

Supplemental Materials

Concentrations and health risk assessment of ambient PM_{2.5}-bound elements in Windsor, Ontario, Canada

Tianchu Zhang^{1, 2}, Yushan Su^{2, *}, James Gilmore², Jerzy Debosz², Michael Noble², Anthony Munoz², Chris Charron², Xiaohong Xu^{1, *}

¹ Department of Civil and Environmental Engineering, University of Windsor, Windsor, ON N9B 3P4, Canada; zhang14g@uwindsor.ca, xxu@uwindsor.ca

² Environmental Monitoring and Reporting Branch, Ontario Ministry of the Environment, Conservation and Parks, Toronto, ON M9P 3V6, Canada; yushan.su@ontario.ca

³ Technical Assessment and Standards Development Branch, Ontario Ministry of the Environment, Conservation and Parks, Toronto, ON M4V 1M2, Canada

* Correspondence: Yushan.Su@ontario.ca, xxu@uwindsor.ca

Table S1. Total sample size and percentages of concentrations $\geq$ MDL for PM_{2.5} and 24 PM_{2.5}-bound elements in Windsor during 19 April 2021–30 April 2023.

PM _{2.5} and elements	Total sample size (N)	$\geq$ MDL (%)
PM _{2.5}	18009	98.8
Ag	9059	8.6
As*^	9059	17
Ba^	9059	42
Br	9059	98.3
Ca	9059	99.5
Cd*^	9059	16
Co*^	9059	0.5
Cr*^	9059	17
Cu	9059	100
Fe	9059	99.9
Hg^	9059	49
K	9059	99.99
Mn^	9059	86.1
Ni*^	9059	50.4
Pb*^	9059	97.7
Rb	9059	11
S	9059	100
Se^	9059	70.5
Si	9059	98.9
Sn	9059	0.011
Sr	9059	73
Ti	9059	94.8
V^	9059	29
Zn	9059	99.8

* Elements used to calculate cancer risks.

^ Elements used to calculate hazard quotients.

Table S2. The mean concentrations and their 95% upper confidence levels (UCL) of PM_{2.5} (µg/m³) and 24 PM_{2.5}-bound elements (ng/m³) in Windsor during 19 April 2021–30 April 2023, for the two scenarios. Scenario 1 (S1): replaced concentrations below MDLs with MDLs. Scenario 2 (S2): replaced concentrations below MDLs using the data distribution of the remaining values, i.e., the Kaplan-Meier (KM) method.

PM _{2.5} and elements	MDL	Mean (S1)	95% UCL (S1)	Mean (S2)	95% UCL (S2)
PM _{2.5}	0.5	9.21	9.29	9.20	9.27
Ag	4.33	4.44	4.45	0.48	0.51
As*^	0.11	0.32	0.35	0.23	0.26
Ba^	0.95	1.9	2.0	1.4	1.5
Br	0.18	2.72	2.77	2.72	2.76
Ca	0.9	70.5	72.5	70.5	72.2
Cd*^	5.75	6.0	6.0	1.2	1.2
Co*^	0.32	0.33	0.33	0.01	0.01
Cr*^	0.29	0.43	0.47	0.19	0.22
Cu	0.27	3.54	3.66	3.54	3.64
Fe	0.76	102.7	106.8	102.7	106.2
Hg^	0.19	0.49	0.50	0.39	0.41
K	2.37	74	76	74	75
Mn^	0.28	4.4	4.6	4.3	4.5
Ni*^	0.23	0.49	0.51	0.38	0.40
Pb*^	0.22	3.4	3.5	3.4	3.5
Rb	0.34	0.36	0.36	0.05	0.06
S	6	490	498	490	497
Se^	0.14	0.66	0.69	0.62	0.64
Si	20	336	345	336	343
Sn	7.46	7.5	7.5	0.0	0.0?
Sr	0.45	0.97	1.01	0.85	0.88
Ti	0.38	3.41	3.56	3.39	3.51
V^	0.29	0.58	0.60	0.37	0.39
Zn	0.23	24.8	26.0	24.8	25.8

* Elements used to calculate cancer risks.

^ Elements used to calculate hazard quotients.

The mean and 95% UCL values in S1 is higher than those in S2 for each of the 24 PM_{2.5}-bound elements.

Table S3. Carcinogen classification and inhalation unit risks ($\mu\text{g}/\text{m}^3$)⁻¹ of the 24 elements.

Elements	Chemical name and compounds	Carcinogen classification [1]	Carcinogen classification and IUR [2]	Carcinogen classification [3]	Carcinogen classification and IUR [4]	IUR [5]
Ag	Silver		D, not likely to be carcinogenic to humans			
As*	Arsenic and Inorganic Arsenic Compounds	Known To Be Human Carcinogens	A known/ likely human carcinogen, 4.3×10^{-3}	Group 1	A known/ likely human carcinogen, 3.3×10^{-3}	6.4×10^{-3}
Ba	Barium		D, not likely to be carcinogenic to humans			
Br	Bromine	Not assessed/not classified				
Ca	Calcium	Not assessed/ not classified				
Cd*	Cadmium and Cadmium Compounds	Known To Be Human Carcinogens	B1, Probable human carcinogen, 1.8×10^{-3}	Group 1	B1, Probable human carcinogen, 4.2×10^{-3}	4.2×10^{-3}
Co*	Cobalt and Cobalt Compounds	Reasonably Anticipated To Be Human Carcinogens		Group 2b	7.7×10^{-3} (OEHHA, 2020)	
Cr*	Chromium Hexavalent Compounds	Known To Be Human Carcinogens	A, known/ likely human carcinogen, 1.2×10^{-2}	Group 1	A, known/ likely human carcinogen, 1.5×10^{-1}	7.6×10^{-2}
Cu	Copper		D, not likely to be carcinogenic to humans			
Fe	Iron and steel founding (occupational exposure during)			Group 1		
Hg	Mercury, elemental		D, not likely to be carcinogenic to humans	Mercury and inorganic mercury compounds Group 3		
K	Potassium	Not assessed/ not classified				
Mn	Manganese		D, not likely to be carcinogenic to humans			
Ni*	Nickel Compounds	Known To Be Human Carcinogens	Nickel refinery dust: A, human carcinogen,	Compounds: Group 1	A, known/ likely human carcinogen,	1.3×10^{-3}

	and Metallic Nickel		2.4 x 10 ⁻⁴	Metallic Group 2B	2.6 x 10 ⁻⁴	
Pb*	Lead and Lead Compounds	Reasonably Anticipated To Be Human Carcinogens	B2, probable human carcinogen - based on sufficient evidence of carcinogenicity in animals	Group 2B	B2, probable human carcinogen 1.2 x 10 ⁻⁵	
Rb	Rubidium	Not assessed/ not classified				
S	Sulfur	Not assessed/ not classified				
Se	Selenium and Compounds		D, not likely to be carcinogenic to humans	Group 3		
Si	Silica, SiO ₂ , Crystalline	Known To Be Human Carcinogens		Group 1		
Sn	Tin	Not assessed/ not classified				
Sr	Strontium	Not assessed/ not classified				
Ti	Titanium dioxide, TiO ₂			Group 2B		
V	Vanadium pentoxide, V ₂ O ₅			Group 2B		
Zn	Zinc and Compounds		D, not likely to be carcinogenic to humans			

Group 1: Carcinogenic to humans

Group 2B: Possibly carcinogenic to humans

Group 3: Not classifiable as to its carcinogenicity to humans

* Elements used to calculate cancer risks in this study.

Green: the largest IUR for that element

Yellow: the smallest IUR for that element

Blue: the only available IUR for that element

When both green and yellow IURs are available for that element, both values were used to calculate cancer risks to produce a range.

Table S4. Reference concentrations (RfC) or equivalent toxic values for PM_{2.5}-bound elements.

Elements	Chemical name and compounds	Reference concentration ^a (µg/m ³ , [2])	Minimal risk levels ^b (µg/m ³ , [6])	Inhalation tolerable concentration ^c (µg/m ³ , [5])	Chronic Inhalation Reference Exposure Level ^d (µg/m ³ , [4])	Other sources (µg/m ³)
Ag	Silver					
As [^]	Arsenic & inorganic arsenic compounds				0.015	
Ba [^]	Barium					RfC: 0.5 [7]
Br	Bromine					
Ca	Calcium					
Cd [^]	Cadmium & cadmium compounds		0.01		0.02	AAQC ^e : 0.005 [8]
Co [^]	Cobalt		0.1			
Cr [^]	Chromium (VI)	particulates 0.1		0.1	0.2	
Cu	Copper and compounds					
Fe	Iron					
Hg [^]	Mercury	Elemental 0.3	0.3		Mercury (Inorganic) 0.03	RfC: 0.3 [7]
K	Potassium					
Mn [^]	Manganese, respirable	0.05	0.3 (large diff)		Manganese & Manganese Compounds, 0.09	
Ni [^]	Nickel		0.01	Metallic 0.018	0.014	AAQC: 0.02 [8]
Pb [^]	Lead					NAAQS ^f : 0.15 [9]
Rb	Rubidium					
S	Sulfur					
Se [^]	Selenium and selenium compounds				20	
Si	Silicon					
Sn	Tin					
Sr	Strontium					
Ti	Titanium					
V [^]	Vanadium		0.1			
Zn	Zinc					

a, the concentration level at or below which no adverse health effects are anticipated for a specified exposure duration [10].

b, an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse noncancer health effects over a specified duration of exposure [6].

c, exposure level at or below which no toxic effects are assumed to occur [5].

d, the amount of chemical in the air that is not likely to cause noncancer health effects even in sensitive populations. Chronic Inhalation Reference Exposure Level is designed to address continuous exposures for up to a lifetime: the exposure metric used is the annual average exposure [11].

e: Ontario's Ambient Air Quality Criteria [8]

f: National Ambient Air Quality Standards of the US [9]

^ Elements used to calculate hazard quotients in this study.

Green: the largest reference concentration for that element

Yellow: the smallest reference concentration for that element

Blue: the only available reference concentration for that element

When both green and yellow RfCs are available for that element, both values were used to calculate hazard quotients to produce a range.

