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Measurement report: Seasonal trends and chemical speciation of chromium(III/VI) in different fractions of urban particulate matter – a case study of Radom, Poland

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Supplementary figures

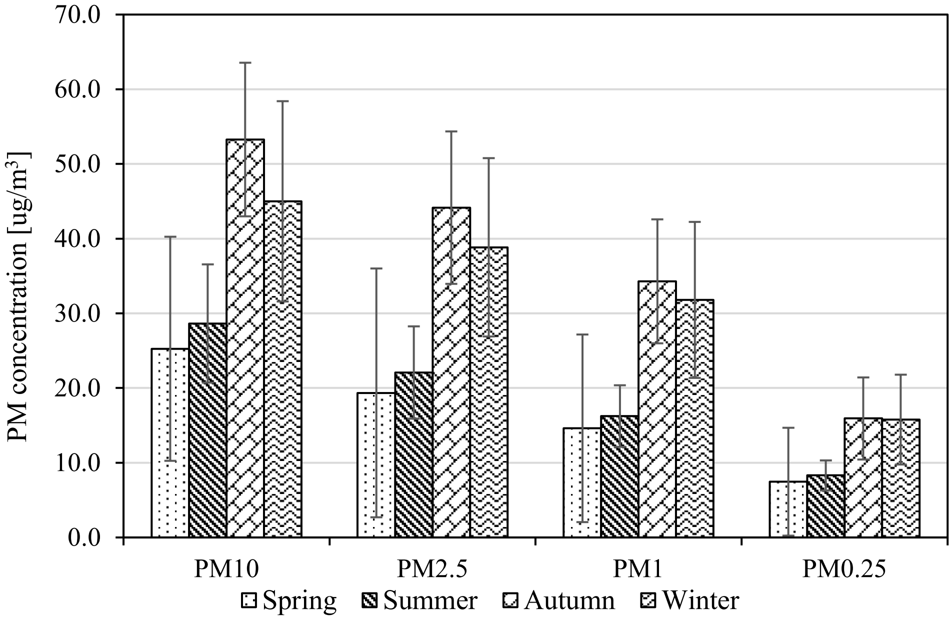

Figure S1. The seasonal variations of particulate matter concentrations suspended in urban air.

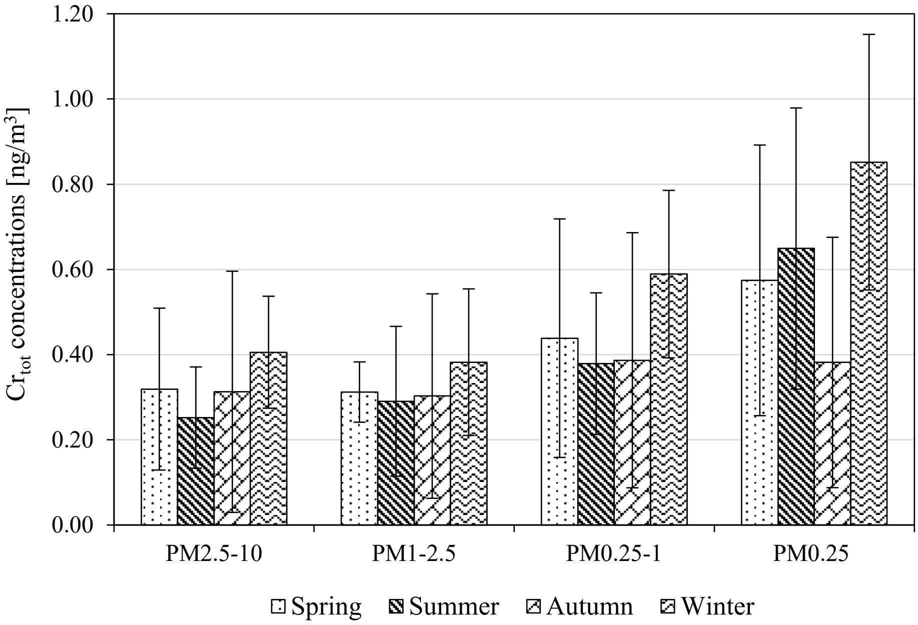

Figure S2. Cr$_{tot}$ concentrations in the particular fractions of the particulate matter studied during the year.

