1   **Identifying decadal trends in deweathered concentrations of criteria air pollutants**

2   **in Canadian urban atmospheres with machine learning approaches**

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11

12 **Abstract**. This study investigates long-term trends of criteria air pollutants, including

13 NO_2, CO, SO_2, O_3 and $PM_{2.5}$, and O_x (=NO_2+O_3) measured in ten Canadian cities

14 during the last two to three decades and associated driving forces in terms of emission

15 reductions, perturbations due to varying weather conditions and large-scale wildfires,

16 and changes in O_3 sources and sinks. Two machine learning methods, the random forest

17 algorithm and boosted regression trees, were used to extract deweathered mixing ratios

18 (or mass concentrations) of the pollutants. The Mann-Kendall trend test of the

19 deweathered and original annual average concentrations of the pollutants showed that,

20 on the time scale of 20 years or longer, perturbation due to varying weather conditions

21 on the decade trends of the pollutants are minimal (within ±2%) in about 70% of the

22 studied cases, although it might be larger (but at most 16%) in the remaining cases.

23 NO_2, CO and SO_2 showed decreasing trends in the last two to three decades in all the

24 cities except CO in Montreal. O_3 showed increasing trends in all the cities except

25 Halifax, mainly due to weakened titration reaction between O_3 and NO. O_x, however,

26 showed decreasing trends in all the cities except Victoria because the increase in O_3 is

27 much less than the decrease in NO_2. In three of the five eastern Canadian cities,

28 emission reductions dominated the decreasing trends in $PM_{2.5}$, but no significant trends

29   in PM$_{2.5}$ were observed in the other two cites. In five western Canadian cities,

30   increasing or no significant trends in PM$_{2.5}$ were observed, likely due to unpredictable

31   large-scale wildfires overwhelming or balancing the impacts of emission reductions on

32   PM$_{2.5}$. In addition, despite improving air quality during the last two decades in most

33   cities, air quality health index of above 10 (representing very high-risk condition) still

34   occasionally occurred after 2010 in western Canadian cities because of the increased

35   large-scale wildfires.

36

39   **1 Introduction**

40   Criteria air pollutants can harm human health and the natural environment. According

41   to Health Impacts of Air pollution in Canada 2021 Report (Heath Canada, 2021), it is

42   estimated that air pollution of NO$_2$, O$_3$ and PM$_{2.5}$ caused 15,300 deaths per year,

43   corresponding to 42 deaths per 100,000 population in Canada in 2016. To protect

44   human health and the environment, the Canadian Council of Ministers of the

45   Environment (CCME) developed the Canadian Ambient Air Quality Standards

46   (CAAQS) for PM$_{2.5}$, O$_3$, SO$_2$ and NO$_2$. CAAQS are supported by four colour-coded

47   management levels with each management level being determined by the amount of a

48   pollutant within an air zone, from which recommendations on air quality management

49   actions are provided. Following this standard, multiphase mitigation measures have

50   been implemented to largely reduce anthropogenic air pollutant emissions in recent

51   decades (ECCC, 2021). Air quality in Canadian urban atmospheres well meets CAAQS

52   in recent years, as reported in Air Quality - Canadian Environmental Sustainability

53   Indictors (ECCC, 2023).

54

55   Nevertheless, the World Health Organization (WHO, 2021) updated the global air

56   quality guidelines (AQG) on NO$_2$, SO$_2$, CO, O$_3$ and PM$_{2.5}$ in 2021, based on

57   accumulated strong evidence that air pollution can affect public health even at very low

58   concentrations. In the WHO 2021 AQG, NO_2 annual average concentration is set as 10

59     $\mu g\ m^{-3}$, equivalent to ~ 5 ppb at annual average temperatures of 6-10 °C across Canada,

60   annual average and 24-hour average $PM_{2.5}$ concentrations are set as 5 $\mu g\ m^{-3}$ and 15 μg

61   m^{-3}, respectively, and peak season mean 8-hr O_3 concentration is set as 60 $\mu g\ m^{-3}$. An

62   urgent issue for all areas of the world is to overcome challenges to further lower ambient

63   NO_2, O_3 and $PM_{2.5}$ concentrations in order to meet the WHO 2021 AQG (Dabek-

64   Zlotorzynska et al., 2019; Griffin et al., 2020; Xu et al., 2019; Jeong et al., 2020; Al-

65   Abadleh et al., 2021; Wang et al., 2021; Zhang et al., 2022; Bowdalo et al., 2022).

66

67   In search of the most efficient mitigation measures for criteria pollutants, the

68   effectiveness of existing measures on air pollution reduction needs to be first examined.

69   For this purpose, long-term trends in concentrations of the criteria air pollutants need

70   to be quantified and the driving forces of the trends, besides anthropogenic emission

71   reductions, should be identified. Several studies have investigated the decadal trends of

72   some criteria pollutants in Canada in the past decade. For example, Chan and Vet (2010)

73   reported upward trends in O_3 mixing ratio from 1997-2006 at dozens of sites in Canada.

74   Xu et al. (2019) and Zhang et al. (2022) also found increasing trends in O_3 mixing ratio

75   from 1996-2016 at multiple sites in Windsor, Ontario, which was attributed to the

76   reduced titration effect of NO with O_3. They also reported that the 95th percentile O_3

77   mixing ratio exhibited a decreasing trend and attributed the decrease to anthropogenic

78   emission reductions. Mitchell et al. (2021) reported that the 99th percentile O_3 mixing

79   ratios exhibited a decreasing trend from 2000-2018 at urban and regional sites in Nova

80   Scotia, but such a trend was not found for low-moderate percentile O_3 mixing ratios.

81   Bari and Kindzierski (2016) found no significant trends in $PM_{2.5}$ mass concentration,

82   although decreasing trends in organic carbon and elemental carbon from 2007-2014 in

83   Edmonton. Jeong et al. (2020) reported 34% decrease in $PM_{2.5}$ mass concentration from

84   2004-2017 in Toronto and attributed the decrease to the reduced coal-fired power plants

85   emissions. Wang et al. (2022a) reported significant decreasing trends in organic and

86   elemental carbon in $PM_{2.5}$ from 2003-2019 at seven urban sites in Canada. Studies on

87   other criteria pollutants are very limited (Feng et al., 2020; Jeong et al.; 2020).

88

89   O_3 mixing ratios, especially at high levels, are strongly affected by meteorological

90   conditions, and thus, trends on the decadal scale can be perturbed by varying weather

91   conditions from year to year (Simon et al., 2015; Xing et al., 2015; Ma et al., 2021; Lin

92   et al., 2022). Inter-annual variations of weather conditions also have strong impact on

93   the decadal trends of other criteria pollutants (Lin et al., 2022). Air quality models are

94   useful tools to analyze emission-driven air quality trends and meteorological impacts

95   (Foley et al., 2015; Astitha et al., 2017; Vu et al., 2019), but most modeling results suffer

96   from large uncertainties which could exceed changes in annual means of simulated

97   pollutant concentrations. Machine learning techniques such as the random forest (RF)

98   algorithm and boosted regression trees (BRTs) have been demonstrated to be a powerful

99   tool to decouple impacts of emission changes and perturbations from varying weather

100   and/or meteorological conditions, enabling the derivation of deweathered trends in air

101   pollutants concentrations (Grange et al., 2018; Grange and Carslaw, 2019; Ma et al.,

102   2021; Mallet, 2021; Shi and Brasseur, 2020; Wang et al., 2020; Munir et al., 2021;

103   Lovric et al., 2021; Hou et al., 2022; Lin et al., 2022). The advantages and limitations

104   of RF algorithm and BRTs have been described in detail in earlier studies (Grange et

105   al., 2018; Grange and Carslaw, 2019). Briefly, BRTs method is fast to train and make

106   prediction, but suffers heavily from overfitting, which may result in unreliable

107   predictions. RF method can control the overfitting, but yields a poor prediction for

108   outliers in large percentiles. Thus, using two methods with different strengths and

109   weaknesses, although their predictions are similar in many ways, can constrain

110   methodology uncertainties and better evaluate perturbations due to varying weather

111   conditions than using only one method, as has been demonstrated in our earlier study

112   (Lin et al., 2022).

113

114   This study attempts to deduct the perturbations due to varying weather conditions on

the observed mixing ratios (or mass concentrations) of some criteria air pollutants in Canada during the past two to three decades and thereby investigates their emission-driven trends. We used the RF algorithm and BRTs to generate the deweathered mixing ratios (or concentrations) of NO_2, SO_2, CO, O_3, O_x and $PM_{2.5}$ during the past decades in ten cities equally distributed in eastern and western Canada. Considering that the machine learning methods may suffer from the weakness in accurately predicting large percentile concentrations of the studied criteria air pollutants, we also applied our previously developed identical-percentile autocorrelation analysis method to better quantify the perturbations due to extreme events such as large-scale wildfires on large percentile $PM_{2.5}$ concentrations (Yao and Zhang, 2020; Lin et al., 2022). The Mann-Kendall (M-K) trend test was then employed to resolve the trends in the deweathered mixing ratios (or mass concentrations). Pearson correlation analysis was further conducted for the deweathered and original mixing ratios (or mass concentrations) of the air pollutants against the corresponding provincial-level emissions. City-level emissions were used in the analysis in cases with large differences between air pollutant concentrations and provincial-level emissions. In addition, the Air Quality Heath Index (AQHI, https://weather.gc.ca/airquality/pages/index_e.html), a health protection tool designed in Canada to advise the public to adjust outdoor activities based on air pollution levels, was also analyzed with particular attention to the trends with AQHI being above 7 and 10, respectively. This study provides a thorough assessment of the emission-driven trends in the studied criteria pollutants on the time scale of two to three decades across Canadian urban atmospheres, knowledge from which is much needed in developing future emission control policies of the concerned pollutants.

2 Methodology

2.1 Monitoring sites and data sources

Ten major cities, including five in eastern Canada (Halifax, Quebec City, Montreal, Toronto and Hamilton) and five in western Canada (Winnipeg, Calgary, Edmonton, Vancouver and Victoria), from the National Air Pollution Surveillance (NAPS) program

143   are selected for investigating decadal trends of the monitored criteria pollutants (Table

144   S1). The NAPS program has long-term air quality data of a uniform standard across

145   Canada (Dabek-Zlotorzynska et al., 2011, 2019; Jeong et al., 2020; Yao and Zhang,

146   2020; Wang et al., 2021, 2022a). The NAPS program includes both continuous and

147   time-integrated measurements of gaseous and particulate air pollutants. Continuous

148   data are available as hourly concentrations and are quality-assured as specified in the

149   Ambient Air Monitoring and Quality Assurance/Quality Control Guidelines

150   (https://open.canada.ca/data/en/dataset/1b36a356-defd-4813-acea-47bc3abd859b).