Table S5. Factor profiles (% of PM_{2.5}-bound element concentrations being assigned to that factor) of PM_{2.5}-bound elements in Windsor based on data collected in 2021 [12]. Bold values are percentages $\geq 40\%$.

Elements	Coal/Heavy Oil Burning	Vehicular Exhaust	Metal Processing	Crustal Dust	Vehicle Brake and Tire Wear
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 S6. Ratios and upper and lower ranges of (a) incremental lifetime CRs and (b) chronic non-cancer HQs, per elements in Windsor during 2021-2023.

(a) Incremental lifetime CRs

Elements	Upper ranges of CRs	Lower ranges of CRs	CR ratios
As	2.24E-06	1.16E-06	1.9
Cd	2.53E-05	1.08E-05	2.3
Co	2.56E-06	2.56E-06	1
Cr(VI)	1.00E-05	8.00E-07	12.5
Ni	6.69E-07	1.24E-07	5.4
Pb	4.17E-08	4.17E-08	1

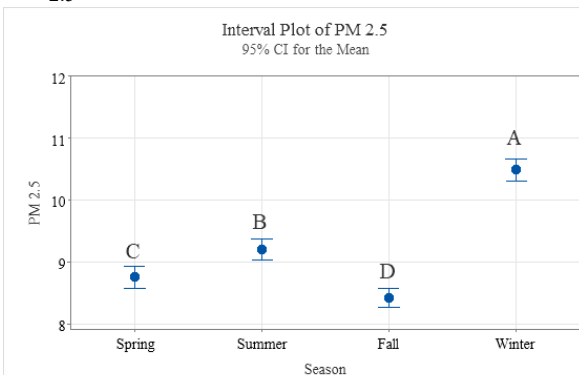
(b) Chronic non-cancer HQs

Elements	Upper ranges of HQs	Lower ranges of HQs	HQ ratios
As	2.33E-02	2.33E-02	1
Ba	4.02E-03	4.02E-03	1
Cd	6.01E-01	3.01E-01	2
Co	3.33E-03	3.33E-03	1
Cr	6.67E-04	3.33E-04	2
Hg	1.67E-02	1.67E-03	10
Mn	9.13E-02	1.52E-02	6
Ni	5.15E-02	2.86E-02	1.8
Pb	2.32E-02	2.32E-02	1
Se	3.44E-05	3.44E-05	1
V	6.03E-03	6.03E-03	1

Table S7. Contributions of each source to PM_{2.5}-bound elemental concentrations, CRs, and non-cancer HQs.

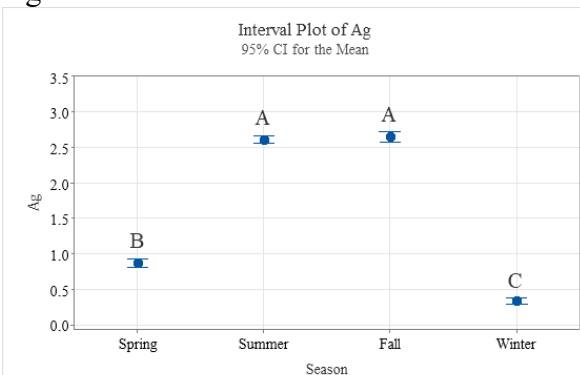
Factor	Contribution to PM _{2.5} element concentrations [rank] (24 elements involved)	Contribution to CR [rank] (6 elements involved)	Contribution to non-cancer HQ [rank] (11 elements involved)
Metal processing	27% [2]	52% [1]	60% [1]
Coal/heavy oil burning	44% [1]	19% [2]	16% [2]
Vehicular exhaust	3% [5]	19% [3]	12% [3]
Crustal dust	21% [3]	7% [4]	5% [5]
Vehicle tire and brake wear	5% [4]	3% [5]	7% [4]

PM_{2.5}



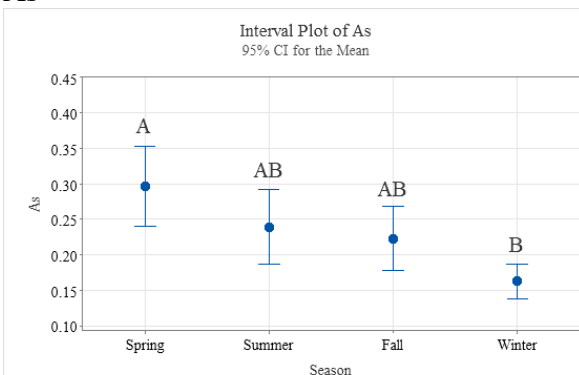
Individual standard deviations are used to calculate the intervals.

Ag



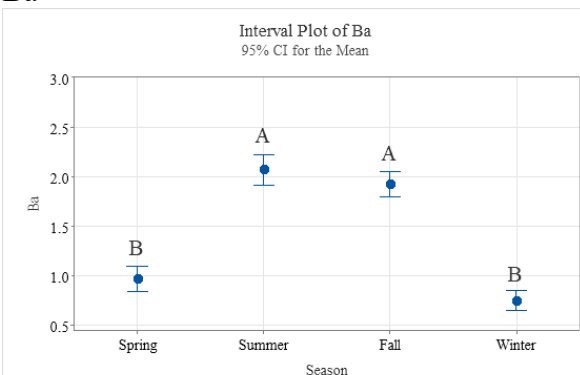
Individual standard deviations are used to calculate the intervals.

As



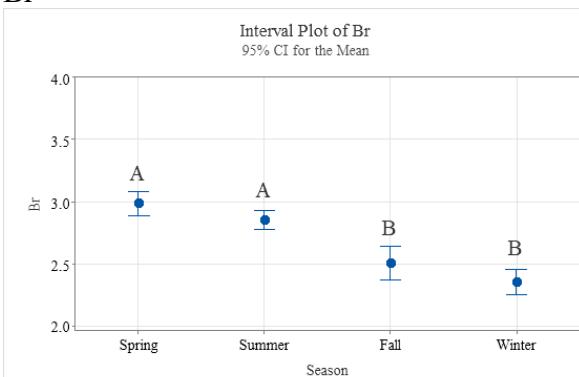
Individual standard deviations are used to calculate the intervals.

Ba



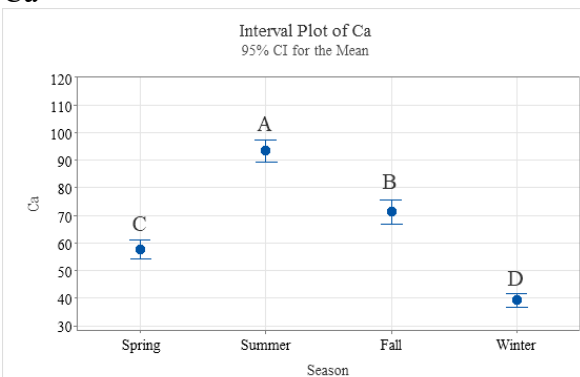
Individual standard deviations are used to calculate the intervals.

Br



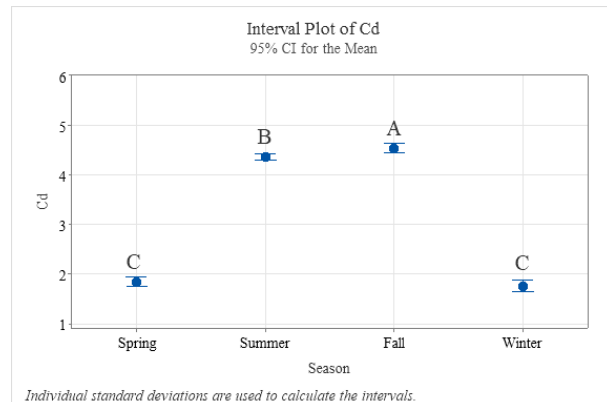
Individual standard deviations are used to calculate the intervals.

Ca

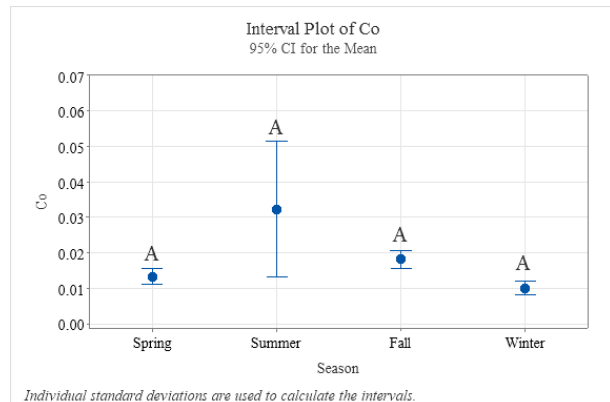


Individual standard deviations are used to calculate the intervals.

