atmosphere

MDPI

Supplementary Materials: Continuous Measurements and Source Apportionment of Ambient $PM_{2.5}$-Bound Elements in Windsor, Canada

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Equations Used to Estimate Uncertainty of Measured Concentrations [1]

When the concentration is less than or equal to the method detection limit (MDL):

$$Uncertainty = \frac{5}{6} \times MDL \tag{1}$$

When the concentration is greater than the MDL:

$$Uncertainty = \sqrt{(Error\ fraction \times concentration)^2 + (0.5 \times MDL)^2} \tag{2}$$

where error fractions for the 24 $PM_{2.5}$-bound elements, black carbon and brown carbons are equal to 10% as suggested by other researchers (e.g., [2,3]).

PMF Model Settings and the Approach to Determining the Optimal Number of Factors

The number of the starting seed was set to 5. An identical solution can be recreated later using the same seed number. Number of base runs was set to 20 because this will allow an evaluation of the variation in Q (goodness-of-fit parameter) as recommended in the PMF user manual [1]. The best run among the 20 runs was selected. In this study, all input species were classified as strong. Model outputs were stored in the format of Excel workbook, which allow an easy access and data processing.

In PMF modeling, the optimal number of PMF resolved factors is decided by the users. In this study, based on the number of potential sources and the number of measured species, the optimal number of PMF resolved factors should be between two and ten. Thus, the PMF model simulations were conducted from two to ten factors to determine an optimal number of factors. IM (maximum individual column mean) and IS (maximum individual column standard deviation) were used to select the number of factors in PMF [4]. When the number of factors increases to the optimal number, IM and IS will experience a drastic drop. In this study, IM and IS values dropped dramatically when number of factors reaching to five (Figure S1). Q (robust) and Q (true) are two additional indicators to reflect the goodness-of-fit by the model, which were also used to identify the optimal number of factors. The smaller Q values indicate a better fit by the PMF model. Similar to IS and IM, a drastic drop of Q (robust) and Q (true) indicating the optimal number of factors is achieved. In this study, there isn't a drastic drop of Q (robust) and Q (true), but the dropping rate becomes slow when the number of factors reaching to six (Figure S2). Five factors were selected based on these indicators (IS, IM, Q robust, and Q true) and the interpretability of the resolved source profiles.

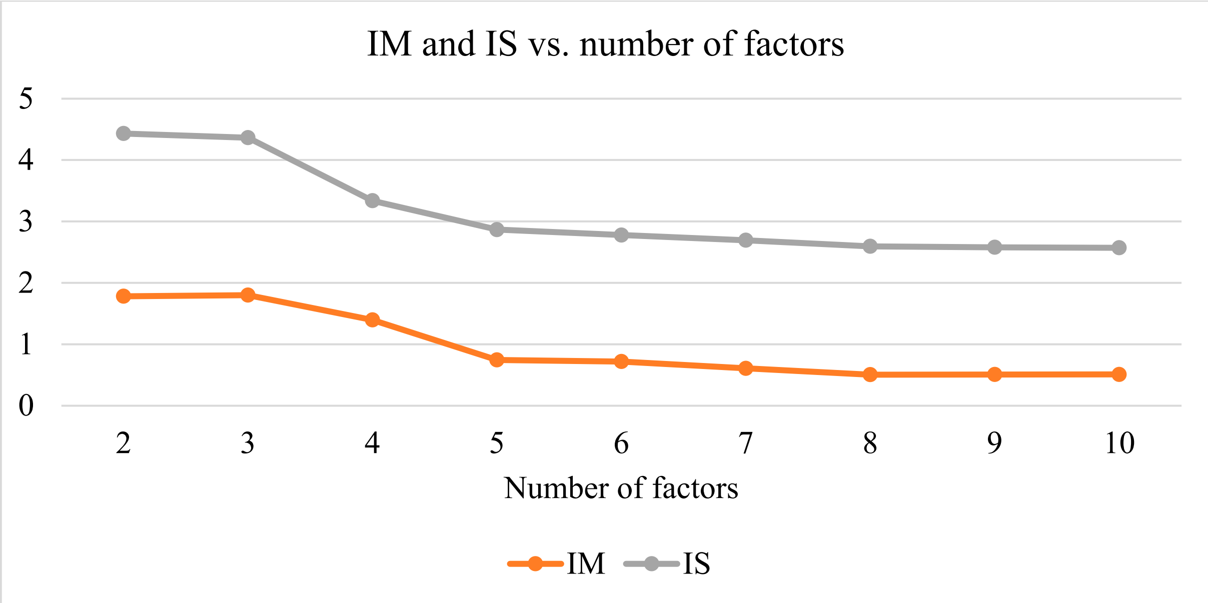


Figure S1. IM and IS vs. number of factors.

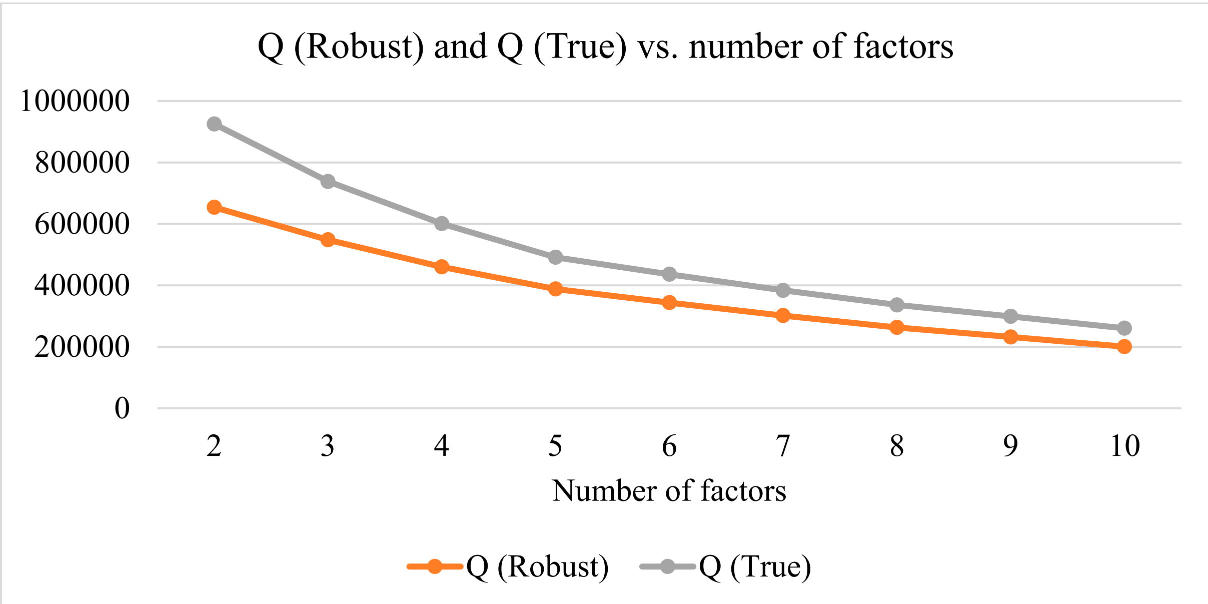


Figure S2. Q (Robust) and Q (True) vs. number of factors.

The PMF factors were interpreted by comparing the major variables (>20% of mass percentage) in each factor to markers and source profiles in the literatures, taking into consideration of emission inventories from National Pollutant Release Inventory (Canada) and National Emissions Inventory (USA).

Table S1. Average concentrations of $PM_{2.5}$-bound elements measured by the Xact 625 analyzer from April to October 2021 at Windsor West, and by the Dichot method as described in Dabek-Zlotorzynska et al., [5] in 2017-2019 at seven 7 stations in Ontario. Site classification and source influences were obtained from Environment and Climate Change Canada website [6].

Element	This Study, Average Xact Concentration at Windsor West (ng/m^3)	Average Dichot Concentrations in 2017–2019 (ng/m^3)						
		Windsor West (Urban, Transport Source Influenced)	Hamilton Downtown (Urban, Point Source Influenced)	Sudbury (Urban, Point Source Influenced)	Toronto North (Urban, General Population Exposure)	Hwy 401 Roadside (Urban, Transport Source Influenced)	Ottawa Downtown (Urban, General Population Exposure)	Simcoe (Suburban, Regional Backgrounds)
Br	3.2	2.3	2.0	1.3	1.5	1.4	1.4	1.6
Ca	89	62	48	15	43	85	38	37
Fe	118	112	70	37	62	223	27	26
K	115	52	48	34	42	43	40	35
Mn	4.6	3.7	2.9	0.9	2.0	2.7	1.2	1.4
Pb	3.9	3.6	3.5	3.2	3.2	3.0	2.7	2.9
S	600	422	509	222	318	330	225	368
Se	0.7	0.9	0.8	0.7	0.7	0.7	0.7	0.7
Si	407	43	33	65	34	57	31	32
Sr	1.6	1.4	1.4	1.0	1.5	1.6	1.3	1.4
Ti	4.1	1.9	1.9	2.0	3.0	8.4	3.4	1.4
Zn	26	23	19	4	20	22	6	7

Table S2. Statistics of 24-h concentrations for 14 $PM_{2.5}$-bound elements with ≥50% MDL in this study and Ontario's Ambient Air Quality Criteria (AAQC) [7].

Element	Minimum (ng/m^3)	Maximum (ng/m^3)	Average (ng/m^3)	Median (ng/m^3)	Standard Deviation (ng/m^3)	24-h AAQC for the $PM_{2.5}$ Fraction (ng/m^3)	24-h AAQC for the PM_{10} Fraction (ng/m^3)	24-h AAQC for the TSP Fraction (ng/m^3)	Derived 24-h AAQC for the $PM_{2.5}$ Fraction (ng/m^3)
Br	0.2	8.6	3.2	2.9	1.7	NA	NA	NA	NA
Ca	8	432	86	59	74	NA	NA	NA	NA
Cu	2.1	21.7	4.0	3.6	2.1	NA	NA	50,000	12,500
Fe	19	1276	116	82	127	NA	NA	4000	1000
Hg	0.3	1.3	0.6	0.6	0.2	NA	NA	NA	NA
K	42	245	91	82	35	NA	NA	120,000	3000
Mn	0.3	28.6	4.4	2.9	4.5	100	200	400	100
Pb	0.8	25.0	3.8	3.4	2.9	NA	NA	500	125
S	29	2313	581	488	443	NA	NA	NA	NA
Se	0.1	3.0	0.7	0.5	0.6	NA	NA	10,000	2500
Si	204	1398	391	353	161	NA	10,000	NA	5000
Sr	0.5	4.0	1.1	0.9	0.6	NA	NA	120,000	30,000
Ti	0.9	20.7	3.9	3.1	3.0	NA	NA	120,000	30,000
Zn	2	123	25	15	26	NA	NA	120,000	30,000

Note: Twenty-four-hour AAQCs are available for 9 out of the 14 elements in the total suspended particulate (TSP) fraction, for two elements in the PM_{10} fraction, and for one element in the $PM_{2.5}$ fraction. The comparison among Mn's AAQCs reveals that the AAQC for the TSP fraction is two times that of the AAQC for the PM_{10} fraction and four times that of the AAQC for the $PM_{2.5}$ fraction. The 24-h AAQC for the $PM_{2.5}$ fraction were calculated from the TSP or PM_{10} fraction if it is not available to compare with daily averages in this study. Four elements do not have AAQC (i.e., Br, Ca, Hg, and S).

