

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

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1 **Abstract.** Particulate nitrate (NO_3^-) is a key target for air pollution control; however,
2 its response to NO_x emission reductions remains uncertain, particularly in cold climates.
3 This study assesses trends of fine- and coarse-mode NO_3^- (f- NO_3^- and c- NO_3^-) during
4 1990-2019 in seven Canadian cities, making use of the long-term data collected by the
5 National Air Pollution Surveillance (NAPS) network, and revealed disproportionate
6 trends between NO_3^- and NO_x emissions across Canada. In Edmonton, annual mean f-
7 NO_3^- decreased by ~60% from 2007–2019 while provincial NO_x emissions declined by
8 only 10–20%; comparable patterns were also observed in five out of the six other cities
9 in the most recent decade. Such disproportionate trends were diagnosed to be caused
10 by reduced primary f- NO_3^- emissions, localized dispersion, and Arctic Oscillation–
11 modulated wind anomalies. Conversely, all cities exhibited a transient f- NO_3^- increase
12 during 1998–2007, coincident with early NO_x controls and consistent with unintended
13 enhancement of primary emissions of f- NO_3^- formed within stationary-combustion
14 plumes. c- NO_3^- was largely insensitive to NO_x reduction in most cities (except
15 Edmonton), with its trends governed by neutralization reactions with alkaline aerosols
16 rather than HNO_3 availability. These findings help interpret the weak or absent response
17 of f- NO_3^- to NO_x emission reductions observed worldwide, particularly in cold-climate
18 regions.

19
20 **Keywords:** particulate nitrate, primary nitrate emission, decadal trends, NO_x emission
21 reduction

22 **1 Introduction**

23 Particulate nitrate (NO_3^-) has been a central focus of pollution control strategies in the
24 past several decades due to its impact on air quality, climate, and ecosystem health
25 (Balamurugan et al., 2022; Dang et al., 2024; Thunis et al., 2021; Zhai et al., 2021; Bell
26 et al., 2007; Chan et al., 2021; Cheng et al., 2024; Dabek-Zlotorzynska et al., 2011;
27 Duce et al., 2008; Font et al., 2024; Harrison et al., 2022; Man et al., 2015; Pullokaran
28 et al., 2024; Squizzato et al., 2018; Sun et al., 2025; Wang et al., 2020; Zaveri et al.,
29 2021; Zhang et al., 2008; Zhou et al., 2022). NO_3^- impacts air quality because it is a
30 major chemical component of particulate matter, particularly fine particles. Besides,
31 photolysis of NO_3^- produces highly reactive oxidants, such as hydroxyl radicals, HOCl,
32 and Cl_2 , thereby enhancing atmospheric oxidation capacity (Chen et al., 2025; Gen et
33 al., 2022; Peng et al., 2022). NO_3^- contributes to climatic effects directly through
34 radiative forcing and indirectly through increasing cloud condensation nuclei (Drugé et
35 al., 2019; Zaveri et al., 2021). For instance, a modeling study showed that nitrate
36 aerosols contributed significantly to shortwave radiative cooling, reaching up to -5 W
37 m^{-2} on a regional scale under clear-sky condition and -0.8 W m^{-2} on global average
38 (Zaveri et al., 2021). NH_4NO_3 formed from condensation of gaseous species of NH_3
39 and HNO_3 can rapidly grow to the sizes of cloud condensation nuclei in cold
40 atmospheres (Höpfner et al., 2019; Wang et al., 2022; Zhu et al., 2014). Additionally,
41 NO_3^- contributes to atmospheric nitrogen deposition, which has ecosystem implications
42 (Bose et al., 2018; Iizuka et al., 2025), and it can even undergo long-range transport in
43 the atmosphere and eventually deposit into oceans or remote continental regions
44 (Jonson et al., 2022; Qi et al., 2018; Iizuka et al., 2025).

45
46 Given the significant reductions of SO_2 emissions worldwide in the past four decades,
47 the impacts of NO_3^- on air quality, climate, and ecosystem health have garnered
48 increasing attention (Aas et al., 2019; Feng et al., 2020; Hand et al., 2024; Sun et al.,
49 2018; Velazquez-Garcia et al., 2023; Wang et al., 2021; Zhai et al., 2021). Unlike
50 sulfate (SO_4^{2-}), which predominantly exists in fine particulate matter ($\text{PM}_{2.5}$), NO_3^-
51 exists in both fine- and coarse-mode particles (referred to as f- NO_3^- and c- NO_3^- ,

52 respectively). As a semi-volatile substance, the fine and coarse fractions of NO_3^- vary
53 with season and location (Peng et al., 2024; Yao and Zhang, 2012a, b; Zhang et al.,
54 2008) because its volatility and partitioning with its gaseous precursors are influenced
55 by ambient meteorological and chemical conditions, including temperature (T), relative
56 humidity (RH), and mixing ratios of HNO_3 and NH_3 (Guo et al., 2016; Seinfeld and
57 Pandis, 2016; Yao et al., 2003; Huo et al., 2025). This complicates the response of f-
58 NO_3^- and c- NO_3^- to changes in NO_x emissions (Balamurugan et al., 2022; Chan et al.,
59 2021; Thunis et al., 2021; Zhai et al., 2021; Huo et al., 2025). Additionally, reduced
60 NO_x emissions may enhance the formation of N_2O_5 at nighttime, a product that can
61 form f- NO_3^- through secondary aerosol formation, thereby further influencing the
62 response of f- NO_3^- to emission reductions (Fan et al., 2020; Shah et al., 2018; Wang et
63 al., 2023; Yan et al., 2023; Zhou et al., 2022; Ward et al., 2025). It has been reported
64 that f- NO_3^- can form from condensable species in fresh stationary combustion plumes,
65 followed by dispersion and evaporation under freezing ambient conditions (Shen et al.,
66 2022; Xiao et al., 2025; Yang et al., 2024; USEPA, 2017). This mechanism has been
67 largely overlooked in studies examining the response of NO_3^- to NO_x emission
68 reductions, particularly in regions with prolonged cold seasons.

69

70 Canada is a nation experiencing long cold winters. Higher concentrations of f- NO_3^-
71 were predominantly observed during cold winter seasons, except during large-scale
72 wildfire events mostly occurring in warm seasons (Bari and Kindzierski, 2016a, b;
73 Dabek-Zlotorzynska et al., 2011; Edgerton et al., 2020; Jeong et al., 2011; Wang et al.,
74 2021). The contributions of primary and/or secondary sources to the elevated f- NO_3^-
75 concentrations in Canadian cold atmospheres remain poorly understood. The primary
76 emissions of f- NO_3^- likely arise from two major processes: (i) the rapid formation of f-
77 NO_3^- through reactions between $\text{HNO}_{3\text{gas}}$ and $\text{NH}_{3\text{gas}}$ within the first few seconds after
78 combustion plumes exit the stack outlet (or vehicle exhaust pipes) and undergo cooling;
79 and (ii) the formation of f- NO_3^- via the reaction $2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HNO}_2$ within
80 droplets produced in fresh cooling combustion plumes, followed by $\text{NH}_{3\text{gas}}$
81 neutralization before these droplets evaporate into ambient aerosols. Note that the fresh

82 plumes contain extremely high concentrations of various air pollutants, enabling the
83 occurrence of the above-mentioned reactions (Seinfeld and Pandis, 2016; Zhang et al.,
84 2021; Zhang et al., 2023).

85
86 The aforementioned knowledge gap hinders our understanding of how changes in
87 primary f-NO₃⁻ emissions influence the annual-scale response of f-NO₃⁻ to NO_x
88 emission reductions. This gap appears to be global rather than unique to Canada, as
89 indicated by the brief review of particulate NO₃⁻ trends and their responses to NO_x
90 emission reductions summarized in Text S1 of the Supporting Information (SI). Two
91 key points emerge. (1) The limited number of trend studies on particulate NO₃⁻ across
92 Canada, including f-NO₃⁻ and total NO₃⁻ (=f-NO₃⁻+c-NO₃⁻) in suspended particles,
93 suggest that long-term changes are neither spatially uniform nor monotonic. (2) The
94 non-linear and sometimes counterintuitive response of particulate NO₃⁻ to NO_x
95 emission controls has been widely reported in the United States, Europe, and China, yet
96 the underlying drivers remain insufficiently constrained. Together, these cross-regional
97 comparisons motivate a Canada-focused synthesis that explicitly evaluates the non-
98 linear influences of co-evolving precursor emissions, gas-particle partitioning, and
99 meteorological variability in interpreting long-term f-NO₃⁻ trends.

100
101 Additionally, significant decreases in NO_x emissions across Canada mainly occurred
102 between 1998 and 2008, with slight time shifting across different provinces (ECCC,
103 2021). PM_{2.5} speciation data since 2003 alone may not fully elucidate the response of
104 NO₃⁻ to reduced NO_x emissions. Fortunately, both f-NO₃⁻ and c-NO₃⁻ data are available
105 from the National Air Pollution Surveillance (NAPS) at 12 urban sites (Dabek-
106 Zlotorzynska et al., 2019; Dabek-Zlotorzynska et al., 2011). Seven of these 12 sites
107 have integrated measurements of particulate chemical components spanning 1-3
108 decades, enabling the examination of long-term trends in f-NO₃⁻ and c-NO₃⁻ in
109 Canadian urban atmospheres and their responses to reduced NO_x emissions.