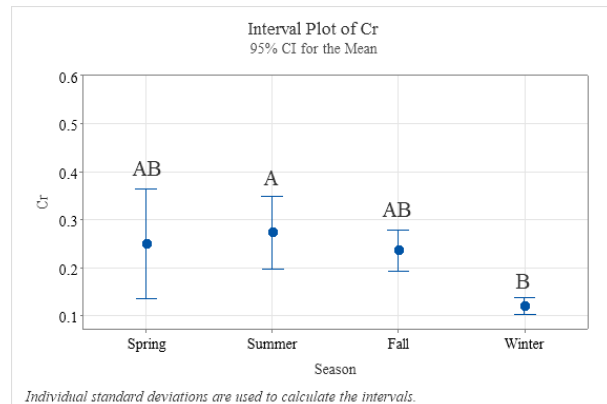
Cd



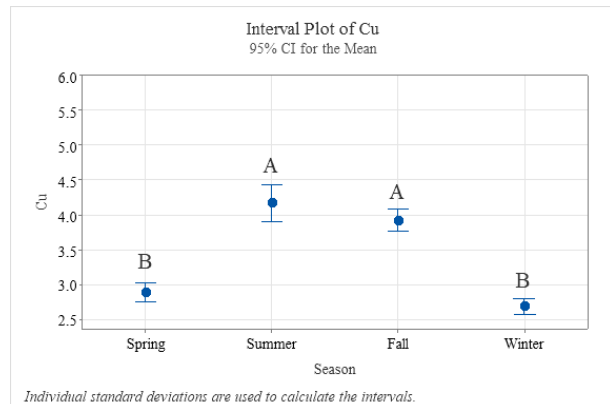
Co



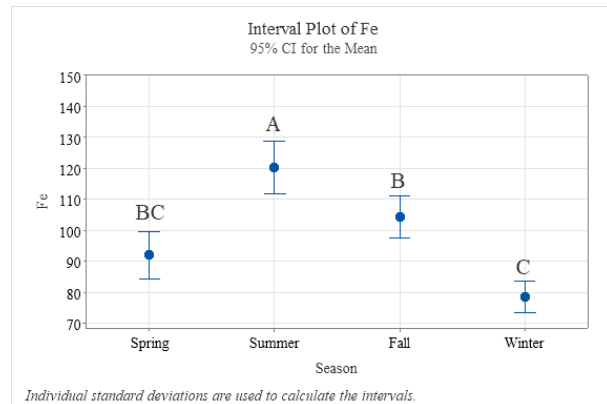
Cr



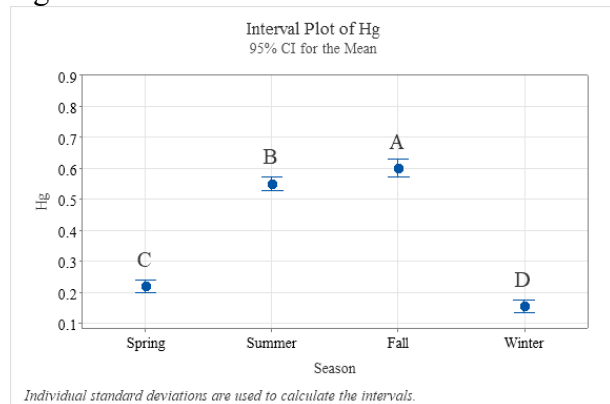
Cu

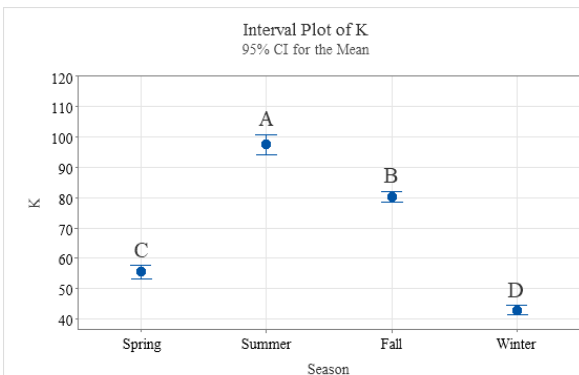


Fe

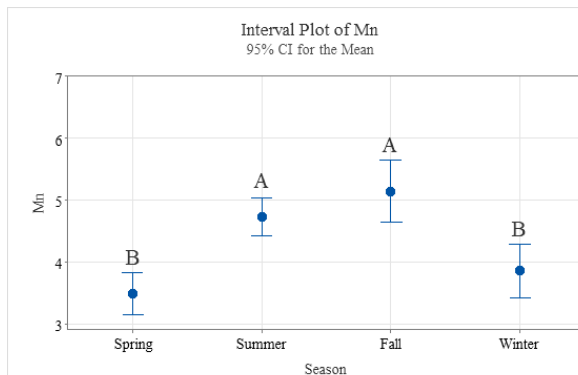


Hg

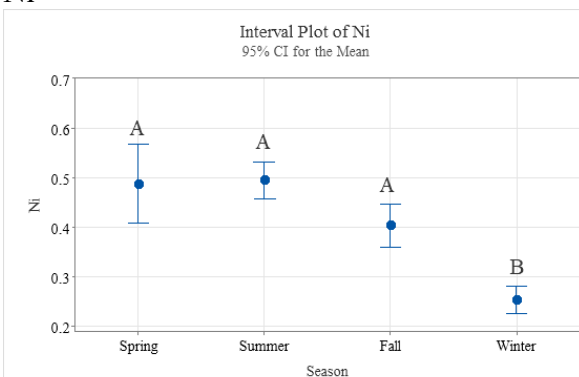


K

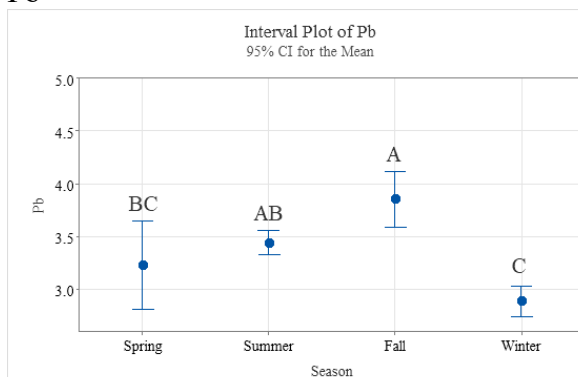
Individual standard deviations are used to calculate the intervals.

Mn

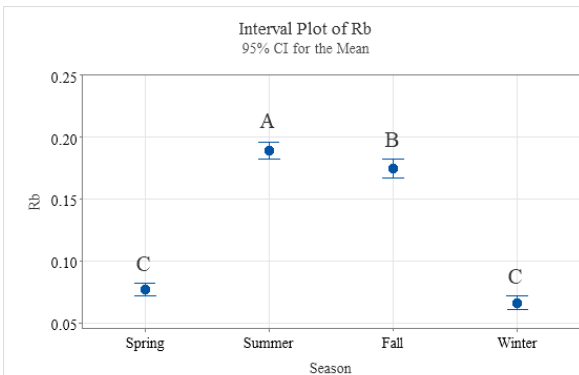
Individual standard deviations are used to calculate the intervals.

Ni

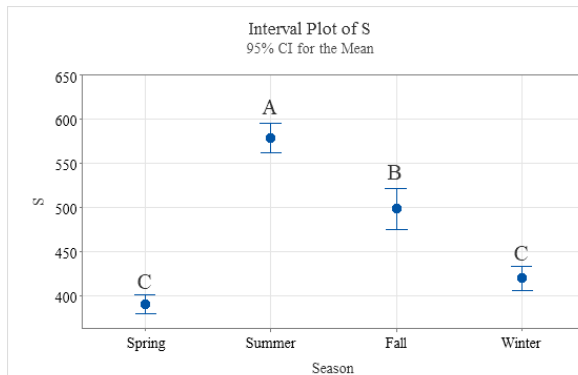
Individual standard deviations are used to calculate the intervals.

Pb

Individual standard deviations are used to calculate the intervals.

Rb

Individual standard deviations are used to calculate the intervals.

S

Individual standard deviations are used to calculate the intervals.

