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Heavy metals in the near-road environment: Results of semi-continuous monitoring of ambient particulate matter in the greater Toronto and Hamilton area

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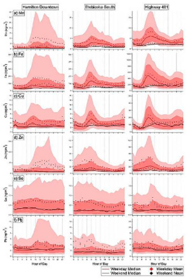
HIGHLIGHTS

- Ambient roadside concentrations of Fe and Cu vary strongly with morning rush hours.
- Correlations between metals and gaseous pollutants are highest at the highway site.
- Zn, Se and Pb do not vary as much as Mn, Fe and Cu at the roadside.
- Scatterplots of metals *vs.* criteria gases suggest the existence of multiple sources.
- sQTBA shows strongest source regions of Fe are local, but regional for Se and Pb.

GRAPHICAL ABSTRACT

Diel variations of concentrations (ng/m^3) of some abundant heavy metals Mn (A), Fe (B), Cu (C), Zn (D), Se (E) and Pb (F) observed at the three near road air monitoring stations on weekdays and weekends during the period of study (dark shade = weekday IQR, light shade = 10th and 90th percentiles).



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ABSTRACT

Six heavy metals - Mn, Fe, Cu, Zn, Se, and Pb among other elemental species were monitored in ambient $PM_{2.5}$ at three near-road ambient air monitoring locations in the Greater Toronto and Hamilton Area (GTHA) with semi-continuous X-ray fluorescence (XRF) instrumentation over a period spanning January 1st, 2014 to June 30th, 2017. Land use in these air monitoring locations includes residential, institutional and industrial, thus, air monitoring is representative of typical urban areas. Ambient metal concentrations were found below Ontario's ambient air quality criteria. Temporal trends however indicated that high concentrations of Fe and Cu correlated with peak commuting and working hours on weekdays. To further understand the potential sources of these metals, scatterplots of metal concentrations and criteria pollutant gases were made on weekdays and weekends. These scatterplots reveal edges that are due to multiple sources of these metals. When these scatterplots are colour-coded by the hour of day, edges associated with the morning rush hour on weekdays for Fe and Cu (also Mn and Zn to a lesser extent) likely due to traffic-related emissions are more clearly-delineated from other edges arising from industrial or regional sources that were prevalent during other times of the day. Finally, an auxiliary receptor model was used to explore the potential source regions of these metals. It was observed that Mn, Fe and Cu had intense potential source regions within the GTHA on weekdays that diminished on the weekends, and in the case of Fe, the potential source regions in the GTHA were sensitive to the morning rush hour period, in-

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dicating that traffic-related emissions are a major source of Fe. Other metals, especially Zn, Se and Pb have source regions that are less sensitive to the morning rush hour period and are usually situated outside the GTHA.

1. Introduction

Heavy metals, generalized herein to comprise most elements in periods 4–7 of the Periodic Table of Elements including transition metals, adjacent metalloids and chalcogens, and the heaviest halogens, are mainly naturally-occurring trace-level elements, many of which exhibit a range of harmful effects. For example, all 15 single chemical elements listed by the International Agency for Research on Cancer as Classes 1–3 carcinogens with the exception of beryllium are heavy metals (International Agency for Research on Cancer, 2017). The toxicity of particulate matter (PM) in cellular media is generally believed to arise from the oxidative stress they induce which is measured by their ability to generate reactive oxygen species (ROS); generally referred to as oxidative potential; OP (Cho et al., 2005; Steenhof et al., 2011). Boogaard et al. (2012) reported that OP of PM correlated well with Cu, Fe, Mn, Cr and Ba. In that study, OP near major urban roads was also highly elevated compared with other urban and background locations. Dithiothreitol-oxidative potential measurements (OP^{DTT}: rate of DTT consumption normalized to the quantity of PM) has been shown to be highly applicable to soluble transition metals in PM (Charrier and Anastasio, 2012). OP^{DTT} measurements made for $PM_{2.5}$ and its water soluble components including Mn, Fe and Cu may also be associated with acute effects e.g., emergency room visits for respiratory disease, asthma and ischemic heart disease two days after exposure (Abrams et al., 2017). Recently, Weichenthal et al. (2018) reported on spatial variations in estimated Fe- and Cu-mediated ROS production of PM via land use regression surfaces for the City of Toronto. Separate from carcinogenicity, other toxic effects of heavy metals include neurotoxic (e.g., Pb; (International Agency for Research on Cancer, 2006)), nephrotoxic (e.g., Cd; (International Agency for Research on Cancer, 2011)) and genotoxic (e.g., Hg; (Crespo-López et al., 2009)) outcomes. The harmful effects of these species may vary with the modes of exposure. In general, heavy metals have relatively low vapour pressures and high densities, thus, they can exist in the particle phase in the atmosphere. These particles are usually mechanically-generated and in ambient air are typically recorded as super-micron (particle diameter > 1 µm), coarse mode particles; although several studies have reported the presence of some heavy metals in the accumulation mode (0.1–1 µm) of fine PM (Saffari et al., 2013; Vecchi et al., 2008). Where inhalation as a major route of exposure is concerned, both occupational and ambient exposure must be considered. Thus, it is important to continually monitor the concentrations of heavy metals in ambient PM.