110

111 In this study we investigated long-term trends in the annual average mass
112 concentrations of f-NO₃⁻ and c-NO₃⁻ in Canadian urban atmospheres, with a particular
113 focus on the responses of f-NO₃⁻ and c-NO₃⁻ to NO_x emission reductions since 1990
114 and the associated mechanisms. The analyses are structured into three major parts: Part
115 1 examines the long-term trends of f-NO₃⁻ and c-NO₃⁻, firstly in Edmonton (Section
116 3.1) and then extended the other six cities (Sections 3.2 and 3.3); Part 2 investigates the
117 key factors influencing f-NO₃⁻ levels in Edmonton (Section 3.4) and the role of primary
118 f-NO₃⁻ emissions in shaping these trends (Section 3.5); and Part 3 provides a
119 comprehensive assessment of uncertainties associated with f-NO₃⁻ and their potential
120 impact on the observed trends (Section 3.6). Finally, a summary of the major findings
121 and potential implications are presented in Section 4.

122 **2 Methodology**

123 **2.1 Monitoring sites and data sources**

124 The present study utilized long-term data monitored at two urban sites in Edmonton (S-
125 90132, Latitude: 53.486, Longitude: -113.465; and S-90130, Latitude: 53.544,
126 Longitude: -113.499), as well as one urban site in each of the other six cities, including
127 Winnipeg (49.898, -97.147), Victoria (48.442, -123.363), Vancouver (49.281, -
128 122.849), Montreal (45.543, -75.572), Quebec City (46.821, -71.221), and Hamilton
129 (45.258, -79.862) (Figures S1 and S2). The first four cities are in western Canada with
130 Edmonton in the province of Alberta, Winnipeg in the province of Manitoba, and
131 Victoria and Vancouver in the province of British Columbia. The other three cities are
132 in eastern Canada with Montreal and Quebec City in the province of Quebec and
133 Hamilton in the province of Ontario.

134

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

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

147

148 In Hamilton, an identical speciation sampler has been used since 2013 to measure ionic
149 components in $\text{PM}_{2.5}$ and gases, with sampling occurring one in every three days. In
150 this city, only elements have been measured in samples collected by the Dichotomous
151 Air Sampler since then. At the other five urban sites selected for this study, speciation
152 $\text{PM}_{2.5}$ data were either unavailable (Winnipeg and Quebec City) or collected one in
153 every six days after 2005 (Victoria, Vancouver, and Montreal). $\text{PM}_{2.5}$ air samplers
154 (Thermo, US) were used in Victoria and Winnipeg after 2012, and $\text{PM}_{2.5}$ samplers
155 (TISCH, US) were used in Vancouver and Montreal after 2016. Corresponding NO_3^-
156 data in $\text{PM}_{2.5-10}$ were not available at these sites since then. In this study, NO_3^- in $\text{PM}_{2.5}$
157 collected by speciation samplers was also referred to as f- NO_3^- . The same definition is
158 applied to f- SO_4^{2-} and f- NH_4^+ , which were used to facilitate the analysis of f- NO_3^- .

159

160 Hourly average mass concentrations of $\text{PM}_{2.5}$ and mixing ratios of NO_2 were also
161 routinely measured at each site, except that no NO_2 mixing ratios were reported at S-
162 90132. In this case, the values from S-90130 were used in this study. For certain parts
163 of the year at the sites in Victoria and Quebec City, NO_2 mixing ratios were also
164 unavailable. In these cases, the mixing ratios of NO_2 measured at different sites within
165 a 1-2 km radius in the same city were used to facilitate the analysis. All the data are
166 publicly available through the National Air Pollution Surveillance (NAPS) program
167 network ([https://data-donnees.ec.gc.ca/data/air/monitor/national-air-pollution-](https://data-donnees.ec.gc.ca/data/air/monitor/national-air-pollution-surveillance-naps-program/?lang=en)
168 [surveillance-naps-program/?lang=en](https://data-donnees.ec.gc.ca/data/air/monitor/national-air-pollution-surveillance-naps-program/?lang=en)) and summarized in Table S1.

169

170 NO_x, SO₂, and NH₃ emissions data at the provincial level in Canada were obtained from
171 [https://www.canada.ca/en/environment-climate-change/services/environmental-
173 indicators/air-pollutant-emissions.html](https://www.canada.ca/en/environment-climate-change/services/environmental-
172 indicators/air-pollutant-emissions.html). The monthly average wind fields were
174 downloaded from <https://psl.noaa.gov/data/gridded/data.narr.html> (Figures 1 and S1),
175 and the Arctic Oscillation (AO) Indexes were obtained from
176 <https://www.ncdc.noaa.gov/teleconnections/ao/> (Figure S1d). Ground-level
177 meteorological data from the airports of these cities were also downloaded from
178 <https://www.wunderground.com/about/data>.

179 It should be noted that existing techniques for measuring ambient HNO_{3gas} are subject
180 to certain artifacts. Specifically, the Na₂CO₃-coated denuder used in speciation
181 samplers is designed to remove acidic gases upstream of PM_{2.5} collection on a Teflon
182 filter, thereby minimizing positive artifacts in the collected PM_{2.5} (Dabek-Zlotorzynska
183 et al., 2019; Dabek-Zlotorzynska et al., 2011). However, measurements obtained using
184 the denuder technique do not exclusively represent HNO_{3gas}. Instead, they include
185 HNO_{3gas}, N₂O_{5gas}, and other acidic gases that react with Na₂CO₃ to form NaNO₃.
186 Consequently, the reported concentrations reflect an upper bound of (HNO_{3gas} +
187 N₂O_{5gas}). To avoid ambiguity, the measured values are denoted as HNO_{3gas}* rather than
188 HNO_{3gas} throughout the following discussion. Importantly, this measurement
189 uncertainty does not materially affect the conclusions of the present study, as HNO_{3gas}*
190 concentrations remain substantially lower than the corresponding particulate nitrate
191 levels during the high-nitrate winter periods examined here (see Section 3.4).
192 Nevertheless, the upper-bound nature of HNO_{3gas}* may introduce bias in gas–particle
193 equilibrium analyses, particularly during winter nighttime high-concentration episodes,
194 when the true HNO_{3gas} mixing ratio may be considerably lower than HNO_{3gas}* due to
195 a potentially substantial contribution from N₂O₅(g).

196 2.2 Statistical analysis

197 Annual average mass concentrations of f-NO₃⁻ and c-NO₃⁻ were calculated from all
198 available data in each calendar year. However, data loss was common in each city and
199 year despite sampling occurring one in every three or six days. To minimize uncertainty
200 from data loss and ensure sufficient data for trend analysis, data for trend analysis were
201 excluded for any year when measurements for two consecutive months were
202 unavailable. To analyze the time series of the annual average mass concentrations of
203 each species, the Mann-Kendall (M-K) analysis was employed. The qualitative trend
204 results determined by the M-K method include: (i) an increasing/decreasing trend with
205 a *P* value of <0.05, (ii) a probable increasing/decreasing trend with a *P* value between
206 0.05 and 0.1, (iii) a stable trend with a *P* value >0.1, as well as a ratio of <1.0 between
207 the standard deviation and the mean of the dataset, and (iv) a no trend with a *P* >0.1 and
208 other conditions (Lin et al., 2022).

209

210 To quantify the overall effect of climate anomalies on the annual average f-NO₃⁻
211 between a pair of two years, our recently developed identical-percentile regression
212 analysis was used (Lin et al., 2022; Yao and Zhang, 2024). In this method, the data
213 sizes of the paired two-year should be the same (e.g., with the same time resolution and
214 filling up all the missing data). The two sets of data, originally in time series, are sorted
215 separately from the smallest to the largest to generate two percentile-based data arrays,
216 which were then used for regression analysis with the intercept being set to be zero.
217 The regression analysis can also be conducted using data in any particular percentile
218 range for exploring different research targets. If the data sizes of the paired two-year
219 are different, the one with a larger size can be modified to match the one with a smaller
220 size using the method presented by Lin et al. (2022) and Yao and Zhang (2024) before
221 applying the regression analysis described above. Moreover, a Random Forest (RF)
222 model was employed to evaluate the relative importance of meteorological and seasonal
223 timing variables in driving f-NO₃⁻ formation (Text S2 of SI), and the Flexible 0-D

224 Atmospheric Model (F0AM) was applied to simulate secondary production of f-NO₃⁻
225 (Text S3 of SI).

226 **3 Results and discussion**

227 **3.1 Complexity of particulate nitrate trends in urban atmosphere of Edmonton**

228 As mentioned in Section 2.1, two sites (S-90130 and S-90132) in Edmonton were
229 selected for investigation due to the discontinued data coverage at both sites. Annual
230 average mass concentrations of f-NO₃⁻ at S-90130 from 1990 to 2005 and at S-90132
231 from 2007 to 2019 were analyzed to illustrate the complexity of particulate nitrate
232 trends in the urban atmosphere (Figure 1a). As mentioned in Section 2.1, data in 2006
233 were missing at both sites. For comparison, annual average mass concentrations of c-
234 NO₃⁻ at S-90130 from 1990 to 2005 are also shown in Figure 1a and those of f-NH₄⁺
235 and f-SO₄²⁻ at S-90130 and S-90132 from 1990 to 2019 are shown in Figure S3. To
236 facilitate analysis, annual average mixing ratios of NO₂ at S-90130 from 1995 to 2019
237 are shown in Figure 1b, and annual provincial total emissions of NO_x, SO₂, and NH₃ in
238 Alberta are also presented (Figures 1b, S3a and S3c, respectively). Correlation analyses
239 between f-NO₃⁻ (or c-NO₃⁻) and provincial total emissions of NO_x in 1990-2005 and
240 between f-SO₄²⁻ and provincial total emissions of SO₂ in 1990-2019 are conducted
241 (Figures 1c and S3b, respectively).