Table S3. Factor profiles (% of species mass concentrations being assigned to that factor) for black carbon (BC) and brown carbons (BrC1 and BrC2), and $PM_{2.5}$-bound elements in Windsor during April–October 2021. Bold values are percentages ≥40%.

Species	Coal/Heavy Oil Burning	Vehicular Exhaust	Metal Processing	Crustal Dust	Vehicle Brake and Tire Wear
BC	19	**72**	3	6	0
BrC1	0	**93**	6	0.10	2
BrC2	2	**90**	0	6	1
Ag	17	6	**73**	3	0
As	18	**75**	0	0	7
Ba	6	31	30	31	2
Br	**69**	14	12	5	0
Ca	6	0	2	**90**	3
Cd	18	11	**71**	0.08	0
Co	0	18	**82**	0	0
Cr	27	27	8	28	10
Cu	13	18	**44**	14	11
Fe	8	4	7	**55**	26
Hg	2	0	**92**	0	6
K	27	17	**42**	15	0
Mn	1	0	7	35	**58**
Ni	19	11	**54**	14	1
Pb	**43**	27	23	5	2
Rb	6	8	**77**	9	0
S	**82**	0	14	2	2
Se	**72**	4	20	0	4
Si	16	1	**56**	27	0
Sn	11	**89**	0	0	0
Sr	17	10	**41**	32	1
Ti	20	7	13	**59**	1
V	**53**	0.8	29	15	2
Zn	3	0.8	12	5	**79**

Table S4. Pearson correlation coefficients of weekly averaged contributions among the five factors identified by the PMF.

	Coal/Heavy Oil Burning	Vehicular Exhaust	Metal Processing	Crustal Dust
Vehicular exhaust	0.504			
Metal processing	0.813	0.601		
Crustal dust	0.525	0.670	0.695	
Vehicle tire and brake wear	0.527	0.553	0.815	0.877

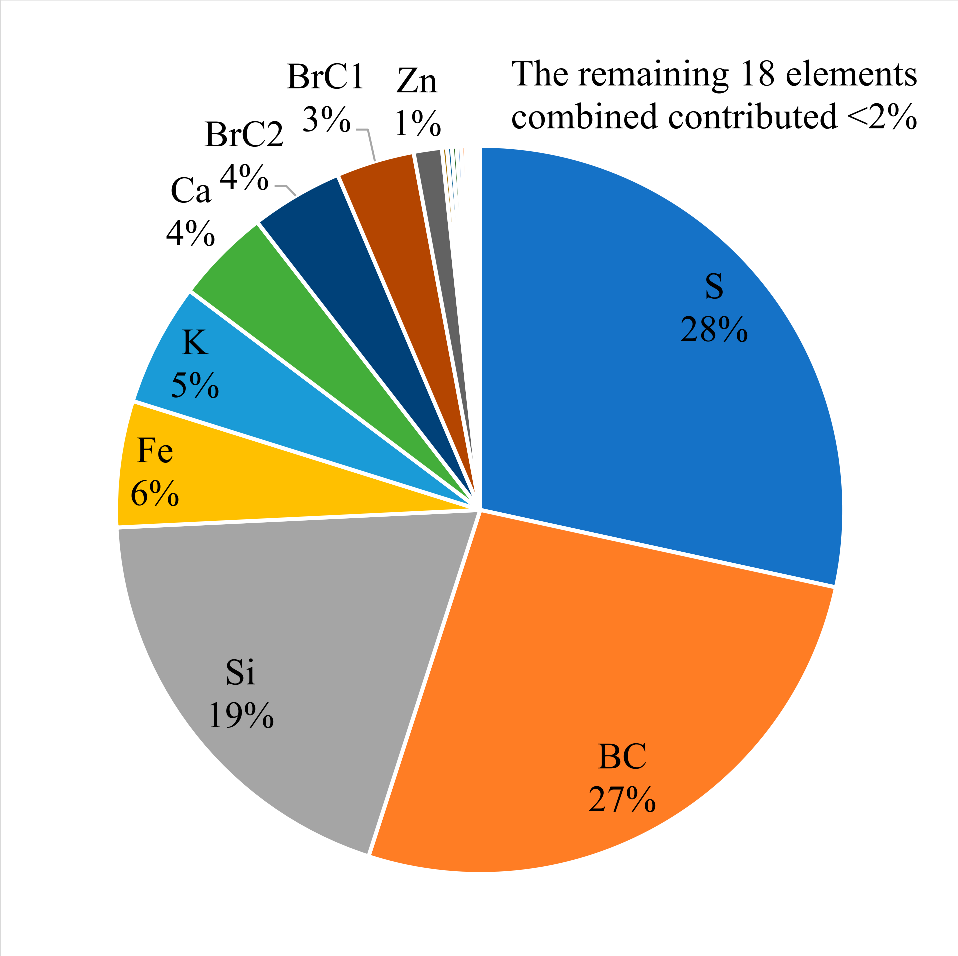
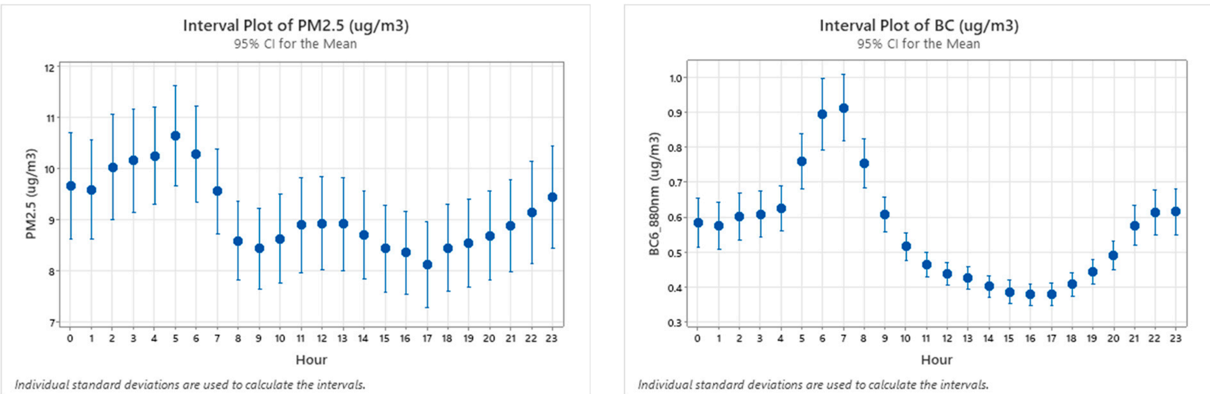
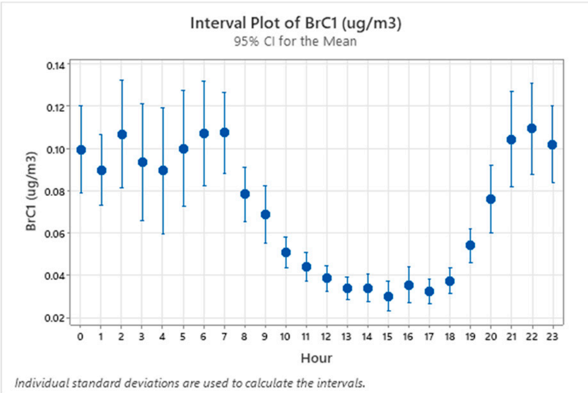
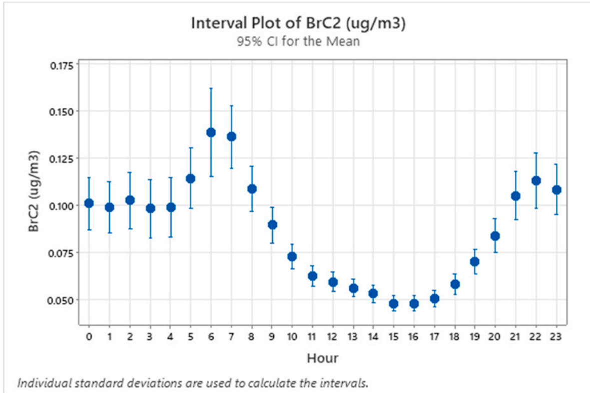
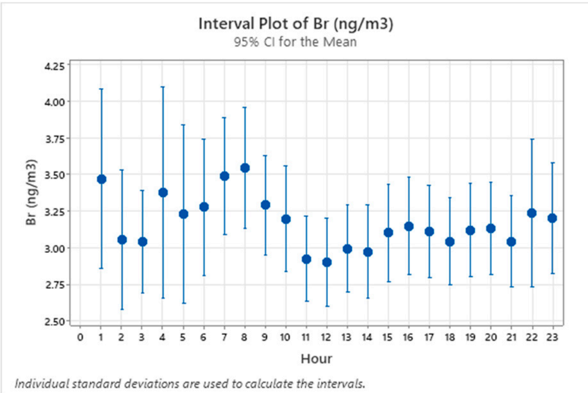


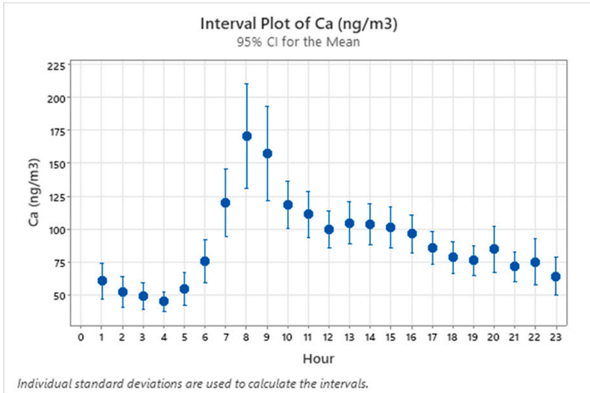
Figure S3. Relative contributions of black carbon (BC) and brown carbons (BrC1 and BrC2) and 24 $PM_{2.5}$-bound elements. The total contributions by the 18 elements (Cu, Mn, Cd, Ti, Pb, Br, Ba, Ag, Sr, Se, Hg, Ni, V, Cr, As, Sn, Rb, and Co) was 1.7%.