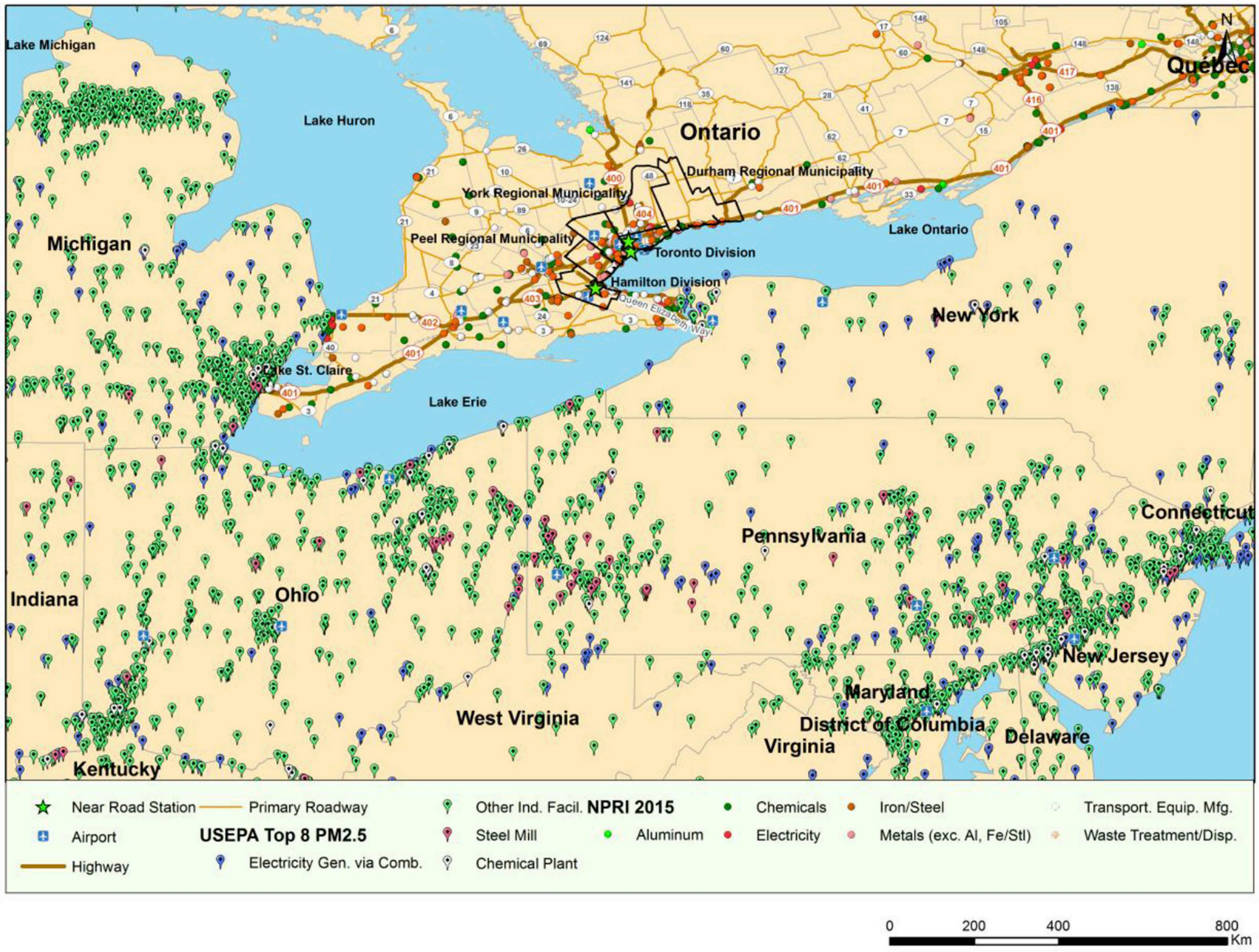

Fig. 1. Map of the Greater Toronto and Hamilton Area (GTHA) showing the three near-road stations used in this study, major roadways and relevant point sources.

For many inhabitants of urban areas, potential exposure to heavy metals will arise via inhalation of atmospheric aerosols from on-road (Boogaard et al., 2012; Weichenthal et al., 2018) transportation-related (tailpipe, mechanical abrasion, road dust resuspension) and industrial emissions in the urban environment, although metro-rail transportation has recently also been shown to be a significant potential source of metal exposure (Loxham et al., 2013; Nieuwenhuijsen et al., 2007; Park et al., 2012; Van Ryswyk et al., 2017). In this work, we report on concentrations and trends of detectable metals at air monitoring locations in Toronto and Hamilton.

The Greater Toronto and Hamilton Area (GTHA; Fig. 1) comprises the adjacent census metropolitan areas (CMAs; Durham, York, Toronto, Peel, Halton and Hamilton) of the two cities and with a combined population of roughly 6.7 million (Statistics Canada, 2017), is the most densely populated region in Canada (Metrolinx, 2008). This region experiences a mix of residential, institutional, industrial and some agricultural land use. Thus, this study was designed to monitor the concentrations of heavy metals in ambient PM obtainable at three locations in the GTHA with continuous instrumentation over multiple years. The overall objective was to determine inter-site and intra-site variations that could be indicative of the different kinds of exposure scenarios in their respective locations and to characterize the heavy metal sources in these urban environments with the aid of auxiliary receptor models. These will help to determine the relative importance of transportation/vehicular emissions or other sources (e.g., industrial and regional) of these heavy metals.

2. Methods

2.1. Sites and data description: Ambient air monitoring stations in three GTHA locations (see Table 1) operated by the Ontario Ministry of the Environment, Conservation and Parks were used in this study based on their population characteristics, proximity to potential sources of heavy metals including roadways and industry, and availability of continuous instrumentation. All the stations were designated as roadside stations as described in the province of Ontario's Annual Air Quality Report (Ontario Ministry of the Environment and Climate Change, 2017), i.e., they were within 100 m of a roadway with traffic volumes > 10000 vehicles/day. Data was collected at three air monitoring stations between 2014 and 2017. The stations were monitored for between two and 3.75 approximately, depending on the installation date of the metal monitoring instrumentation.

Hamilton Downtown is an urban ambient air monitoring station in Hamilton, Ontario. The site is located approximately 3 km from one of Canada's largest urban industrial zones comprising steel mills, waste treatment and disposal facilities and chemical manufacturing industries. Etobicoke South is an urban ambient air research station on the outlying boundaries of the City of Toronto. The site is located in an open area surrounded by major truck depots to the north and a concrete processing facility 400 m to the south-east. Finally, the Highway 401 station is an urban ambient air research station in Toronto, Ontario fitted with instrumentation capable of near-real-time speciation of ambient $PM_{2.5}$ (Sofowote et al., 2018). It is a near-road station positioned 10 m from Highway 401, a major roadway, which at this location has eighteen lanes.

2.2. Instrumentation: The metals data were obtained using two Xact 625 and one upgraded Xact 620 (Cooper Environmental Systems, Oregon, USA) ambient metals monitoring systems. The principles of operation of these monitors have been described in more detail elsewhere (Missouri Department of Natural Resources, 2009; Sofowote et al., 2014; Yadav et al., 2009). The instruments were fitted with a $PM_{2.5}$ size cut inlet and collected particulate mass on filters to monitor ambient air for a prescribed period. Elements are quantified by X-ray fluorescence (XRF). The Xact 625 monitors were optimized and operated to continuously determine metals at a sampling period of 1-h. The system is capable of determining ambient concentrations of potassium (K), calcium (Ca). vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), selenium (Se), cadmium (Cd), tin (Sn), antimony (Sb), barium (Ba), mercury (Hg), and lead (Pb). Silicon (Si) and sulphur (S) could also be detected by the Xact 625 monitor but results are likely not quantitative as per the manufacturer's recommendations.

At the Hamilton station, Environment and Climate Change Canada's (ECCC) National Air Pollution Surveillance (NAPS; (Dabek-Zlotorzynska et al., 2011)) program operated a PM dichotomous sampler from which non-continuous (24-h, once every 3 days) $PM_{2.5}$ elemental concentration data were obtained via analyses by energy dispersive XRF (Dichot-EDXRF) and inductively coupled plasma mass spectrometry (ICP-MS). In this work, these elemental concentrations data were used for comparisons with the collocated daily-averaged Xact 625-derived concentrations.

2.3. Statistical methods: To aid the understanding of the data from the Xact instruments at these three locations in the GTHA, a series of non-parametric statistical tests were performed. Trend analyses performed with the Mann-Kendall test coupled with the Sen's estimator for trend (Sen's slope) are a straightforward approach to determining the significance and magnitude of a trend respectively, in which the latter (Sen's slope) is computed for a given data set based on monotonicity (Gilbert, 1987). A non-parametric two-way ANOVA in the form of the Friedman's test could also be applied to the data from each station for repeated measures (Friedman, 1937; Gilbert, 1987) to observe intra-site variability. With this test, conditions such as years and weeks can be simultaneously tested on the sampling distribution to determine significant changes spanning the desired time frame at each site.

For determining broad significant differences in the sampling distributions of data collected across stations for the entire sampling period, a non-parametric one-way ANOVA in the form of the Kruskal-Wallis (Gilbert, 1987; Kruskal and Wallis, 1952) test coupled with a post-hoc test such as the Dunn multiple-comparison test (Dunn, 1964) was done. The test objective in this case was to determine significant differences using the individual stations as the test condition. The Kruskal-Wallis test was also used to determine intra-site seasonal differences. The supplement features an extended discussion of these nonparametric methods.

3. Results and discussion

At these three monitoring stations, the elements listed in Table 2

Table 1
Ambient metals monitoring near-road stations in the Greater Toronto and Hamilton Area (GTHA) used in this study and their characteristics.