242

243 At S-90130, annual average f-NO₃⁻ and c-NO₃⁻ was $0.48 \pm 0.25 \mu\text{g m}^{-3}$ (average \pm
244 standard deviation) and $0.15 \pm 0.05 \mu\text{g m}^{-3}$, respectively, during 1990 - 2005. No trend
245 or stable trend was found for these species ($P > 0.10$), likely due to a bell-shaped change
246 in provincial total NO_x emissions from 1990 to 2005. In fact, a significant correlation
247 was found between annual average c-NO₃⁻ and provincial total NO_x emissions during
248 1990-2005 ($P < 0.01$). However, a significant correlation between annual average f-
249 NO₃⁻ and provincial NO_x emissions was obtained only during 1992-2005 ($P < 0.01$),
250 but not for the entire period during 1990-2005 with the values in 1990-1991 being
251 substantially deviating from the regression curve. Such a deviation is yet to be

252 explained. Notably, f-NO₃⁻ and c-NO₃⁻ 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-NO₃⁻ and
255 c-NO₃⁻ is discussed in detail in Section 3.2.

256

257 At S-90132, annual average f-NO₃⁻ was $1.3 \pm 0.40 \mu\text{g m}^{-3}$ during 2007 - 2019. f-NO₃⁻
258 exhibited a decreasing trend ($P < 0.01$), with a Sen's Slope of $0.063 \mu\text{g m}^{-3} \text{ yr}^{-1}$,
259 resulting in an overall decrease of approximately 60% during this period. In
260 comparison, the monitored NO₂ 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-NO₃⁻ and c-NO₃ 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 NO₂ mixing ratios and provincial NO_x total emissions. Notably,
266 NO₂ 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-NO₃⁻ 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 NO₃⁻ (Sections 3.6). It should be noted that the annual average f-NO₃⁻ 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-NO₃⁻, annual average f-SO₄²⁻ exhibited a relatively smooth decreasing trend
280 ($P < 0.01$), with a Sen's slope of $0.029 \mu\text{g m}^{-3} \text{ yr}^{-1}$ 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

282 mostly consistent with a $0.021 \mu\text{g m}^{-3} \text{yr}^{-1}$ decrease in the provincial total SO_2 emissions
283 from 1990 to 2019. Additionally, a moderately strong correlation was found between
284 the annual average f-SO_4^{2-} and the provincial total SO_2 emissions over the three decades
285 ($P < 0.01$, Figure S3b). The f-SO_4^{2-} trend in the urban atmosphere reflects the mitigation
286 effect, as has also been reported for rural atmospheres in Canada (Cheng and Zhang,
287 2017; Feng et al., 2020). f-SO_4^{2-} , typically formed through in-cloud aqueous reactions
288 and with non-volatile properties, is generally associated with regional sources, and thus
289 tends to be spatially homogeneously distributed in urban scales (Bell et al., 2007; He et
290 al., 2001; Park et al., 2004). This may explain the much smaller gaps in the annual
291 average f-SO_4^{2-} between the two nearby urban sites, as compared to the case of f-NO_3^-
292 .

293
294 Annual average f-NH_4^+ exhibited a decreasing trend ($P < 0.05$) if combining data at S-
295 90130 from 1990 to 2005 and at S-90132 from 2007 to 2019 (Figure S3c). However,
296 the trend was stable at both sites during the two separate periods ($P > 0.10$). From 1990
297 to 2019, the provincial total NH_3 emissions increased by approximately 40% (Figure
298 S3c). The phenomenon of the decoupled trends between f-NH_4^+ and NH_3 emissions
299 widely occurred in Canada and the U.S. in the recent decades, as reported in Yao and
300 Zhang (2019). This is because the level of f-NH_4^+ was mainly controlled by those of
301 SO_4^{2-} and NO_3^- through neutralization reactions, especially under NH_3 -rich conditions
302 (Bari and Kindzierski, 2016b; Dabek-Zlotorzynska et al., 2011; Edgerton et al., 2020).
303 The equivalent ratios of NH_4^+ to $(\text{SO}_4^{2-} + \text{NO}_3^-)$ in two selected years support this
304 hypothesis (Figure S4).

305 **3.2 Trends of f-NO_3^- and c-NO_3^- in urban atmospheres of Winnipeg – an inland** 306 **city in western Canada**

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

311 term average of $0.19 \pm 0.04 \mu\text{g m}^{-3}$ during 1990–2012. A probable increasing trend in
312 annual average c-NO₃⁻ was identified ($P = 0.06$). Over the same period, both the annual
313 average mixing ratio of NO₂ at this site and provincial total NO_x emissions in Manitoba
314 exhibited decreasing trends ($P < 0.01$) (Figure 1e), and they correlated with each other
315 strongly ($R^2 = 0.90$, $P < 0.01$). The absence of a corresponding decrease in f-NO₃⁻
316 concentration compared to NO_x emissions is likely attributable to enhanced primary
317 emissions of f-NO₃⁻-containing aerosols, as discussed in Sections 3.3 and 3.5 below.
318 This is clearly supported by the following evidence: from 1999 to 2004, annual average
319 f-NO₃⁻ increased by approximately 200%, even as provincial NO_x emissions and NO₂
320 mixing ratios declined by about 10%. Accordingly, the trend in f-NO₃⁻ concentrations
321 was analyzed in two separate periods: 1990–2002 and 2003–2018. The year of 2003 is
322 allocated into the second rather than the first period based on the curve of annual
323 variation shown in Figure 1d. In the first period (1990–2002), f-NO₃⁻ showed a probable
324 decreasing trend, with a Sen’s Slope of $0.017 \mu\text{g m}^{-3} \text{ year}^{-1}$ and a total decline of about
325 80%. This sharp decrease cannot be explained by the relatively modest 10–20%
326 reductions in NO₂ and NO_x during the same period, suggesting that highly localized
327 factors and/or uncertainties caused by coarse resolution data (1 in every 6 days) were
328 likely the dominant contributors. The related uncertainty analysis is presented in
329 Section 3.6 below. In the second period (2003–2018), f-NO₃⁻ exhibited a decreasing
330 trend with a Sen’s Slope of $0.018 \mu\text{g m}^{-3} \text{ year}^{-1}$, amounting to an overall reduction of
331 approximately 70%, which also exceeded the ~50% reduction in NO₂ mixing ratios at
332 the same site and the ~30% reduction in provincial NO_x emissions. The
333 disproportionate trends between f-NO₃⁻ and NO_x emissions observed in Winnipeg are
334 similar to the case in Edmonton discussed above.

335

336 When the time series of daily concentrations of f-NO₃⁻ and c-NO₃⁻ were examined for
337 a low-concentration year (1996) and a high-concentration year (2007) (Figure 1f-g),
338 elevated concentrations of f-NO₃⁻ were predominantly observed during the cold
339 months. High concentrations of f-NO₃⁻ were likely from primary sources, as discussed
340 in Section 3.5 below, considering the similar climate in inland western Canada. This,

341 however, needs to be confirmed using $\text{HNO}_{3\text{gas}}^*$ data, which are not available at this
342 site. In contrast, elevated concentrations of c-NO_3^- typically occurred during warmer
343 months. Again, no significant correlation was observed between f-NO_3^- and c-NO_3^- in
344 any year ($R^2 < 0.1$, $P > 0.05$). Given the probable increasing trend in annual average c-
345 NO_3^- despite decreasing NO_x emissions at both city and provincial scales, and
346 considering the seasonal pattern of elevated levels, it is likely that the trend in c-NO_3^-
347 was governed by the availability of alkali aerosols associated with suspended road dust
348 and road-salt particles capable of neutralizing $\text{HNO}_{3\text{gas}}^*$, rather than by changes in
349 $\text{HNO}_{3\text{gas}}^*$ itself. As further illustrated in Section 3.4 below for the case of Edmonton,
350 stagnant winter meteorological conditions did not coincide with elevated $\text{HNO}_{3\text{gas}}^*$
351 concentrations, likely due to the accompanying sub-freezing temperatures. Moreover,
352 stagnant and freezing conditions are not conducive to the suspension of road dust and
353 road-salt particles during winter. This interpretation is also supported by findings
354 reported in literature at rural sites in Canada (Cheng and Zhang, 2017; Feng et al., 2020)
355 and urban and rural sites in the U.S. (Sickles II and Shadwick, 2015) and U.K. (Tang et
356 al., 2018), where positive correlations between $\text{HNO}_{3\text{gas}}^*$ and NO_2 have been observed,
357 suggesting that a reduction in NO_x would not typically lead to enhanced $\text{HNO}_{3\text{gas}}^*$
358 formation.

359 **3.3 Time window for unintended effects of NO_x mitigation on f-NO_3^- aerosols in** 360 **Canadian urban atmospheres and associated shaped trends of f-NO_3^- and c-NO_3^-**

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

370 example, in the province of Quebec, the annual average f-NO₃⁻ increased by
371 approximately 150% in Quebec City from 1998 to 2003 and by around 300% in
372 Montreal from 1998 to 2002. During the same period, annual average mixing ratio of
373 NO₂ decreased by approximately 10% in both cities, while provincial total NO_x
374 emissions remained nearly unchanged. In the province of Ontario, annual average f-
375 NO₃⁻ in Hamilton remained relatively low at 0.69 ± 0.09 µg m⁻³ during 1995–1999, but
376 rose sharply to 1.6 µg m⁻³ in 2001, with a notable dip to 0.85 µg m⁻³ in 2002 possibly
377 due to climate anomaly, bounced back to 1.7 µg m⁻³ in 2004 and stabilized at 1.6 µg m⁻³
378 in 2005. During the period from 1999 - 2005, both observed NO₂ mixing ratios in
379 Hamilton and provincial NO_x emissions in Ontario began to decline by 20–30%. A
380 similar pattern was also found in western coastal urban areas such as Victoria and
381 Vancouver, both located in British Columbia, between 1998 and 2002 (Figure 2), where
382 annual average f-NO₃⁻ increased by approximately 100% while NO₂ mixing ratios and
383 provincial NO_x emissions declined by 10–30%. These widespread, disproportionate
384 trends between f-NO₃⁻ and NO_x emissions across multiple cities strongly suggest that,
385 during this early control window, NO_x mitigation measures may have been
386 accompanied by an unintended increase in primary f-NO₃⁻ emissions, potentially
387 associated with condensable particulate matter (CPM) and/or byproducts of emission
388 control technologies. However, no direct facility measurement data were made 20-year
389 ago to verify this hypothesis. In fact, the USEPA only issued the method protocol for
390 determining condensable particulate matter in 2017. Evidence from recent studies in
391 developing countries further indicates that early-stage NO_x controls (e.g., NH₃-SCR
392 operated at >300 °C) can be susceptible to imperfect ammonia dosing and the formation
393 of associated byproducts (Yang et al., 2016). This provides a plausible mechanistic
394 explanation, although the specific causes in Canada and the United States cannot be
395 definitively determined in the absence of historical CPM measurements. Accordingly,
396 trend analysis of particulate nitrate should treat this period separately, with a
397 demarcation line drawn at approximately 2002 or later.