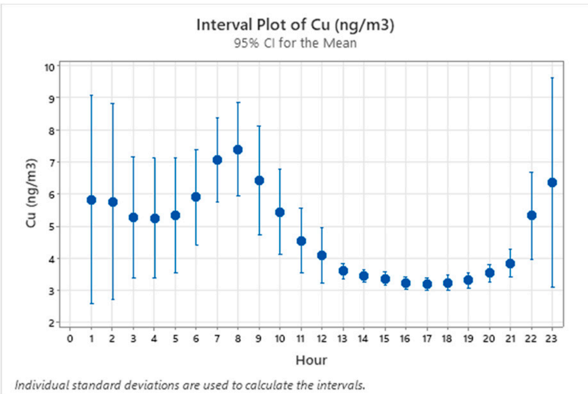


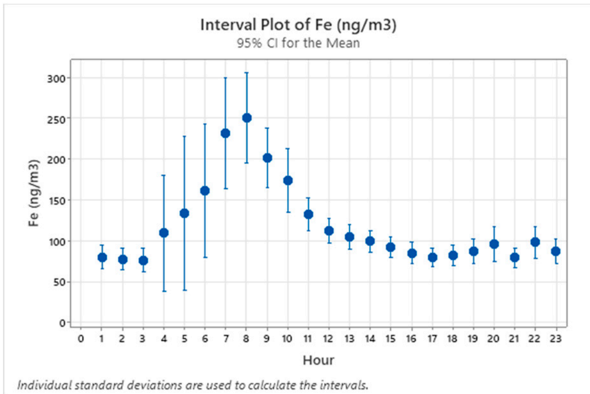

Interval Plot of BrC1 (ug/m3)
95% CI for the Mean
BrC1 (ug/m3)
Hour
Individual standard deviations are used to calculate the intervals.

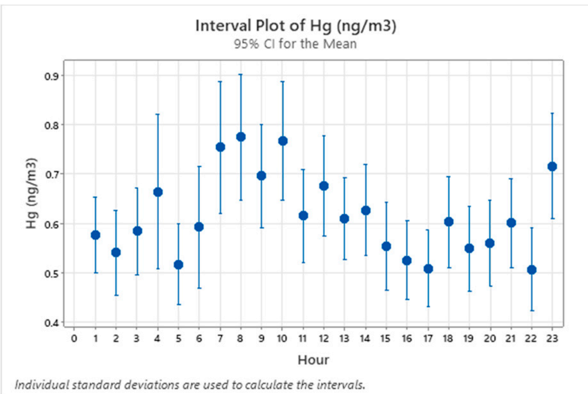

Interval Plot of BrC2 (ug/m3)
95% CI for the Mean
BrC2 (ug/m3)
Hour
Individual standard deviations are used to calculate the intervals.


Interval Plot of Br (ng/m3)
95% CI for the Mean
Br (ng/m3)
Hour
Individual standard deviations are used to calculate the intervals.


Interval Plot of Ca (ng/m3)
95% CI for the Mean
Ca (ng/m3)
Hour
Individual standard deviations are used to calculate the intervals.


Interval Plot of Cu (ng/m3)
95% CI for the Mean
Cu (ng/m3)
Hour
Individual standard deviations are used to calculate the intervals.


Interval Plot of Fe (ng/m3)
95% CI for the Mean
Fe (ng/m3)
Hour
Individual standard deviations are used to calculate the intervals.


Interval Plot of Hg (ng/m3)
95% CI for the Mean
Hg (ng/m3)
Hour
Individual standard deviations are used to calculate the intervals.

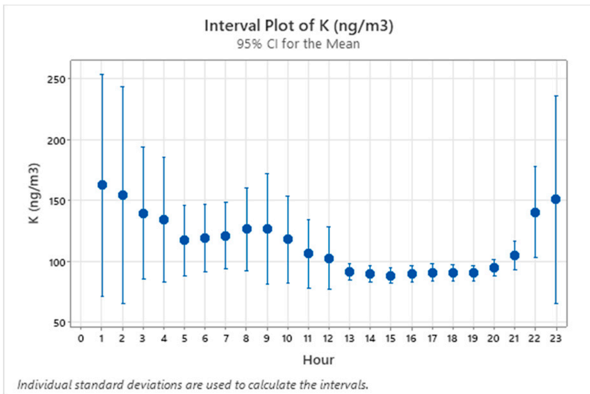

Interval Plot of K (ng/m3)
95% CI for the Mean
K (ng/m3)
Hour
Individual standard deviations are used to calculate the intervals.

Figure S4. Diurnal variations of $PM_{2.5}$, BC, brown carbons (BrC1 and BrC2), and $PM_{2.5}$-bound element concentrations. The dots indicate the mean values and the error bars represent the 95% confidence intervals.

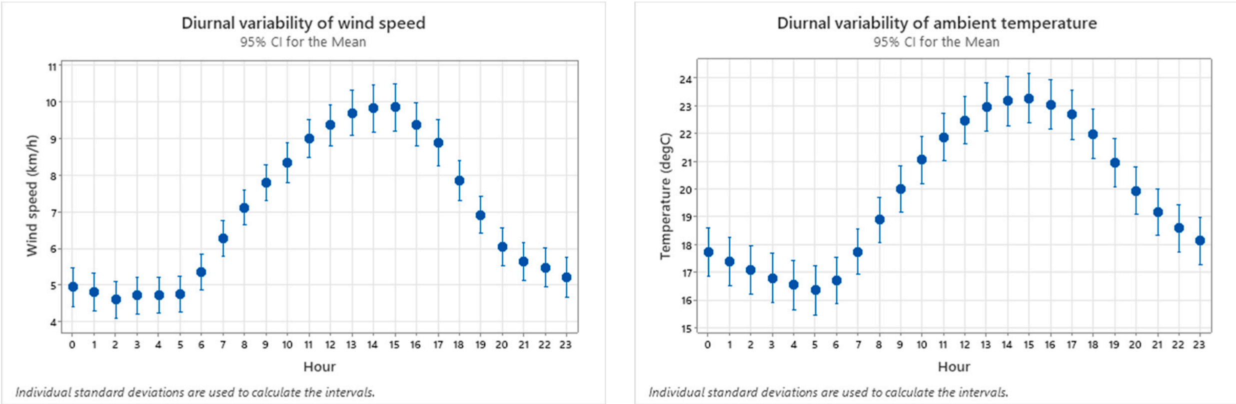
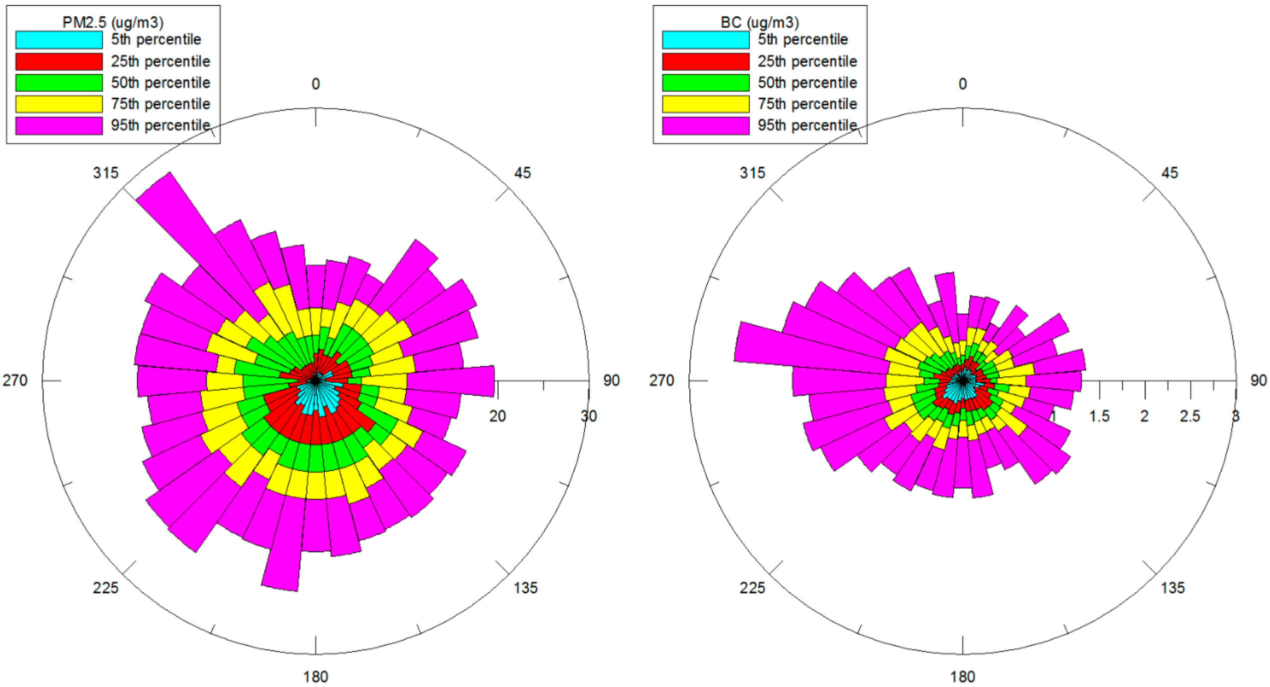
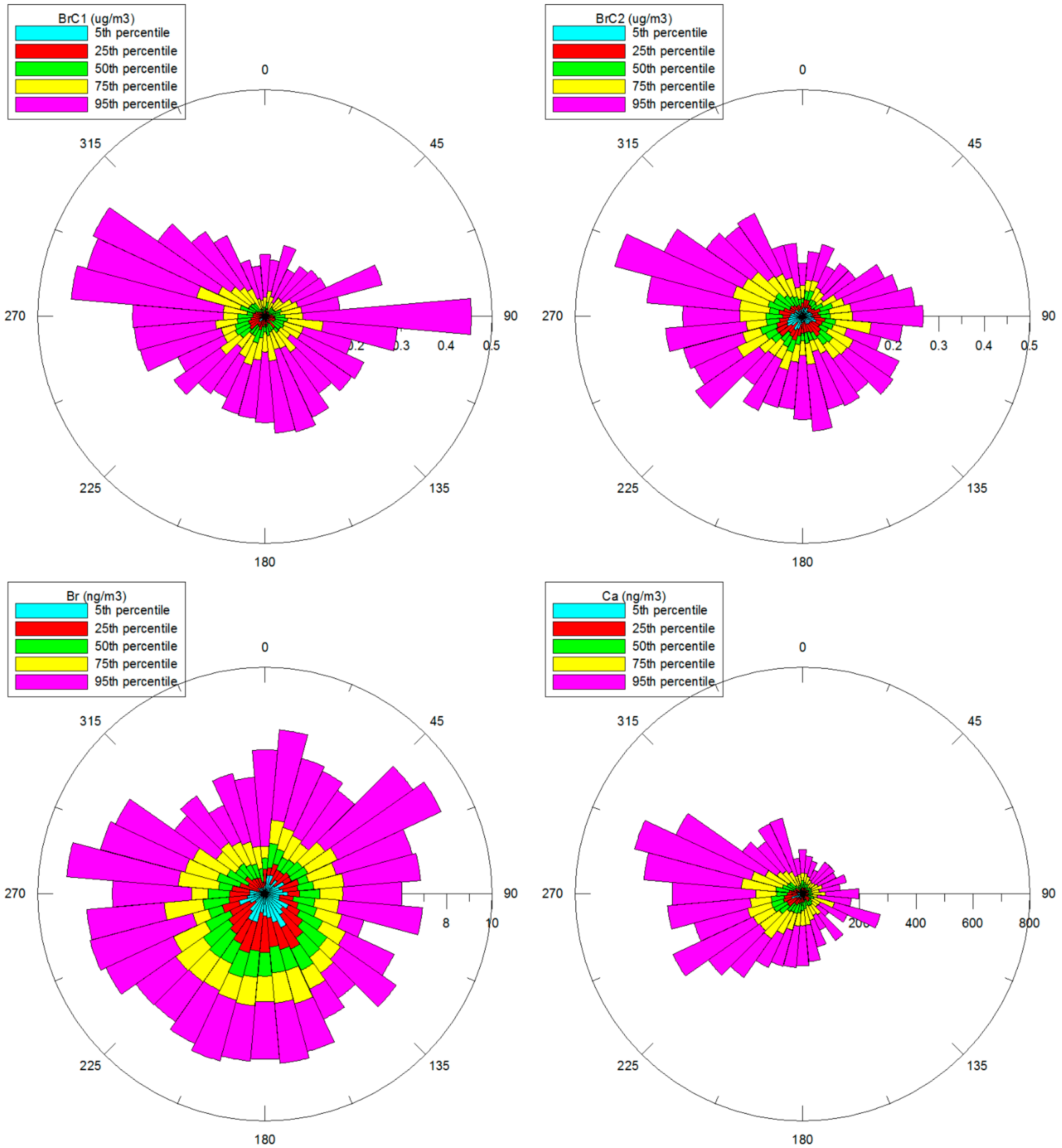
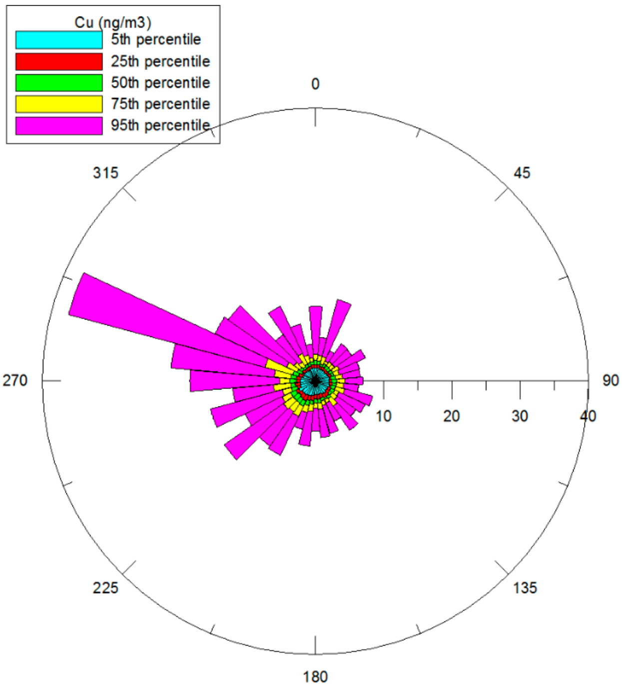
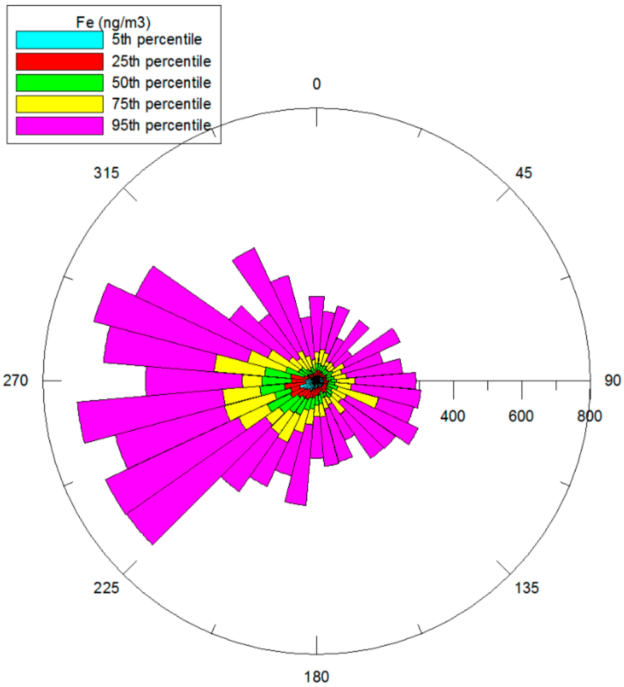