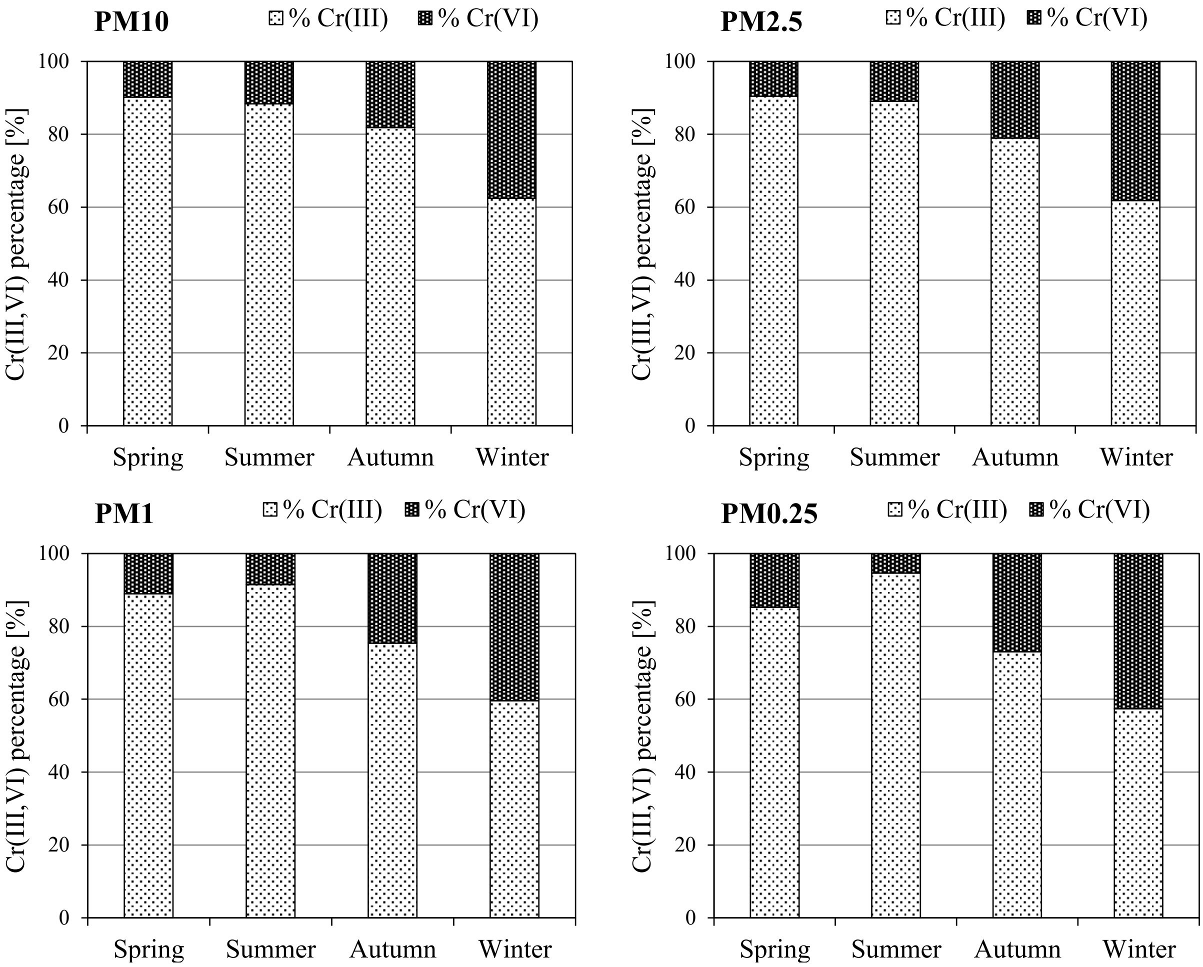

Figure S3. Chromium(III/VI) speciation in the airborne particulate matter in Radom over a year.