398

399 In contrast to this early-phase behavior, several lines of evidence suggest that primary
400 f-NO₃⁻ emissions have likely declined in recent years. At the national scale, Canada's
401 electricity supply has shifted markedly toward CO₂-emission-free sources (now
402 exceeding 80%), which are also largely free of NO_x emissions. This transition should
403 reduce primary nitrate-related emissions from the power sector (Canada Electricity
404 Advisory Council, 2024). In addition, the rapidly increasing share of zero-emission
405 vehicles, accounting for 10.8% of new vehicle registrations in 2023, is expected to
406 further decrease primary f-NO₃⁻ emissions from the transportation sector (Statistics
407 Canada, 2024). Consistent with these broader trends, observations in Edmonton show
408 that the decline in annual mean f-NO₃⁻ concentrations over the past decade has been
409 substantially larger than the corresponding decrease in NO₂. This divergence supports
410 the interpretation that reductions in primary f-NO₃⁻ emissions have likely been an
411 important contributing factor.

412

413 Setting the demarcation line at 2003 in Quebec City (noting the substantial data loss in
414 2002 for this city) and at 2002 in Montreal, the annual average f-NO₃⁻ decreased by
415 more than 70% over the subsequent 16- or 17-year period, largely agree with the 40-
416 60% reductions in NO₂ mixing ratios and provincial NO_x emissions during the same
417 period. The slight differences in their decreasing rates could be attributed to unintended
418 changes in primary emissions of f-NO₃ aerosols as discussed above, non-linear
419 atmospheric chemistry process involving other chemical species, and data uncertainties,
420 etc. Notably, the annual average c-NO₃⁻ showed no significant trend during these
421 periods in either city, suggesting that c-NO₃⁻ levels may have been more strongly
422 influenced by the presence of alkali aerosols capable of neutralizing HNO_{3gas}^{*} rather
423 than by the availability of HNO_{3gas}^{*} itself. Data prior to 2002 (Montreal) or 2003
424 (Quebec City) were insufficient in duration to support robust trend analysis;
425 nevertheless, the influence of unintended mitigation effects during this period was still
426 evident. In comparison, if removing the demarcation line and considering the whole
427 data record together, annual average f-NO₃⁻ would show no clear trend from 1995 to
428 2018 in Quebec City and a stable trend from 1997 to 2018 in Montreal. Over the full

429 period, annual average f-NO₃⁻ and c-NO₃⁻ were $0.41 \pm 0.19 \mu\text{g m}^{-3}$ and $0.19 \pm 0.05 \mu\text{g}$
430 m^{-3} , respectively, in Quebec City and $0.57 \pm 0.38 \mu\text{g m}^{-3}$ and $0.28 \pm 0.06 \mu\text{g m}^{-3}$,
431 respectively, in Montreal.

432

433 Similarly, if setting a demarcation line at the year of 2002 for Victoria and Vancouver,
434 f-NO₃⁻ would show either a significant decreasing trend or a probable decreasing trend,
435 with a total decrease of around 40% in both cities from 2002 to 2018. These declines
436 were broadly consistent with the 30–40% decreases in both NO₂ mixing ratios and
437 provincial NO_x emissions during the same period. From 1990 to 2002, f-NO₃⁻ showed
438 either no trend or a stable trend, which was consistent with the trend in the provincial
439 NO_x emissions, but inconsistent with the observed decreasing trend in NO₂ mixing ratio
440 during this period. If looking at the full data record of c-NO₃⁻ together (from 1990 to
441 2012 in Victoria or 2015 in Vancouver), either no trend or a stable trend was identified
442 in either city, regardless of using the full data record or just data after the year 2002.
443 The absence of a clear decreasing trend in c-NO₃⁻ concentration, despite significant
444 NO_x emissions, appears to be a common feature across Canadian urban environments.
445 Unlike the other cities aforementioned where annual average concentrations of f-NO₃⁻
446 were much higher than those of c-NO₃⁻, in Victoria, annual average concentrations of
447 f-NO₃⁻ and c-NO₃⁻ were similar, oscillating around $0.23 \pm 0.06 \mu\text{g m}^{-3}$ (1990 to 2018)
448 and $0.25 \pm 0.05 \mu\text{g m}^{-3}$ (1990 to 2012), respectively. In contrast, annual average
449 concentrations of f-NO₃⁻ ($0.16 \pm 0.05 \mu\text{g m}^{-3}$ in 1990 - 2018) were significantly smaller
450 than that of c-NO₃⁻ ($0.31 \pm 0.05 \mu\text{g m}^{-3}$ in 1990 - 2015) ($P < 0.01$) in Vancouver, and the
451 same conclusion can be generated if only using data in 1990-2015.

452

453 In Hamilton, no statistically significant trends were identified for f-NO₃⁻ and c-NO₃⁻,
454 whether considering the full time series or just the period post-2005. This is somewhat
455 different than the cases in the other cities discussed above, suggesting potentially strong
456 impact of local sources, besides the other main factors discussed above, considering
457 that Hamilton is an industrial city with heavy density of industries. Annual average f-

458 NO_3^- and c-NO_3^- in this city were $0.88 \pm 0.35 \mu\text{g m}^{-3}$ and $0.46 \pm 0.12 \mu\text{g m}^{-3}$,
459 respectively, during the period of 1995 to 2019.

460 **3.4 Key factors influencing annual average f- NO_3^- and its trends in Edmonton**

461 To explore key factors influencing the annual average f- NO_3^- and its trends in
462 Edmonton, we selected data from two representative years (2010 and 2015) at site S-
463 90132 for comparative analysis. The year 2010 was chosen because in this year
464 abnormally high annual average f- NO_3^- was observed compared to all the other years
465 during the period of 2007-2019, suggesting possible impact by climate anomaly in this
466 year. The year 2015 was chosen because in this year annual average f- NO_3^- represents
467 the median value of a five-year period of 2015-2019, likely reflecting the average
468 climatic conditions, knowing that the annual average NO_2 mixing ratio observed at a
469 nearby site (S-90130) and the provincial total NO_x emissions were nearly constant
470 during 2015-2019. From 2010 to 2015, the decrease in NO_2 mixing ratios in Edmonton
471 (11%) was consistent with the decline in Alberta's provincial NO_x emissions (10%). In
472 contrast, the annual mean concentration of f- NO_3^- decreased much more sharply (by
473 58%), falling from $2.1 \mu\text{g m}^{-3}$ in 2010 to $0.89 \mu\text{g m}^{-3}$ in 2015.

474

475 Through the comparative analysis, seasonal variations of f- NO_3^- , various single-factor
476 effects on f- NO_3^- , and the impact of climate anomalies on f- NO_3^- were explored. As
477 shown in Figures 3a and 3b, higher concentrations of f- NO_3^- were predominantly
478 observed during cold months, including January to March and November to December,
479 in both 2010 and 2015. These higher concentrations during the five cold months
480 contributed to 81% and 88% of the annual averages in 2015 and 2010, respectively.
481 Thus, the annual trends in f- NO_3^- were mainly determined by higher concentrations of
482 f- NO_3^- in cold months in Edmonton. Based on wind fields shown in Figures S1 and S2,
483 air masses reaching to this site in the cold winter should come from the remote northern
484 areas with low pollution levels due to the strong northwest wind, which should have
485 lowered concentrations of f- NO_3^- in the urban atmosphere. Thus, the high
486 concentrations of f- NO_3^- observed at this site should be caused by local accumulation

487 under stagnant weather conditions. Therefore, the emissions of f-NO₃⁻-contained
488 aerosols related to mitigation measures, the precursors and formation pathways of f-
489 NO₃⁻, and meteorological conditions during the winter period should be considered as
490 key factors determining the annual average f-NO₃⁻.

491

492 We then correlated the 24-hr integrated daily concentrations of f-NO₃⁻ with ambient T,
493 wind speed (WS), RH, and gaseous HNO₃ (HNO_{3gas}) to explore various single-factor
494 effects on f-NO₃⁻ (Figure 3). A demarcation line was observed at -3°C in 2010 and
495 0.5°C in 2015, with substantially lower f-NO₃⁻ concentration at T on the right than left
496 side of the line (Figures 3a and 3e). Lower ambient T favored the gas-aerosol
497 partitioning of NH₄NO₃ in PM_{2.5} (Seinfeld and Pandis, 2016; Shah et al., 2018).
498 However, lower ambient T also weakened photochemical reactions due to reduced
499 amounts of intermediate volatility organic compounds or semi-volatile organic
500 compounds in the gas phase (McDonald et al., 2018; Wernis et al., 2022). This
501 reduction in photochemical activity subsequently lowered the concentration of HNO_{3gas}
502 to some extent, e.g., the concentrations of HNO_{3gas} observed at T > 20°C increased by
503 over a factor of four relative to those at T < -10°C in 2015 as shown in Figures 3e. The
504 sources of f-NO₃⁻ and its formation pathways during the winter period will be revisited
505 in Section 3.5. The causes for the different T values of the demarcation line between
506 2010 and 2015 are not clear. The concentrations of f-NO₃⁻ decreased with increasing
507 WS due to the dispersion effect, and no elevated concentrations were observed once
508 WS is stronger than 5 m/s (Figures 3b and 3f). The concentrations of f-NO₃⁻ had little
509 dependence on ambient RH (Figure 3c and 3g), e.g., the highest concentrations in both
510 years occurred at RH of 70-80% instead of >80%. The lowest concentrations of f-NO₃⁻
511 appearing at RH < 60% is because RH < 60% typically occurred at ambient T greater
512 than 0°C in Edmonton. In addition, the relative importance of 15 major variables on f-
513 NO₃⁻ concentration was examined using a Random Forest model, as detailed in Text S2
514 of SI. The ambient T ranked as the dominant factor, followed by PM_{2.5} mass
515 concentration, NO₂ mixing ratio, boundary layer height, etc.