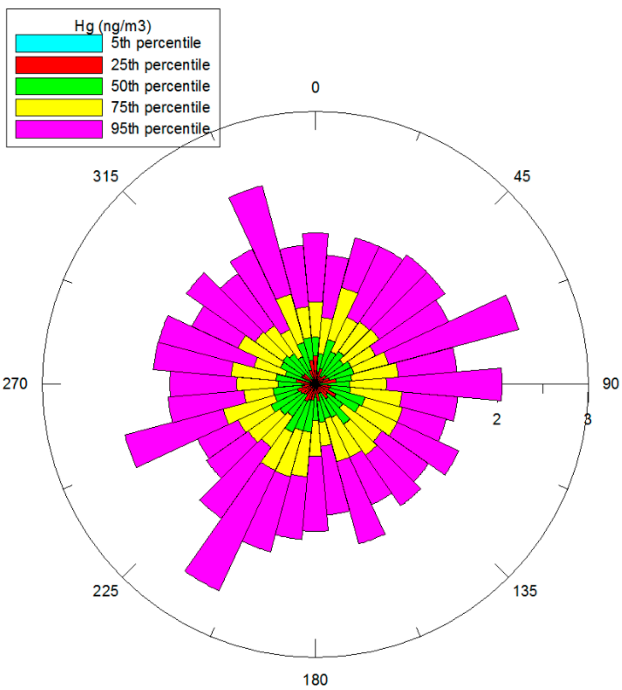
Figure S5. Diurnal variations of wind speed (**left**) and ambient temperature (**right**). The dots indicate the mean values and the error bars represent the 95% confidence intervals.

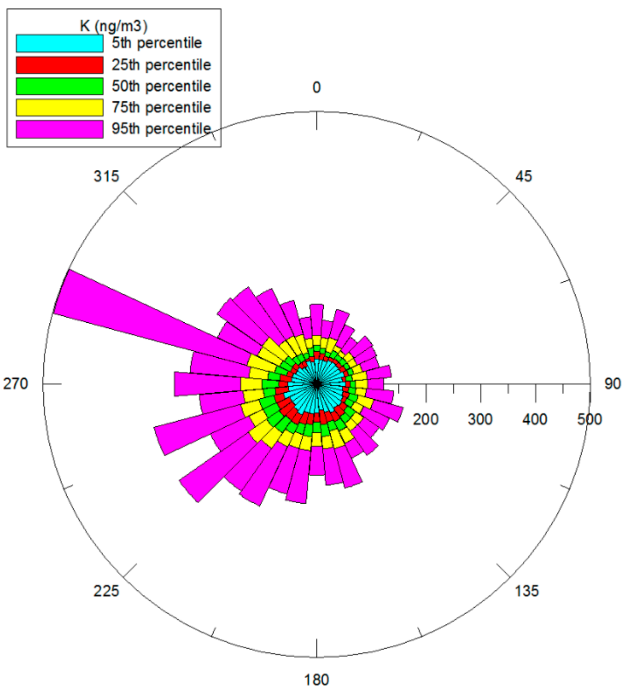


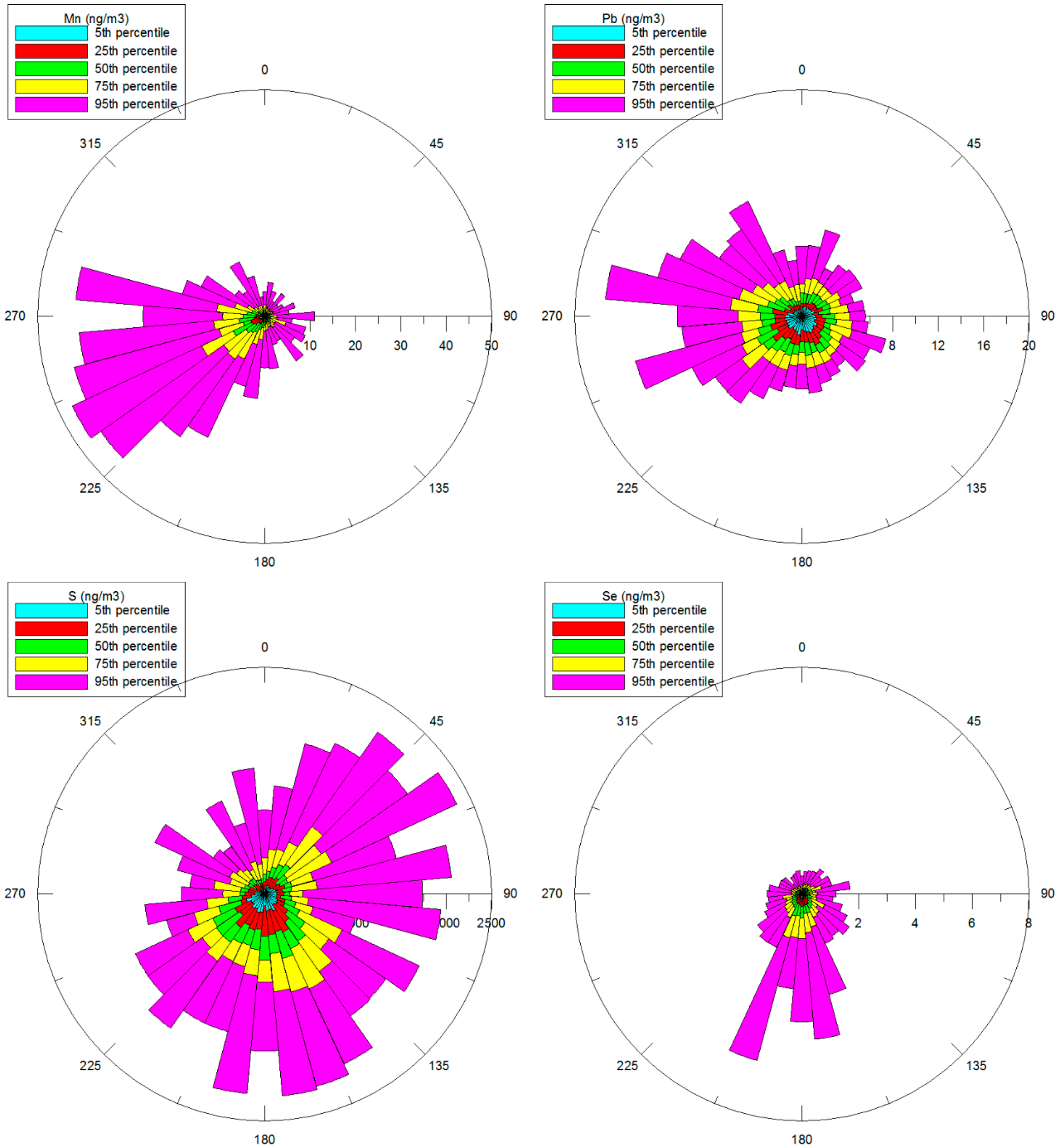

BrC1 (ug/m3)
5th percentile
25th percentile
50th percentile
75th percentile
95th percentile
0
45
90
135
180
225
270
315
0.4
0.5
BrC2 (ug/m3)
5th percentile
25th percentile
50th percentile
75th percentile
95th percentile
0
45
90
135
180
225
270
315
0.2
0.3
0.4
0.5
Br (ng/m3)
5th percentile
25th percentile
50th percentile
75th percentile
95th percentile
0
45
90
135
180
225
270
315
8
10
Ca (ng/m3)
5th percentile
25th percentile
50th percentile
75th percentile
95th percentile
0
45
90
135
180
225
270
315
400
600
800