Station name	Latitude	Longitude	Station classification	Distance from roadway (m)	AADT[a] or estimate	Monitoring period
Hamilton Downtown	43°15′28.0″	−79°51′42.0″	Roadside	47	> 10,000 [b]	17/07/2014–09/08/2017
Etobicoke South	43°36′39.1″	−79°31′19.0″	Roadside	33	14,517 [c]	01/01/2014–11/08/2017
Highway 401	43°42′34.0″	−79°32′36.6″	Roadside	10	411,600 [d]	08/06/2015–09/08/2017

[a] Annual average daily traffic.
[b] Ontario Ministry of the Environment and Climate Change (2017).
[c] City of Toronto. Transportation Services (2013).
[d] Ministry of Transportation of Ontario (2016).

Table 2
Data properties of six elemental species monitored by the Xact ambient metals analyzers at the three near-road air monitoring stations in the GTHA and Ontario's ambient air quality criteria (AAQC) and guidelines. All instruments were fitted with a $PM_{2.5}$ inlet.

Species	Site	Data available (%)	Concentration > MDL (%)	MDL[a] (ng/m^3)	Median (ng/m^3)	Maximum (ng/m^3)	Minimum (ng/m^3)	24-Hr AAQC[b] (ng/m^3)	0.5-Hr Standard /Guideline (ng/m^3)[c]
Mn	Hamilton DTN	79.49	56.24	0.28	0.83	624.37	0	100 ($PM_{2.5}$)	1200
	Etobicoke S.	63.1	57.58		1.43	77.95	0		
	Highway 401	75.32	74.8		2.96	110.82	0		
Fe	Hamilton DTN	79.49	79.46	0.76	49.63	7818	0	4000	10000
	Etobicoke S.	63.1	63.03		66.19	1987	0		
	Highway 401	75.32	75.31		187.34	2559	0.33		
Cu	Hamilton DTN	79.49	79.49	0.27	2.76	303.23	0.02	50000	100000
	Etobicoke S.	62.91	60.28		3.19	438.99	0		
	Highway 401	75.24	75.24		8.4	233.48	0.81		
Zn	Hamilton DTN	79.49	79.41	0.23	9.2	2811	0.01	120000	100000
	Etobicoke S.	63.1	62.98		9.57	1342	0		
	Highway 401	75.24	75.19		11.46	1202	0.07		
Se	Hamilton DTN	79.49	55.49	0.14	0.32	66.44	0	10000	*20000*
	Etobicoke S.	63.1	36.59		0.21	28.04	0		
	Highway 401	75.25	50.57		0.24	44.47	0		
Pb	Hamilton DTN	79.49	79.28	0.22	2.48	137.1	0	500	1500
	Etobicoke S.	63.1	57.56		1.39	957.23	0		
	Highway 401	75.12	75.11		2.33	48.93	0.16		

[a] MDLs are manufacturer-reported values for 60-min sampling time.
[b] Ontario ambient air quality criteria.
[c] Values in italics indicate a screening level (SL) or guideline while non-italicized values are standards related to Ontario Regulation 419/05.

were the heavy metals detectable by the Xact 625 with concentrations that were usually above detection limits ≥50% of the time (Mn, Fe, Cu, Zn, Se, and Pb). A more complete elemental list can be found in the supplement (Table S1) and a thorough breakdown of the data coverage over the monitoring periods is given in Fig. S1. Table 2 also details instrumental performance in terms of the sampling completeness (data availability) and measure of sensitivity (concentration > method detection limit (MDL)) of the Xact 625 monitors for the study periods.

Results of comparisons of the daily-averaged Xact 625-derived concentrations at Hamilton Downtown with collocated, non-continuous (24-h, once every 3 days) dichotomous NAPS $PM_{2.5}$ elemental data obtained by Dichot-EDXRF and ICP-MS indicated that the Xact 625 overestimated Zn (*compared to* Dichot-EDXRF, ICP-MS), underestimated Se (Dichot-EDXRF, ICP-MS), and Pb (Dichot-EDXRF) but agreed well for Mn and Fe (Dichot-EDXRF, ICP-MS). and Cu (ICP-MS). A detailed discussion of these comparisons is available in the supplement.

At all three sites, no metals or elemental species were found to exceed either Ontario's ambient air quality criteria (AAQC) or standards/guidelines (Standards Development Branch; Ontario Ministry of the Environment and Climate Change, 2016, 2012). Hourly measurement data were either averaged to 24-h resolution for comparison with AAQC values, or were compared directly with 0.5-h guideline values. These results suggest that the health impacts of these ambient PM metals may be relatively low at these locations. However, it is still important to study the intra- and inter-site trends of these heavy metals over the years to determine whether concentrations are on an upward, stable or downward trend at these locations.

3.1. Intra-site comparisons: As stated earlier, non-parametric tests were used to determine the trends of metals where enough data was available. These tests included the Mann-Kendall tests and the Sen's slope (Gilbert, 1987) for the twelve-month period between March 2016 and February 2017 for reasons discussed in detail in the supplement.

The Kruskal-Wallis non-parametric ANOVA was used to compare yearly concentrations of these six heavy metals at each station. Comparisons of metal concentrations were done with weekly-averaged values and a summary is presented in Table 3 below. Detailed pairwise comparisons with the Dunn's post-hoc test for these metal concentrations over the years of study can be found in Table S4. At all stations, 2–3 significant differences were found and only Fe and Se were not significantly different over time regardless of location.

Similar analyses were performed on the hourly concentrations of these metals grouped by seasons. Further Dunn's post-hoc test was used to compare metal concentrations at pairs of stations (Table S5). The test statistic could not be computed for Se at all three stations and Mn at Highway 401 due to large amounts of zero-valued concentrations that generate too many tied ranks in the data. All stations showed significant differences, except for Zn and Pb concentrations at Highway 401 in the summer, spring and fall.

Further analyses of intra-site variations were performed with the Friedman's non-parametric test for repeated measures. Detailed results are included in the supplement (Table S6).

3.2. Inter-site comparisons: The Kruskal-Wallis/Dunn tests were again used to compare concentrations of these metals across the three stations. All stations showed significant differences, except for Zn in 2017 and Pb concentrations at Highway 401 and Hamilton Downtown (Table S7). The significant differences are likely due to the dissimilarities in sources and their emissions affecting these stations. Also, the relationships between stations did not change much over the years. This consistency may be a sign of well-established, long-term sources such as the major roadways and industry located near these stations. The test statistic could not be computed for Se in all three years and Mn in 2015 and 2016 due to large amounts of zero-valued concentrations that generate too many ties of ranks in the data.

3.3. Diel and seasonal variations of metal concentrations: Given

Table 3
Results of Kruskal-Wallis ANOVA yearly comparisons of six heavy metals from the Hamilton Downtown, Etobicoke South and Highway 401 near-road air monitoring stations using weekly-averaged concentrations.