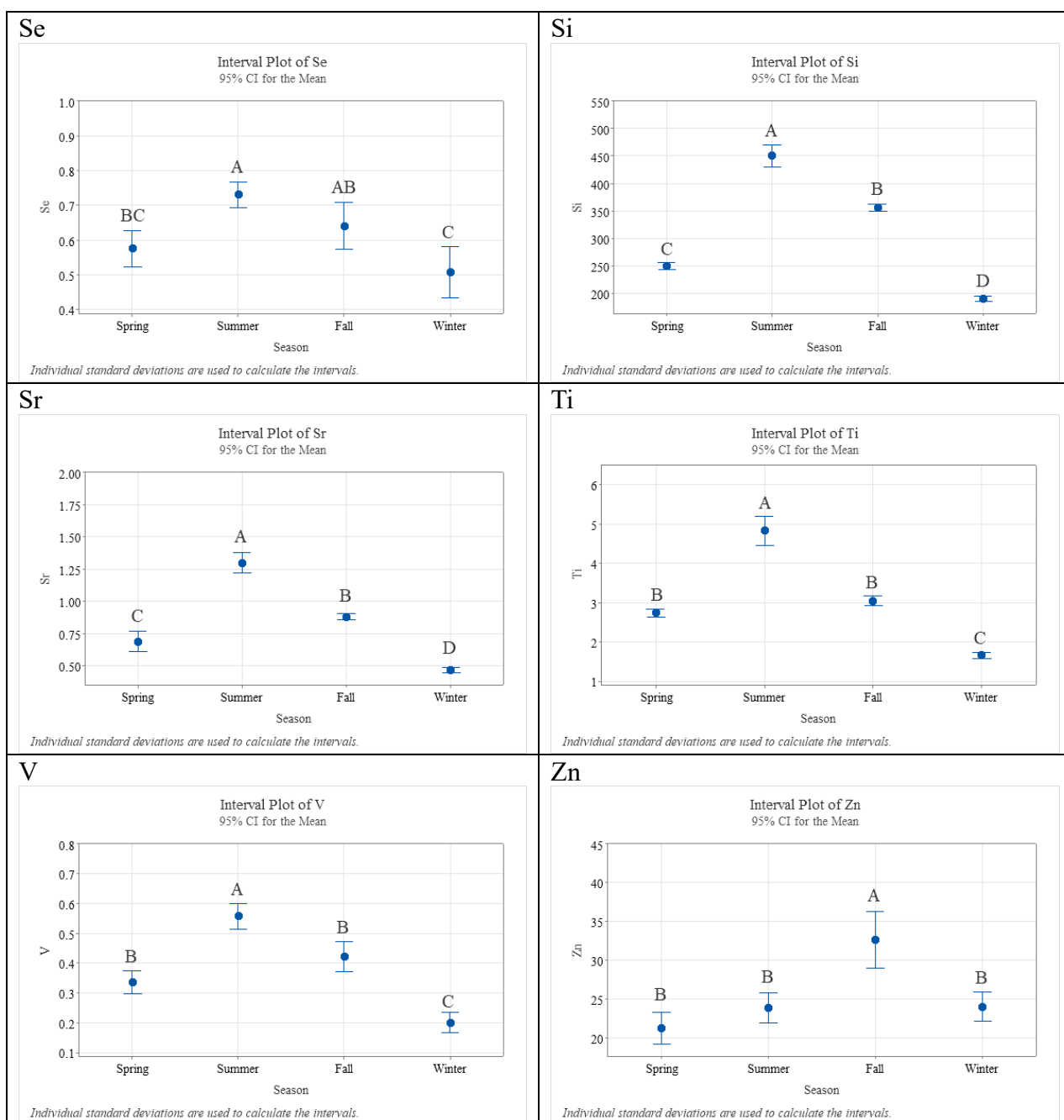
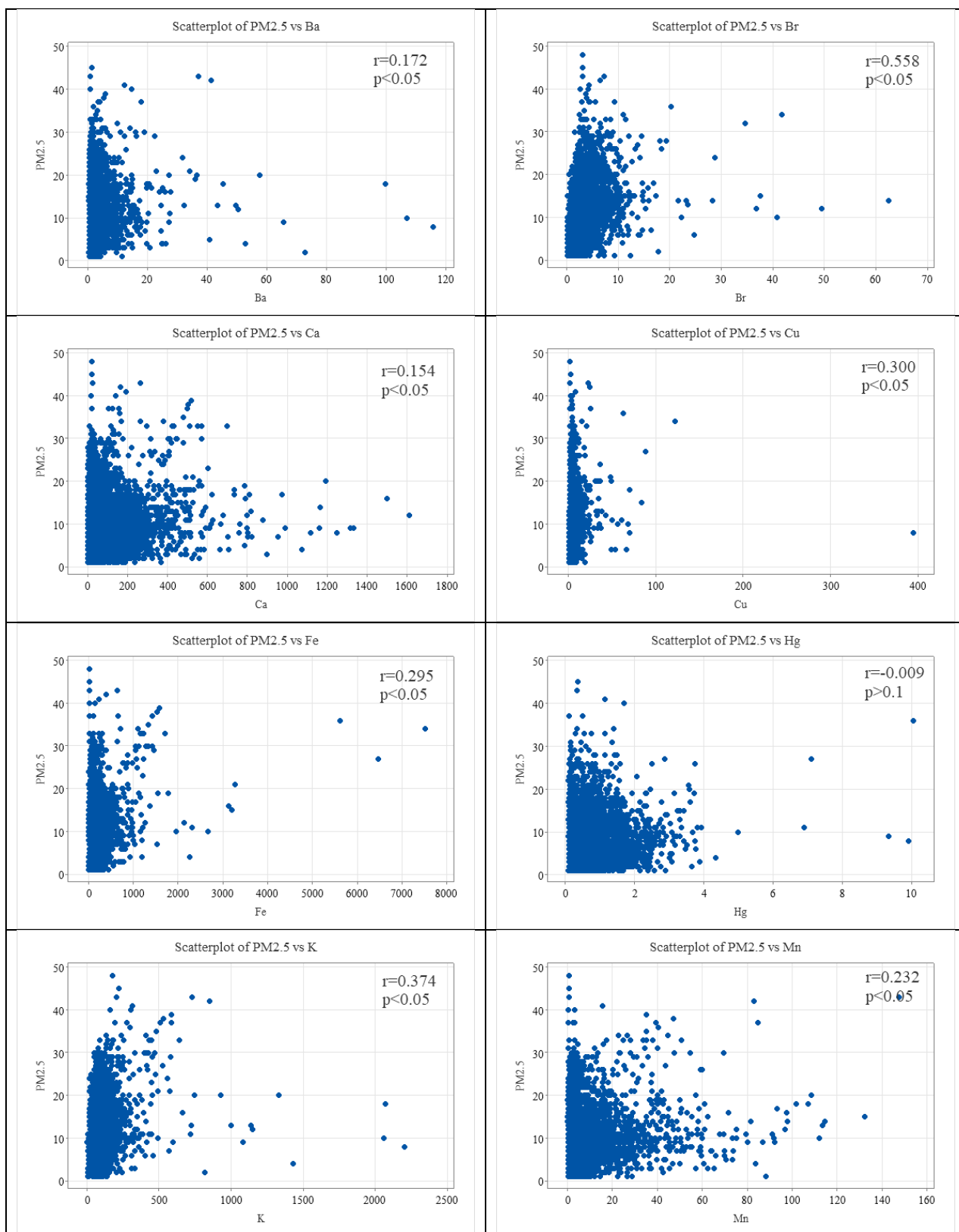


Figure S1. Seasonal variability of PM_{2.5} mass and PM_{2.5}-bound element concentrations (solid circles) and 95% confidence interval (error bars) in Windsor during April 2021-April 2023. The letters indicate Tukey's grouping.



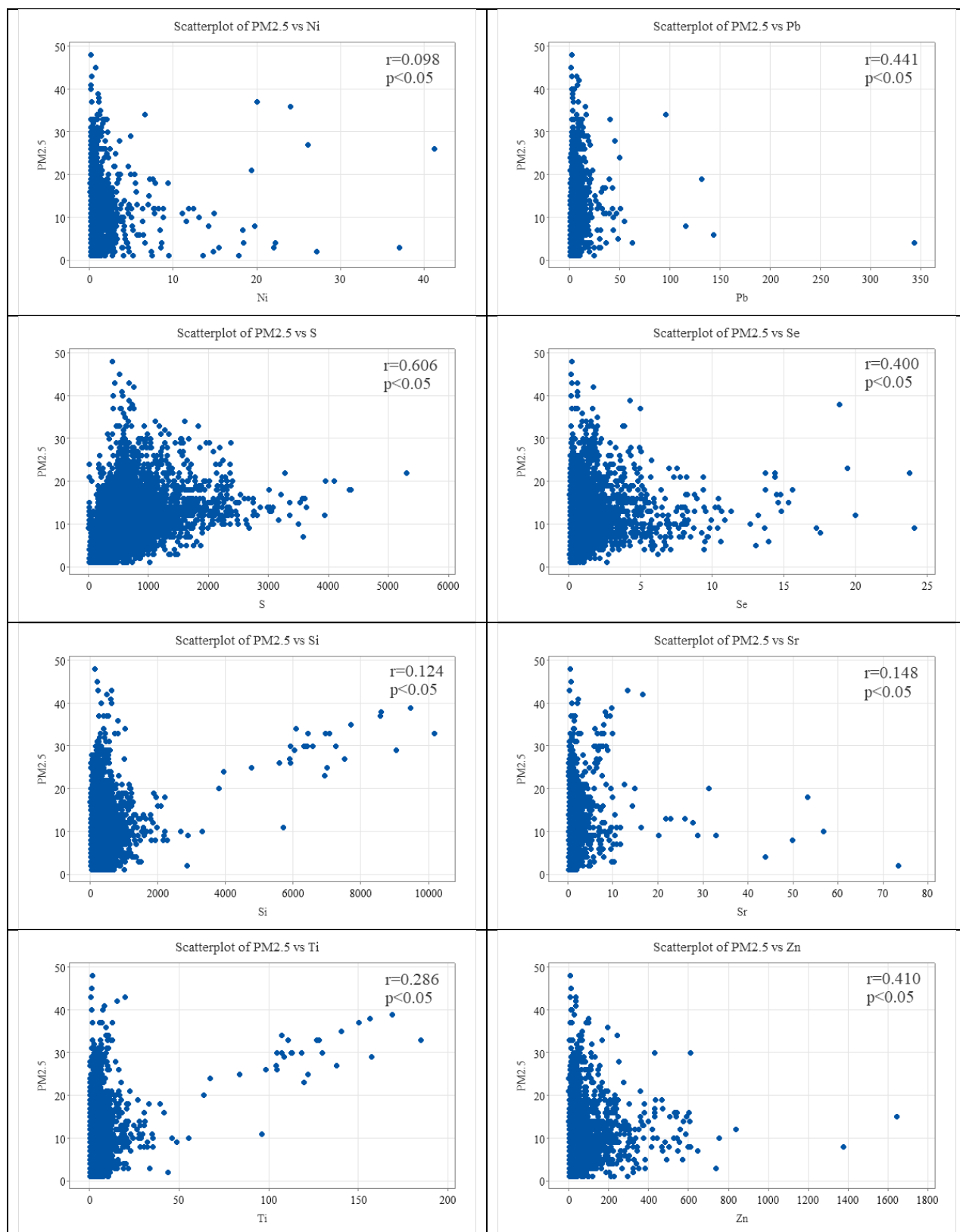
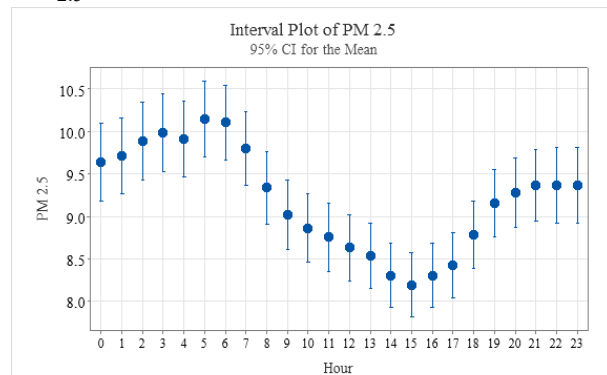


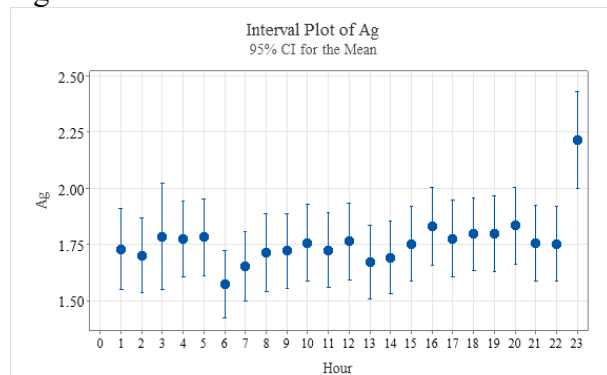
Figure S2. Scatter plots and Spearman correlation coefficients among concentrations of hourly PM_{2.5} mass ($\mu\text{g}/\text{m}^3$) and 16 selected elements (ng/m^3).