Cu (ng/m3)
5th percentile
25th percentile
50th percentile
75th percentile
95th percentile
0
45
90
135
180
225
270
315
10
20
30
40


Fe (ng/m3)
5th percentile
25th percentile
50th percentile
75th percentile
95th percentile
0
45
90
135
180
225
270
315
400
600
800


Hg (ng/m3)
5th percentile
25th percentile
50th percentile
75th percentile
95th percentile
0
45
90
135
180
225
270
315
2
3


K (ng/m3)
5th percentile
25th percentile
50th percentile
75th percentile
95th percentile
0
45
90
135
180
225
270
315
200
300
400
500


Mn (ng/m3)
5th percentile
25th percentile
50th percentile
75th percentile
95th percentile
0
45
90
135
180
225
270
315
10
20
30
40
50
Pb (ng/m3)
5th percentile
25th percentile
50th percentile
75th percentile
95th percentile
0
45
90
135
180
225
270
315
8
12
16
20
S (ng/m3)
5th percentile
25th percentile
50th percentile
75th percentile
95th percentile
0
45
90
135
180
225
270
315
2500
Se (ng/m3)
5th percentile
25th percentile
50th percentile
75th percentile
95th percentile
0
45
90
135
180
225
270
315
2
4
6
8

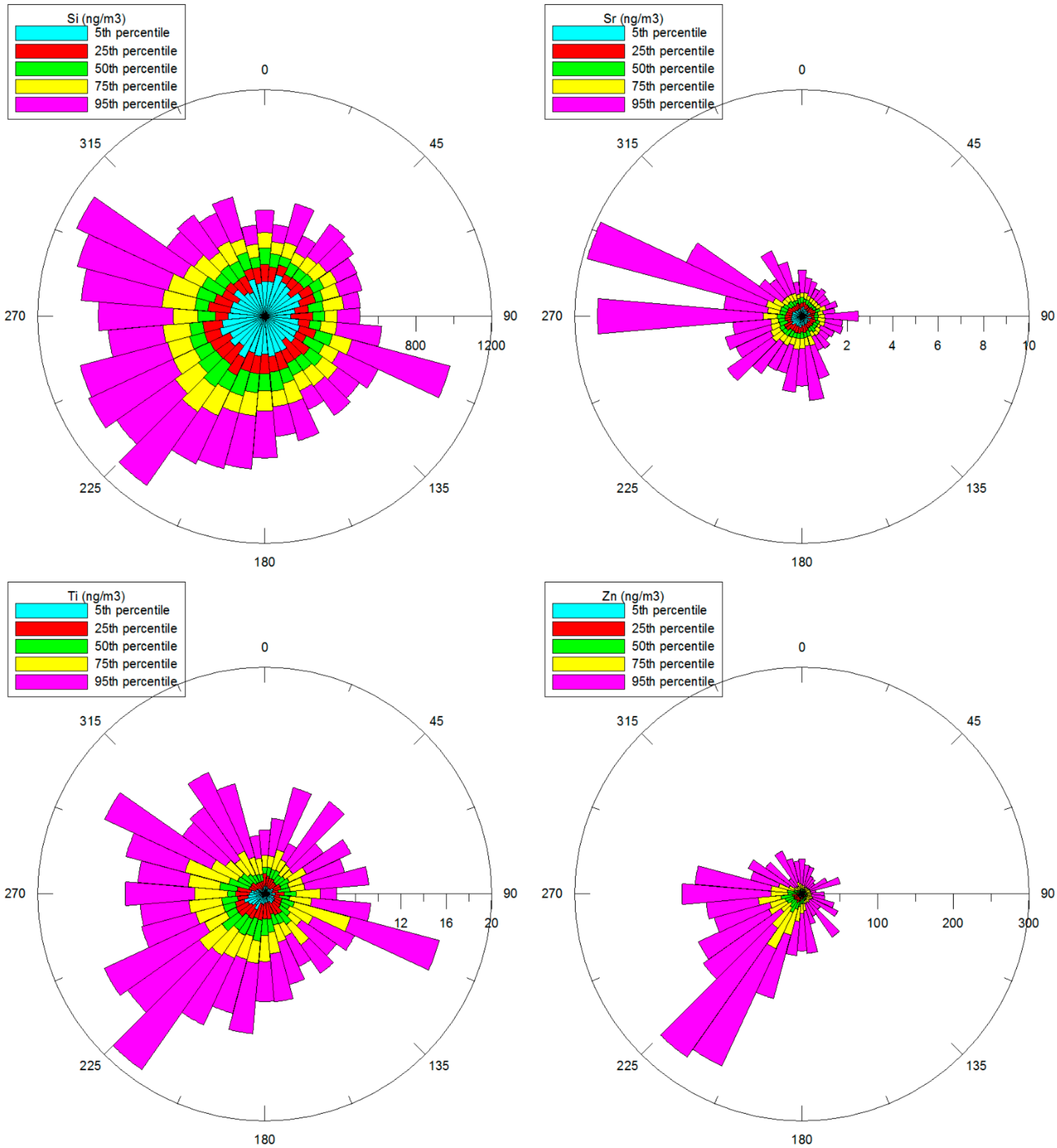
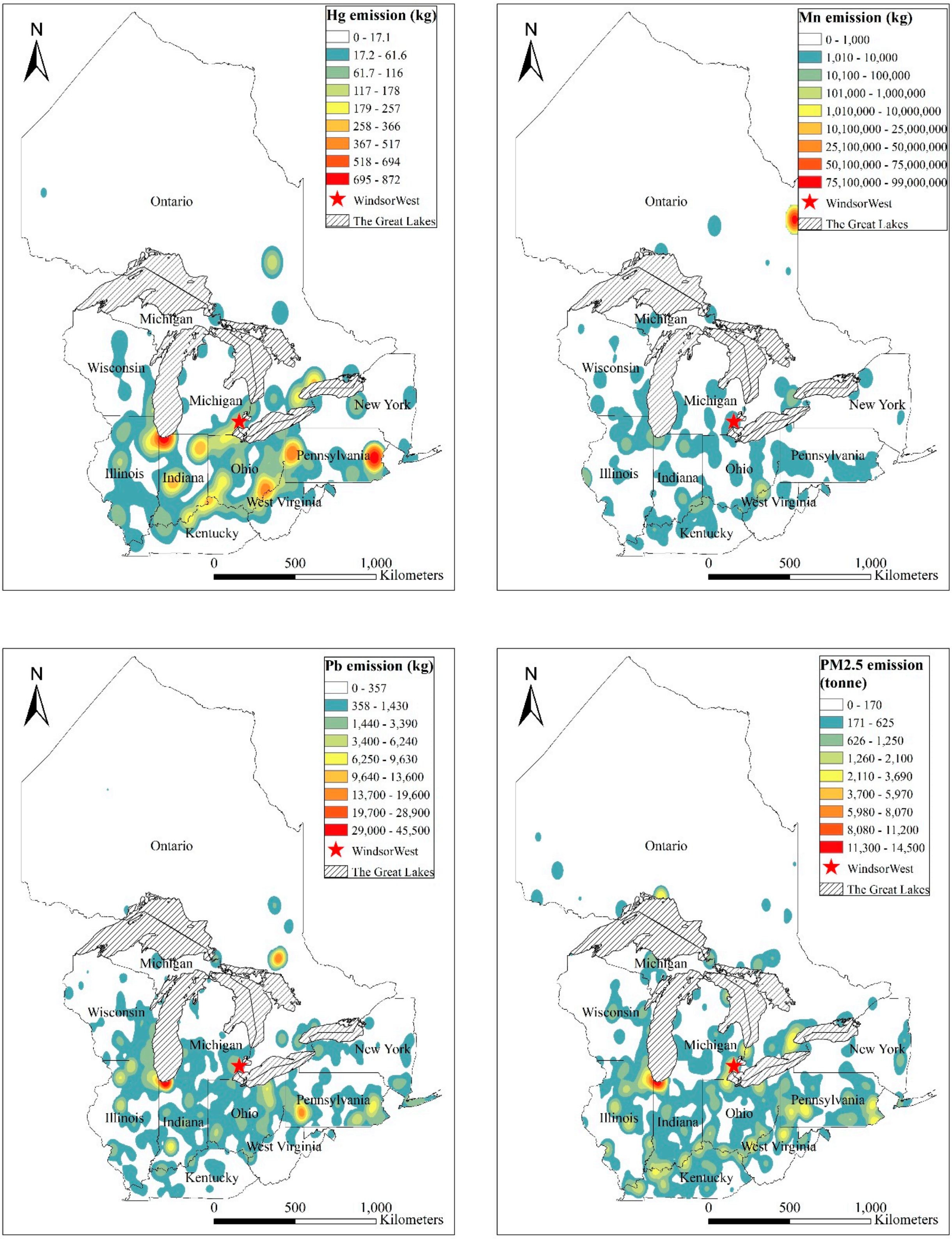
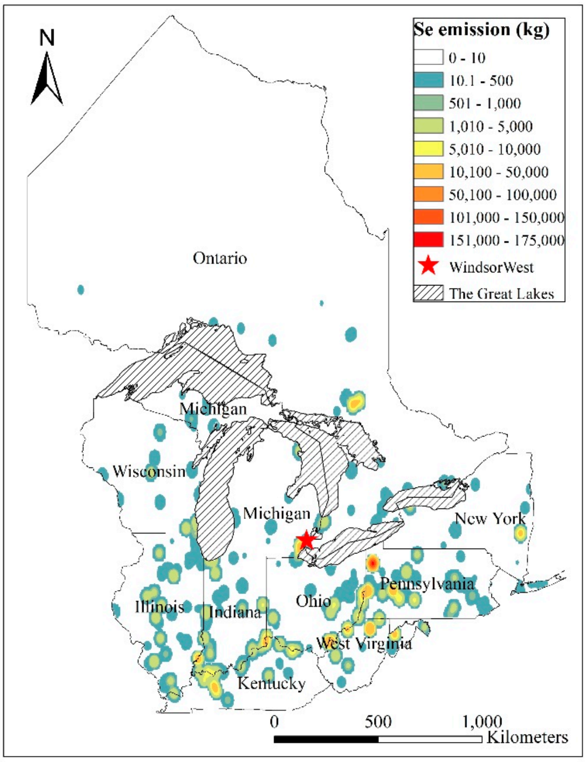


Figure S6. Pollution roses of $PM_{2.5}$ mass, black carbon, brown carbons, and 14 selected $PM_{2.5}$-bound elements.