	Hamilton Downtown	Etobicoke South	Highway 401
	2014–2017	2014–2017[a]	2015–2017
Mn	**SD**	NSD	**SD**
Fe	NSD	NSD	NSD
Cu	NSD	**SD**	**SD**
Zn	**SD**	**SD**	NSD
Se	NSD	NSD	NSD
Pb	NSD	**SD**	**SD**

[a] At Etobicoke South, 2015 data were removed because only 6 weeks were available. NSD indicates that no significant difference was detected. SD signifies that a significant difference was detected. α = 0.05.

these findings of inter-site comparisons, it was important to explore in more detail the diel variations of these metals to determine exactly when divergences occur at the three locations. Understanding when these differences occur will provide critical insights into determining their causes and apportioning metal sources. Fig. 2 compares the weekday and weekend diel variations of Mn, Fe, Cu Zn, Se and Pb at these three near-road stations. The solid lines are medians, the dashed lines are means, the darker shaded areas in Fig. 2 are the weekday interquartile range (IQR) and the lighter shaded areas bound the weekday 10th and 90th percentiles. Fig. S13 is a complementary plot to

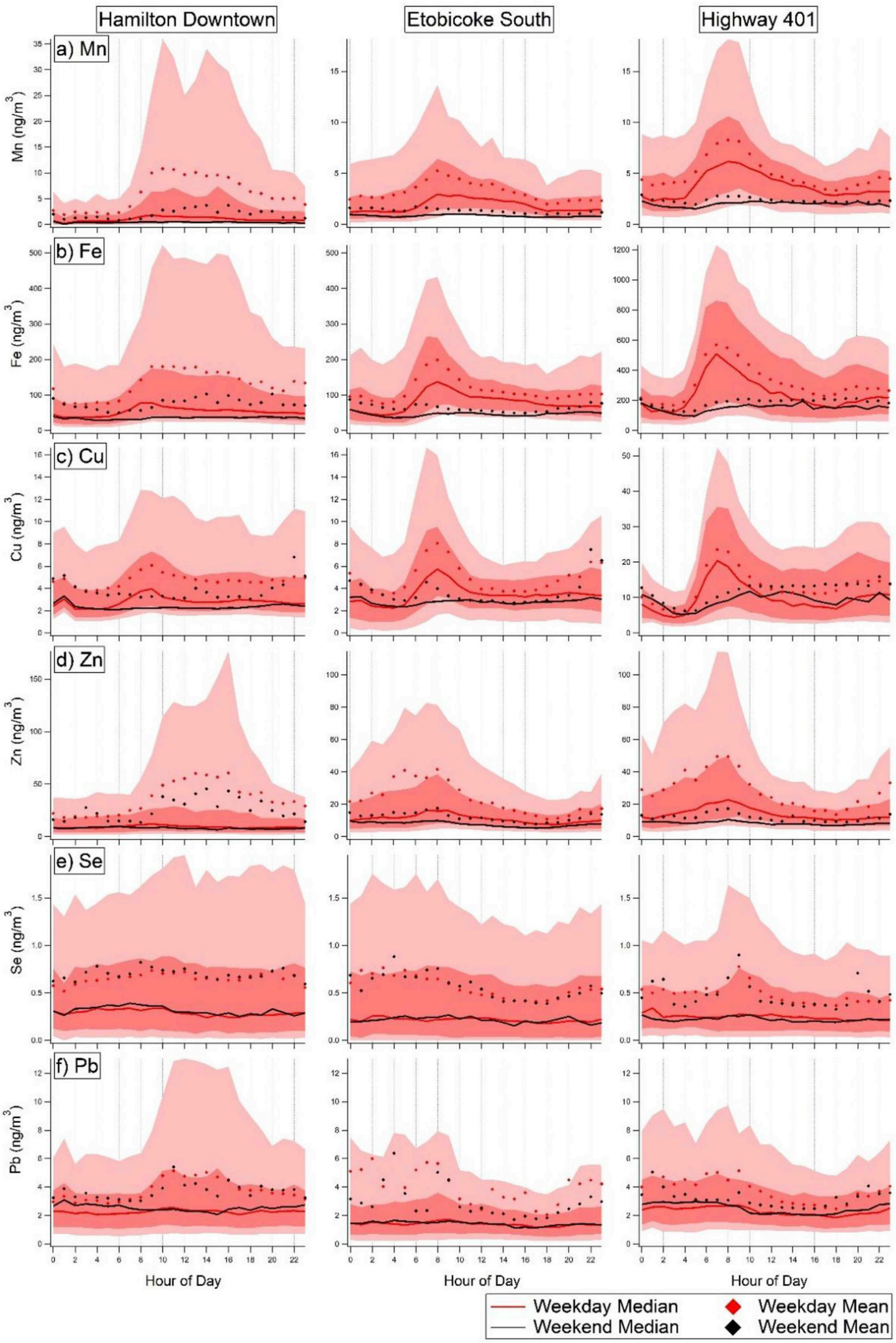

Fig. 2. Diel variations of concentrations (ng/m^3) of some abundant heavy metals Mn (A), Fe (B), Cu (C), Zn (D), Se (E) and Pb (F) observed at the three near road air monitoring stations on weekdays and weekends during the period of study (dark shade = weekday IQR, light shade = 10th and 90th percentiles).

Fig. 2 wherein the shaded areas are weekend IQR and 10th/90th percentile ranges. It is clear from median levels (red solid line) in these plots that Fe (Fig. 2B) and Cu (Fig. 2C) experience a morning spike in concentration peaking between 6 and 9 a.m. exclusively on weekdays that is well-defined at the Highway 401 station (peak at 7 a.m.) and to a lesser extent at the Etobicoke South (peak at 8 a.m.) and Hamilton Downtown (peak at 9 a.m.) stations. These times coincide with the morning rush hour at these locations indicating that vehicular traffic may have an important impact on the measured concentrations. Compared with the evening rush hour, the morning rush hour period appears to experience greater pollutant concentrations likely due to low mixing heights that exacerbate pollutant concentrations near the surface and higher weekday morning volumes of heavy duty vehicles (Sofowote et al., 2018; also Fig. S14F).

Also, median and higher (75th – 90th percentile) concentrations of Fe and Cu are highest at the Highway 401 station, likely due to a combination of its greater proximity to the roadway and the higher vehicular traffic volumes observed at this location (see Table 1). Indeed, the effect of weekday activities can be clearly observed when the diel profiles of higher concentrations on weekdays and weekends are compared for Mn, Fe, Cu and Zn at the Highway 401 station, and the Etobicoke South station to a lesser extent. For these four metals, a peak is observed after dawn (before mid-morning) on weekdays that is absent on weekends. This weekday/weekend difference in profile shape is less distinct for Mn and Zn at Hamilton Downtown, where higher concentrations (75th – 90th percentile) of Mn, Fe and Zn occur at later times of the day (late morning to evening). This consistency in profile at Hamilton suggests that their source is fairly constant and independent of weekday/weekend distinctions. In general, the relationship of metals with high vehicular traffic (typified by the morning rush hour) periods on weekdays does not hold for Se and Pb (Fig. 2E and F) at any of the stations or for median concentrations of Mn and Zn at Hamilton Downtown. Profiles of higher concentrations for Se (Fig. 2E and figure S13E) and Pb (Fig. 2F and Figure S13F) on weekdays and weekends are generally similar at each station with the exception of weekday Pb at Hamilton Downtown that has relatively high 11:00 – 16:00 concentrations.

To further understand the potential sources of these metals, hourly concentrations were compared against five criteria gas pollutants (ground-level O_3, NO, NO_2, CO and SO_2) collected at the same air monitoring stations (only O_3, NO and NO_2 were sampled at Etobicoke South). NO, CO and SO_2 are primary combustion byproducts that may arise from mobile/vehicular or industrial sources while O_3 and NO_2 are indicative of secondary processing in the atmosphere. In Ontario, NO and CO tend to be more closely associated, though not exclusively, with mobile emissions while SO_2 is typically indicative of heavy diesel emissions, coal combustion/coking that may arise from industrial metallurgy or coal-fired power generation sources. Since Ontario has phased out all coal power generation and only allows the use of ultra-low sulphur diesel fuels for use in the transportation sector within the province (Ontario Ministry of the Environment and Climate Change, 2017), the relevant sources of SO_2 are likely smelting-related or possibly regional in origin.