PM_{2.5}



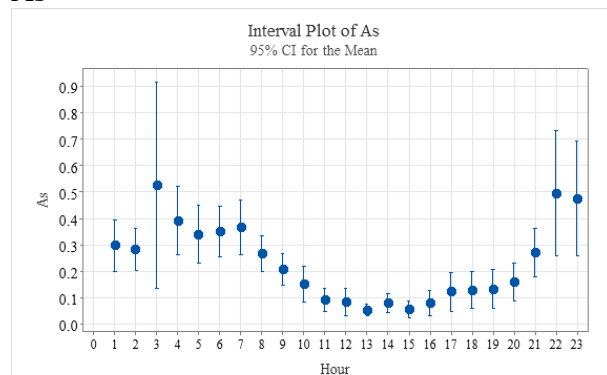
Individual standard deviations are used to calculate the intervals.

Ag



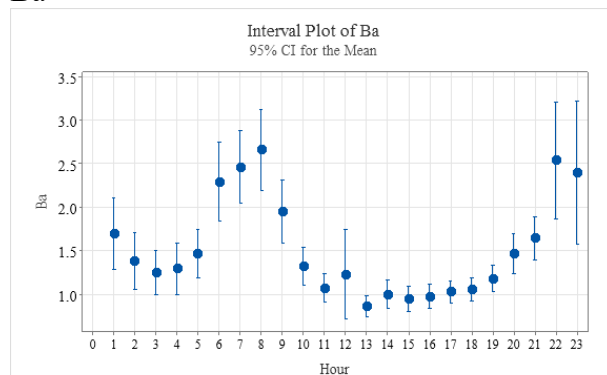
Individual standard deviations are used to calculate the intervals.

As



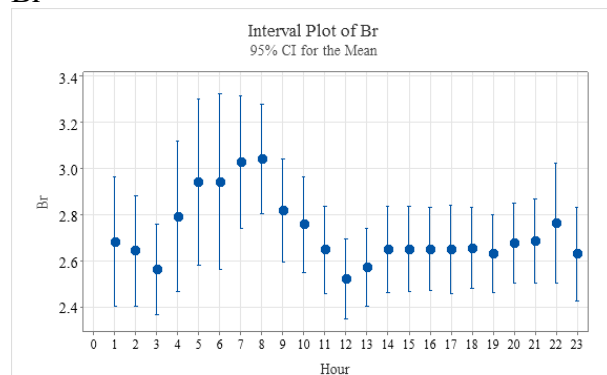
Individual standard deviations are used to calculate the intervals.

Ba



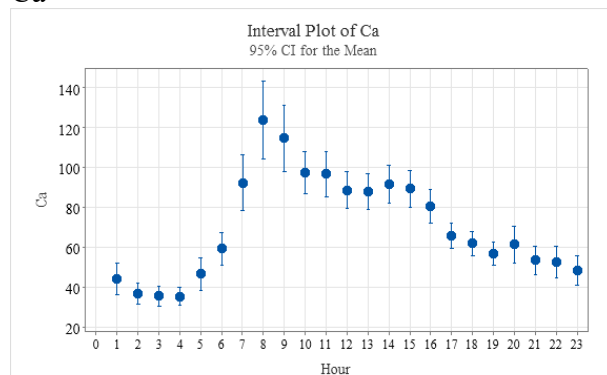
Individual standard deviations are used to calculate the intervals.

Br

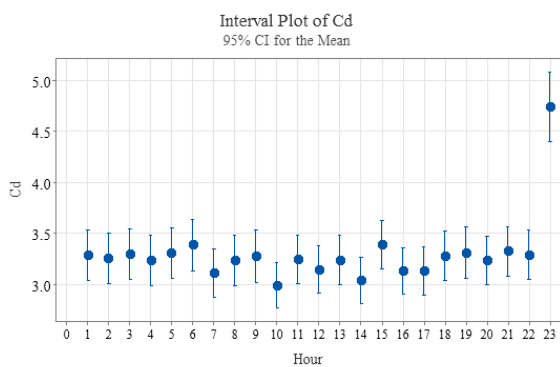


Individual standard deviations are used to calculate the intervals.

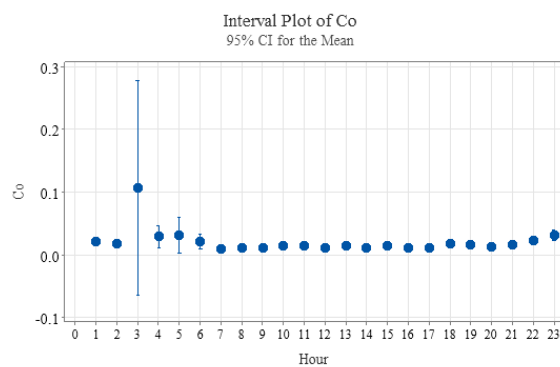
Ca



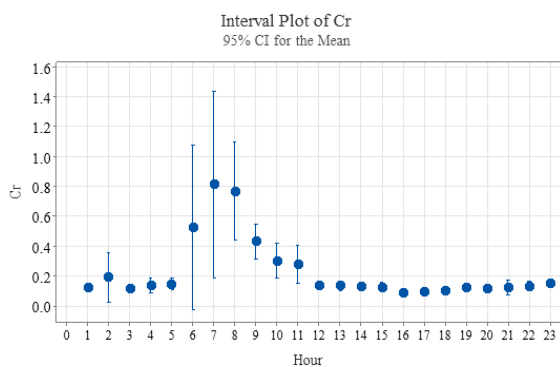
Individual standard deviations are used to calculate the intervals.

Cd

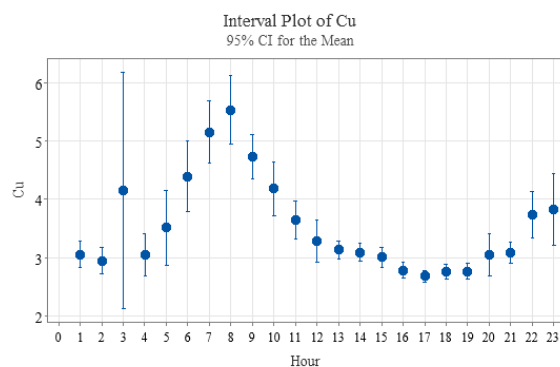
Individual standard deviations are used to calculate the intervals.

Co

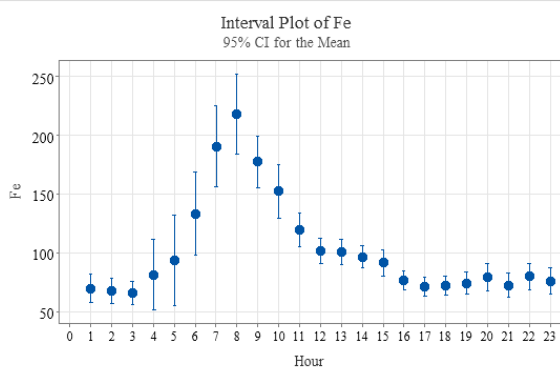
Individual standard deviations are used to calculate the intervals.

Cr

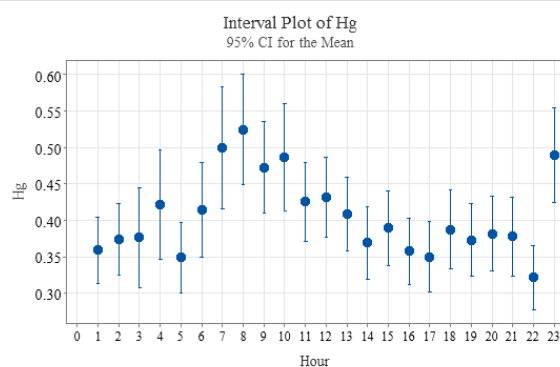
Individual standard deviations are used to calculate the intervals.