Hg emission (kg)
0 - 17.1
17.2 - 61.6
61.7 - 116
117 - 178
179 - 257
258 - 366
367 - 517
518 - 694
695 - 872
WindsorWest
The Great Lakes
N
Ontario
Michigan
Wisconsin
Michigan
New York
Pennsylvania
Illinois
Indiana
Ohio
West Virginia
Kentucky
0 500 1,000 Kilometers
Mn emission (kg)
0 - 1,000
1,010 - 10,000
10,100 - 100,000
101,000 - 1,000,000
1,010,000 - 10,000,000
10,100,000 - 25,000,000
25,100,000 - 50,000,000
50,100,000 - 75,000,000
75,100,000 - 99,000,000
WindsorWest
The Great Lakes
N
Ontario
Michigan
Wisconsin
Michigan
New York
Pennsylvania
Illinois
Indiana
Ohio
West Virginia
Kentucky
0 500 1,000 Kilometers
Pb emission (kg)
0 - 357
358 - 1,430
1,440 - 3,390
3,400 - 6,240
6,250 - 9,630
9,640 - 13,600
13,700 - 19,600
19,700 - 28,900
29,000 - 45,500
WindsorWest
The Great Lakes
N
Ontario
Michigan
Wisconsin
Michigan
New York
Pennsylvania
Illinois
Indiana
Ohio
West Virginia
Kentucky
0 500 1,000 Kilometers
PM2.5 emission (tonne)
0 - 170
171 - 625
626 - 1,250
1,260 - 2,100
2,110 - 3,690
3,700 - 5,970
5,980 - 8,070
8,080 - 11,200
11,300 - 14,500
WindsorWest
The Great Lakes
N
Ontario
Michigan
Wisconsin
Michigan
New York
Pennsylvania
Illinois
Indiana
Ohio
West Virginia
Kentucky
0 500 1,000 Kilometers



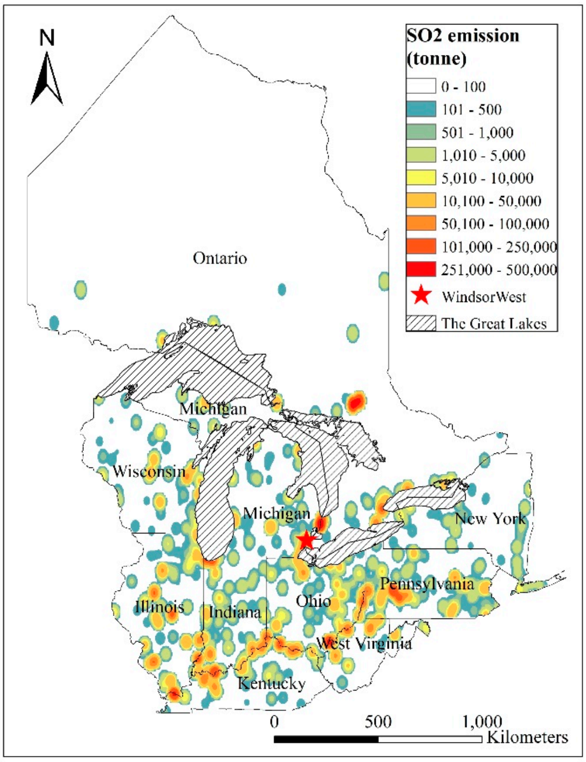


Figure S7. NPRI and NEI emission maps of Hg, Mn, Pb, $PM_{2.5}$, Se, and SO_2 in Ontario in 2020 and surrounding nine US states in 2017.

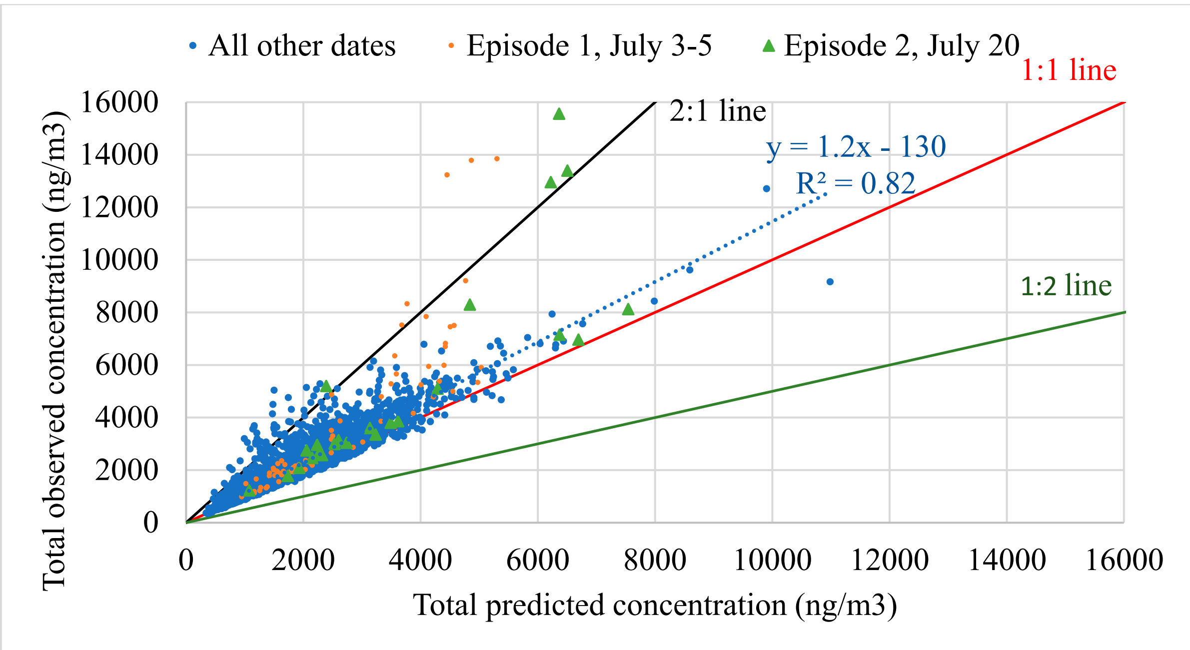


Figure S8. Scatter plots of hourly total observed concentrations vs. hourly total predicted concentration. The two episodes are labelled in orange and green, respectively. When concentrations were greater than 4000 ng/m^3, most of the hourly concentrations during the two episodes deviate further away from the 1:1 line. Episodes were identified with two considerations: (1) hourly concentrations were at least 20 times higher than the averaged concentrations during the study period of April–October 2021 for more than 5 h; and (2) multiple elements simultaneously showed high hourly concentrations.

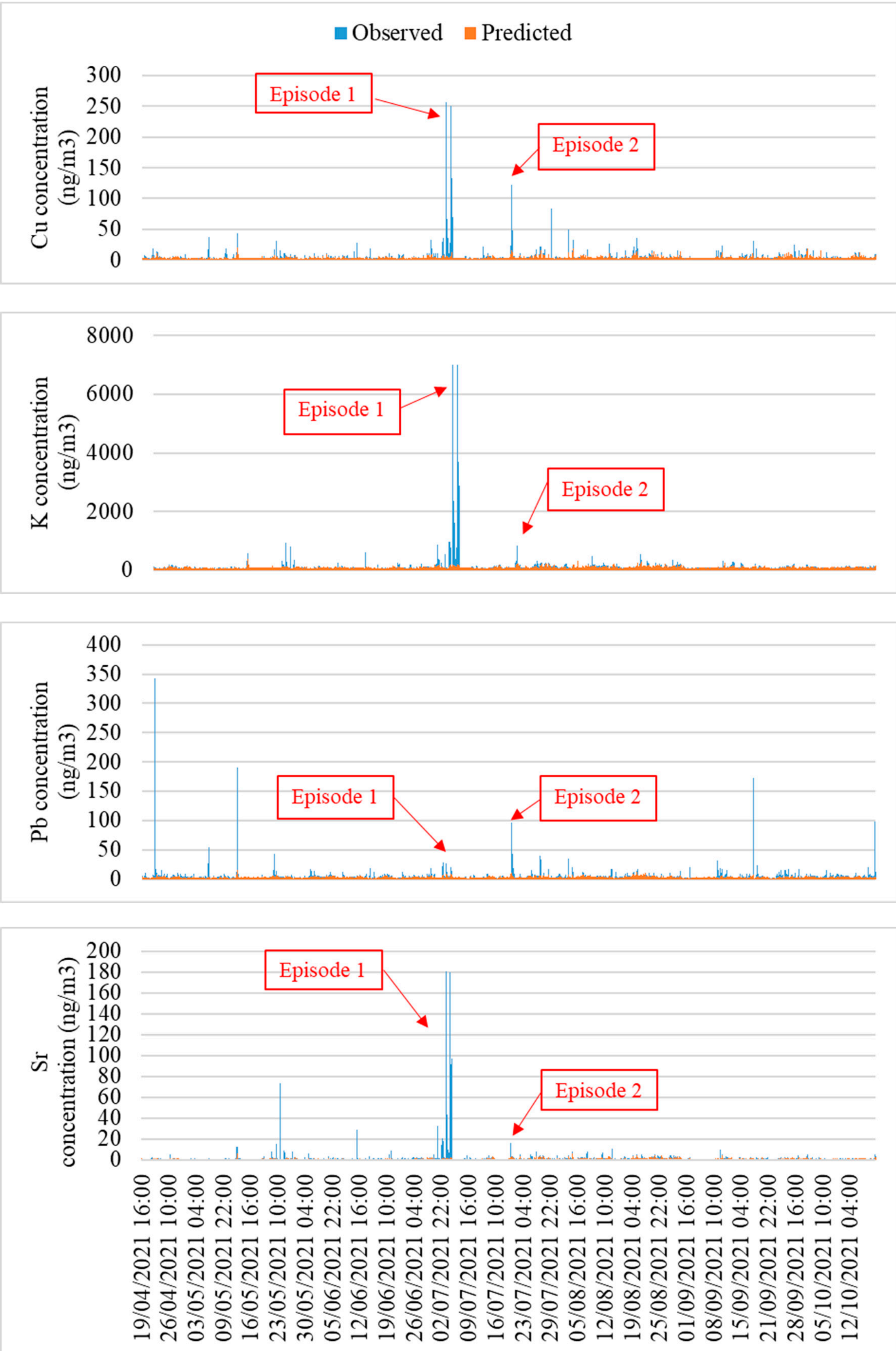
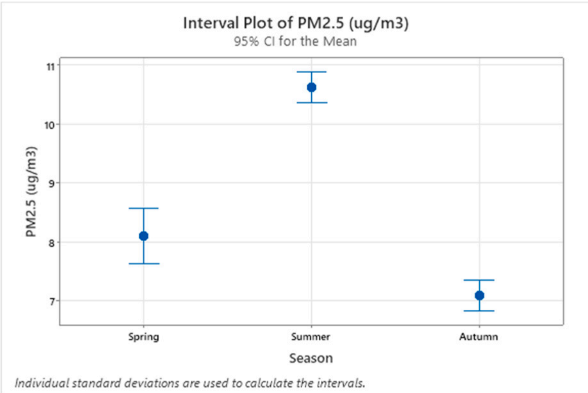
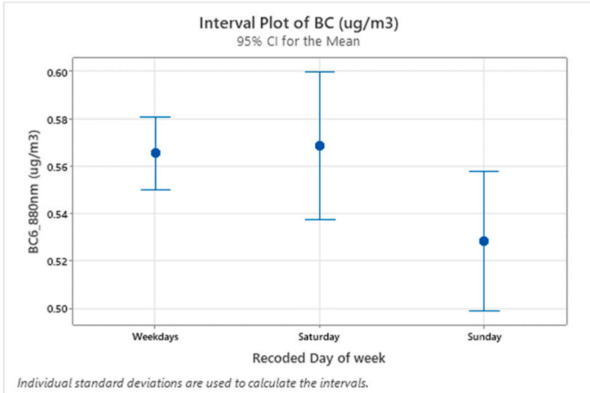
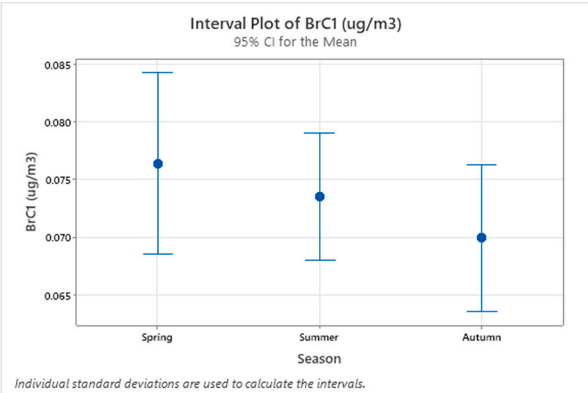