Table 4 is an array of Pearson correlation coefficient (r) matrices of these heavy metals and the aforementioned criteria gases as well as a few meteorological parameters – ambient temperature (ATEM), relative humidity (RH) and wind speed (WS) observed on weekdays and weekends while Fig. 3 are scatter plots of the comparisons of these six heavy metals with NO. In Table 4, $r > |0.4|$ are highlighted in boldface. This is an arbitrary but fairly low value to indicate sufficient correlation.

Across all three stations, there were more correlations with $r > |0.4|$ on weekdays than on weekends. Usually, there were no meaningful correlations of these metals with O_3 and the meteorological parameters. Noteworthy exceptions were observed at the Highway 401 station for O_3 with either Fe or Cu on weekdays. In these exceptions, a negative correlation was observed indicating that an inverse relationship existed between the metal species in question and the O_3. This suggests that the metals were emitted from primary sources since O_3 is also lost due to the titration effect with NO. Fe consistently showed positive correlations on weekdays with NO at all stations (although $r < 0.4$ at Hamilton) and also had positive correlations with CO at Hamilton Downtown and Highway 401 (CO was not measured at Etobicoke South). Cu also largely follows the same patterns as Fe but weekday correlations with NO at Etobicoke South are < 0.4.

Table 4

Pearson correlation (r) matrices of hourly concentrations of the six heavy metals against criteria pollutant gases and some meteorological parameters observed at the three air monitoring stations on weekdays and weekends during the period of study. Values of $r > |0.4|$ have been highlighted in boldface.

Location	Variable	WKD						WKE					
		Mn	Fe	Cu	Zn	Se	Pb	Mn	Fe	Cu	Zn	Se	Pb
Hamilton	O_3	−0.09	−0.14	−0.19	−0.06	−0.08	−0.15	−0.01	−0.03	−0.09	−0.01	0.01	−0.07
	NO	0.23	0.31	0.30	0.15	0.16	0.27	0.16	0.14	0.15	0.15	0.07	0.20
	NO_2	0.35	**0.43**	**0.42**	0.28	0.39	**0.47**	0.24	0.26	0.20	0.20	0.26	0.37
	CO	**0.47**	**0.55**	**0.50**	**0.42**	**0.42**	**0.54**	**0.45**	**0.40**	0.26	**0.45**	0.34	**0.52**
	SO_2	**0.53**	**0.51**	0.30	**0.45**	**0.46**	**0.59**	**0.47**	0.39	0.13	**0.49**	0.34	**0.53**
	ATEM	0.13	0.14	0.11	0.11	0.17	0.13	0.14	0.14	0.01	0.13	0.14	0.18
	RH	−0.05	0.00	0.08	−0.03	0.13	0.03	−0.06	0.01	0.08	−0.05	0.10	0.07
	WS	−0.05	−0.10	−0.19	−0.02	−0.21	−0.13	0.01	−0.04	−0.15	0.01	−0.15	−0.14
Etobicoke S.	O_3	−0.20	−0.28	−0.18	−0.18	−0.07	−0.07	−0.17	−0.26	−0.16	−0.19	−0.12	−0.07
	NO	**0.40**	**0.55**	0.31	0.32	0.14	0.04	0.28	**0.40**	0.20	0.27	0.14	0.06
	NO_2	0.39	**0.50**	0.29	0.28	0.21	0.07	0.37	**0.51**	0.21	0.37	0.25	0.10
	ATEM	0.14	0.22	0.09	−0.01	0.08	−0.03	0.05	0.16	0.09	−0.02	−0.02	−0.03
	RH	0.10	0.01	0.01	0.02	0.13	0.05	0.12	0.09	0.01	0.14	0.12	0.05
	WS	−0.27	−0.35	−0.18	−0.17	−0.17	−0.03	−0.20	−0.34	−0.17	−0.21	−0.17	−0.05
Highway 401	O_3	−0.33	**−0.44**	**−0.42**	−0.21	−0.02	−0.07	−0.29	−0.32	−0.28	−0.17	−0.03	−0.03
	NO	**0.58**	**0.78**	**0.73**	0.35	0.06	0.03	**0.56**	**0.61**	**0.50**	0.24	0.06	−0.01
	NO_2	**0.50**	**0.61**	**0.58**	0.28	0.16	0.08	**0.50**	**0.49**	0.38	0.29	0.14	0.11
	CO	**0.55**	**0.68**	**0.69**	0.33	0.13	0.12	**0.57**	**0.61**	**0.54**	0.25	0.10	0.10
	SO_2	0.23	0.09	0.06	0.11	0.18	0.22	0.16	0.05	0.01	0.12	0.12	0.10
	ATEM	0.07	0.09	0.10	−0.04	0.08	−0.00	0.12	0.11	0.10	0.02	−0.02	0.05
	RH	0.01	−0.15	−0.18	0.06	0.15	0.17	−0.09	−0.29	−0.33	0.07	0.08	0.18
	WS	−0.25	−0.22	−0.20	−0.17	−0.13	−0.17	−0.27	−0.18	−0.13	−0.21	−0.08	−0.19