151

152   Multiple monitoring sites exist in most cities, but only one urban background site was

153   selected in each city mentioned above based on the following criteria: with the most

154   complete dataset of the five selected criteria pollutants (NO_2, CO, SO_2, O_3 and $PM_{2.5}$),

155   with the longest data record, and with valid data in each year (Table S1). In cases with

156   a data gap longer than a year, e.g., in Quebec City, Halifax and Calgary, data at a nearby

157   urban background site (within 1 km) were then used to fill the gap. If no site within 1

158   km is available, then the data gap is left unfilled. SO_2, CO, NO_x and $PM_{2.5}$ emission

159   data at the provincial level in Canada are obtained from

160   https://www.canada.ca/en/environment-climate-change/services/environmental-

161   indicators/air-pollutant-emissions.html. City-level air pollutant emissions from various

162   registered facilities since 2002 were obtained from

163   https://www.canada.ca/en/services/environment/pollution-waste-

164   management/national-pollutant-release-inventory.html.

165

166   Besides the monitored criteria pollutants described above, AQHI is also calculated in

167   this study at three-hour resolution using the following formula (Stieb et al., 2008; To et

168   al., 2013):

169    $AQHI = (100/10.4) \times ([(e^{0.000537 \times O3}-1) + (e^{0.000871 \times NO2}-1) + (e^{0.000537 \times PM2.5}-1)]$, in which

170   O_3 and NO_2 represent their respective three-hour average original mixing ratios (in ppb)

171   and $PM_{2.5}$ represents its three-hour average original concentration (in $\mu g\ m^{-3}$). The

172 calculated AQHI is rounded to the nearest positive integer. AQHI between 1-3

173 represents excellent air quality that is safe for outdoor activities. Outdoor activities may

174 be reduced at AQHI between 4-6 for certain population with some health issues. AQHI

175 between 7-10 and >10 correspond to high and very high health risk conditions,

176 respectively. Note that four alternative AQHI-Plus amendments have been proposed for

177 wildfire seasons and the AQHI-Plus values are always larger than the corresponding

178 AQHI values (Yao et al., 2020). One of AQHI-Plus amendments has been implemented

179 in late 2016 in British Columbia. The AQHI-Plus amendments are not used in this study

180 since it is not implemented across the whole Canada.

181

182 **2.2 Statistical analysis**

183 In this study, two popular machine learning packages, including the "rmweather" R

184 package (Grange et al., 2018) and the "deweather" R package (Carslaw and Ropkins,

185 2012; Carslaw and Taylor, 2009), were used to perform the RF algorithm and the BRTs,

186 respectively. Besides the monitored hourly average mixing ratio (or mass concentration)

187 of a pollutant, temporal variables (hour, day, weekday, week and month) and

188 meteorological parameters (wind speed, wind direction, ambient temperature, relative

189 humidity and dew point) are also needed as additional independent inputs to the

190 machining learning process. The hourly meteorological data were obtained from the

191 meteorological observational station at a nearby airport in each city, which are

192 accessible from the NOAA Integrated Surface Database (ISD) by using the "worldmet"

193 R package (Carslaw, 2021). The meteorological data from the nearest airport in every

194 city should reflect synoptic weather conditions, which have been used in existing

195 machine learning studies (Vu et al., 2019; Mallet, 2020; Wang et al., 2020; Dai et al.,

196 2021; Ma et al., 2021). Additional meteorological parameters such as boundary layer

197 height, total cloud cover, surface net solar radiation, surface pressure, total precipitation

198 and air mass clusters have also been used in some studies to improve the performance

199 of the machine learning methods (Hou et al., 2022; Shi et al., 2021; Lin et al., 2022).

200 These additional meteorological parameters were not included in the present study, but

201 could be included in future analyses. Nevertheless, good performance can still be

202 achieved in the present study mainly because of multi-decade length of the datasets, as

203 demonstrated by an example shown in Fig. 1. Note that the inputs for the two packages

204 were randomly divided into two groups and the user cannot control the division, i.e.,

205 the training dataset that used 80% of the data and a testing dataset that used the

206 remaining 20%. Thus, the testing datasets were different between the RF algorithm and

207 the BRTs. Note that all input parameters and output variables, i.e., the predicted hourly

208 average mixing ratio (or mass concentration) of a pollutant, for testing were the same

209 as those used for learning. Moreover, the training and testing were conducted for every

210 pollutant at every site.

211

212 Five statistical metrics, including coefficient of determination (R^2), root mean square

213 error (RMSE), mean bias (MB), mean fractional bias (MFB) and mean fractional error

214 (MFE), were calculated to evaluate the performance of the two machine learning

215 methods. In the literature, criteria and goal values have not been set for the statistical

216 metrics for the purpose of evaluating machine learning prediction performance.

217 Alternatively, the criteria and goal values for MFE and MFB proposed by USEPA are

218 adopted here, which are MFE≤75% and MFB≤±60% for the criteria value and MFE≤50%

219 and MFB≤±30% for the goal value (USEPA, 2007).

220

221 Fig. 1 shows predictions against observations of NO_2 mixing ratio in Halifax using the

222 testing datasets during 1996-2017, as an example for evaluating the performance of the

223 two machine learning methods (P value <0.01 for all the correlation). MFB and MFE

224 values were far below their respective goal values for both RF algorithm and BRTs set

225 by USEPA. R^2 and RMSE were 0.86 and 5.1, respectively, for both methods. MB is -

226 0.04 for RF algorithm and 0.1 for BRTs. The values of these metrics indicated that the

227 predictions well reproduced the observations. However, the two machine learning

228 methods overall underpredicted NO_2 mixing ratios to a small extent based on the

229 regression lines slightly below the 1:1 line. The underestimation was mainly due to

230 sporadic large values in the measurement of NO_2 mixing ratio, which did not provide

231 sufficient samples for the machine learning methods to learn and yield good predictions.

232 For all the pollutants in all the cities investigated in this study, the machine learning

233 predictions generally met the goal values set by USEPA, except for $PM_{2.5}$ in some

234 western Canadian cities such as Calgary and Edmonton with the predictions only

235 meeting criteria values because of the perturbation from large-scale wildfires.

236

237 Following the approach described in earlier studies (Hou et al., 2022; Lin et al., 2022),

238 the two machine learning methods were run for 1000 times with meteorological

239 variables randomly resampled from the entire datasets during the study period. The

240 average model prediction from the 1000 model runs represents the meteorologically

241 normalized pollutant concentration at a particular time. We also tested averaging 2000

242 and 3000 model predictions, which produced consistent results with those of using 1000

243 model predictions. Thus, averaging 1000 model predictions was used for

244 meteorological normalization in this study.

245

246 As mentioned above, the machine learning methods suffer from the weakness in

247 accurately predicting high concentration values in large percentiles. We thus applied

248 the identical-percentile autocorrelation analysis method developed in our previous

249 study to quantify the perturbations due to extreme events such as large-scale wildfires

250 on the large percentile concentration values (Yao and Zhang, 2020; Lin et al., 2022).

251 This method has five steps for data processing and analysis. The first step is to construct

252 a long-term average data series at hourly resolution covering 365 days by averaging the

253 corresponding hourly data from all the years of the study period. The second step is to

254 pair a data series at any given year to the long-term average data series, and if there

255 were any data gaps (missing hours) in the former data series, data for these hours in the

256 latter series were also removed so that the two data series have exactly the same size.

257 The third step is to rearrange all the hourly data from the smallest to the largest value

258 in each of the data series generated in step 2, and then conduct correlation analysis

between the pair of data series. Inflection points in the large and small percentile zone were first visibly identified/guessed, and referenced as upper and lower inflection points, respectively. The pair of data between the lower and upper inflection points were correlated repeatedly by varying values of the two inflection points in search for highest R^2 values. The fourth step is to predict the large percentile values exceeding the upper inflection point using the regression equation with the highest R^2 generated in step 3. The final step is to obtain the perturbations due to extreme events on the large percentile concentrations by subtracting the observed values from the predicted values.

Fig. 2 shows three examples calculating the perturbations due to varying weather conditions and large-scale wildfires on the large percentile concentrations of $PM_{2.5}$ in 1998, 1999 and 2019 in Edmonton. Large-scale wildfires occurred in 1998 and 2019 (Fig. S1), but no record in 1999. In 1998, data points outside the 4.5th-94th percentile range were screened out through steps 1-3, and the remaining data points were used to obtain a regression equation, which shows $[PM_{2.5}]_{\text{data in 1998}} = [PM_{2.5}]_{\text{long-term average}} \times 3.9-18$ ($R^2=0.96$, P<0.01) (Fig. 2a). $[PM_{2.5}]_{\text{data in 1998}}$ and $[PM_{2.5}]_{\text{long-term average}}$ represent the same identical percentile values of $PM_{2.5}$ in re-organized data series of 1998 and the long-term average through steps 1-3, respectively. The similar definition is applicable for $[PM_{2.5}]_{\text{data in 1999}}$ and $[PM_{2.5}]_{\text{data in 2019}}$ presented below. In 1999, data points within the 4.5th-99.7th percentile range resulted in a regression equation of $[PM_{2.5}]_{\text{data in 1999}} = [PM_{2.5}]_{\text{long-term average}} \times 3.1-15$ ($R^2=0.97$, P<0.01) (Fig. 2c). In 2019, data points within the 5.4th–96th percentile range resulted in $[PM_{2.5}]_{\text{data in 2019}} = [PM_{2.5}]_{\text{long-term average}} \times 2.2-12$ ($R^2=0.94$, P<0.01) (Fig. 2e). Note that step 3 is critical to obtain these excellent correlations (Fig. 2a, 2c and 2e) as compared with those absent of step 3 (Fig. 2b, 2d and 2f).