516

517 It should be noted that gas–particle equilibrium between $\text{HNO}_3\text{--NH}_3$ and submicron
518 NH_4NO_3 is unlikely to be achieved at temperatures below $-10\text{ }^\circ\text{C}$, given the relatively
519 long equilibration timescales. Based on the results of characteristic timescales analysed
520 by Wexler and Seinfeld (1990, 1992) and dynamically simulated by Meng and Seinfeld
521 (1996), particles with diameters of approximately $0.5\text{--}0.7\text{ }\mu\text{m}$ generally require hours
522 to approach equilibrium – typically on the order of $\sim 1\text{--}6\text{ h}$ with a more conservative
523 upper bound of $\sim 6\text{--}20\text{ h}$. Under such low-temperature conditions, the assumption of
524 instantaneous thermodynamic equilibrium becomes questionable; therefore,
525 equilibrium thermodynamic modelling was not applied here. At even lower
526 temperatures, the equilibration timescale would extend to tens of hours for highly
527 viscous or glassy particles, as suggested by Li and Shiraiwa (2019).

528

529 Correlation analysis between simultaneously measured f-NO_3^- and $\text{HNO}_{3\text{gas}}^*$ showed
530 that f-NO_3^- concentrations higher than $4\text{ }\mu\text{g m}^{-3}$ occurred when $\text{HNO}_{3\text{gas}}^*$ concentrations
531 were lower than $0.4\text{ }\mu\text{g m}^{-3}$ in both years (Figures 3d and 3h). Thus, the high f-NO_3^-
532 concentrations were not likely caused from the secondary formation of f-NO_3^- from
533 $\text{HNO}_{3\text{gas}}^*$ in ambient air, as further discussed in Section 3.5 below. Considering that the
534 concentrations of $\text{NH}_{3\text{gas}}$ (data not shown here) were generally more than one order of
535 magnitude higher than those of $\text{HNO}_{3\text{gas}}^*$, $\text{NH}_{3\text{gas}}$ should not be the limiting factor for
536 f-NO_3^- formation, and was therefore excluded from further analysis below.

537

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

547 phase observed in the last four decades (Figure S1d). Typically, the belt of strong winds
548 circulating around 55°N latitude weakens during such a phase, which allows colder
549 Arctic air masses to penetrate further south into the mid-latitudes (Higgins et al., 2002).
550 The substantial decrease in WS during the winter period of 2010 likely contributed to
551 the higher annual average f-NO₃⁻ in this year. It is noticed that the recorded ambient T
552 in Edmonton in this winter was similar to the climatic mean value
553 (<https://www.wunderground.com/about/data>), further supporting the hypothesis that it
554 is the weakened WS caused by AO anomaly, rather than changes in T, that enhanced the
555 accumulation of f-NO₃⁻.

556

557 To further examine the effects of the AO anomaly on f-NO₃⁻ accumulation in 2010
558 relative to that in 2015, we conducted the identical-percentile regression analysis
559 between the two years (Figures 4c-e). With the intercept being forced to zero, similar
560 to the approach commonly used in chemical experiments for establishing the standard
561 curve (Yao et al., 2011), the slope of the regression equation was 2.74 if using all the
562 data (0th to 100th percentiles), 1.56 if using the central 50% data (25th to 75th percentiles),
563 and 1.41 if only using the lower 50% data (0th to 50th percentiles). The differences in f-
564 NO₃⁻ concentration between the two years were clearly enlarged when higher
565 concentrations were included, due to the AO anomaly effect in the winter of 2010.
566 Assuming a log-normal distribution of the data, the lower percentiles and higher
567 percentiles data, i.e., 0th to 2.5th percentiles and 97.5th to 100th percentiles, are normally
568 excluded from 95% confidence level. This is because these data points have lower
569 probability densities and their corresponding values are more vulnerable to climate
570 anomaly impact such as AO with negative and positive phases. The highest probability
571 density should always occur at the 50th percentile, where the corresponding value
572 should be least affected by AO. To minimize potential error from using a single value,
573 we used the average values of the 47.5th-52.5th percentiles, which were 0.63 μg m⁻³ in
574 2010 and 0.45 μg m⁻³ in 2015. The ratio of these two values (=1.4) was nearly identical
575 to the slope of the regression equation using data from the 0th to 50th percentiles
576 presented above. Thus, the annual average f-NO₃⁻ in 2010 was recalculated by the

577 corresponding value in 2015 being multiplying by a factor of 1.4 in order to deduct the
578 AO anomaly effect. The recalculated annual average f-NO₃⁻ in 2010 would decrease
579 from the original value of 2.1 µg m⁻³ to 1.2 µg m⁻³. Interestingly, removing the AO
580 effect in 2010 would only have a minor impact on the decadal trends from 2007 to 2019,
581 e.g., the Sen's Slope only showed small changes: which was 0.063 µg m⁻³ year⁻¹ using
582 the original annual average values including the year 2010, 0.060 µg m⁻³ year⁻¹ if
583 excluding the year 2010, and 0.057 µg m⁻³ year⁻¹ if replacing the year 2010 value with
584 1.2 µg m⁻³.

585

586 Overall, the AO largely affected the annual average f-NO₃⁻ in 2010. Nevertheless, such
587 an impact only has marginal effects on the decadal trends of f-NO₃⁻, as the AO typically
588 oscillates between negative and positive phases within 2-3 years (Figure S1d). The
589 enhanced or weakened effects of AO in 2-3 years can be largely canceled out in
590 extracting the decadal trend of f-NO₃⁻. The overall effect appeared to be too small to
591 explain the above-mentioned disproportionate responses of the annual average f-NO₃⁻
592 to the reduced NO_x emissions, and more exploration on this issue is presented in
593 Sections 3.5 and 3.6 below.

594

595 **3.5 Rethinking the role of primary emissions of NH₄NO₃ during the cold season in** 596 **Canadian urban atmospheres**

597 From the analysis presented in the previous section we concluded that the high
598 concentrations of f-NO₃⁻ in the winter were mainly due to local accumulation under
599 stagnant meteorological conditions, rather than long-range transport driven by
600 northwesterly winds. This raised the fundamental question: what is the role of primary
601 emissions in combustion plumes or secondary formation of NH₄NO₃ in ambient air in
602 contributing to f-NO₃⁻ in Canadian urban atmospheres during the cold season? To
603 answer this question, we proposed a hypothesis, i.e., whether HNO_{3gas}* concentrations
604 significantly increased under conditions with low f-NO₃⁻ concentrations compared to
605 cases with high f-NO₃⁻ concentrations, and then examined the hypothesis below.

606 Theoretical analysis and implications of the hypothesis were provided in supplementary
607 information (Text S3 of SI).

608

609 To examine the weaker hypothesis outlined above, we first divided the 2010
610 observations into two temperature regimes: $T < 0^{\circ}\text{C}$ and $0^{\circ}\text{C} < T \leq 4^{\circ}\text{C}$. Observations
611 with $T < 0^{\circ}\text{C}$ were further divided into two subsets based on f-NO_3^- concentrations,
612 using the thresholds of $> 4 \mu\text{g m}^{-3}$ and $\leq 4 \mu\text{g m}^{-3}$. These three groups were then
613 compared, i.e., Group 1: $T < 0^{\circ}\text{C}$ and $\text{f-NO}_3^- > 4 \mu\text{g m}^{-3}$, in which case there were 19
614 samples with average $\text{HNO}_{3\text{gas}}^*$ and f-NO_3^- concentrations being $0.15 \pm 0.09 \mu\text{g m}^{-3}$ and
615 $8.8 \pm 4.4 \mu\text{g m}^{-3}$, respectively; Group 2: $T < 0^{\circ}\text{C}$ and $\text{f-NO}_3^- < 4 \mu\text{g m}^{-3}$, in which case
616 there were 26 samples with average $\text{HNO}_{3\text{gas}}^*$ and f-NO_3^- concentrations being $0.15 \pm$
617 $0.12 \mu\text{g m}^{-3}$ and $1.3 \pm 0.7 \mu\text{g m}^{-3}$, respectively; and Group 3: $0^{\circ}\text{C} < T \leq 4^{\circ}\text{C}$, in which
618 case there were 13 samples with average $\text{HNO}_{3\text{gas}}^*$ and f-NO_3^- concentrations being
619 $0.15 \pm 0.11 \mu\text{g m}^{-3}$ and $1.3 \pm 1.7 \mu\text{g m}^{-3}$, respectively. Apparently, the average $\text{HNO}_{3\text{gas}}^*$
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 $\text{HNO}_{3\text{gas}}^*$ 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 $T > 0^{\circ}\text{C}$ 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 $T \leq 4^{\circ}$ 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 (\pm SD)
630 concentrations of f-NO_3^- and $\text{HNO}_{3\text{gas}}^*$ were $8.7 \pm 4.1 \mu\text{g m}^{-3}$ and $0.16 \pm 0.11 \mu\text{g m}^{-3}$
631 for Group 1, $1.4 \pm 0.95 \mu\text{g m}^{-3}$ and $0.17 \pm 0.16 \mu\text{g m}^{-3}$ for Group 2, and $0.9 \pm 1.1 \mu\text{g m}^{-3}$
632 3 and $0.15 \pm 0.10 \mu\text{g m}^{-3}$ for Group 3, respectively. Even with the expanded dataset,
633 mean $\text{HNO}_{3\text{gas}}^*$ 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.