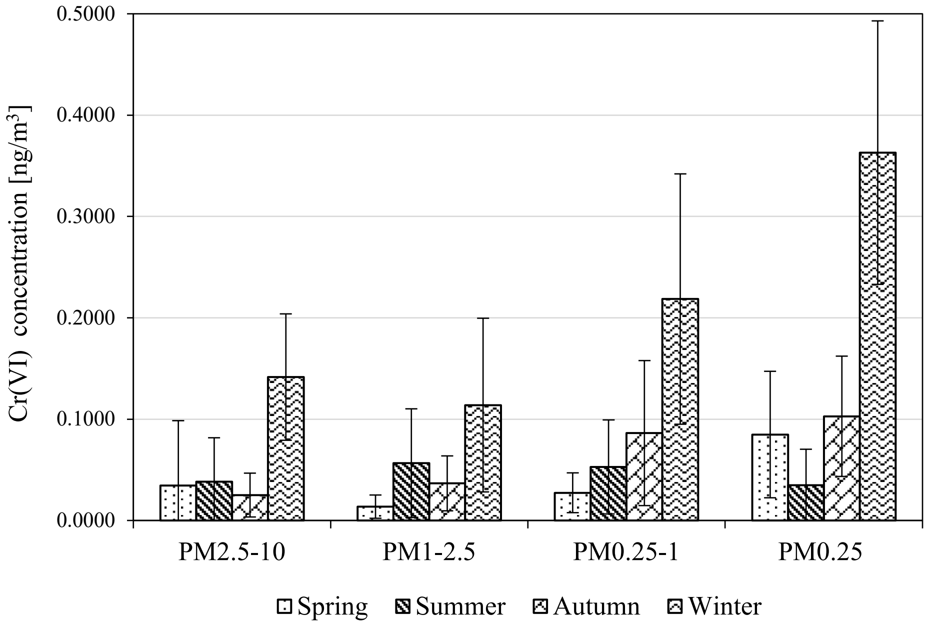

Figure S4. Cr(VI) concentrations in the particulate matter fractions studied during a year.