The perturbation due to the extreme weather conditions or the extreme events on the 100th percentile $PM_{2.5}$ value, i.e., the maximum value in this study, at a particular year (y) can be calculated as:

288   $[PM_{2.5}]_{\text{perturbation at 100th,y}} = [PM_{2.5}]_{\text{predicted at 100th,y}} - [PM_{2.5}]_{\text{observed at 100th,y}}$

289   $[PM_{2.5}]_{\text{predicted at 100th,y}} = [PM_{2.5}]_{\text{long-term average at 100th}} \times k_y + b_y$

290   where $[PM_{2.5}]_{\text{observed at 100th,y}}$ represents the 100th percentile PM$_{2.5}$ value observed in y

291   year, and k_y and b_y represent the slope and intercept, respectively, of the regression

292   equation with the highest R^2 in the y year generated through steps 1-3. Similarly, the

293   perturbation inherent from the large percentile values from the final upper inflection

294   point (m^{th}) to 100th percentile in a particular year can be calculated as:

295   $[PM_{2.5}]_{\text{perturbation at} \geq \text{mth, y}} = [PM_{2.5}]_{\text{predicted at} \geq \text{mth, y}} - [PM_{2.5}]_{\text{observed at} \geq \text{mth, y}}$,

296   $[PM_{2.5}]_{\text{predicted at mth,y}} = [PM_{2.5}]_{\text{long-term average at mth}} \times k_y + b_y$

297   The calculated values from $[PM_{2.5}]_{\text{perturbation at} \geq \text{mth,y}}$ to $[PM_{2.5}]_{\text{perturbation at 100th,y}}$ in the y

298   year were averaged as $[PM_{2.5}]_{\text{perturbation average,y}}$. The perturbation contribution to the

299   corresponding original annual average equals to $[PM_{2.5}]_{\text{perturbation average,y}} \times (1\text{-}m\%)$ in y

300   year, and the values were 3.0 μg m^{-3} in 1998, 0.2 μg m^{-3} in 1999 and 1.7 μg m^{-3} in 2019

301   in Edmonton, corresponding to strong, minimal and moderate perturbations,

302   respectively, from large wildfires.

303

304   The M-K trend test is a non-parametric test applicable to any type of data distribution

305   and is employed to resolve the trends in the time series of the deweathered and original

306   annual average concentration of each pollutant. Qualitative trends revolved by the M-

307   K trend test include 1) an increasing or decreasing trend with a P value of <0.05, and 2)

308   no significant trend including a probably increasing or decreasing trend, a stable trend,

309   and a no-trend with all the other conditions (Aziz et al., 2003; Kampata et al., 2008;

310   Yao and Zhang, 2020). The extracted trends and associated driving factors are discussed

311   in detail below.

312

313   **3. Results**

314   *3.1 Trends in deweathered and original NO$_2$ mixing ratios*

315   Fig. 3a and 3b show decadal variations in the original annual averages of NO$_2$ mixing

316   ratios in the ten Canadian cities. The BRTs-deweathered and RF-deweathered hourly

317 averages of NO_2 mixing ratios are shown in Fig S2, in which the deweathered results

318 were also interpreted in terms of increased or reduced emissions of NO_x. The decadal

319 trends resulted from annual averages of BRTs-deweathered, RF-deweathered and

320 original NO_2 mixing ratios are listed in Table 1.

321

322 The deweathered and original annual average NO_2 mixing ratios in any of the 10 cities

323 both showed consistent decreasing trends in the last 2-3 decades ($P<0.05$ through M-K

324 trend test). The BRTs-deweathered and RF-deweathered annual averages highly

325 correlated with the original values with $R^2>0.95$ and $P<0.01$ (Table 1). The slopes of

326 zero-intercept regression equations between the deweathered and original annual

327 average NO_2 mixing ratios were mostly within 0.98-1.04, indicating $\leq 4\%$ differences

328 between the deweathered and original annual values. These results indicated that the

329 perturbation due to varying weather conditions only exerted minor influences on the

330 original annual averages. The only exception is the RF-deweathered annual averages in

331 Halifax (with a slope of 1.08); however, this may not suggest that the perturbation due

332 to varying weather conditions was as high as 8% since the BRTs-deweathered annual

333 averages in the same city showed a slope of only 1.03, indicating that the uncertainties

334 in the slope associated with the RF-deweathered averages can be as large as 5% (8%

335 minus 3%) because of its poor prediction for large outlier values.

336

337 The annual decreasing rates in the deweathered and original NO_2 mixing ratios in the

338 studied cities varied from 0.31 to 0.74 ppb year $^{-1}$, and the overall percentage decreases

339 ranged from 37% to 62% during the last two to three decades (Table 1). Our results

340 suggested that varying weather conditions likely played a negligible role in the annual

341 decreasing rates of NO_2 mixing ratio in two eastern (Montreal and Hamilton) and four

342 western (Winnipeg, Calgary, Vancouver and Victoria) Canadian cities, as can be seen

343 from the very close annual decreasing rates between the deweathered and original

344 annual average mixing ratios, despite methodology uncertainties in generating

345 deweathered mixing ratios as mentioned above. In the remaining four cities, the annual

346　decreasing rates were always larger in the original than the deweathered annual average

347　NO_2 mixing ratio, with the largest differences in Toronto (0.07-0.10 ppb year[-1]),

348　followed by Halifax (0.06-0.10 ppb year[-1]), Edmonton (0.06-0.08 ppb year[-1]) and

349　Quebec City (0.02-0.07 ppb year[-1]), suggesting that varying weather conditions

350　contributed appreciably to the annual decreasing rate. The annual decreasing rates were

351　highly city-dependent, but there were no significant differences between eastern and

352　western cities ($P>0.05$). With continuously decreasing NO_2 mixing ratios in the last

353　decades (Fig. 3), annual average NO_2 fell to below 10 ppb by 2019 in half of the studied

354　cities (Halifax, Montreal, Quebec City, Winnipeg and Victoria), meeting the WHO 2021

355　guideline. Additional efforts are still needed to lower the NO_2 level in the rest of the

356　cities, especially in Toronto and Edmonton in which annual average NO_2 were still as

357　high as 15 ppb in 2019.

358

359　NO_2 in urban atmospheres were mainly formed by the rapid titration reaction of NO

360　with O_3, with NO largely released from anthropogenic emissions, especially the

361　transport sector (Pappin et al., 2016; Casquero-Vera et al., 2019; Dabek-Zlotorzynska

362　et al., 2019; Feng et a., 2020; Griffin et al., 2020; Al-Abadleh et al., 2021). The

363　correlations between the annual average NO_2 mixing ratios and corresponding

364　provincial NO_x emissions were thereby analyzed below (Table 1). Note that the on-line

365　air pollutant emission inventory in Canada reports the emissions since 1990 (ECCC,

366　2021) so the correlation analysis only covers the period of 1990-2019. Strong

367　correlations ($R^2=0.82$-0.98) were obtained in all of the five eastern Canadian cities. The

368　overall decreasing percentages of the deweathered and original NO_2 mixing ratios in

369　Halifax and Quebec City were roughly the same as that of the provincial grand total

370　NO_x emissions and transportation NO_x emissions, but in Montreal, Toronto and

371　Hamilton the former decreasing percentages were smaller than the latter ones. In

372　contrast, the overall decreasing percentages in NO_2 mixing ratio in the five western

373　Canadian cities were substantially larger than the corresponding decreasing percentages

374　of the provincial grand total NO_x emissions and transportation NO_x emissions, and the

375 correlation (R^2=0.54-0.94) between NO_2 mixing ratio and provincial emission were not

376 as good as those in eastern cities. The extreme case occurred in Calgary, where NO_2

377 mixing ratio decreased by 31-33% during 1990-2007 when the grand total NO_x

378 emissions and transportation NO_x emissions in Alberta increased by 11% and 5%,

379 respectively, noting that a much short period of data were used in this than other cities.

380 The city-level NO_x emissions recorded from various facilities in Calgary increased from

381 68 tons in 2002 to 262 tons in 2007 (Table S2), which cannot explain the decrease in

382 NO_2 mixing ratios.

383

384 *3.2 Trends in deweathered and original mixing ratios of CO and SO_2*

385 As mentioned earlier, CO and SO_2 in Canadian cities well meet the CAAQS in recent

386 years. The original annual average mixing ratios of CO and SO_2 in the ten cities

387 generally met the WHO 2021 air quality guidelines in the last decade, except SO_2 in

388 Hamilton (Fig. S4). Thus, the analysis results on deweathered and original mixing ratios

389 of SO_2 and CO in the nine cities and CO in Hamilton were only briefly summarized

390 below, leaving SO_2 in Hamilton to be discussed separately.

391

392 The annual averages of the deweathered CO mixing ratios were reasonably consistent

393 with the original annual averages in five cities, e.g., the slopes of the deweathered

394 mixing ratios against the original ones varied from 0.97 to 1.03 in Montreal, Hamilton,

395 Winnipeg, Edmonton, Vancouver and Victoria, although somewhat large differences

396 between the deweathered and original mixing rations were seen in Quebec City with a

397 slope of 1.12 (RF vs. Origin) and Toronto with a slope of 0.92 (BRTs vs. Origin). The

398 original and deweathered annual averages of CO decreased by ≥82% in the last 2-3

399 decades in six cities, including Halifax (90-92%), Calgary (90-91%), Winnipeg (84-

400 88%), Edmonton (86-86%), Toronto (83-86%) and Vancouver (82-83%) (Table S3),

401 followed by 66-70% in Hamilton and less than 60% in Quebec City (56-58%) and

402 Victoria (57-59%). Large percentage decreases in baseline CO mixing ratios across

403 North America were reported before (Zhou et al., 2017). The deweathered and original

annual averages of CO mixing ratio significantly correlated with the corresponding provincial grand total emissions and transportation emissions of CO (R^2 =0.68-0.96, P<0.01) in these nine cities. The overall percentage decreases in CO mixing ratio in Quebec City and Victoria were approximately the same as those in the corresponding provincial transportation emissions of CO; however, the former percentage decreases were evidently larger than the latter ones in the other seven cities mentioned above. In Montreal, no significant trends were obtained in the deweathered and original CO mixing ratios during 1995-2010 (P>0.05), despite that the provincial total CO emissions and transportation CO emissions decreased by 37% and 53%, respectively, during the same period.