From Fig. 3, it is clear that multiple edges exist in the scatterplots

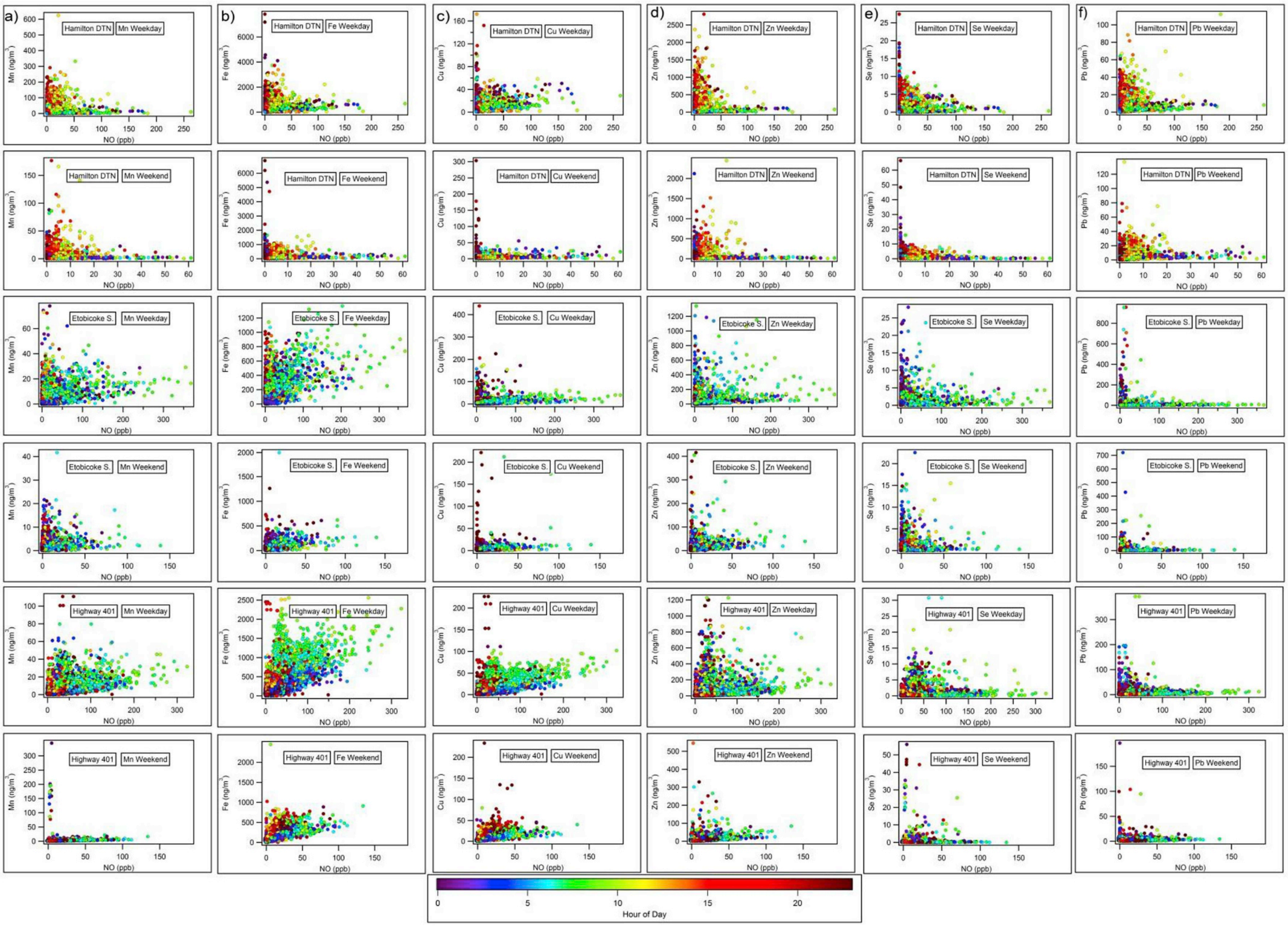

Fig. 3. Weekday and weekend scatter plots of hourly concentrations of a. manganese (Mn), b. iron (Fe), c. copper (Cu), d. zinc (Zn), e. selenium (Se) and f. lead (Pb) *vs.* NO; coloured by hour of day observed at the Hamilton Downtown, Etobicoke South and Highway 401 stations during the period of study.

with NO. Additional scatterplots are included in the supplement (Figures S15 – S17) for SO_2, CO and NO_2 respectively. Edges are boundary regions or hyperplanes (Henry, 2003) within a given dataset and are usually characterized by unique slopes (Wang et al., 2011). Thus, the data is likely a mixture of sources where two or more edges occur. When the data are grouped by time (hour) of day, edges begin to emerge in the scatterplots.

Edges suggest that there were at least two sources in effect for the species being compared on the x- and y-axes – one with relatively high metal concentrations but low NO, and the other with low metal concentrations but high NO because they vary almost independently of one another. At Hamilton Downtown, two near-perpendicular edges can be seen for most metals that appear unchanged regardless of day of the week. For Fe (Fig. 3B) and Cu (Fig. 3C), however, the blue-green dots (06:00 – 09:00 a.m.; i.e., morning rush hour) appear to form a gentle edge on weekdays that is absent on the weekends. On weekdays at the other locations, multiple edges can also be observed but the blue-green dots form distinct edges for Fe and Cu that, in the case of Highway 401, are among the steepest. This indicates that the morning rush hour is a major source of these two metals along the highway. Good NO – Fe and NO – Cu agreements along the highway are also observable on weekends but the blue-green dots do not form the steepest edge. For Mn (Fig. 3A) and Zn (Fig. 3D), the rush-hour dots yield less distinct edges on weekdays at Highway 401 compared to Fe and Cu. Se and Pb are largely uncorrelated with the criteria gas pollutants (e.g. Fig. 3E and F) and meteorological parameters (Table 4) except at Hamilton Downtown where correlations with SO_2 and CO are observed for Pb independent of day of week, suggesting that Hamilton may possess a local source of these species.

In summary, the scatterplots of criteria gases with these six metals reveal multiple edges at all stations, indicating that more than a single source of metals may be impacting the stations. At the highway, local traffic-related impacts are usually directly observable with the morning rush hour on weekdays forming a leading edge for Fe and Cu, and to a much lesser extent, Mn and Zn. On both weekdays and weekends, Se and Pb appear independent of the criteria gases with the exception of Hamilton where these and other metals appear to have very distinct multiple edges.

Seasonal variations of weekday/weekend patterns of the concentrations of these six metals are shown in Fig. S18 as box and whisker plots. In general, the seasonal medians of Se and Pb (Figs. S18E and S18F) do not vary much regardless of day of week at the Highway 401 and Etobicoke South stations. At Hamilton Downtown, the weekend medians for Se and Pb in the summer are greater than on weekdays in summer and all other days in the remaining seasons. Also, at the Highway 401 and Etobicoke South stations, Mn, Fe, and Zn clearly have greater median concentrations on weekdays compared to weekends in all seasons, an indication that at these locations, these metals may be more closely-related with traffic volumes of heavy duty vehicles that also show a significant weekend decrease along the highway (Sofowote et al., 2018). In contrast, seasonal weekday and weekend median concentrations of Cu do not vary much at these three stations indicating a source with similar emissions patterns in both day types, although Cu is sensitive to morning rush hour traffic (Fig. 2). Light duty vehicles (C_2

in Fig. S14) could potentially be an important source of Cu since their volumes are elevated during the morning rush hour but do not vary significantly from weekdays to weekends. Cu is a main component of brake lining fibres (Thorpe and Harrison, 2008) and also, Cu is used in the copper-sweetening process to remove mercaptans from gasoline fuel and other distillates (Schindler, 1945; Technical Committee of Petroleum Additive Manufacturers in Europe, 2013). In general, greatest 75th – 90th percentile concentrations for all six metals are observed on weekdays in the spring at the Hamilton Downtown station while at Etobicoke South and the Highway 401 stations, these higher concentrations are greatest on weekdays in the fall.

3.4. Spatial source apportionments of metals in the GTHA: The investigation into sources can be greatly aided by auxiliary receptor models wherein time series of observed ambient concentrations are paired with meteorological variables such as surface wind speeds and directions or with air mass back trajectories (Ashbaugh et al., 1985; Pekney et al., 2006; Sofowote et al., 2015, 2014). The model discussed in this work is the simplified form of the quantitative transport bias analysis sQTBA; (Zhao et al., 2007; Zhou et al., 2004). It should be noted that unlike the original QTBA, the simplified version does not explicitly account for deposition and transformation of aerosols during transport. Also, sQTBA shows source regions as well as locations or pathways of stagnated air masses that significantly contribute to aerosol/particulate matter concentrations at the receptor site (Keeler and Samson, 1989).

Seventy-two-hour air mass back trajectories were obtained from NOAA HYSPLIT with an arrival height of 500 m a.g.l. for each of the air monitoring stations and inputted in the sQTBA ensemble model. Grid (lat-long) coordinates used were 0.15° × 0.15°, translating to ~12 km × 16 km in the GTHA. Full details of the execution of this model for multiple locations have been discussed elsewhere (Healy et al., 2017; Sofowote et al., 2015, 2014).