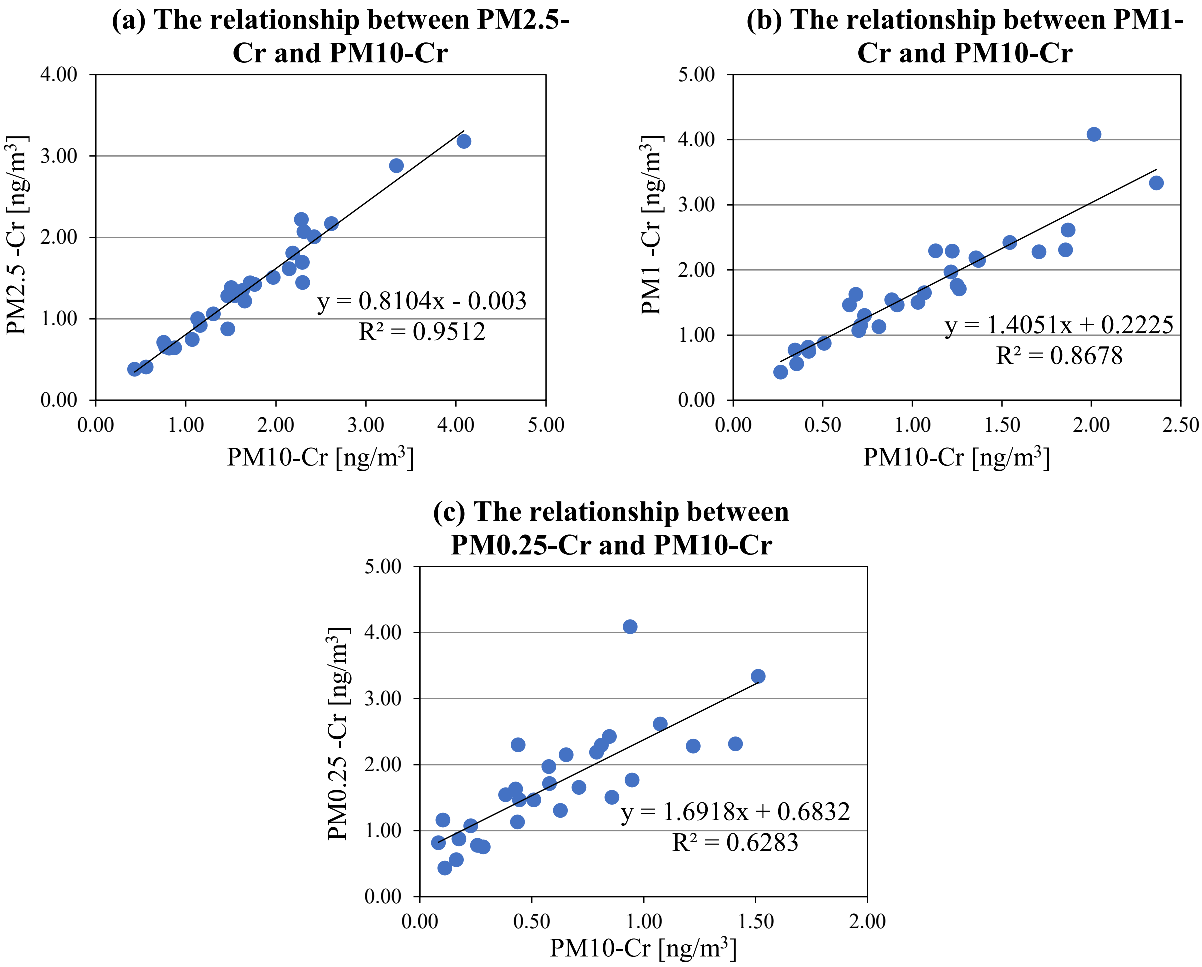

Figure S5. Correlation curves between total chromium concentration in PM10 and in finer airborne particulate matter fractions (a) PM2.5 (b) PM1 and (c) PM0.25.