The deweathered and original annual average mixing ratios of SO_2 decreased by 89-97% in the last 2-3 decades in four cities, including Winnipeg (95-97%), Vancouver (90-95%), Toronto (89-95%) and Halifax (90-93%), followed by 79-86% in Montreal, 78-85% in Quebec City, 73-82% in Victoria, 62-64% in Calgary and 52-55% in Edmonton (Table S4). Large percentage decreases in SO_2 mixing ratio have been reported in rural atmospheres across North America during the last 2-3 decades (Xing et al., 2015; Feng et al., 2020). Since 1990, the overall decreasing percentages in SO_2 mixing ratio in Halifax, Toronto, Calgary and Vancouver were evidently larger than those of the corresponding provincial grand total SO_2 emissions. In Montreal, Quebec City, Winnipeg and Edmonton, the percentage decreases in SO_2 mixing ratio were close to those in the corresponding provincial grand total SO_2 emissions during the same periods. Although SO_2 mixing ratio in Victoria decreased by 73-82% during 1999-2019, the corresponding provincial grand total SO_2 emission did not decrease much during the same period. However, the city-level SO_2 emissions from registered facilities in Victoria decreased from 217 tons in 2002 to near zero in 2019 (Table S2), supporting the decreases in SO_2 mixing ratios. Note that the differences between the two deweathered mixing ratios of SO_2 were enlarged to some extent in comparison with other pollutants, e.g., with the differences being 10-12% for SO_2, but only 2-5% for

NO2 (as presented above), in Montreal, Toronto and Winnipeg. The increased

uncertainties led to the difference between the RF-deweathered and original SO_2 mixing

ratios being up to 16% in Winnipeg, based on the slope of 1.16 listed in Table S4. The

difference between the BRTs-deweathered and original SO_2 mixing ratios was, however,

only 4%, suggesting that the perturbation due to varying weather conditions might be

within 4%-16%. Again, the RF algorithm suffers from the weakness in predicting large

outlier values.

In Hamilton, the annual average of the deweathered SO_2 mixing ratios were highly

consistent with those of the original data as indicated by the close to 1.0 slopes. The

deweathered and original annual averages of SO_2 mixing ratios decreased by 23-28%

during 1996-2019, which were substantially smaller than the 81% decrease of the

corresponding provincial grand total SO_2 emissions during the same period. Such a

large discrepancy indicates that the reduction in SO_2 emission in Hamilton likely

substantially lagged behind the average provincial level. This is indeed the case since

SO_2 emissions from registered facilities in Hamilton (Table S2) fluctuated around

$8.67 \pm 1.75 \times 10^3$ tons year^{-1} during 2002-2009 and then increased to $1.14 \pm 0.13 \times 10^4$ tons

year^{-1} during 2010-2018. This also caused the weak correlations between annual

average SO_2 mixing ratio in this city and provincial total SO_2 emission ($R^2 = 0.42$-0.57,

P<0.05). In addition, the original annual average SO_2 mixing ratio increased from 3.2-

3.5 ppb in 2016-2017 to 4.8-5.0 ppb in 2018-2019 when provincial total SO_2 emission

changed little. Thus, reducing local SO_2 emissions in Hamilton is critical to further

lower SO_2 mixing ratio in this city in order to meet the CAAQS and the WHO 2021

guideline, despite the existence of other factors such as regional transport (Zhou et al.,

2017; Ren et al., 2020).

3.3 Trends in deweathered and original O_3 and O_x mixing ratios

The original annual averages of O_3 and O_x are shown in Fig. S5 and the analysis results

of deweathered and original annual averages are listed in Table S5. Increasing trends in

the deweathered and original annual average O_3 mixing ratio were obtained in nine cities during the last 2-3 decades, with Halifax as an only exception that showed no significant trend (P>0.05) during 2000-2017. Theoretically, the increasing trends in the O_3 mixing ratios could be caused by the enhanced tropospheric photochemical formation of O_3 and/or the weakened titration reaction between O_3 and NO due to the substantial reduction of NO emissions (Simon et al., 2015; Zhou et al., 2017; Sicard et al., 2020; Mitchell et al., 2021; Wang et al., 2022b) (more discussion in Section 4.2 below). In contrast, the decreasing trends in the deweathered and original annual average O_x mixing ratios were generally obtained, except in Victoria where there was no significant trend (P>0.05) during 2000-2017. The opposite long-term trends between O_3 and O_x suggested that the increase in O_3 is much less than the decrease in NO_2, which does not support the hypothesis of the enhanced tropospheric formation of O_3.

The deweathered and original annual average O_3 mixing ratios increased by 10 ppb in Edmonton from 1981-2019, 8 ppb in Hamilton from 1996-2019 and Calgary from 1986-2014, and <7 ppb in the other cities (Fig. S5, Table S5). The increased O_3 mixing ratio was likely caused by the reduced titration reaction between O_3 and NO, considering the reduced photochemical formation of O_3 in the troposphere (Simon et al., 2015; Xing et al., 2015). Varying weather conditions likely exerted a negligible influence on the decade increases in O_3 mixing ratio in Edmonton, Hamilton, Calgary and Vancouver on the basis of the almost identical increases in deweathered and original annual averages. However, the comparison between deweathered and original annual averages also showed that varying weather conditions did cause an increase of 2 ppb out of the total of 7 ppb increase in the original annual average O_3 in Winnipeg from 1985-2018, and 1 ppb increase in Montreal from 1997-2010 and in Toronto from 2003-2019. In contrast, varying weather conditions likely caused 1 ppb decrease in Quebec City from 1995-2019 and in Victoria from 1999-2019.

The deweathered and original annual average O_x mixing ratio decreased by 10-12 ppb

in Vancouver from 1986-2019, 10 ppb in Halifax from 2000-2019 and in Toronto from 2003-2019, 8-10 ppb in Edmonton from 1981-2019 and <6 ppb in the other cities (Fig. S5 and Table S5). Based on the simultaneously monitored NO mixing ratios and the method reportedly used for estimating the primary NO_2 emission (Kurtenbach et al., 2012; Simon et al., 2015; Casquero-Vera et al., 2019; Xu et al., 2019), the reduced primary NO_2 emissions likely accounted for only 1-2 ppb decrease in O_x in the ten cities and generally acted a minor contributor to the decrease in O_x.

3.4 Trends in deweathered and original PM$_{2.5}$ mass concentrations

Opposite decadal trends were observed between eastern and western Canadian cities in the deweathered and original $PM_{2.5}$ mass concentrations (Table 2, Fig. 3c, 3d and Fig S6). In eastern Canadian cities, either decreasing or no significant trends were obtained in the last two decades. The decreasing trends (P<0.05) were identified in the RF-deweathered, BRTs-deweathered and original annual average $PM_{2.5}$ in Montreal from 2005-2019 and in Hamilton from 1998-2019. The overall decreases were only 2 μg m^{-3} with the decreasing rate of 0.22-0.25 μg m^{-3} year^{-1} in Montreal and 3-4 μg m^{-3} and 0.14-0.15 μg m^{-3} year^{-1} in Hamilton. The decreasing trends (P<0.05) were also identified in the RF-deweathered and BRTs-deweathered $PM_{2.5}$ in Toronto from 2000-2019 with an overall decrease of only 2 μg m^{-3} and a decreasing rate of only 0.10-0.11 μg m^{-3} year^{-1}. However, no significant trend (P>0.05) was identified in the original annual average $PM_{2.5}$ in Toronto, implying that the perturbation due to varying weather conditions likely cancelled out the mitigation effects of air pollutants. Note that there were no decreasing trends in the provincial total primary $PM_{2.5}$ emissions in Quebec and Ontario during the periods when $PM_{2.5}$ mass concentration decreased in the above-mentioned three cities. This was not surprising because the major chemical components in $PM_{2.5}$ were derived mainly from secondary sources (Dabek-Zlotorzynska et al., 2019; Jeong et al., 2020; Wang et al., 2021). The decreasing provincial emissions of SO_2, NO_x and volatile organic emissions in Quebec and Ontario likely have reduced the amounts of their oxidized products in $PM_{2.5}$ (Xing et al., 2015; Yao and Zhang, 2019, 2020; Feng

520 et al., 2020; Jeong et al., 2020; ECCC, 2021; Wang et al., 2021, 2022a). No significant

521 trends ($P>0.05$) were identified in the deweathered and original $PM_{2.5}$ concentrations

522 in Halifax from 2008-2018 and in Quebec City from 1998-2019, which need further

523 investigation.

524

525 In western Canadian cities, either increasing or no significant trends were extracted in

526 the deweathered and original annual average $PM_{2.5}$ mass concentrations. Increasing

527 trends ($P<0.05$) were identified in the RF-deweathered, BRTs-deweathered and original

528 annual average $PM_{2.5}$ in Winnipeg from 2001-2018 with an overall increase of only 1-

529 2 $\mu g\ m^{-3}$ and an increasing rate of 0.09-0.10 $\mu g\ m^{-3}\ year^{-1}$. Increasing trends ($P<0.05$)

530 were identified in the RF-deweathered and original annual average $PM_{2.5}$ in Victoria

531 from 1999-2019 with an overall increase of only 1 $\mu g\ m^{-3}$ and an increasing rate of

532 0.07-0.08 $\mu g\ m^{-3}\ year^{-1}$, but no significant trend was identified in the BRTs-deweathered

533 annual average $PM_{2.5}$. An increasing trend was obtained only in the RF-deweathered

534 annual average $PM_{2.5}$ in Vancouver from 2004-2019, and no significant trends were

535 identified in the BRTs-deweathered and original annual average $PM_{2.5}$. The

536 inconsistency between the trends extracted from the three different annual average

537 $PM_{2.5}$ data series was mostly because of the small magnitudes of the actual interannual

538 changes and thus the trends, which are on the same order of magnitude as the

539 methodology uncertainties. Considering the decreasing trends in NO_2, CO and SO_2

540 mixing ratios discussed above and the reported decreasing trends in secondary chemical

541 components of $PM_{2.5}$ in Western Canada (Wang et al., 2021, 2022a), the increasing

542 trends in the deweathered and/or original annual average $PM_{2.5}$ observed in some

543 western Canadian cities were likely caused by increased natural emissions, such as from

544 the increased large-scale wildfires in recent years.

545

546 It is noticed that a few spikes always appeared in the BRTs-deweathered $PM_{2.5}$

547 concentrations in the five western Canadian Cities since 2010 (Fig. S6). Most of these

548 spikes were associated with large-scale wildfire emissions (Littell et al., 2009; Collier

549   et al., 2016; Landis et al., 2018; Matz et al., 2020). For example, wildfires caused large

550   and rapid increases in $PM_{2.5}$ mass concentration from ≤10 μg m^{-3} to >400 μg m^{-3} in

551   Edmonton during 10-12 August 1998 and on 30 May 2019 (Fig. S1). During these

552   periods, the BRTs method predicts the spikes of $PM_{2.5}$. However, the RF method

553   seemingly failed to learn the wildfire signals and missed predicting the spikes

554   associated with largely increased natural emissions because of its inherent weakness.