Cu

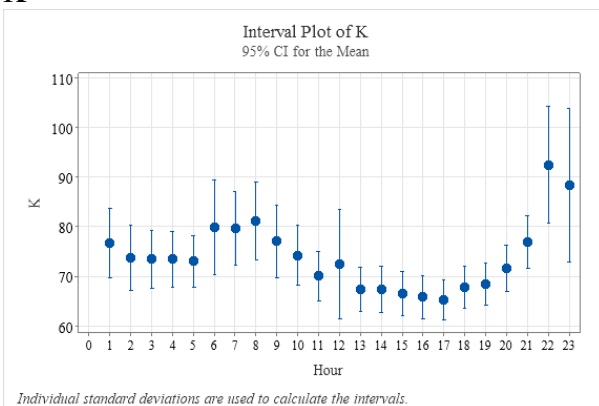
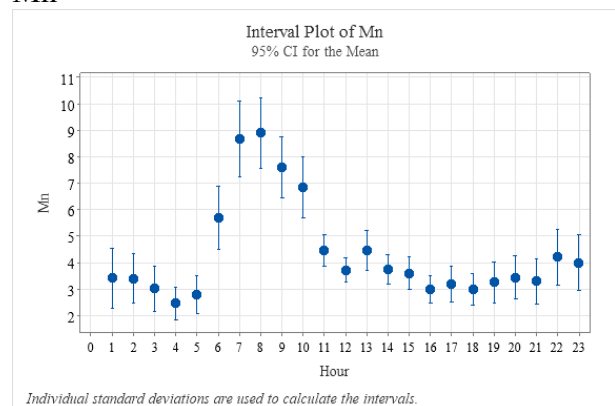
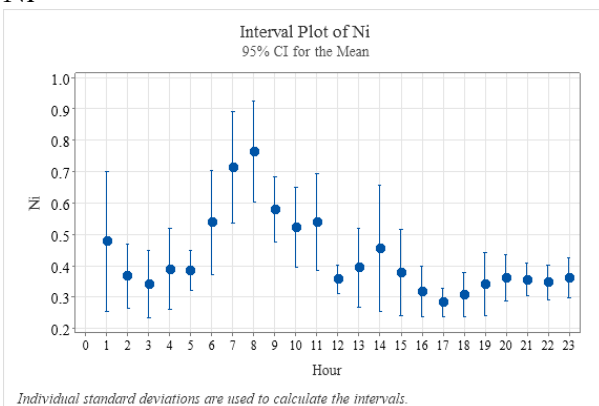
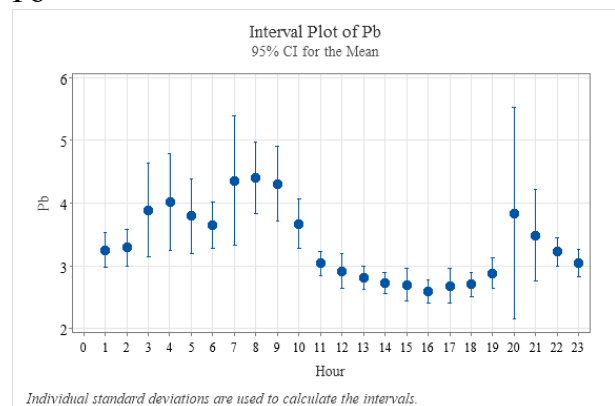
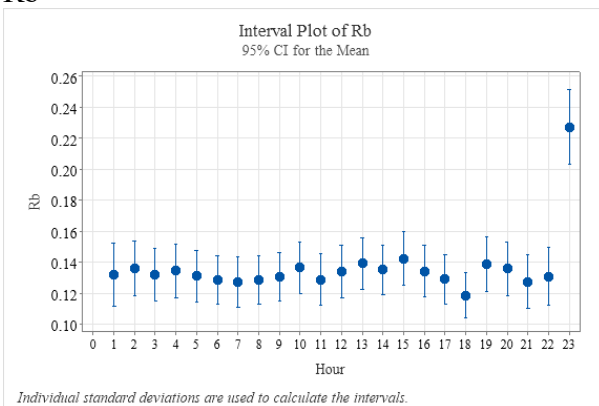
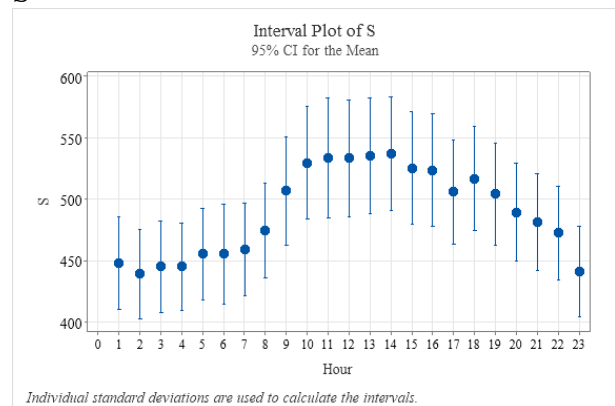
Individual standard deviations are used to calculate the intervals.

Fe

Individual standard deviations are used to calculate the intervals.

Hg

Individual standard deviations are used to calculate the intervals.

K**Mn****Ni****Pb****Rb****S**

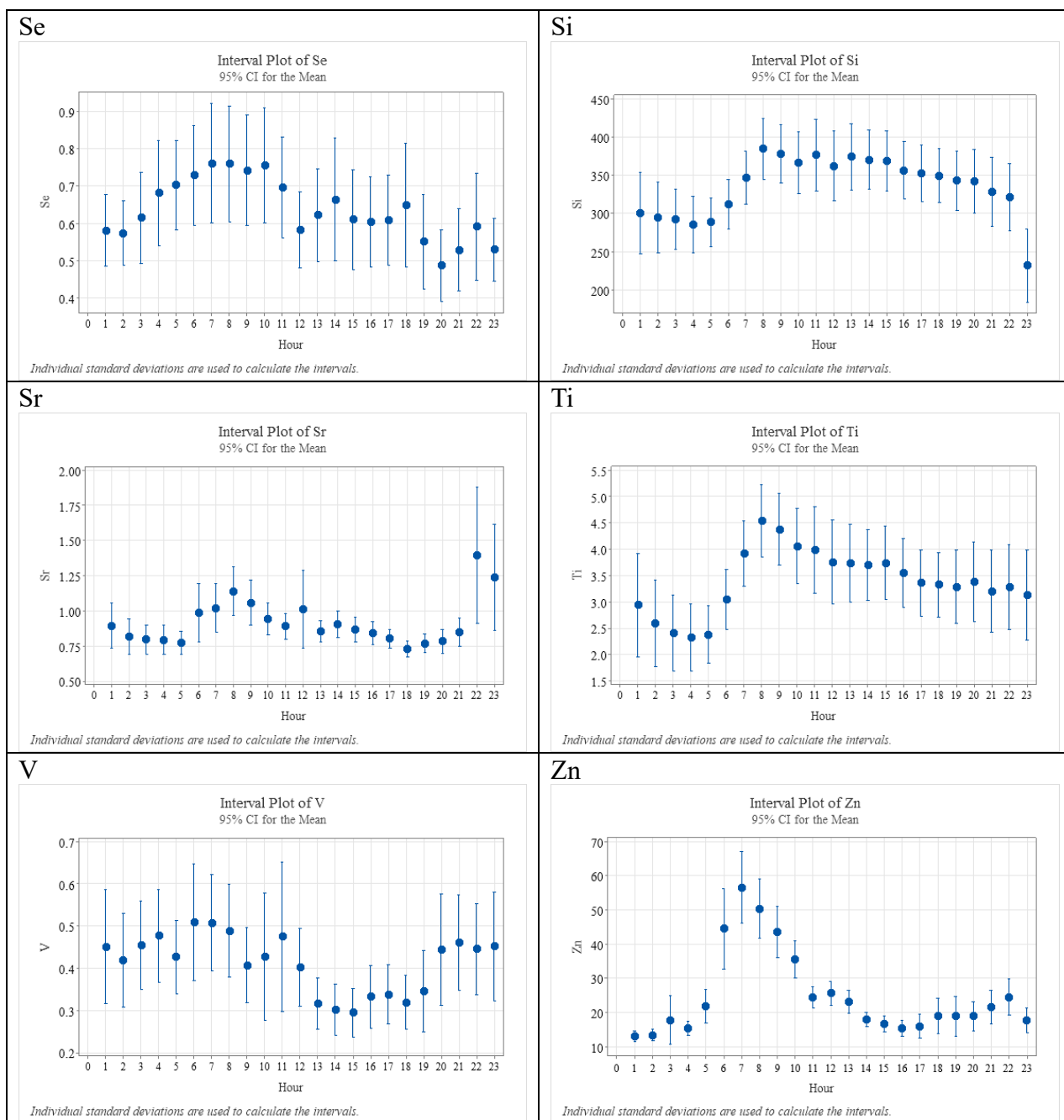
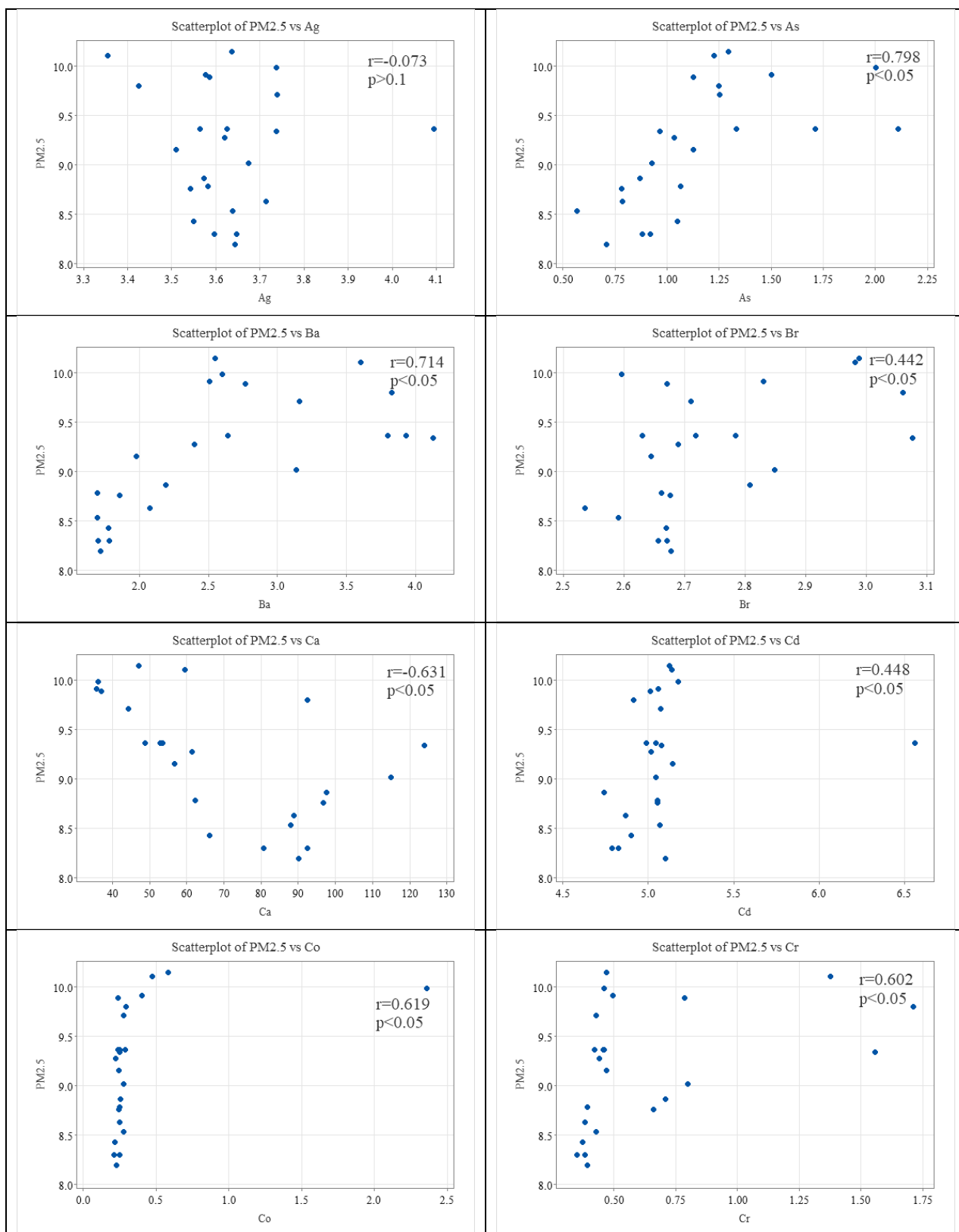
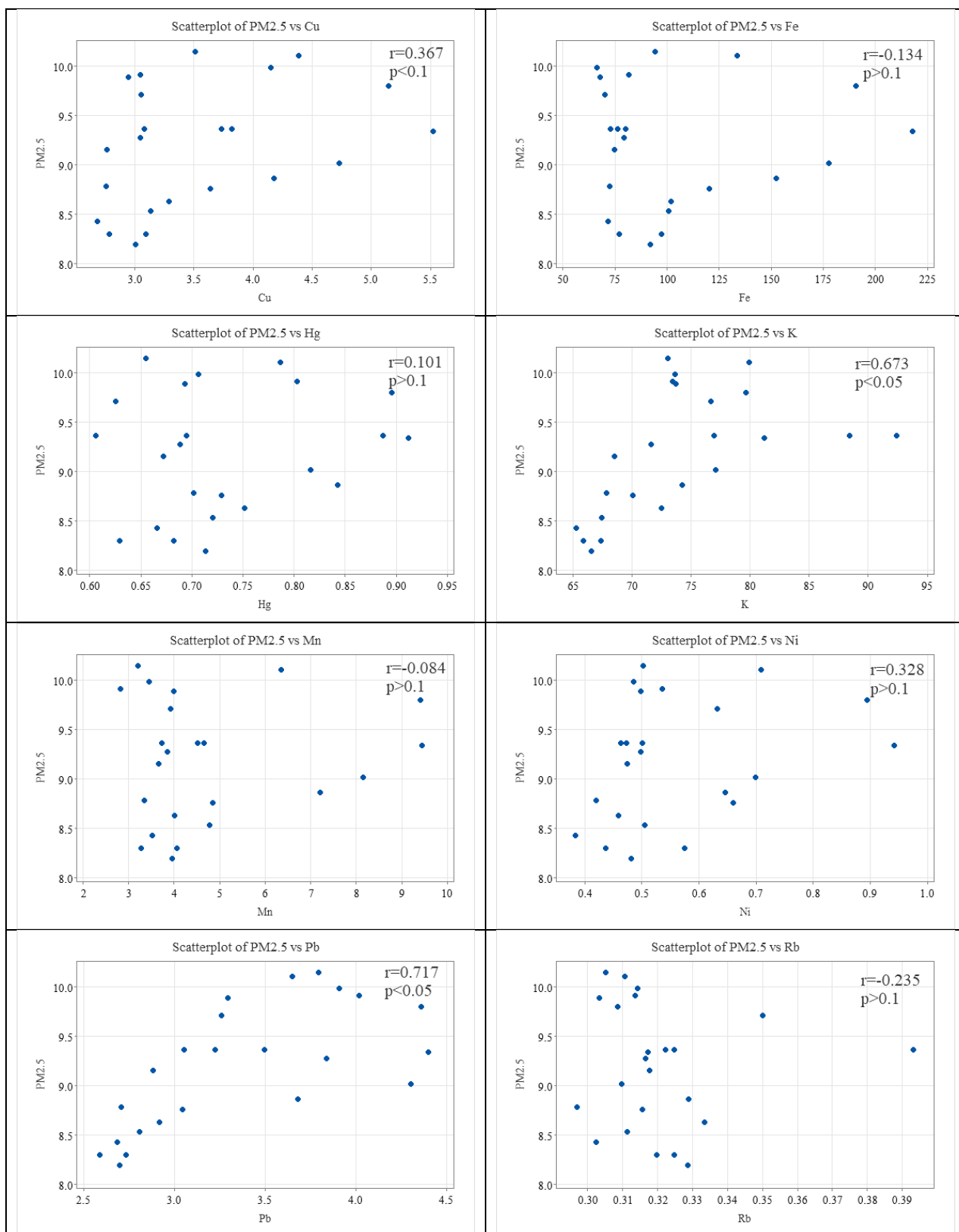