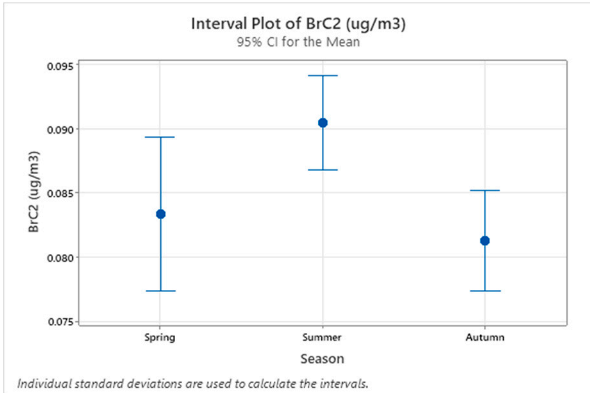
Figure S9. Time-series of hourly observed concentrations vs. predicted concentration for Cu, K, Pb and Sr.

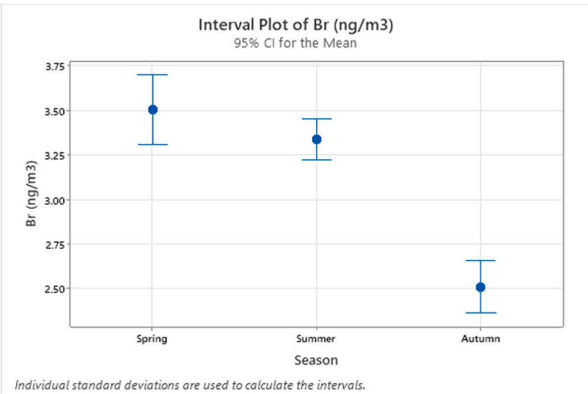
Figure S10. Diurnal variations of source contributions (ng/m^3) of each source in Windsor. The dots indicate the mean values and the error bars represent the 95% confidence intervals.

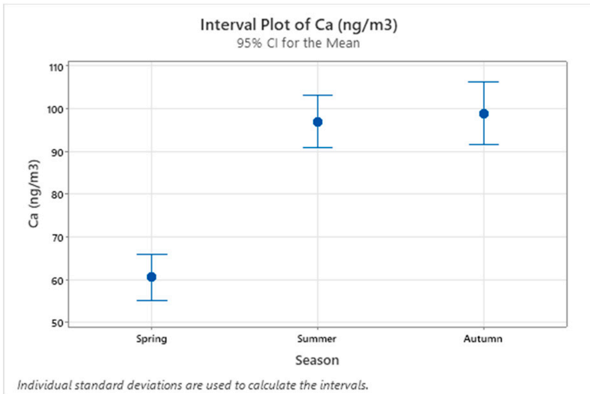

Interval Plot of PM2.5 (ug/m3)
95% CI for the Mean
PM2.5 (ug/m3)
11
10
9
8
7
Spring
Summer
Autumn
Season
Individual standard deviations are used to calculate the intervals.

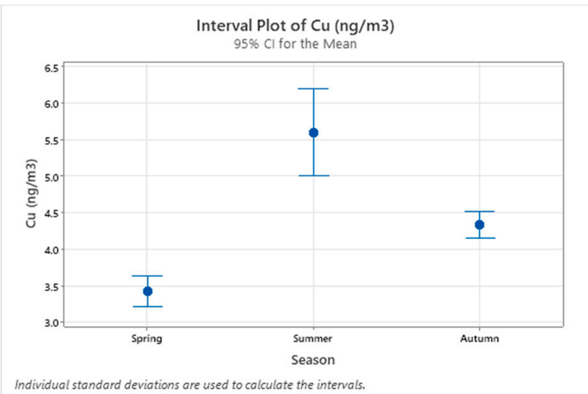

Interval Plot of BC (ug/m3)
95% CI for the Mean
BC6_880nm (ug/m3)
0.60
0.58
0.56
0.54
0.52
0.50
Weekdays
Saturday
Sunday
Recoded Day of week
Individual standard deviations are used to calculate the intervals.

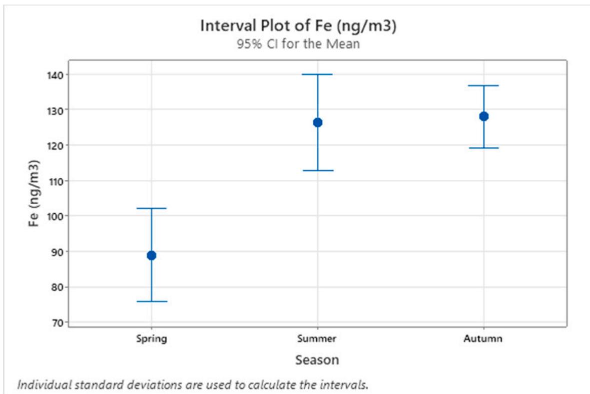

Interval Plot of BrC1 (ug/m3)
95% CI for the Mean
BrC1 (ug/m3)
0.085
0.080
0.075
0.070
0.065
Spring
Summer
Autumn
Season
Individual standard deviations are used to calculate the intervals.

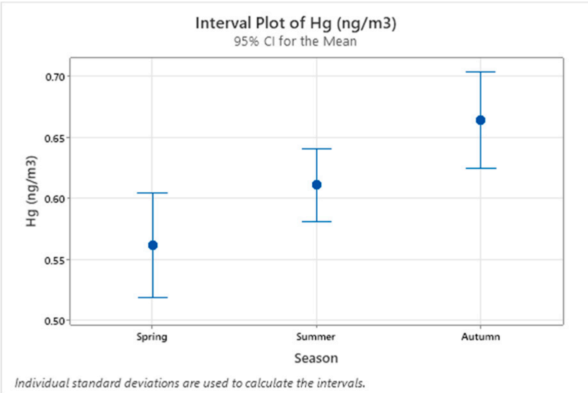

Interval Plot of BrC2 (ug/m3)
95% CI for the Mean
BrC2 (ug/m3)
0.095
0.090
0.085
0.080
0.075
Spring
Summer
Autumn
Season
Individual standard deviations are used to calculate the intervals.

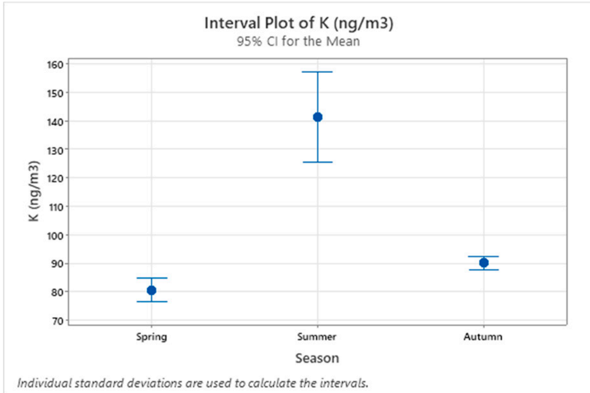

Interval Plot of Br (ng/m3)
95% CI for the Mean
Br (ng/m3)
3.75
3.50
3.25
3.00
2.75
2.50
Spring
Summer
Autumn
Season
Individual standard deviations are used to calculate the intervals.

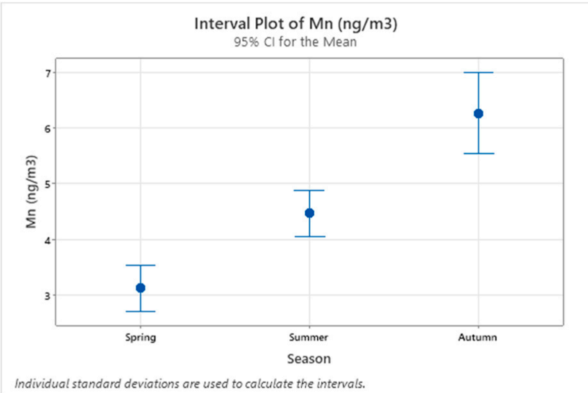

Interval Plot of Ca (ng/m3)
95% CI for the Mean
Ca (ng/m3)
110
100
90
80
70
60
50
Spring
Summer
Autumn
Season
Individual standard deviations are used to calculate the intervals.

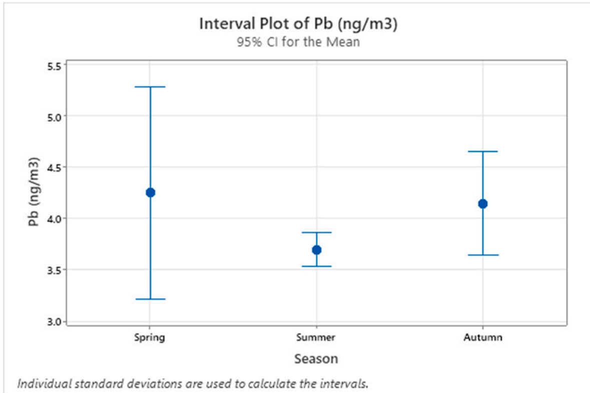

Interval Plot of Cu (ng/m3)
95% CI for the Mean
Cu (ng/m3)
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
Spring
Summer
Autumn
Season
Individual standard deviations are used to calculate the intervals.

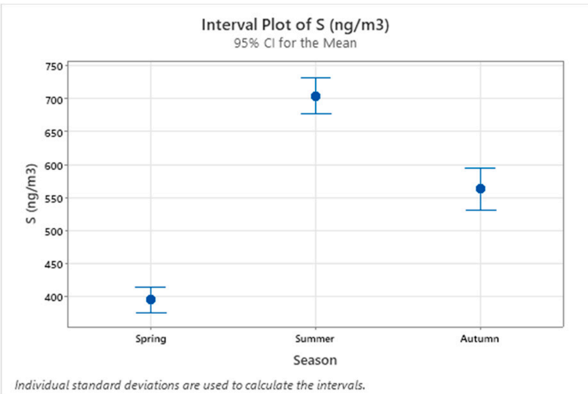

Interval Plot of Fe (ng/m3)
95% CI for the Mean
Fe (ng/m3)
140
130
120
110
100
90
80
70
Spring
Summer
Autumn
Season
Individual standard deviations are used to calculate the intervals.