555

556   To further explore the causes for the different trends in $PM_{2.5}$ between eastern and

557   western Canadian cities, the 95th-100th percentile $PM_{2.5}$ mass concentration data in each

558   year were averaged into annual value and were examined below. The top 5% $PM_{2.5}$

559   exhibited decreasing trends (P<0.05) in four eastern Canadian cities and no significant

560   trend (P>0.05) in Halifax (Fig. S7). The decreasing trends further confirmed the

561   mitigation effects of air pollutants on $PM_{2.5}$. However, annual average $PM_{2.5}$ was still

562   as high as 8.8 μg m^{-3} in Hamilton in 2019, 7.0-7.7 μg m^{-3} in Quebec City, Toronto and

563   Montreal, and 5.6 μg m^{-3} in Halifax. If keeping the same decreasing rates as mentioned

564   above, it would take another 1-3 decades to lower annual average $PM_{2.5}$ by 2-4 μg m^{-3}

565   in order to meet the WHO 2021 guideline.

566

567   No significant trends (P>0.05) were identified in the 95th-100th percentile $PM_{2.5}$ mass

568   concentrations in the five western Canadian cities. Note that a large standard deviation

569   of the 95th-100th percentile $PM_{2.5}$ mass concentration was found in some years in the

570   five western cities, indicating a high variability. However, this is not the case in the

571   eastern Canadian cities. The episodic $PM_{2.5}$ events likely canceled out the mitigation

572   effects in the western Canadian cities. The annual average $PM_{2.5}$ were 6.6-6.8 μg m^{-3} in

573   2019 in Winnipeg, Edmonton and Victoria, which need great additional mitigation

574   efforts in order to reduce to a level below 5 μg m^{-3} in the presence of the episodes caused

575   by natural emissions. Note that the annual average $PM_{2.5}$ was already lower than 5 μg

576   m^{-3} in Vancouver, and that the annual average was 8.4 μg m^{-3} at the study site in Calgary

577   in 2014. The value slightly decreased to 7.6 μg m^{-3} in 2019 at another site ~5 km from

578   the study site in Calgary.

579

580   *3.5 Trends in AQHI in the ten Canadian cities*

581   Decreasing trends in AQHI were obtained in nine cities ($P<0.05$), with Calgary as an

582   only exception (Figs. S9 and S10). The annual average AQHI decreased by 8-29%

583   during the last two decades to the levels of 1.8 to 3.0 during 2017-2019 in the nine cities.

584   In Calgary, the annual averages AQHI narrowed around 3.4±0.2 during 1998-2010. In

585   the five eastern cities, AQHI above 10 occurred at <0.3% frequency before 2010, but

586   none after 2010. AQHI between 7-10 occurred at <4% frequency before 2010, and

587   below 0.5% after 2010. In the five western cities, AQHI above 10 occurred at <0.3%

588   frequency, and AQHI between 7-10 occurred at <2% frequency during the last two

589   decades. Note that AQHI above 10 still occurred at <0.3% frequency even after 2010

590   because of the large-scale wildfires. In fact, the occurrence frequencies of AQHI

591   between 7-10 and above 10 were a bit higher after 2010 (<0.3%) than before 2010 in

592   Vancouver and Victoria due to the increased wildfire events in the most recent decade.

593

594   On seasonal average, AQHI above 10 occurred most in summer (from June to August)

595   in most cities, e.g., Victoria (1.1%), Vancouver (0.8%), Edmonton (0.7%) and Winnipeg

596   (0.1%) in 2018. AQHI above 10 also occurred in winter (from December to February

597   next year) and spring (from March to May) in some cities, e.g., Edmonton (0.3% in the

598   spring of 2019 and 0.1-0.3% in the winter of 2012-2013) and Winnipeg (0.1% in the

599   spring of 2018).

600

601   **4. Discussion**

602   *4.1 Perturbations due to varying weather conditions on the decadal trends*

603   Perturbations due to varying weather conditions on the decadal trends of the studied

604   pollutants are presented in detail in Section 3 above, and key findings are briefly

605   summarized here. The perturbations are defined as the percentage differences between

606   the trends of the original and deweathered annual average concentrations. In ~70% of

607 the studies cases covering all the selected criteria pollutants in the ten cities, the

608 perturbation due to varying weather conditions had an influence of within ±2% on the

609 decadal trends of the original annual averages over the 20-year period. In the remaining

610 cases, relatively larger perturbations were identified, but at most 16%, keeping in mind

611 that a portion of the percentage differences between the trends of the original and

612 deweathered annual average concentrations was likely caused by errors inherent from

613 BRTs and RF predictions.

614

615 Specifically, in all the cases except CO in Quebec City (for which the calculated

616 perturbation is 7% from BRTs and 12% from RF), at least one of the two machining

617 leaning methods generated a perturbation of smaller than 5%. For example, the top

618 three largest perturbations obtained from using one of the two machining leaning

619 methods were all for SO_2, including 16% from RF in Winnipeg, 14% from BRTs in

620 Montreal and 13% from RF from BRTs in Toronto; however, the corresponding

621 perturbations from using another one of the two machining leaning methods were quite

622 smaller (4%, 0.2% and 3%, respectively), indicating possible large methodology

623 uncertainties. Thus, perturbations due to varying weather conditions should be

624 generally small on the two-decade time scale in most cases.

625

626 *4.2 Trend analysis of O_3 net sinks and sources*

627 As reported in literature, a large fraction of ground-level O_3 at middle-high latitude

628 zones comes from secondary reactions associated with natural sources (Barrie et al.,

629 1988; Van Dam et al., 2013; Cooper et al., 2005; Seinfeld and Pandis, 2006; Mitchell

630 et al., 2021). The natural signal usually has a spring maximum related to stratosphere-

631 troposphere exchange as well as increasing photochemistry, among other potential

632 factors (Chan and Vet, 2010; Monks et al., 2015; Strode et al., 2018; Xu et al., 2019).

633 The contributions from stratosphere-troposphere exchange are approximately 40 ppb,

634 while the sinks associated with natural and anthropogenic factors in the atmospheric

635 boundary layer may decrease the ground-level O_3 to levels lower than 40 ppb (Barrie

et al., 1988; Van Dam et al., 2013; Chan and Vet, 2010; Monks et al., 2015; Mitchell et al., 2021). On the other hand, enhanced tropospheric photochemical reactions under favorable meteorological conditions may increase the ground-level O_3 to levels higher than 40 ppb, causing severe O_3 pollution (Monks et al., 2015; Simon et al., 2015; Seinfeld and Pandis 2006; Xu et al., 2019). In fact, 40 ppb has been widely used as the threshold value for assessing O_3 impacts on ecosystem health (e.g., AOT40 index) (Avnery et al., 2011). Thus, O_3 data with mixing ratios lower and higher than 40 ppb were analyzed separately below, with the former case representing net O_3 sinks occurring in the atmospheric boundary layer and the latter one representing net O_3 sources occurring therein (Table 3).

In the cases with O_3 mixing ratios ≥ 40 ppb, the deweathered and original values, however, exhibited decreasing trends (P<0.05) in all of the five eastern cities and two western cities (Victoria and Vancouver) (Figs. 4 and S8 and Table 3). The overall decreases in O_3 with mixing ratios ≥ 40 ppb were 2 ppb in Halifax from 2000-2017, in Montreal and Quebec City from 1995-2019, and in Victoria from 1999-2019 (figure not provided), 4 ppb in Toronto from 2003-2019, 5-6 ppb in Hamilton from 1987-2019, and 12 ppb in Vancouver from 1986-2019 (but only 2 ppb from 2000-2019). Again, a few spikes and troughs occurred in the BRTs-deweathered values possibly because of unpredictably increased and decreased emissions of O_3 precursors, respectively. In the cases with O_x mixing ratios ≥ 40 ppb, the decreasing trends were obtained in all of the ten cities. These results further implied that the tropospheric photochemical formation of O_3 likely reduced in seven of the ten cities during the last two to three decades.

In the cases with O_3 mixing ratios ≥ 40 ppb in the remaining three western cities, the decreasing trends (P<0.05) were obtained in the BRTs-deweathered and original values and no significant trend (P>0.05) in the RF-deweathered values in Winnipeg; the decreasing trend was obtained only in the original values in Calgary; and no significant trends in the deweathered and original values in Edmonton. These trend results implied

665   that the responses of the fraction of O_3 to emission reductions of its precursors were too

666   weak to be confirmed, especially in the presence of perturbation due to varying weather

667   conditions.

668

669   In the cases with O_3 mixing ratios < 40 ppb, the trends were almost the same as those

670   from using the full dataset of O_3 mixing ratios. This consistency suggested that the

671   increasing trends in O_3 mixing ratio in the nine Canadian cities were mainly due to the

672   reduced O_3 sinks.

673

674   *4.3 The perturbation from large-scale wildfires on PM$_{2.5}$ trend in western Canadian*

675   *cities*

676   Wildfire emissions become important contributors to air pollution in North America

677   with global warning and increased extreme weather conditions such as heatwaves and

678   severe droughts (Andreae and Merlet, 2001; Littell et al., 2009; Marlon et al., 2013;

679   Barbero et al., 2015; Abatzoglou and Williams, 2016; Randerson et al., 2017; Mardi et

680   al., 2021). For example, Meng et al. (2019) estimated that wildfires accounted for 17.1%

681   of the total population-weighted exposure to PM$_{2.5}$ for Canadians during 2013-2015

682   and 2017-2018. The large contribution was not surprising because large wildfires can

683   rapidly increase hourly PM$_{2.5}$ mass concentration from a few μg m^{-3} to >400 μg m^{-3}

684   (Landis et al., 2018 and Fig. S1). The estimated annual economic cost attributable to

685   PM$_{2.5}$ pollution reached \$410M-\$1.8B for acute health impacts and \$4.3B-\$19B for

686   chronic health impacts in western Canada (Landis et al., 2018; Matz et al., 2020). In the

687   U.S., wildfire emissions were reported to account for up to 25% of annual primary

688   PM$_{2.5}$ emissions (U.S. EPA, 2014).

689

690   Due to the wide occurrence of small-scale wildfires, most of the emitted air pollutants

691   from these sources and subsequent long-range transport can be considered as natural

692   background pollution. The key issue is to quantify the abnormally increased

693   contributions from large-scale wildfires to annual average PM$_{2.5}$ in each year and their

694 perturbations on long-term trends in PM$_{2.5}$. Using the method described in Section 2,

695 the perturbation contributions in Winnipeg were estimated to be around 0.5±0.4 µg m$^-$

696 ^{3} in 2001-2018, with larger values of 1.1-1.3 µg m^{-3} associated with large-scale wildfires

697 in 2002, 2012 and 2018 (Fig. 5a). The larger perturbation contributions in 2012 and

698 2018 indeed led to an increasing trend in PM$_{2.5}$ from 2001-2018 in this city (Table 2).