The maps in Fig. 4 are seasonal sQTBA plots for Fe classified by weekdays and weekends. This metal is believed to have strong local and regional sources. Similar seasonal weekday/weekend maps for Mn, Cu, Zn, Se and Pb can be found in Figures S19 – S23. In these maps, sQTBA outputs have been overlaid on point sources from emissions inventories compiled by Environment and Climate Change Canada (Environment

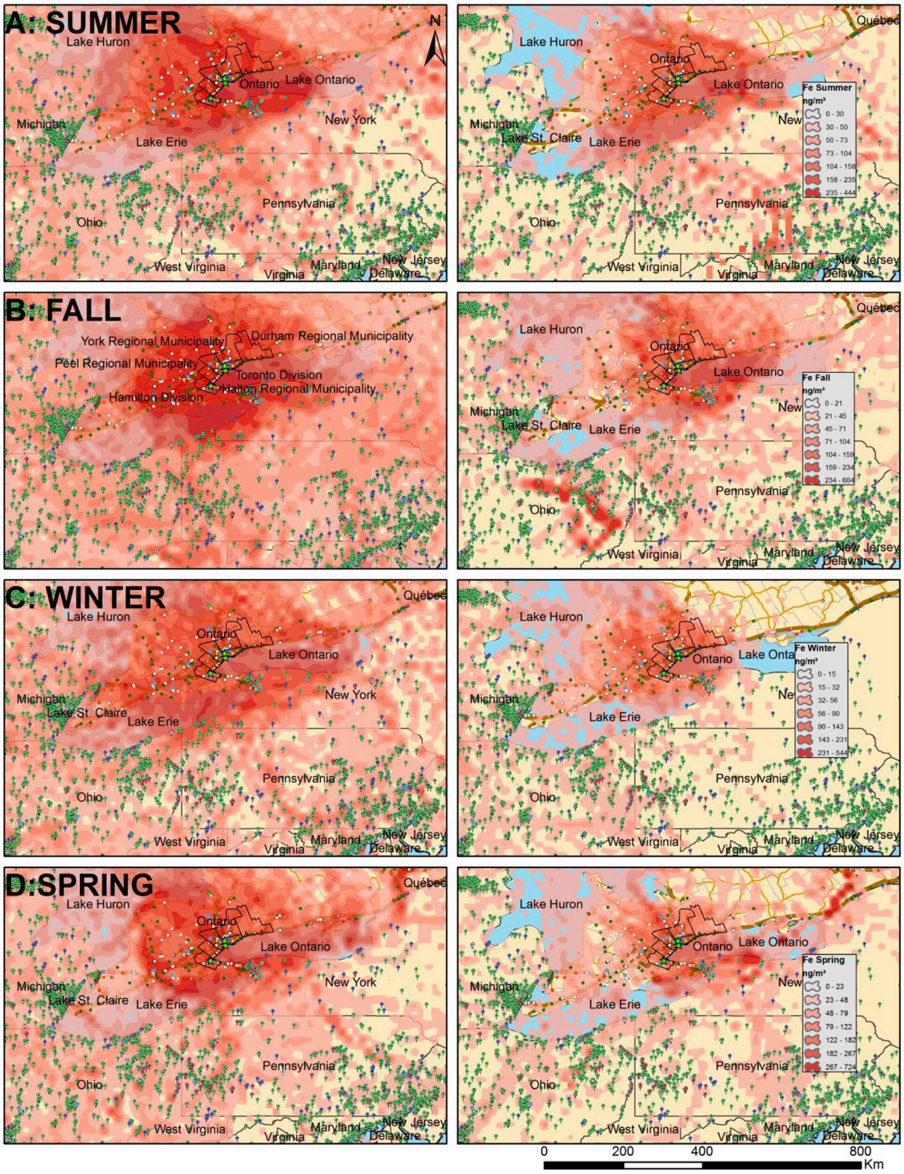

Fig. 4. Seasonal weekday (left) and weekend (right) sQTBA plots of Iron (Fe) concentrations observed at the three air monitoring stations in the GTHA (outlined in black) during the period of study. A: Summer (JJA); B: Fall (SON); C: Winter (DJF); and D: Spring (MAM). Values in parenthesis for the seasons are calendar months. Point sources are defined in Fig. 1.

and Climate Change Canada, 2017) and the USEPA (2016). Airports in this region have also been added from Google Earth Pro (Google, 2018). Fig. 4 indicates that in addition to regional and transboundary sources in the US Midwest, Fe has strong sources specifically within Toronto on weekdays but reduced concentration intensities on the weekends in all four seasons. This corroborates local traffic in Toronto and Hamilton as a major source of Fe. A likely reason for this is the resuspension of iron-rich road dust and breakdown of moving metallic vehicular components and parts. The weekday concentration intensities of locations (i.e., source regions) in and around Hamilton are greater than at Toronto in summer and spring, suggesting that Hamilton may experience additional sources and/or is more subject to stagnant air flows since Hamilton has a greater potential to experience more frequent inversions due the effect of the Niagara Escarpment that essentially walls in the downtown core compared to locations in Toronto that have a flatter topography. To further understand the impact of local traffic sources on the GTHA, the sQTBA analyses for weekdays were redone without the morning rush hour period. Fig. 5 shows the results for Fe. The other metals can be found in Figures S24 – S28. In the case of Fe, a reduction in concentration intensities around Toronto (especially in Peel, Halton in the summer – Fig. 5A and York in spring – Fig. 5D) is observable when data corresponding to the morning rush hour period are removed. The unchanged concentration intensities likely delineate the other source regions less dominated by traffic. These other regions contain point sources ranging from metal smelting/manufacturing to power generation on both sides of the border.

For Mn (Figs. S19 and S24) and Cu (Figs. S20 and S25), the most intense concentrations also occur on weekdays within and beyond the GTHA in the summer and fall for Mn or summer and spring for Cu. Mn (Fig. S19) usually has stronger intensities in Hamilton than in Toronto while for Cu (Fig. S20), the concentrations in most parts of the Cities of Toronto and Hamilton are high and are of similar intensity regardless of day of week (except for higher intensities on spring weekdays in Hamilton).

In the fall, the most intense concentrations for Cu are observed on the weekends in the Niagara-Buffalo region, well east of Hamilton. When the morning rush hour period is removed from the weekdays, source intensities for Mn in the GTHA and surroundings (Fig. S24) do

