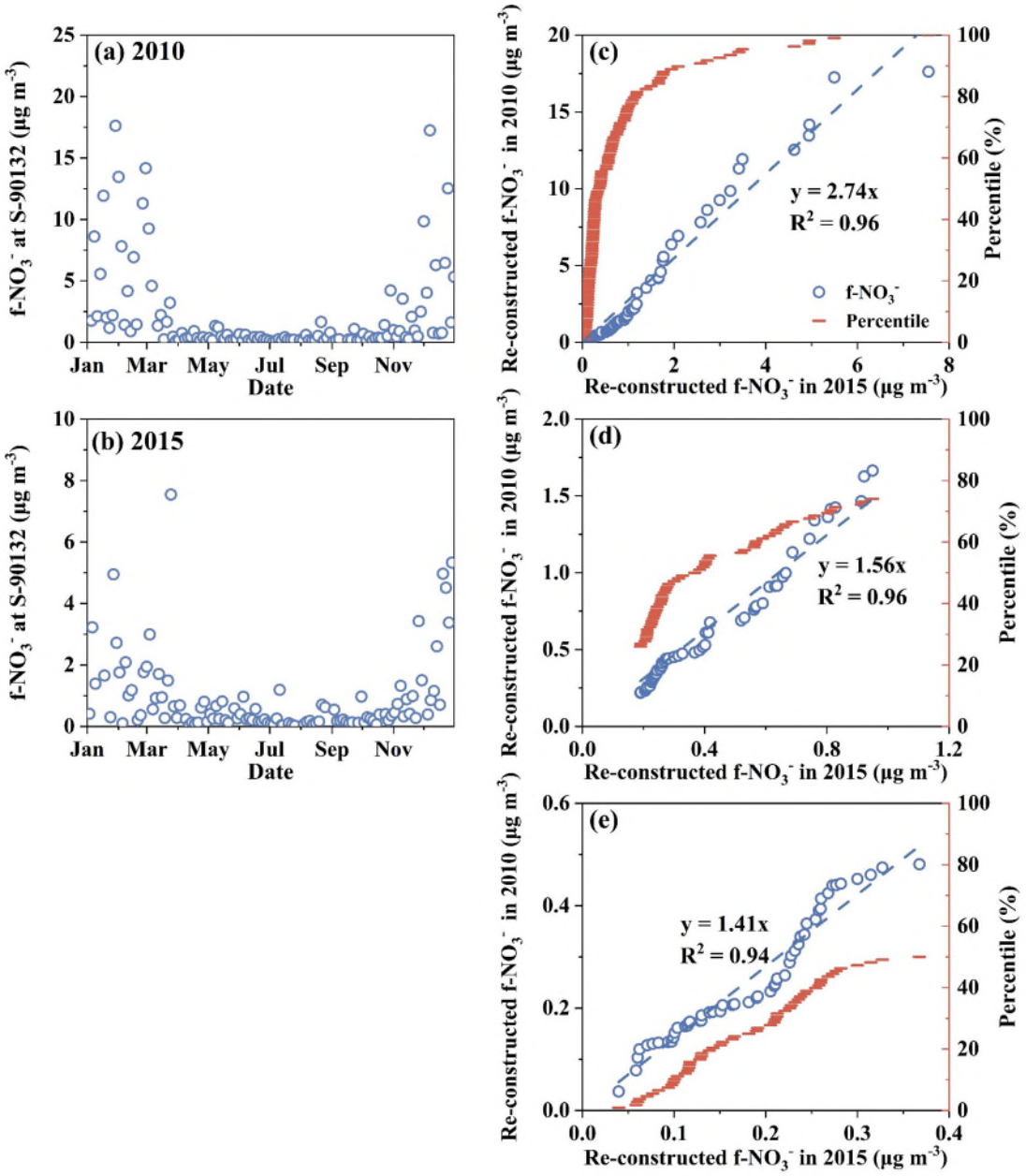

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