699 The perturbation contributions were, however, smaller than 0.2 µg m^{-3} in 2001, 2003,

700 2005, 2006, 2008, 2009, 2014 and 2017, and such small values may be related to

701 varying weather conditions rather than large-scale wildfires.

702

703 In Edmonton, the perturbation contributions were around 1.0±0.9 µg m^{-3} in 1998-2019

704 (Fig. 5b). However, the largest contribution was 3.0 µg m^{-3} in 1998, followed by 2.4 µg

705 m^{-3} in 2018 and 2.1 µg m^{-3} in 2004, respectively, because of large-scale wildfires. The

706 perturbation contributions from large-scale wildfires were large enough to cancel out

707 the mitigation effect of air pollutants on annual averages of PM$_{2.5}$ in Edmonton. In

708 Calgary, the perturbation contributions were around 1.2±0.7 µg m^{-3} in 1998-2013,

709 depending on if large-scale wildfires occurred in any particular year. For example, the

710 perturbation contributions were smaller than 0.2 µg m^{-3} in 1999, 2007 and 2013, while

711 the contributions reached 2.2-2.3 µg m^{-3} in 1998 and 2010.

712

713 In Victoria, the perturbation contributions were around 0.7±0.2 µg m^{-3} in 1998-2019.,

714 The perturbation contribution in each year was, however, larger than 0.4 µg m^{-3},

715 suggesting that the wildfires were always important contributors. In Vancouver, the

716 perturbation contributions largely decreased to 0.3±0.5 µg m^{-3} in 2004-2019. However,

717 the maximum value still reached 1.7 µg m^{-3} in 2017, followed by 1.4 µg m^{-3} in 2018

718 and 0.5 µg m^{-3} in 2015. The large perturbation likely overwhelmed or canceled out the

719 effects of emission reductions on annual average PM$_{2.5}$.

720

721 **5. Conclusions**

Through analysis of deweathered and original annual average concentrations of selected criteria air pollutants measured in ten major cities in Canada during the last 2-3 decades, we have generated the following decadal trends for these pollutants: 1) decreasing trends in NO_2, CO and SO_2 mainly due to reduced primary emissions across Canada, except no significant trend in CO in Montreal; 2) increasing trends in O_3 mainly due to the reduced titration effect across Canada, except no significant trend in O_3 in Halifax; and 3) roughly opposite trends in $PM_{2.5}$ between eastern and western Canada, resulted from the combined effects of emission reductions and the occurrence of large-scale wildfires.

The overall percentage decrease in NO_2 during the last 2-3 decades among the 10 cities ranged from 37% to 62%, and the annual decreasing rates varied from 0.31 ppb year^{-1} to 0.74 ppb year^{-1}. The overall percentage decrease in CO varied from 57% to 92% and the annual decreasing rate ranged from 0.010 ppm year^{-1} to 0.076 ppm year^{-1} between nine cities. The corresponding numbers for SO_2 are from 23% to 93% and from 0.04 ppb year^{-1} to 0.63 ppb year^{-1} among the 10 cities. By only considering O_3 mixing ratio $\geq$ 40 ppb, annual average O_3 decreased by 2-4 ppb in most cities during the past two-three decades, but not in Calgary and Edmonton, and no consistent decreasing trend was identified in Winnipeg, implying that the mitigation effects of air pollutants on O_3 were too weak to be confirmed.

The mitigation effects on $PM_{2.5}$ were detected on the basis of the identified decreasing trends in three of the five eastern cities regardless of using original or deweathered annual average data, but this is not the case in the other two eastern cities. In the five western cities, the perturbation due to large-scale wildfires greatly affected original annual average $PM_{2.5}$ and was large enough to cancel out the mitigation effects in some years, leading to no decreasing trends and in some cases even increasing trends.

Excluding Calgary, the annual average AQHI showed a significant decrease by 8-29% during the last two decades to levels between 1.8 and 3.0 in 2017-2019. However, large-scale wildfire events still occasionally elevated AQHI to a level of above 10 (very high risk) (<0.3% frequency) in western Canadian cities after 2010. Thus, large-scale wildfires have become a key factor in causing severe air pollution in Canadian cities, as was seen in the most recent very large-scale wildfires occurred in Canada from the later spring to the earlier summer in 2023 that resulted in severe air pollution across Canada and New York through long-range transport. Urgent work should be conducted for assessing the impacts of large-scale wildfires on human health and climate change, besides investigating their occurrence and control mechanisms and transport pathways. In-depth studies are also needed to explore the causes of the non-decreasing trends in O_3 with mixing ratios $\geq$ 40 ppb in some western Canadian cities, results from which are critical for making future control policies.

Data availability. the data used in this paper are downloadable from https://open.canada.ca/data/en/dataset/1b36a356-defd-4813-acea-47bc3abd859b) and https://www.canada.ca/en/environment-climate-change/services/environmental-indicators/air-pollutant-emissions.html.

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Table 1. Regression of (BRTs and RF) deweathered against original annual average NO_2 mixing ratios, annual decreasing rate (ppb year^{-1}) and overall decreasing percentage (%) of deweathered and original NO_2 mixing ratios (P<0.05 for all the decreasing trends), correlation (R^2) of deweathered and original NO_2 mixing ratios against provincial total NO_x emissions and transportation NO_x emissions (P<0.05 except those marked with "/" for which p>0.05), and percentage decreases (%) of the provincial total NO_x emissions and transportation NO_x emissions (P<0.05 for all the decreasing trends except increasing trends in NO_x emission from 1990-2010 in Winnipeg and Calgary[#]) in ten Canadian cities during the last decades ([##]since 1990; bold font numbers represent cases with smaller deceasing percentages in NO_2 mixing ratios than in corresponding provincial emissions, italic numbers represent R^2>0.8, and italic bold numbers represent an increasing trend).

City	Regression of deweathered against original mixing ratio (P<0.01)		Annual decreasing rate (ppb year^{-1}) and overall decreasing percentage (%) (P<0.05)			Correlation (R^2) of mixing ratios against provincial total and transportation NO_x emissions (P<0.05)			Percentage decreases (%) of provincial total and transportation emissions[&&]
	BRTs	RF	BRTs	RF	original	BRTs	RF	original	
Halifax (1996-2017)	y=1.03×x	y=1.08×x	0.49, 62	0.45, 58	0.55, 50	*0.83, 0.84*	*0.84, 0.85*	*0.86, 0.87*	54, 56
Montreal (1995-2019)	y=0.99×x	y=1.04×x	*0.34,* **44**	*0.32,* **42**	*0.34,* **39**	*0.90, 0.85*	*0.91, 0.86*	*0.87, 0.82*	**47, 52**
Quebec (1996-2019)	y=0.98×x	y=1.02×x	0.44, 51	0.39, 45	0.46, 46	*0.97, 0.97*	*0.97, 0.98*	*0.95, 0.95*	47, 52
Toronto (2004-2019)	y=1.02×x	y=1.04×x	*0.67,* **40**	*0.64,* **39**	*0.74,* **37**	*0.96, 0.96*	*0.97, 0.98*	*0.94, 0.94*	**52, 52**
Hamilton (1996-2019)	y=1.00×x	y=1.02×x	*0.53,* **42**	*0.55,* **44**	*0.54,* **42**	*0.95, 0.97*	*0.95, 0.96*	*0.92, 0.93*	**58, 57**
Winnipeg (1984-2018)	y=0.99×x	y=1.00×x	0.37, 57	0.34, 57	0.34, 50	*0.90, 0.93*	*0.91, 0.94*	*0.85, 0.89*	43, 43[#]
Edmonton (1994-2019)	y=1.02×x	y=1.00×x	0.45, 41	0.47, 40	0.53, 45	*0.57, 0.73*	*0.54, 0.73*	*0.63, 0.73*	10, 29
Calgary (1986-2007)	y=1.00×x	y=1.01×x	0.60, 31	0.60, 32	0.61, 33	/	/	/	***-11, -5***[#]
Vancouver (1986-2019)	y=1.00×x	y=1.01×x	0.36, 49	0.36, 47	0.37, 49	0.63, 0.75	0.63, 0.74	0.54, 0.66	23, 27[##]
Victoria (1993-2019)	y=1.01×x	y=1.02×x	0.31, 0.49	0.31, 0.45	0.31, 0.51	0.58, 0.69	0.58, 0.69	0.54, 0.65	23, 33[##]

Table 2. Regression of (BRTs and RF) deweathered against original annual average $PM_{2.5}$ mass concentrations, annual decreasing rate (µg m^{-3} year^{-1}) and overall decrease (µg m^{-3}) of deweathered and original $PM_{2.5}$ mass concentrations, and percentage decreases (%) of the provincial total $PM_{2.5}$ emissions in ten Canadian cities during the last decades (decreasing trends were obtained with P<0.05 except those marked with "/" for which P>0.05; and bold font numbers represent cases with increasing trends).

City	Regression of deweathered against original mixing ratio (P<0.01)		Annual decreasing rate (µg m^{-3} year^{-1}) and overall decrease (µg m^{-3})			Decreasing percentage (%) of provincial total $PM_{2.5}$ emissions
	BRTs	RF	BRTs	RF	original	
Halifax (2008-2018)	y=1.00×x	y=1.02×x	/	/	/	27
Montreal (2005-2019)	y=1.00×x	y=1.01×x	0.24, 2	0.22, 2	0.25, 2	/
Quebec (1998-2019)	y=1.00×x	y=1.01×x	/	/	/	/
Toronto (2000-2019)	y=1.00×x	y=1.01×x	0.11, 2	0.10, 2	/	/
Hamilton (1998-2019)	y=1.00×x	y=1.01×x	0.15, 4	0.14, 3	0.15, 3	/
Winnipeg (2001-2018)	y=1.04×x	y=1.04×x	**-0.10, -2**	**-0.10, -2**	**-0.09, -1**	**-11**
Edmonton (1998-2019)	y=1.01×x	y=1.03×x	/	/	/	**-40**
Calgary (1998-2014)	y=1.00×x	y=1.03×x	/	/	/	**-38**
Vancouver (2004-2019)	y=0.99×x	y=1.02×x	/	**-0.08, -1**	/	28
Victoria (1999-2019)	y=1.00×x	y=1.03×x	/	**-0.08, -1**	**-0.07, -1**	42

Table 3. Trends in deweathered and original annual average O_3 and O_x mixing ratios at levels below and above 40 ppb in ten Canadian cities during the last decades ([#]decreasing tends with $P<0.05$; [##]no trend or stable trend with $P>0.10$; [###]increasing trend with $P<0.05$).