636

637 The above analysis results suggest that the trend of f-NO₃⁻ in Edmonton was likely
638 governed by the primary emissions of f-NO₃⁻ aerosols, as well as the extents of their
639 volatilization and dispersion during the cold season. The dependence of volatilization
640 of f-NO₃⁻ on ambient T and dispersion on WS has been recently confirmed in
641 observational and modeling studies (Huo et al., 2025; Peng et al., 2024; Shen et al.,
642 2022). As mentioned in the Introduction, the primary emissions of f-NO₃⁻ likely have
643 two major sources (or processes). The first source is also conventionally defined as
644 condensable particulate emission and associated with the combustion of (N₂ + O₂),
645 which produces various oxidized nitrogen species, including HNO_{3gas}^{*}, NO_x, etc.
646 (USEPA, 2017). The amount of primary NH₄NO₃ formed from HNO_{3gas}^{*} in cooling
647 plumes theoretically depends on the combustion technology, the use of catalytic
648 reduction systems employing NH₃, and the ambient T (Zhang et al., 2021; Tayyeb Javed
649 et al., 2007; Palash et al., 2013), which may not be controlled by NO_x emission levels.
650 In some reported cases, mitigation measures reduced NO_x emissions, but
651 simultaneously increased primary emissions of f-NO₃⁻ (Feng et al., 2020; Palash et al.,
652 2013; Tayyeb Javed et al., 2007; Yang et al., 2024; Zhao et al., 2020). As evidences
653 presented in Sections 3.3, this phenomenon likely occurred across various Canadian
654 urban atmospheres. In contrast, the second source in fresh cooling plumes is directly
655 linked to NO_x emissions through the chemical conversion of NO₂ in cooling plume
656 droplets, although it is highly sensitive to the lifetime of these droplets (Shen et al.,
657 2022; Wang et al., 2016; Wang et al., 2020). In addition, primary nitrate aerosols from
658 traffic emissions were reportedly unimportant in urban atmospheres across Canada and
659 U.S. (Jeong et al., 2020; Chalbot et al., 2013), leaving only one possibility that primary
660 nitrate aerosols were mainly derived from stationary combustion sources.

661

662 Although secondary f-NO₃⁻ formation should always occur to some extent in ambient
663 air, the relative contribution from this process to the total f-NO₃⁻ is very small during
664 the periods with high f-NO₃⁻ concentrations. As shown in Text S4 of SI, the modeled
665 maximum potential contribution from secondary formation can only account for a small

666 fraction of the observed f-NO₃⁻ (<15% in the baseline runs, and <45% even in the
667 empirical-estimate runs known to have overpredictions in general). These results
668 support the hypothesis presented above that primary f-NO₃⁻ was the dominant
669 contributor to the high f-NO₃⁻ concentration in winter. Moreover, higher f-NO₃⁻
670 concentrations were generally observed under low wind speeds (WS <1-2 m s⁻¹). Given
671 that the sampling site is about 17 km from the farthest urban edge, the transport time
672 for both primary and secondary f-NO₃⁻ to reach the site was therefore estimated to be
673 approximately 2–4 h. This timescale is far too short for substantial secondary formation
674 of f-NO₃⁻ in such cold ambient air (T < -10 °C), unless in-source processes dominated
675 (Shen et al., 2022; USEPA, 2017; Zhang et al., 2023). Within this 2–4 h transport
676 window, the amount of HNO_{3gas}* dry deposition should also be minimum, especially
677 under low-temperature conditions.

678

679 **3.6 Uncertainties affecting f-NO₃⁻ trends in Edmonton**

680 Three categories of uncertainties that may affect the observed trends of f-NO₃⁻ in
681 Edmonton were analyzed: (i) differences in observational results between the speciation
682 sampler and the Dichotomous sampler, (ii) spatial inhomogeneity due to highly
683 localized factors, and (iii) artifacts introduced by the sampling frequency (e.g., every
684 third or sixth day), which may influence the calculation of annual averages. For
685 category (i) uncertainty, PM_{2.5} mass concentrations measured by the two different
686 instruments at site S-90132 in 2010 showed strong agreement for most samples, with
687 occasional discrepancies at lower concentration levels (Figure S6). Specifically, when
688 the regression intercept was forced to zero, the resulting equation was $y = 1.02 * x$ (R² =
689 0.94), and the difference in annual average concentrations was less than 10% (10.3 µg
690 m⁻³ from the Dichotomous sampler vs. 11.1 µg m⁻³ from the speciation sampler).

691

692 For category (ii) uncertainty, Figure S7 compares real-time PM_{2.5} mass concentrations
693 measured simultaneously at two sites 7 km apart (S-90132 and S-90130) from 2011 to
694 2014. Other years were excluded due to significant data loss at one or both sites.

695 Regression slopes between the two sites (with intercepts forced to zero) are 0.86, 0.82,
696 0.58, and 0.67, with corresponding differences in annual average concentrations of
697 21%, 15%, 40%, and 39% in 2011, 2012, 2013, and 2014, respectively. The significant
698 year-to-year differences between the two sites are unlikely caused by mitigation
699 policies, climate variability, or changes in the atmospheric formation pathways of
700 PM_{2.5}, but rather by spatial inhomogeneity driven by highly localized factors that varied
701 from year to year (Yeganeh et al., 2025). The influence of such localized effects appears
702 to be substantial and may represent an important, yet often overlooked, contributor to
703 the disproportionately large decreases in the annual average f-NO₃⁻ relative to
704 reductions in provincial total NO_x emissions over decadal timescales. More broadly,
705 pronounced intra-urban spatial heterogeneity has been documented for many ionic
706 aerosol components (with sulfate generally exhibiting a more regional character),
707 underscoring the importance of high-resolution urban monitoring for interpreting long-
708 term trends. At the same time, compared with routine PM mass measurements,
709 sustained long-term, high-resolution chemical speciation monitoring requires
710 substantially greater investment in instrumentation, maintenance, and operational
711 resources, making such measurements more challenging to maintain over multi-year
712 periods. This practical limitation highlights the need to carefully consider site
713 representativeness and spatial heterogeneity when interpreting long-term nitrate trends
714 derived from fixed-site observations.

715

716 It is noted that while the annual average PM_{2.5} mass concentrations were significantly
717 higher at S-90130 than S-90132 ($P < 0.01$) during 2010-2014, the opposite trend was
718 observed for the annual average f-NO₃⁻, e.g., higher at S-90132 during 2007–2019
719 compared to those at S-90130 during 1990–2005. The highest annual average f-NO₃⁻
720 concentration at S-90130 appeared in 2000 and that at S-90132 appeared in 2010
721 (Figure 1a). The mass fractions of f-NO₃⁻ in PM_{2.5} were 0.050 ± 0.065 in 2000 and 0.13
722 ± 0.13 in 2010 (Figure S4), indicating that PM_{2.5} at S-90132 contained more f-NO₃⁻
723 aerosols during 2007-2019 than at S-90130 during 1990-2005, strongly supporting the
724 hypothesis that mitigation measures reduced NO_x emissions in Edmonton, while

725 simultaneously increased primary f-NO₃⁻ emissions from the first source (see Section
726 3.3) after 2005.

727

728 Concerning category (iii) uncertainty, no continuous measurements of f-NO₃⁻ were
729 available to assess its magnitude. We thus used continuous measurements of PM_{2.5} data
730 at S-90130 as a proxy for this evaluation. Given that the annual average PM_{2.5} mass
731 concentration in 2010 was approximately 50% larger than in 2011, the analysis was
732 conducted using data from 2011 to 2020 instead of 2010 to 2020. Daily average PM_{2.5}
733 mass concentrations were first calculated for every day of the year. Then for each year,
734 annual average PM_{2.5} mass concentrations were calculated from daily average
735 concentrations using (i) full dataset, (ii) one in every three days data (three subsets),
736 and (iii) one in every six days data (six subsets). Thus, a total of 10 sets of annual
737 average PM_{2.5} data series was created for the period of 2011-2020, which was then used
738 for decadal trend analysis. The trend derived from the full dataset showed a decreasing
739 trend with a Sen's Slope of 0.43 μg m⁻³ year⁻¹. Consistent decreasing trends were also
740 obtained from using the one in every three days subset data series, with Sen's Slope
741 values of 0.46, 0.46, and 0.42 μg m⁻³ year⁻¹, respectively, indicating an error of less than
742 8%. When using the one in every six days subset data series, five out of six data subsets
743 also showed a decreasing trend, with Sen's Slope values of 0.47, 0.50, 0.45, 0.45, and
744 0.44 μg m⁻³ year⁻¹, respectively, indicating an error of less than 10% in most cases.
745 However, one subset data series showed a probable decreasing trend, with a Sen's Slope
746 of 0.38 μg m⁻³ year⁻¹.