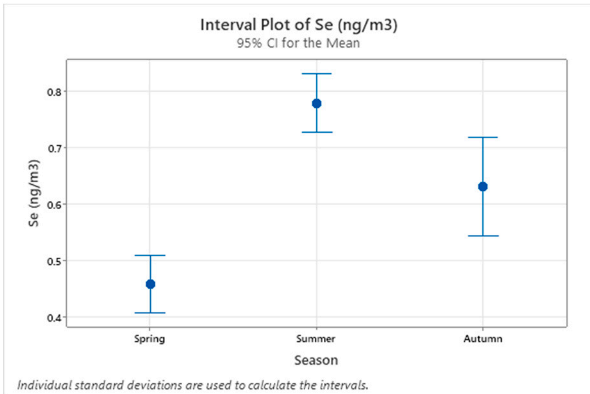

Interval Plot of Hg (ng/m3)
95% CI for the Mean
Hg (ng/m3)
0.70
0.65
0.60
0.55
0.50
Spring
Summer
Autumn
Season
Individual standard deviations are used to calculate the intervals.

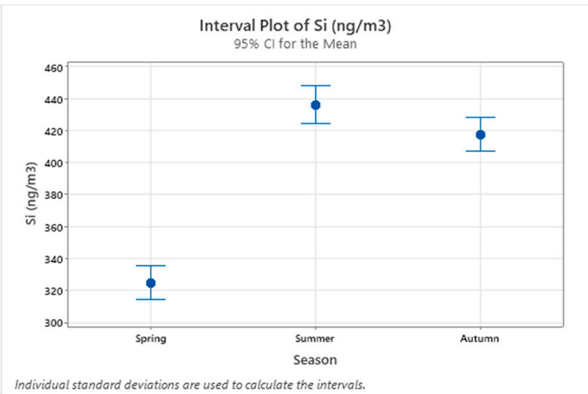

Interval Plot of K (ng/m3)
95% CI for the Mean
K (ng/m3)
160
150
140
130
120
110
100
90
80
70
Spring
Summer
Autumn
Season
Individual standard deviations are used to calculate the intervals.

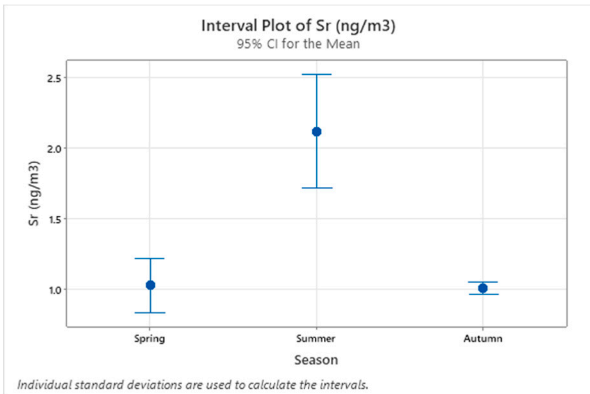

Interval Plot of Mn (ng/m3)
95% CI for the Mean
Mn (ng/m3)
7
6
5
4
3
Spring
Summer
Autumn
Season
Individual standard deviations are used to calculate the intervals.


Interval Plot of Pb (ng/m3)
95% CI for the Mean
Pb (ng/m3)
5.5
5.0
4.5
4.0
3.5
3.0
Spring
Summer
Autumn
Season
Individual standard deviations are used to calculate the intervals.


Interval Plot of S (ng/m3)
95% CI for the Mean
S (ng/m3)
750
700
650
600
550
500
450
400
Spring
Summer
Autumn
Season
Individual standard deviations are used to calculate the intervals.


Interval Plot of Se (ng/m3)
95% CI for the Mean
Se (ng/m3)
0.8
0.7
0.6
0.5
0.4
Spring
Summer
Autumn
Season
Individual standard deviations are used to calculate the intervals.


Interval Plot of Si (ng/m3)
95% CI for the Mean
Si (ng/m3)
460
440
420
400
380
360
340
320
300
Spring
Summer
Autumn
Season
Individual standard deviations are used to calculate the intervals.


Interval Plot of Sr (ng/m3)
95% CI for the Mean
Sr (ng/m3)
2.5
2.0
1.5
1.0
Spring
Summer
Autumn
Season
Individual standard deviations are used to calculate the intervals.

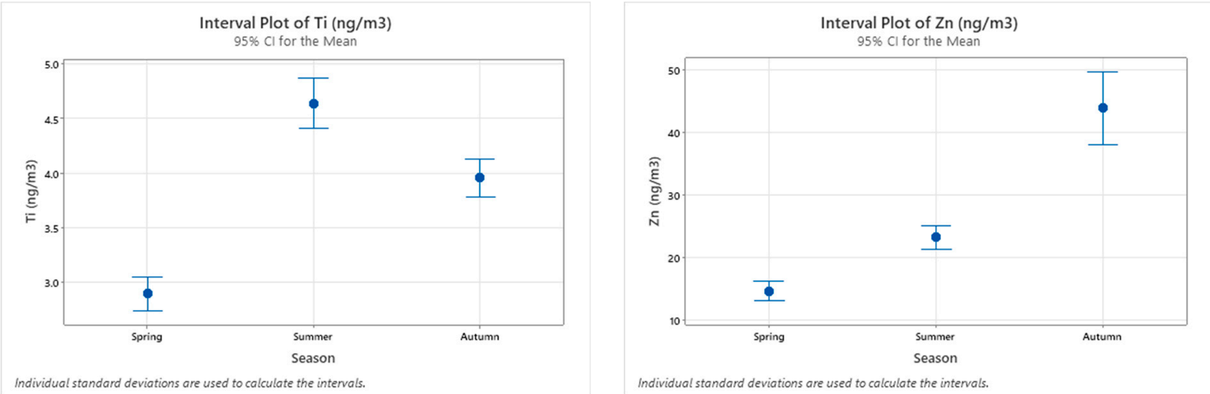
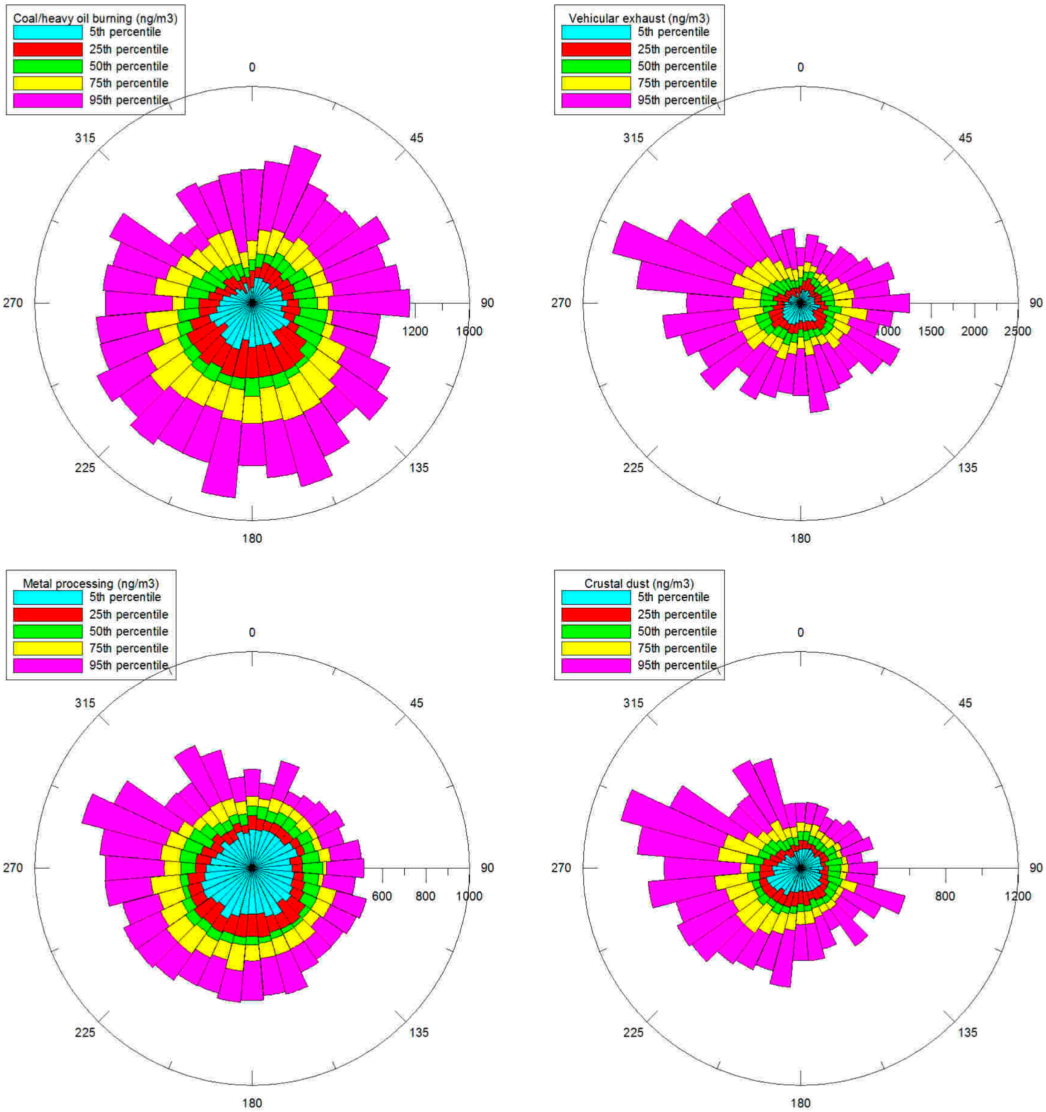


Figure S11. Seasonal variations of $PM_{2.5}$, BC, brown carbons (BrC1 and BrC2), and $PM_{2.5}$-bound element concentrations in Windsor during the study period. The dots indicate the mean values and the error bars represent the 95% confidence intervals.



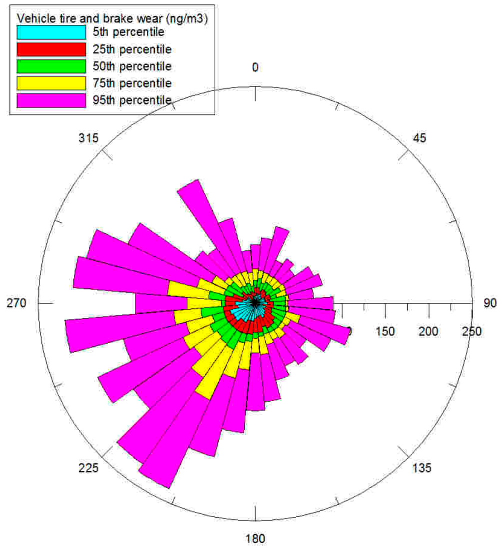


Figure S12. Pollution roses of source contributions in Windsor, Canada.

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