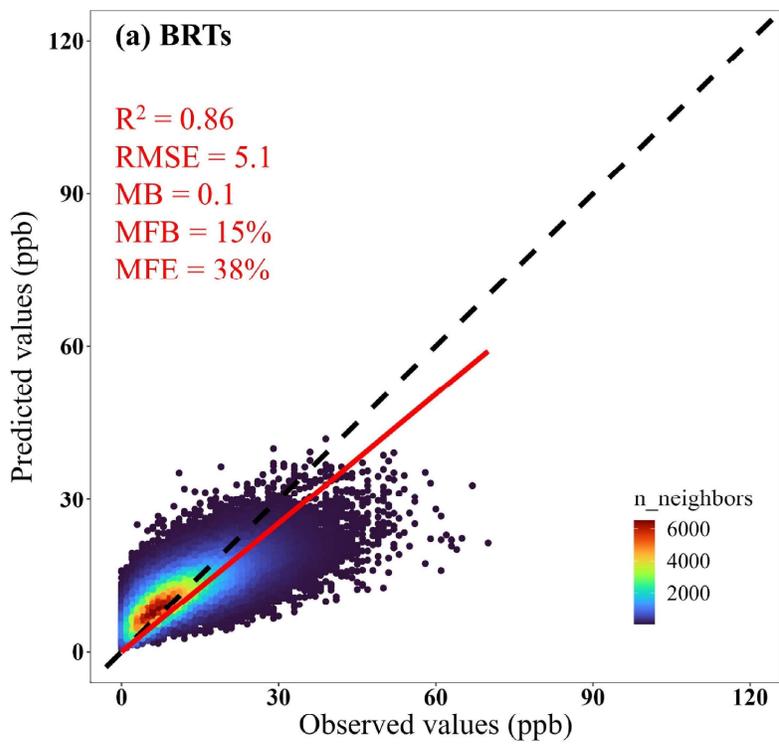| | O_3 | | | | | | O_x | | | | | |
| | ≥ 40 ppb | | | < 40 ppb | | | ≥ 40 ppb | | | < 40 ppb | | |
	BRTs	RF	Original	BRTs	RF	Original	BRTs	RF	Original	BRTs	RF	Original
Halifax (2000-2017)	↓[#]	↓	↓	/[##]	/	/	↓	↓	↓	↓	↓	↓
Montreal (1997-2010)	↓	↓	↓	↑[###]	↑	↑	↓	↓	↓	/	/	/
Quebec (1995-2019)	↓	↓	↓	↑	↑	↑	↓	↓	↓	/	↓	/
Toronto (2003-2019)	↓	↓	↓	↑	↑	↑	↓	↓	↓	↓	↓	↓
Hamilton (1996-2019)	↓	↓	↓	↑	↑	↑	↓	↓	↓	/	/	/
Winnipeg (1985-2018)	↓	/	↓	↑	↑	↑	↓	↓	↓	↓	↓	/
Edmonton (1981-2019)	/	/	/	↑	↑	↑	↓	↓	↓	↓	↓	↓
Calgary (1986-2014)	/	/	↓	↑	↑	↑	↓	↓	↓	↓	↓	↓
Vancouver (1986-2019)	↓	↓	↓	↑	↑	↑	↓	↓	↓	↓	↓	↓
Victoria (1999-2019)	↓	↓	↓	↑	↑	↑	↓	↓	↓	/	/	/

List of Figures

Fig. 1. Performance evaluation of the predicted NO_2 hourly mixing ratios by BRTs and RF algorithm against those observed in Halifax during 1996-2017. Red lines represent linear regression, and color bar reflects data number density. Note that different observational data sets are shown between (a) and (b) because the inputs for the two packages (BRTs and RF) are randomly divided into two groups for training and testing.

Fig. 2. Correlations between hourly $PM_{2.5}$ concentration in a single year and 22-year average $PM_{2.5}$ concentration in each hour of the year in Edmonton. Left columns show percentile series of $PM_{2.5}$ in 1998, 1999 and 2019, respectively, against the corresponding 22-year average series. Right column shows time series of $PM_{2.5}$ in 1998, 1999 and 2019, respectively, against the corresponding 22-year average series. Blue straight dashed lines in a, c and e represent the regression curves within linear ranges and their extensions out of the ranges; vertical arrows represent the distance of the predicted values from the regression curve. Blue straight lines and dark blue dashed lines in b, d and f represent the regression curves and 1:1 lines, respectively.
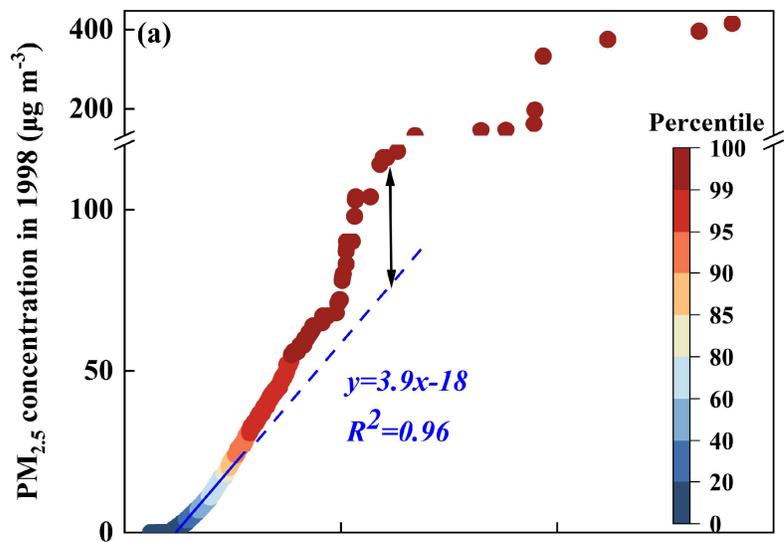
Fig. 3. Trends of original annual average NO_2 (upper row) and $PM_{2.5}$ (lower row) in five eastern (left column) and five western (right column) Canadian Cities.