Figure S3. Diurnal variability of PM_{2.5} mass and PM_{2.5}-bound element concentrations (solid circles) and 95% confidence interval (error bars) in Windsor during April 2021-April 2023.





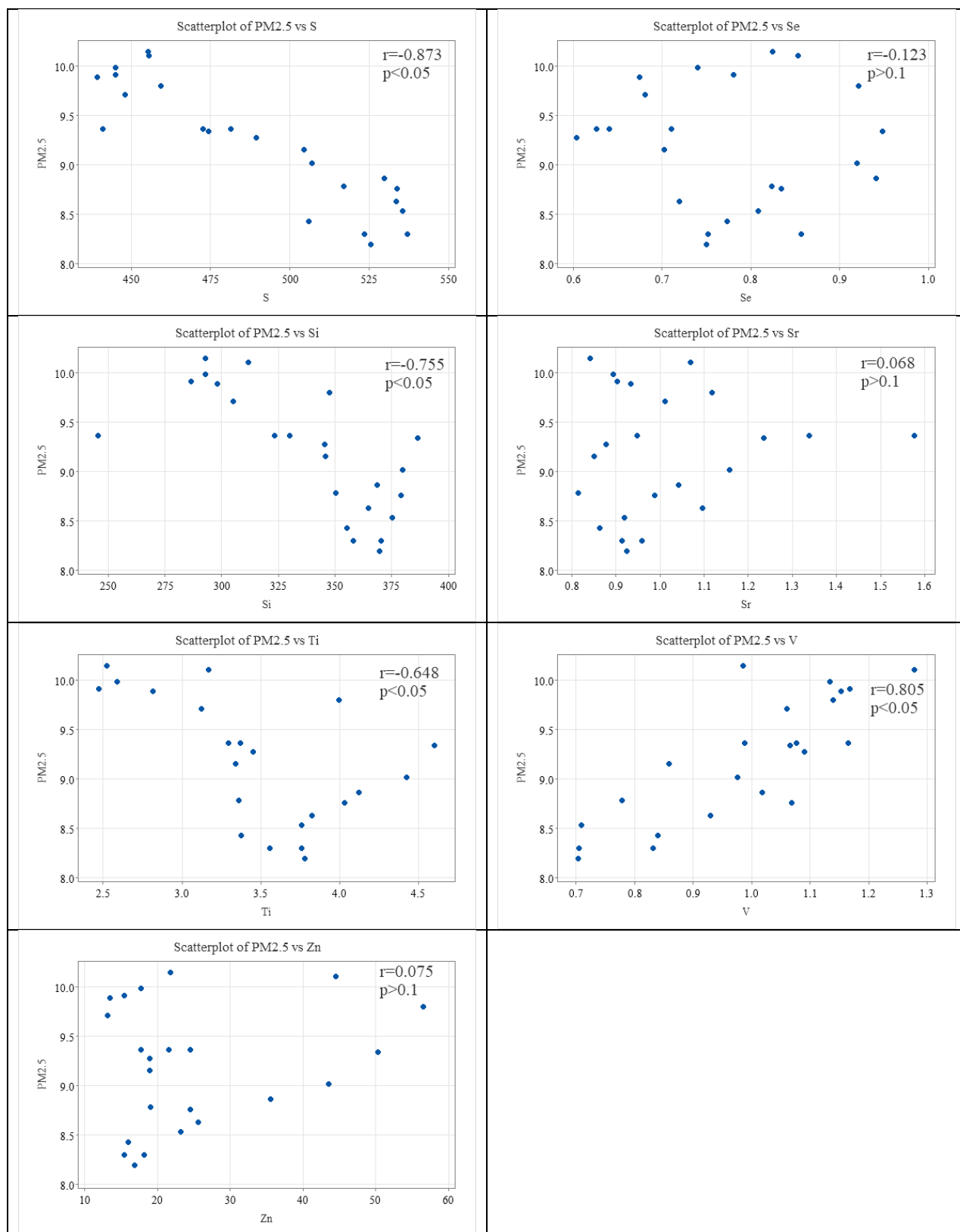


Figure S4. Scatter plots and Spearman correlation coefficients of hour-of-day mean concentration among PM_{2.5} mass ($\mu\text{g}/\text{m}^3$) and 23 elements (ng/m^3).

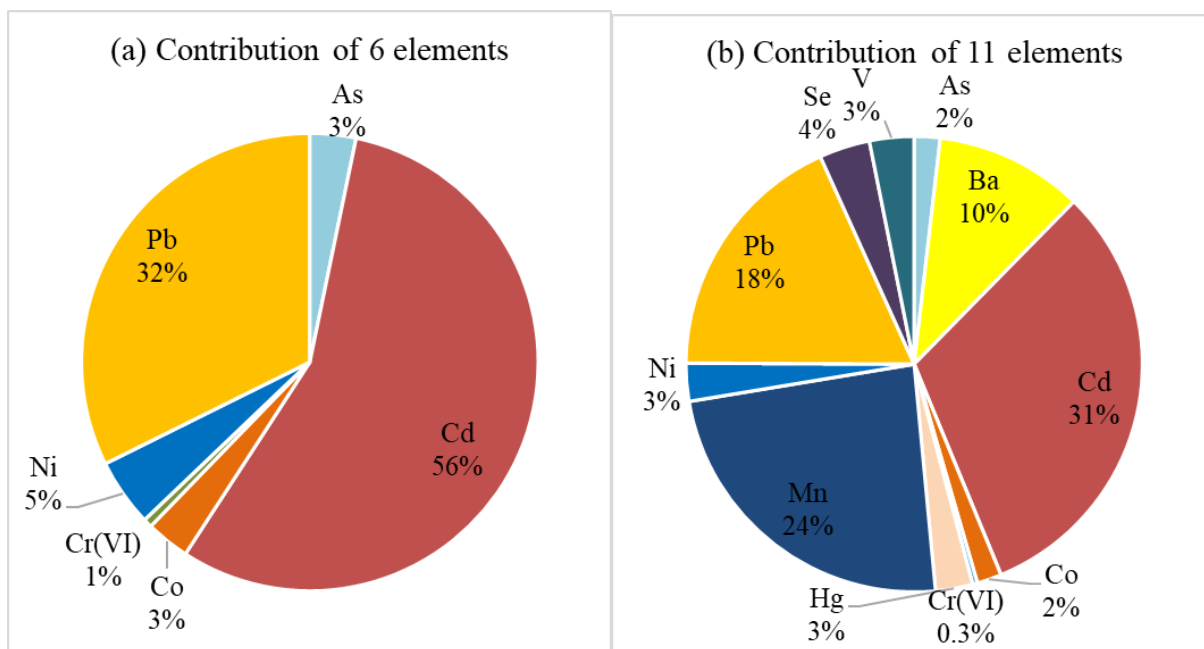


Figure S5. Concentration contributions of (a) six elements used to calculate cancer risks, and (b) 11 elements used to calculate non-cancer hazard quotients.