747

748 Using the same approach described above, we also compared the decadal trends
749 obtained from using one in every three days data, which are readily available, with those
750 from using one in every six days data, which are arbitrarily split from the former data
751 set into two subsets. One of the two subsets for f-NO₃⁻ showed a decreasing trend with
752 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
753 year⁻¹; however, the other subset exhibited a stable trend. For f-SO₄²⁻, both subsets
754 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 $0.022 \mu\text{g}$
756 $\text{m}^{-3} \text{year}^{-1}$. 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 $\text{f-NO}_3^-/\text{f-SO}_4^{2-}$ 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 $\text{f-NO}_3^- > 4 \mu\text{g m}^{-3}$ exhibited $\text{f-NO}_3^-/\text{f-SO}_4^{2-}$ 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 (Pun et al., 2009; Smyth et al., 2009; Walker et al., 2012;
784 Kim et al., 2014, 2023; ECCO, 2016; Shah et al., 2018; Luo et al., 2019; Russell et al.,

785 2019; Pappin et al., 2024; Semeniuk et al., 2025). (2) The standard GEOS-Chem
786 v12.0.0 simulation substantially overestimated surface $\text{PM}_{2.5} \text{NO}_3^-$ over the U.S. (1.89
787 $\mu\text{g m}^{-3}$ vs. $0.70 \mu\text{g m}^{-3}$), with pronounced spatial heterogeneity: outside California, the
788 normalized mean bias reached +176%, whereas California exhibited an opposite bias
789 of -62%, implying region-dependent dominant error sources (e.g., meteorology,
790 emissions, and/or thermodynamics) (Walker et al., 2012; Luo et al., 2019). (3)
791 simulated particulate NO_3^- often responds to NO_x controls in a strongly non-linear, and
792 sometimes counterintuitive manner, posing a persistent “acidity–partitioning”
793 challenge for trend attribution. For instance, in the northeastern United States,
794 observations show that PM_{10} nitrate increased by 95% (urban) and 57% (rural) from
795 2005 to 2015 despite declining NO_x emissions, and this behavior was attributed to
796 changes in aerosol acidity and gas–particle partitioning feedbacks that can offset the
797 expected effect of precursor reductions (Kim et al., 2023). Finally, condensable
798 particulate nitrate, as defined in US EPA Method 202 (US EPA, 2017), as well as its
799 enhanced fraction under sub-freezing conditions, is generally not represented in current
800 emission inventories. Given its potential importance, as suggested by our analysis
801 presented above, incorporating temperature-dependent condensable nitrate into
802 emission inventories is likely necessary to improve the representation and prediction of
803 f- NO_3^- in 3-D air quality modelling.

804

805 **4 Findings and implications**

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

810

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

813 1998–2007, likely due to altered combustion plume chemistry favoring rapid f-NO₃⁻
814 formation in cold-climate conditions. Significant declines in f-NO₃⁻ (e.g., 60% in
815 Edmonton) outpaced NO_x reductions in the most recent decade, driven by diminishing
816 primary emissions, highly localized factors, and AO induced dispersion effects.

817

818 (ii) Decoupled c-NO₃⁻ and NO_x reductions in all the cities except Edmonton: c-NO₃⁻
819 remained stable or increased slightly while NO_x emissions were reduced. c-NO₃⁻ trends
820 were likely controlled by the abundance of alkali aerosols, highlighting the limited
821 efficacy of NO_x-focused policies for controlling c-NO₃⁻.

822

823 (iii) Critical role of primary f-NO₃⁻ emissions in winter in all the cities: Over 80% of
824 the annual f-NO₃⁻ burden was originated from cold-season primary emissions, with
825 minimal contribution from secondary formation process, emphasizing the need for
826 season-specific mitigation strategies. However, confirmation of this role requires three-
827 dimensional air quality modeling with updated emission inventories that explicitly
828 incorporate condensable particulate matter under subzero ambient temperatures.

829

830 Collectively, these findings call for a paradigm shift in air quality management.
831 Effective mitigation strategies must explicitly address primary particulate nitrate
832 sources, incorporate gas–particle partitioning dynamics under cold-climate conditions,
833 and account for interactions with alkali-containing aerosols. Policy frameworks should
834 further prioritize enhanced real-time measurements of PM_{2.5} chemical composition to
835 better resolve localized and seasonal variability, particularly in regions experiencing
836 prolonged winter conditions. In parallel, coordinated unmanned aerial vehicle (UAV)
837 and ground-based observations of CPM under contrasting temperature and atmospheric
838 dispersion regimes are essential to provide direct observational evidence of its role and
839 contributions.

840

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

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

851 *Competing interests.* One of the coauthors is a member of the editorial board of ACP.

852

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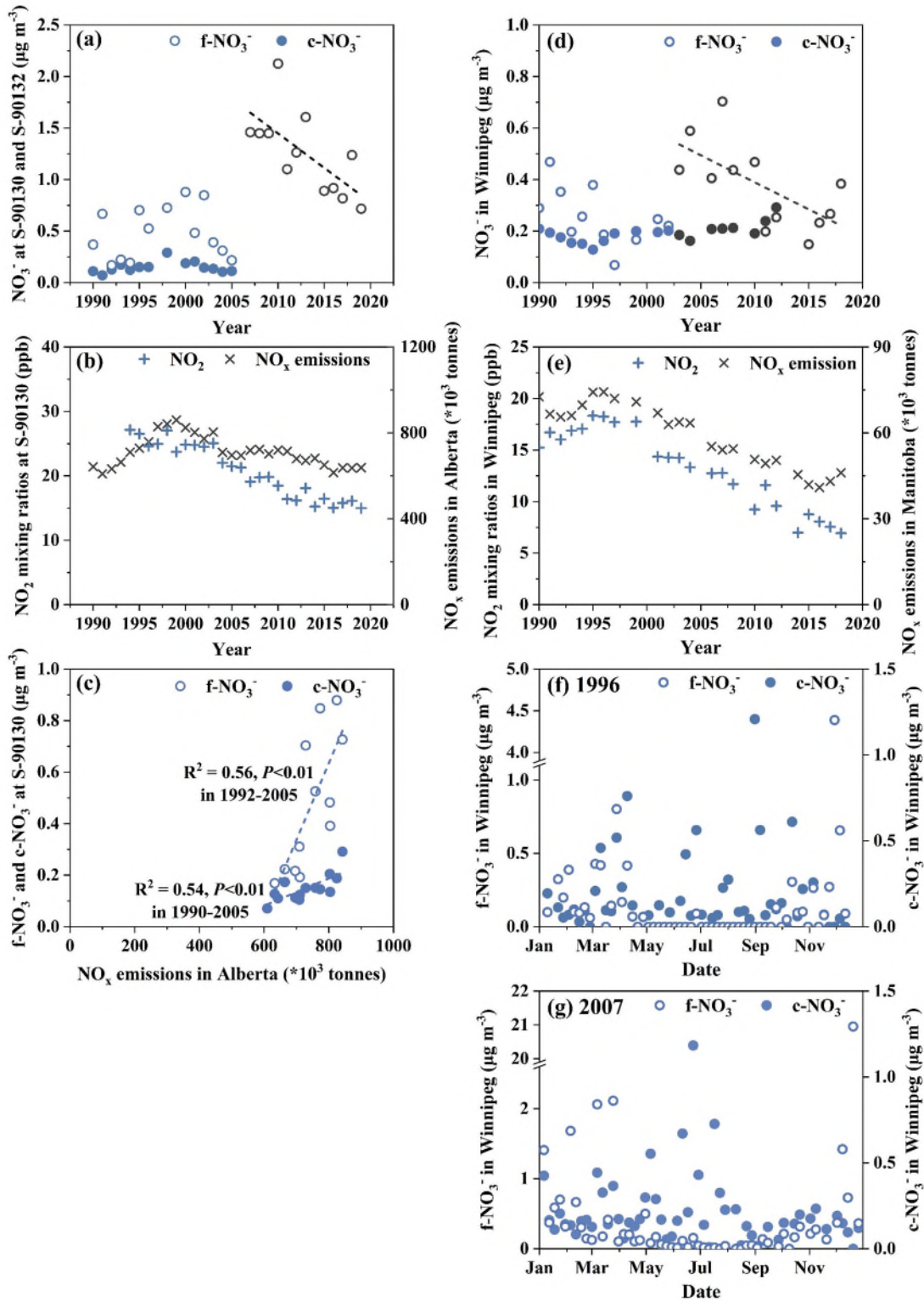