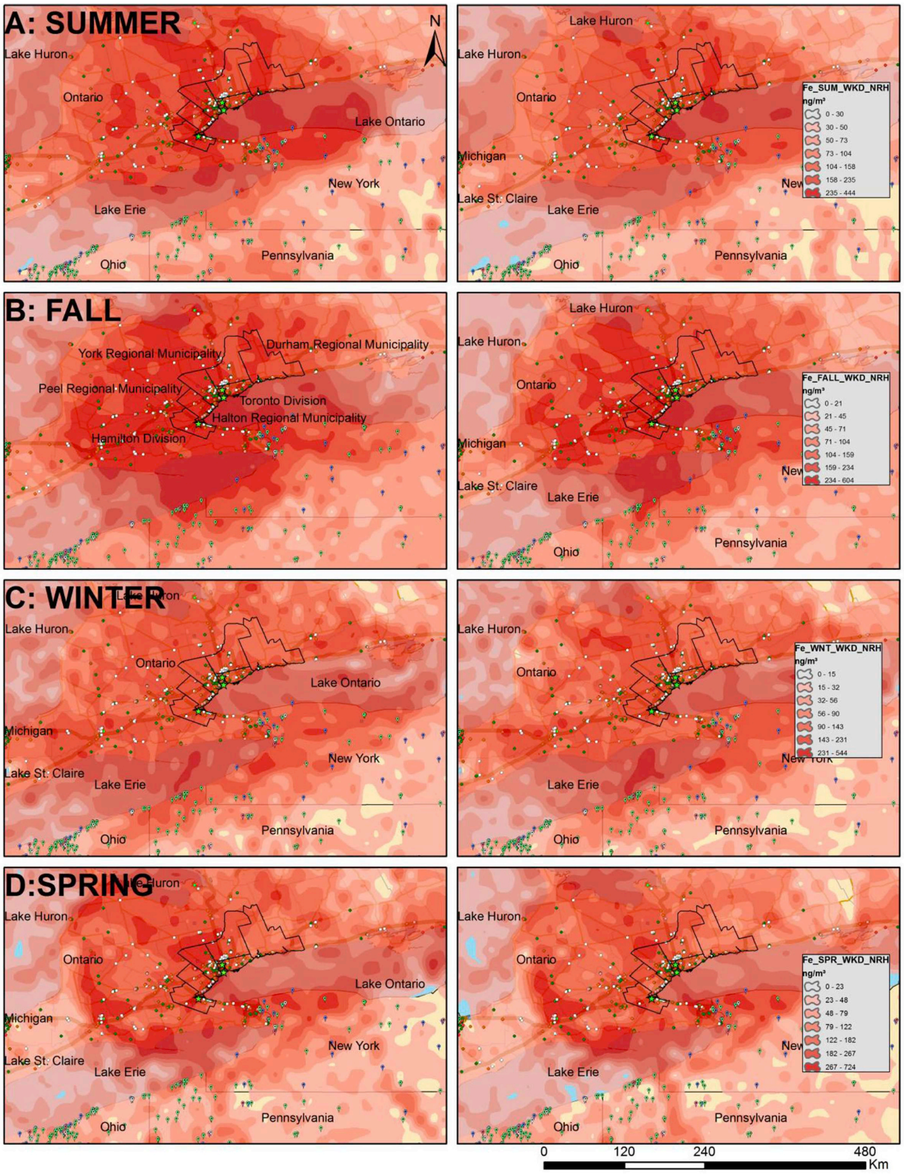

Fig. 5. Seasonal weekday (left) and weekday without the morning rush hour data (right) sQTBA plots of Fe concentrations observed at the three air monitoring stations in the GTHA (outlined in black) during the period of study. A: Summer (JJA); B: Fall (SON); C: Winter (DJF); and D: Spring (MAM). Values in parenthesis for the seasons are calendar months. Point sources are defined in Fig. 1.

not change appreciably. However, a reduction in the concentration intensities for Cu in the GTHA and surrounding areas is observed on summer weekdays (Fig. S25) indicating some dependence of Cu on traffic. In the other seasons however, weekday Cu concentration intensities in the GTHA with and without rush hour are similar. Industrial point sources, such as transport equipment manufacturing and smelting appear to dominate Cu source regions in and outside the GTHA.

Similar to Mn, Zn usually has higher concentration areas around Hamilton compared to Toronto regardless of day of week, except in the wintertime when a very intense potential local source in Toronto and York is found on weekdays (Fig. S21). In Hamilton, topography and steel-making where Zn is used in galvanization may play significant roles. In general, Zn differs from Fe, Cu and Mn because its most intense source regions are usually outside the GTHA and the concentration intensities are usually greatest on the weekends (Fig. S21). Also, unlike Fe and Cu, no appreciable difference in source regions or intensities are observed when the morning rush hour period is removed (Fig. S26) suggesting less dependence on local mobile/traffic emissions; except in winter around the Toronto/York border where reductions in intensity can be observed. This higher wintertime Zn associated with rush hour periods on weekdays may be a reflection of longer idling times and/or harder cold starts of internal combustion engines, given that Zn is an important component of engine lubricating oils (Barnes et al., 2001).

The remaining two species – Se (Fig. S22) and Pb (Fig. S23) also have source regions that are most intense on weekends with the exception of Pb in winter and spring where strong source regions south and east of Hamilton respectively can be observed on weekdays. The weekday/weekend concentration intensities of these species in Toronto and Hamilton are generally similar, indicating that the sources of these metals are fairly constant regardless of day of week, although, on weekends in the fall and weekdays in the winter, Se and Pb respectively have very strong transboundary source regions from the US Midwest. Additionally, in the fall, strong source regions of Pb are observed on weekends in Peel Region and the US side of Lake Ontario. The high Pb regions observed on fall weekends overlie some small and regional airports. Aviation gasoline (avgas) used mainly in piston-engine airplanes is a well-known source of Pb emissions (Carr et al., 2011) that has recently been associated with adverse health impacts such as high blood Pb levels of children that live within 500 m of an airport (Miranda et al., 2011). Finally, as with Mn and Zn, no visible differences are observed when the morning rush hour period is removed from the sQTBA inputs for Se (Fig. S27) and Pb (Fig. S28) on weekdays, indicating that their concentrations which have relatively low intensities in the GTHA, are largely independent of rush hour traffic and mobile emissions by extension.

In summary, the sQTBA outputs suggest that although all six heavy metals have regional sources, strong source areas for Fe and Cu also exist within the GTHA itself. These GTHA sources are also sensitive to the morning rush hour, suggesting that local vehicular traffic along the roadways in these areas is the likely source. The other metals do not have strong GTHA sources but regional ones dominated largely by industrial point sources which also do not change regardless of inclusion of the morning rush hour period.

4. Conclusions

Six heavy metals - Mn, Fe, Cu, Zn, Se, and Pb were consistently detected with the Xact 625 Ambient Metals Monitor at three near-road ambient air monitoring locations in the GTHA for a period spanning 3 years. Comparing the Xact 625 concentrations of these six metals with the traditional analytical methods revealed that the Xact 625 data were more comparable to the ICP-MS than the Dichot-EDXRF. For these metals, exceedances of Ontario's 24-h AAQC were not observed and no exceedance of half-hour standards occurred at any of these locations. Temporal trends however indicated that high concentrations of Fe and Cu correlated with peak commuting and working hours.

Non-parametric intra-site comparisons using the Kruskal-Wallis ANOVA and Dunn's multiple comparison tests on weekly averages of metal concentrations for all years available in this study indicated that most metals did not consistently show a significant difference in their distributions from one year to the next, with Fe and Se being the most resistant to statistical differences. Further intra-site comparisons revealed only very few similarities existed in the distributions of these metals between seasons at the three stations. Inter-site variations of Mn, Fe, Cu, Zn and Pb showed significant differences for most metals across monitoring stations over the entire study period.

When these metal concentrations were compared with criteria air pollutant gases, multiple edges were observed in the data, indicating at least more than one source of pollution at each of the stations. In general, these metals were largely independent of SO_2 at the Highway but showed some association at Hamilton (with the exception of Cu). Also, Fe and Cu had their strongest correlations with NO and CO at the Highway 401 indicating good dependence on mobile sources. The traffic-related emissions source characterization of Fe and Cu at Highway 401 were further supported by their higher weekday NO and CO correlations compared to the weekends. In general, the highway experiences an intense rush hour period between 6 and 9 a.m. and greater volumes of heavy duty vehicles on weekdays. This morning rush hour period form distinct edges in scatterplot comparisons of Fe or Cu with NO at the Highway 401 station on weekdays that is absent on weekends.

Exploring potential sources of high metal concentrations with trajectory ensemble models (sQTBA in this work) helps reveal where high spatial concentration intensities occur over a given domain thus delineating areas with potential local or long-range/regional sources. In general, Mn, Fe and Cu have higher concentration intensities in the GTHA on weekdays that diminish on the weekends, suggesting influence from a traffic source. With very few exceptions, Zn, Se and Pb concentration intensities in the GTHA are largely constant regardless of weekday/weekend distinctions, indicating that they are more related to industrial and regional sources. Additionally, on weekdays, the strongest potential source regions of Fe in all seasons, and Cu in the summer are sensitive to the inclusion of concentrations measured during the morning rush hour period but are largely invariant for Mn, Zn, Se and Pb. Indeed, for Zn, Se and Pb, the strongest potential source regions are usually observed on the weekends and are situated outside the GTHA, frequently with transboundary origins.

This work shows that local traffic-related sources are an important contributor of heavy metals such as Fe and Cu, and this should inform development of proper mitigation strategies such as improved traffic management especially during the rush hour periods. This study will also be useful in the design of effective control measures for the other heavy metals that seem to have a more industrial and/or regional origin.

Declarations of interest

None.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.aeaoa.2019.100005.

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