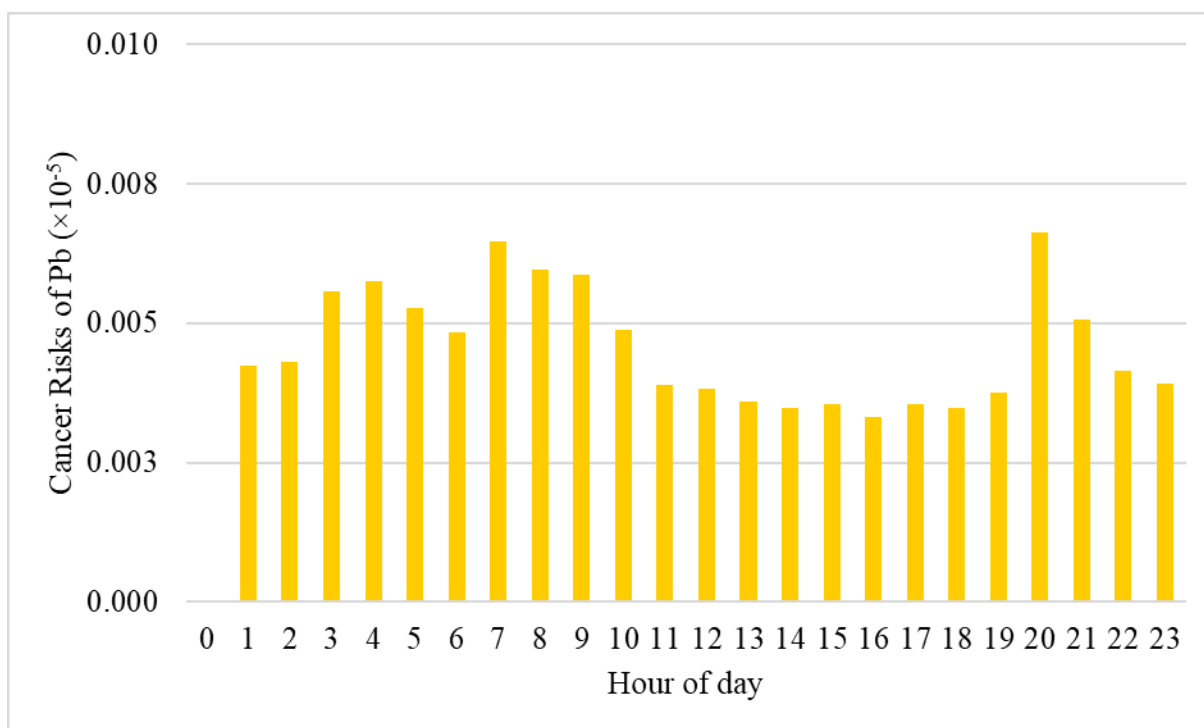


Figure S6. Diurnal variability of incremental lifetime CRs of Pb.

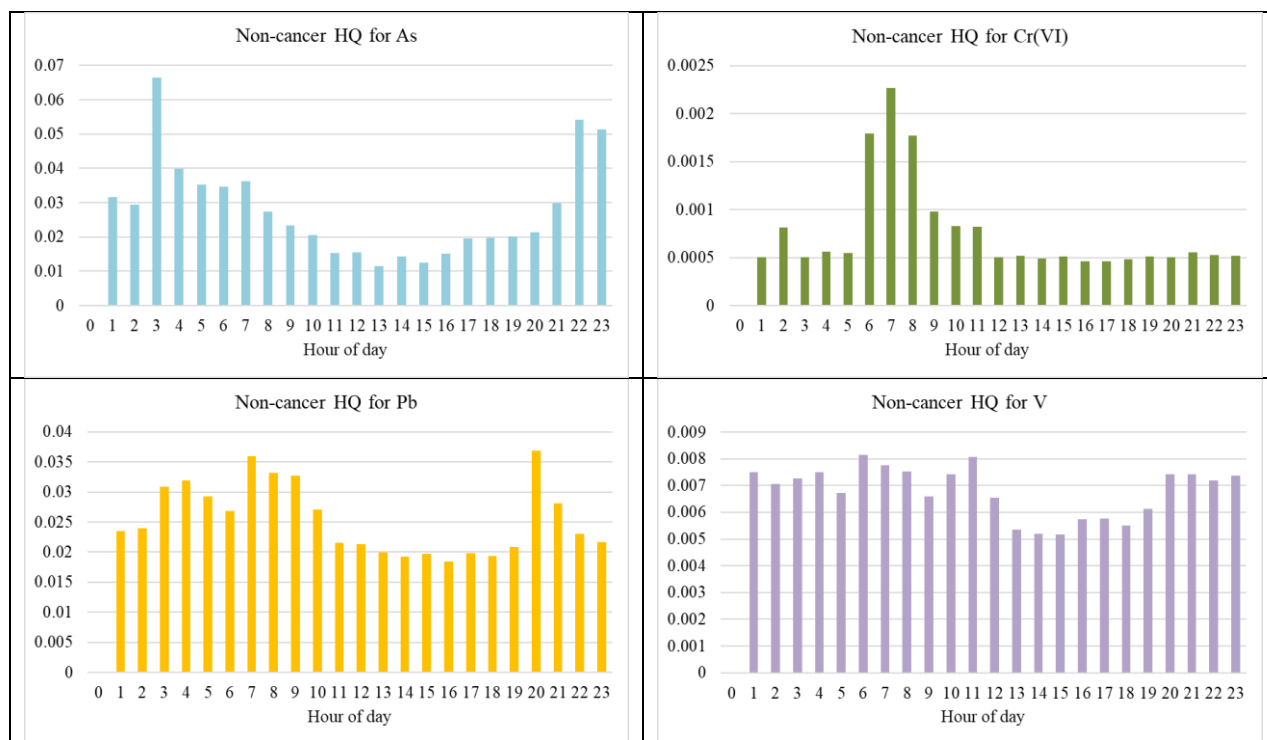


Figure S7. Diurnal variability of chronic non-cancer HQs for As, Cr(VI), Pb and V.

References

1. United States Department of Health and Human Service (DHHS), 2021. 15th Report on Carcinogens. https://ntp.niehs.nih.gov/sites/default/files/ntp/roc/content/listed_substances_508.pdf. Accessed on January 16, 2025.
2. United States Environmental Protection Agency (USEPA) (2019). IRIS assessments. https://cfpub.epa.gov/ncea/iris_drafts/atoz.cfm?list_type=alpha. Accessed on January 16, 2025.
3. World Health Organization (WHO), (2024). IARC monographs on the identification of carcinogenic hazards to humans. <https://monographs.iarc.who.int/list-of-classifications>. Accessed on January 16, 2025.
4. California Office of Environmental Health Hazard Assessment (OEHHA), (2024). Chemicals. <https://oehha.ca.gov/chemicals>. Accessed on January 16, 2025.
5. Health Canada (HC), (2021). Federal Contaminated Site Risk Assessment in Canada: Toxicological reference values (TRVs). https://publications.gc.ca/collections/collection_2021/sc-hc/H129-108-2021-eng.pdf. Accessed on January 16, 2025.
6. Agency for Toxic Substances and Disease Registry (ATSDR), (2024). Minimal Risk Levels (MRLs) for Hazardous Substances. <https://wwwn.cdc.gov/TSP/MRLS/mrlslisting.aspx>. Accessed on January 16, 2025.

7. United States Environmental Protection Agency (USEPA) (1997). Health Effects Assessment Summary Tables, FY 1997 Update.
<https://rais.ornl.gov/documents/HEAST1997.pdf>. Accessed on January 16, 2025.
8. Ontario Ministry of the Environment, Conservation and Parks (MECP), (2020). Ambient Air Quality Criteria. <https://files.ontario.ca/mecp-ambient-air-quality-criteria-list-en-2020-05-01.pdf>. Accessed on January 16, 2025.
9. United States Environmental Protection Agency (USEPA) (2024). NAAQS Table.
<https://www.epa.gov/criteria-air-pollutants/naaqs-table>. Accessed on January 16, 2025.
10. California Office of Environmental Health Hazard Assessment (OEHHA), (1999). Air Toxics Hot Spots Program Risk Assessment Guidelines.
<https://oehha.ca.gov/media/downloads/crn/acuterel.pdf>. Accessed on January 16, 2025.
11. California Office of Environmental Health Hazard Assessment (OEHHA), (2021). Air assessment of air contaminants.
<https://www.sdapcd.org/content/dam/sdapcd/documents/capp/meetings/portside-csc/032119/032119-OEHHA-Risk-Assessments.pdf>. Accessed on January 16, 2025.
12. Zhang, T., Su, Y., Debosz, J., Noble, M., Munoz, A., & Xu, X. (2023). Continuous Measurements and Source Apportionment of Ambient PM_{2.5}-Bound Elements in Windsor, Canada. *Atmosphere*, 14(2), 374.