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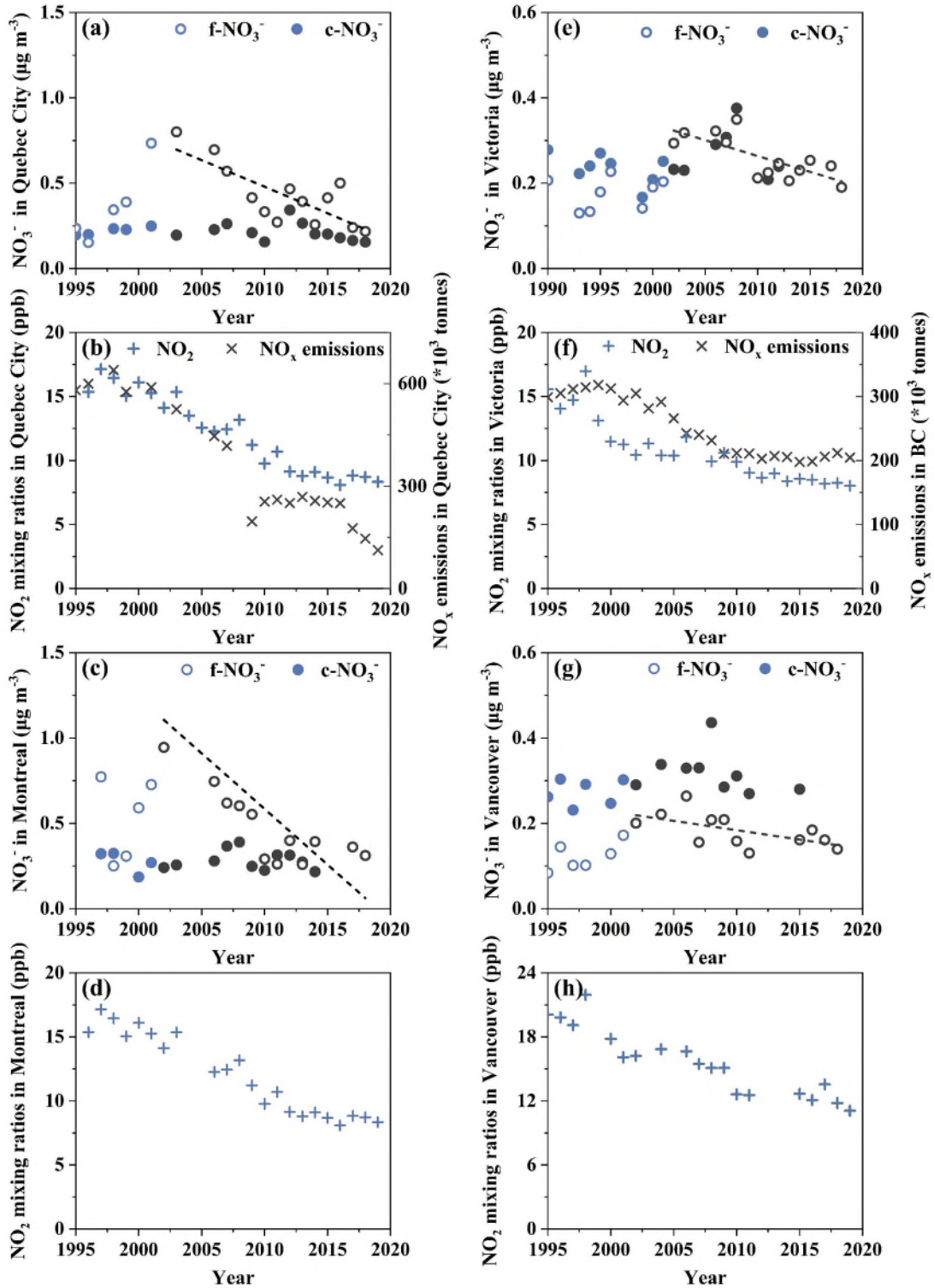


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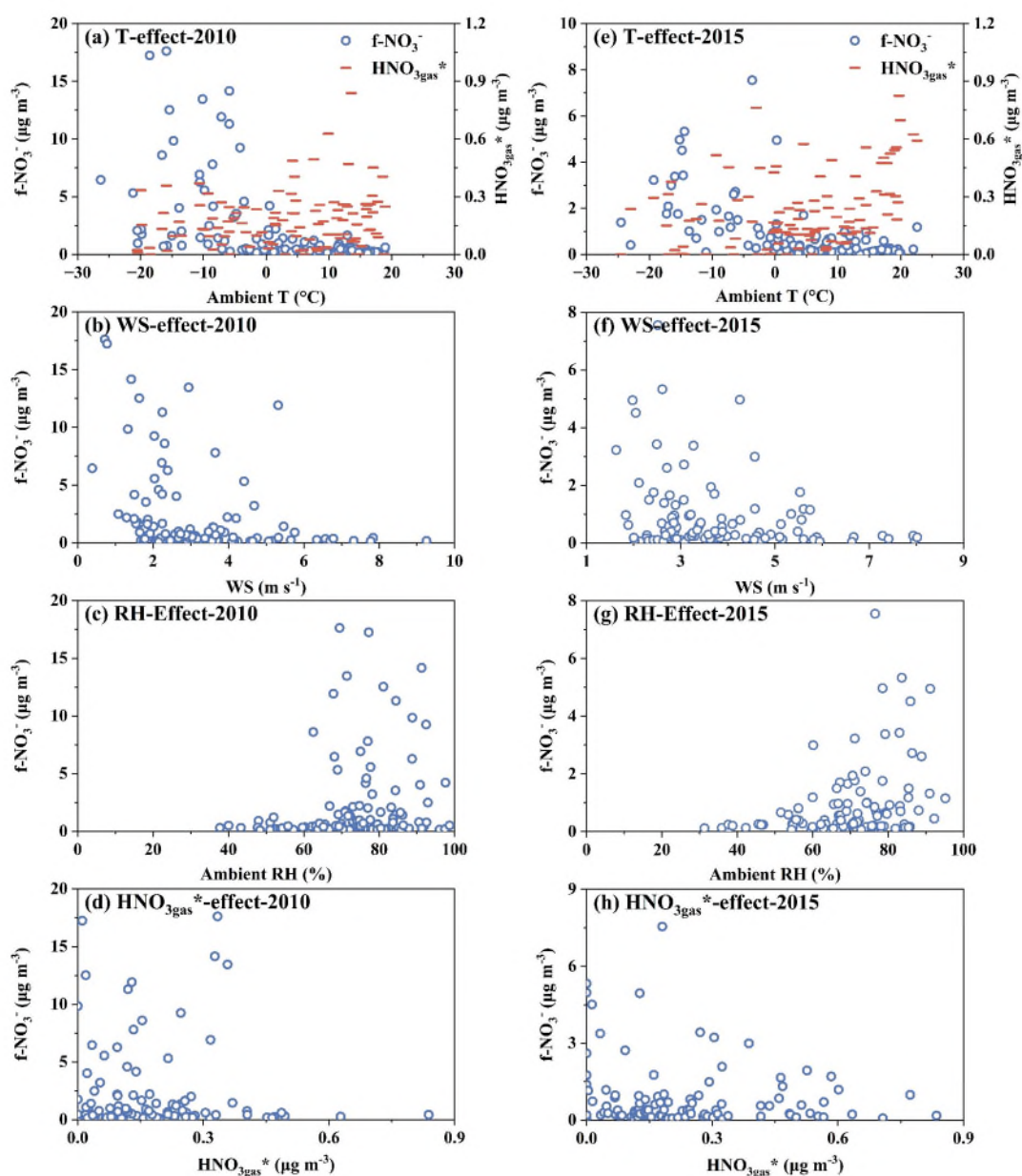


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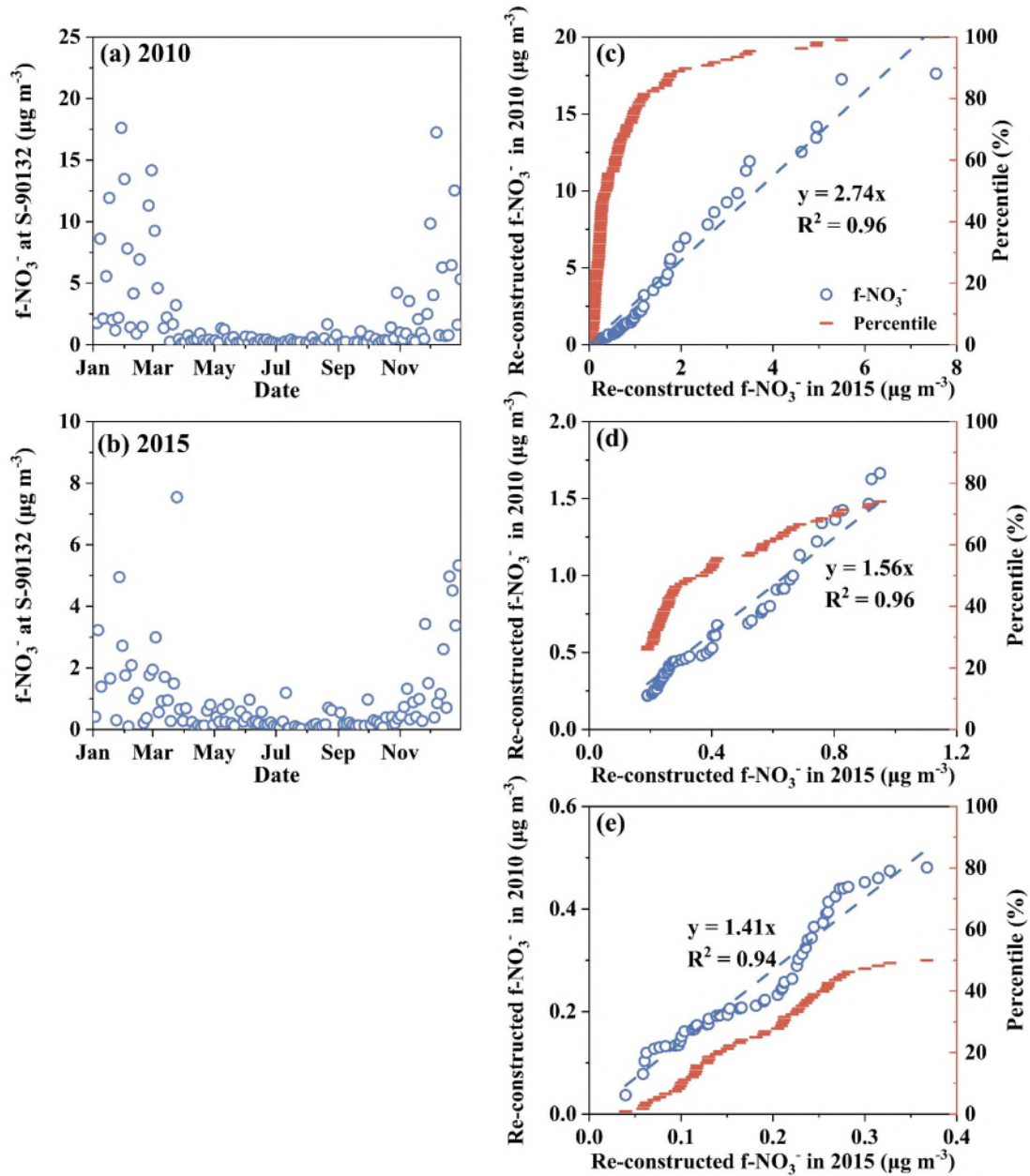


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