Fig. 4 Deweathered hourly mixing ratios of O_3 (left column) and O_x (right column) at levels ≥ 40 ppb in five eastern Canadian cities.
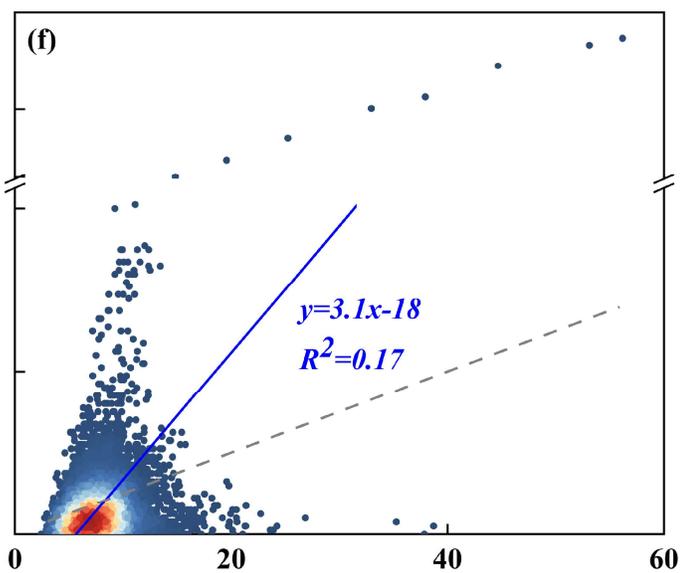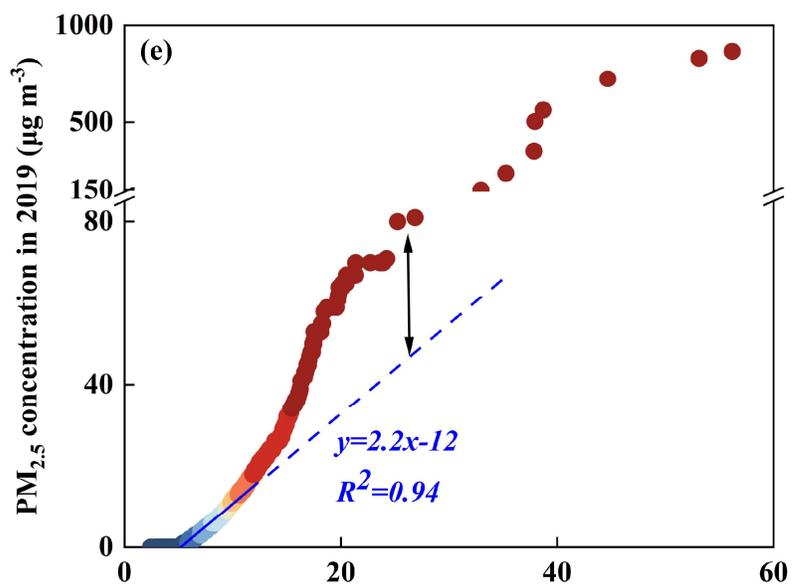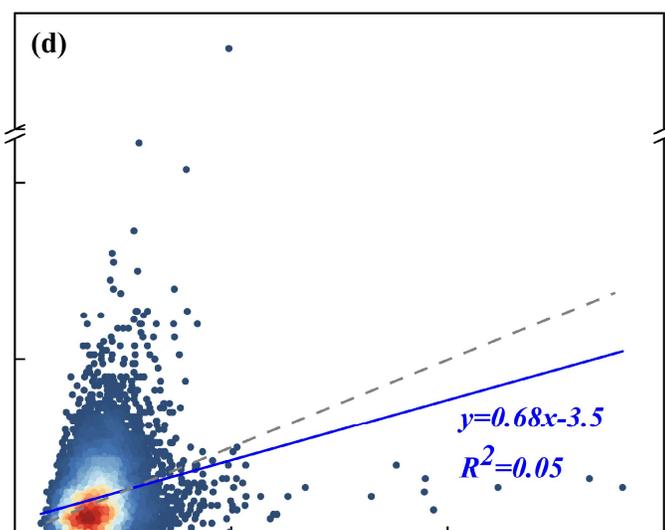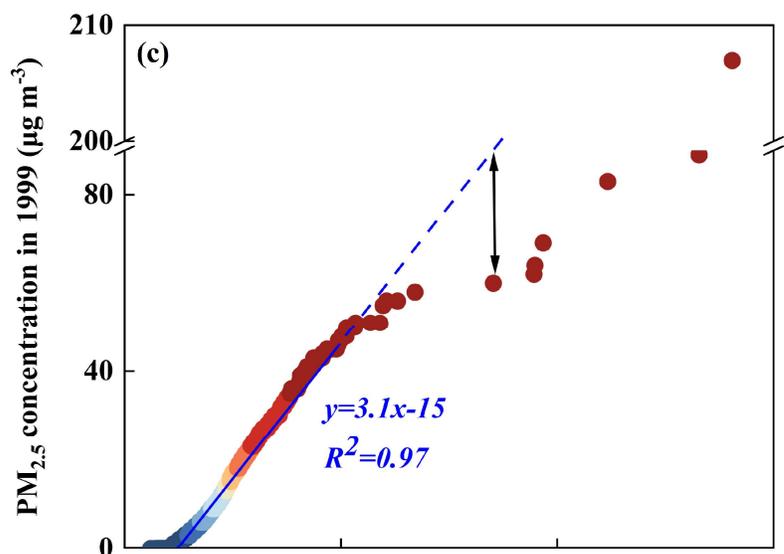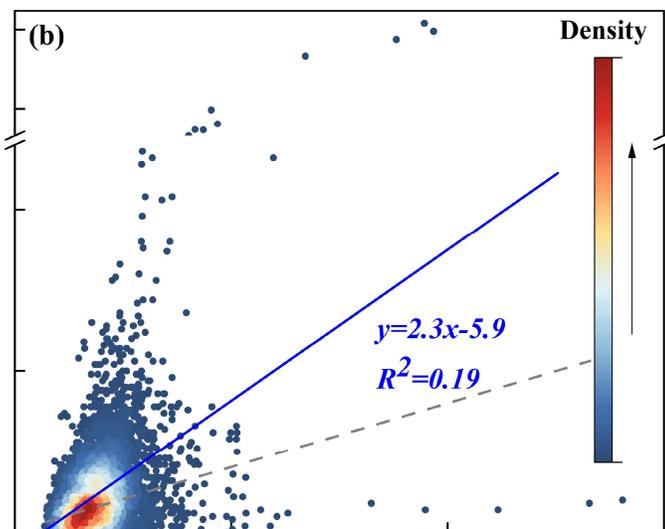
Fig. 5. The calculated perturbation contribution to the corresponding original annual average $PM_{2.5}$ concentration (left column) and the mean and standard derivation of the calculated perturbation (right column) in five western Canadian cities.
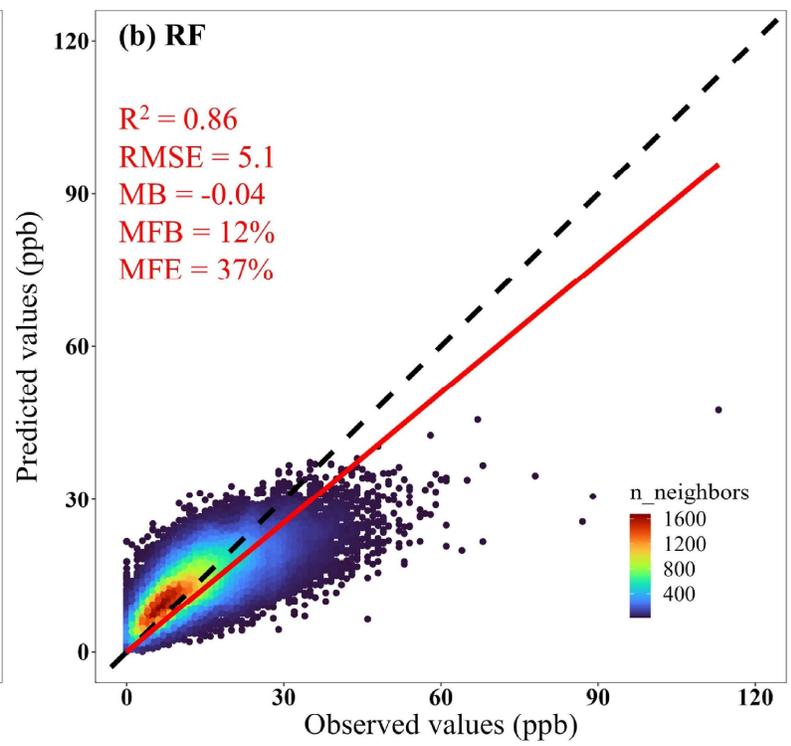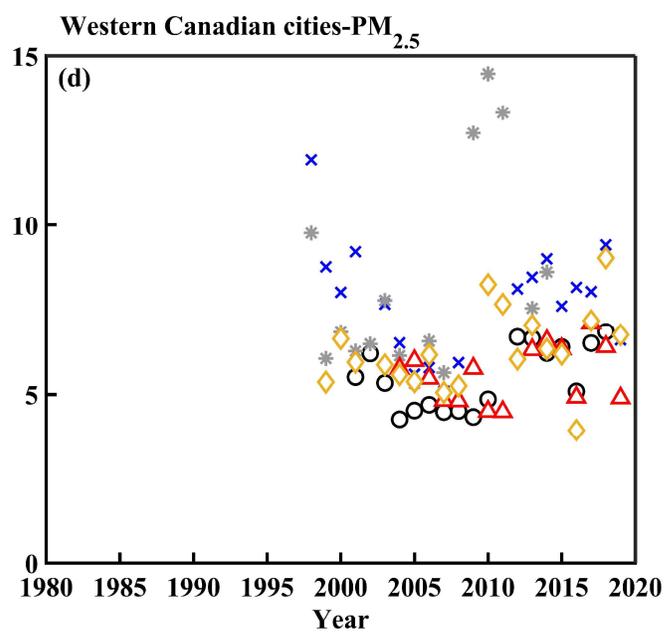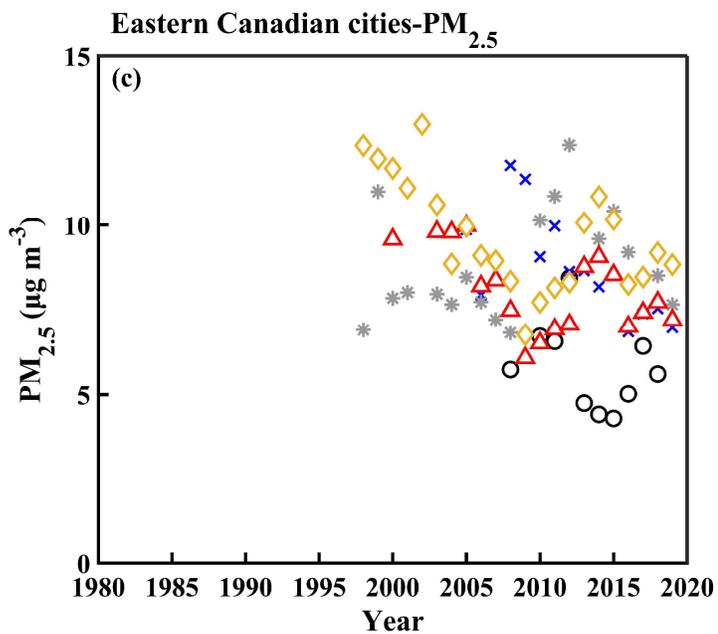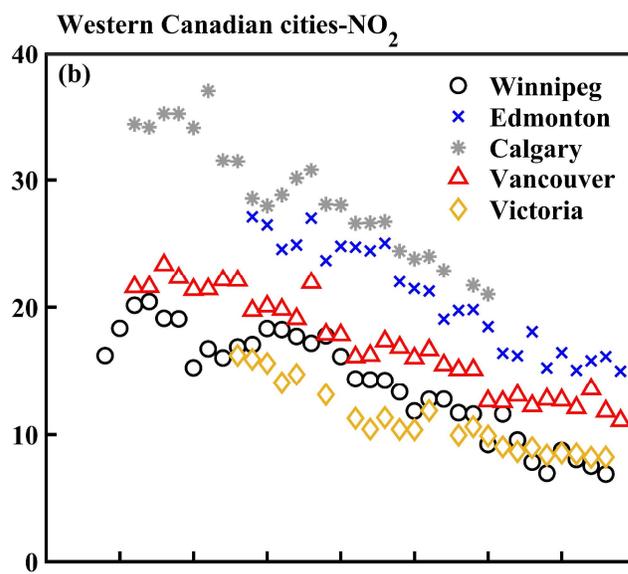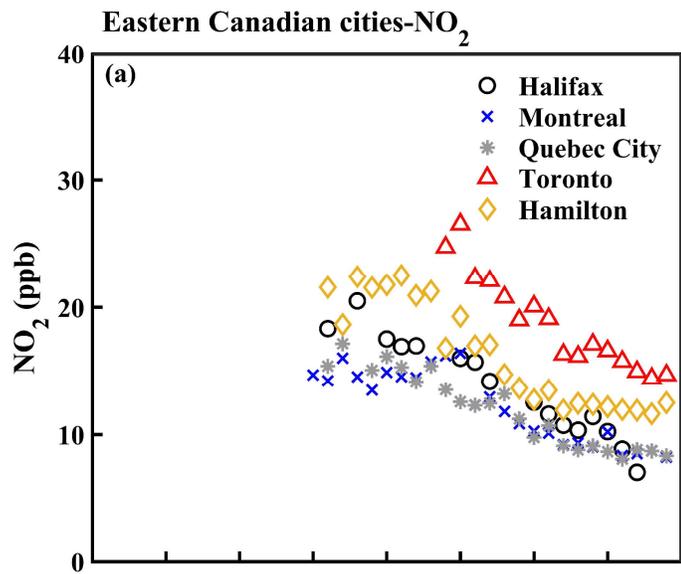
Percentile series — **Time series**

(a) PM$_{2.5}$ concentration in 1998 (μg m^{-3})

$y=3.9x-18$
$R^2=0.96$

Percentile: 100, 99, 95, 90, 85, 80, 60, 40, 20, 0

(b) Density

$y=2.3x-5.9$
$R^2=0.19$

(c) PM$_{2.5}$ concentration in 1999 (μg m^{-3})

$y=3.1x-15$
$R^2=0.97$

(d)

$y=0.68x-3.5$
$R^2=0.05$

(e) PM$_{2.5}$ concentration in 2019 (μg m^{-3})

$y=2.2x-12$
$R^2=0.94$

(f)

$y=3.1x-18$
$R^2=0.17$

PM$_{2.5}$ concentration in 1998-2019 (22-year average in each hour) (μg m^{-3})

Eastern Canadian cities-NO$_2$

Western Canadian cities-NO$_2$

Eastern Canadian cities-PM$_{2.5}$

Western Canadian cities-PM$_{2.5}$