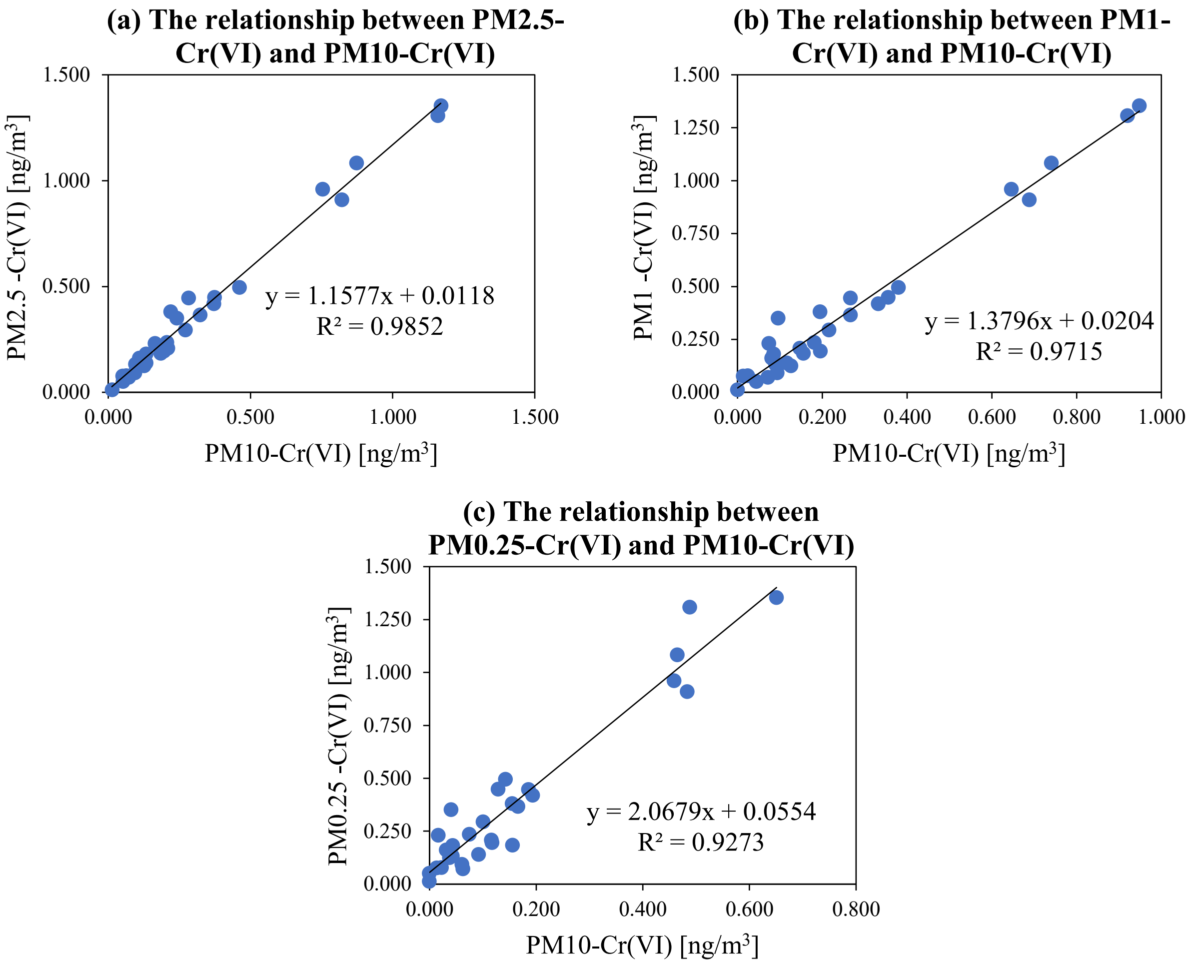

Figure S6. Correlation curves between chromium(VI) concentration in PM10 and in finer airborne particulate matter fractions: (a) PM2.5. (b) PM1 and (c) PM0.25.

Supplementary tables

Table S1. The concentration of chromium in PM according the literature data.

Location (City/Country)	Sampling site	Fraction	Concentration (mean ± SD) Cr [ng/m^3]	Cr(VI) [ng/m^3]	Reference
Agra, India	agricultural site	PM2.5	19.3	-	[Sah et al., 2019]
Baoding, China	rural-urban fringe zone	PM2.5	33.5 (winter); 6.3 (summer)		[Xie et al., 2019]
Beijing and Qingdao, China	urban area, the anthropogenic emission sources	PM2.5	3.831 (Beijing) 3.707 (Qingdao)	0.140±0.065 0.091±0.073	[Wang et al., 2023]
Beijing, China	winter haze days	PM2.5	41.6		[Duan et.al., 2014]
Beijing, China	urban area	TSP PM2.5	21.4 6.9		[Schleicher et al., 2011]
Budapest, Hungary	an area with high traffic density	PM10	5.7 (winter) 7.7 (summer)		[Muránszky et al., 2011]
Edinburgh, U.K.	urban background air in the city	PM2.5 PM10	0.49 1.6		[Heal et al., 2005]
Ewekoro, Nigeria	industrial town	PM2.5	11.4		[Anake et al., 2020
Flemish region, Belgium	near and far from an anthropogenic source	PM10	96 34	1.2 5.2	[Tirez et al., 2011]
Guangzhou, China	urban area	PM2.5	7.693		[Feng et al., 2009]
Hamilton, Canada	industrial areas	PM10	5-19	0.1-1.6 av. 0.55	[Bell end Hipfner, 1997]
Isfahan, Iran	industrial areas	TSP	20.6-31.7	5.4 – 8.2	[Talebi, 2003]
Katowice, Poland	urban traffic site	PM1 PM2.5	6.9±2.0 (winter); 5.5±0.6 (summer) 8.5±2.1 (winter) 8.2±4.8 (summer)		[Widziewicz et al., 2016]
Katowice, Poland	traffic emissions, urban area	PM1 PM2.5 PM10	4.48 (highway); 6.73 (crossroads); 1.87 (highway); 2.05 (crossroads); 2.39 (highway); 2.86 (crossroads)		[Rogula-Kozłowska, 2015]
Ljubljana, Slovenia	urban background location in the city	PM10	6.22		[Turšič et al., 2008]
Nanjing, China	industrial zone and main transportation hub	PM2.5	26.61±6.718 (Xianlin); 26.14±6.781 (Gulou)		[Li et al., 2015]
New Jersey (Meadowlands district), USA	close to a major U.S. Highway	PM2.5		0.13±0.06 (summer) 0.02±0.01 (winter)	[Yu et al., 2014]
New Jersey, USA	urban area	PM10		0.94-1.41 ng/m^3 (winter) 0.86-1.56 ng/m^3 (summer)	[Huang et al., 2014]
Ota, Nigeria	industrial estate	PM2.5	9.03		[Anake at al., 2017]
Regensburg, Germany	urban areas	TSP	0.21-1.58	0.16-1.22	[Nusko and Heuman, 1997]
Rome and Fontechiari, Italy	urban area and a rural environment	PM2.5 PM10	3.1 (rural) 5.7 (urban) 2.9 (rural) 7.4 (urban)		[Astolfi et al., 2006]

Rome and Tunis Italy	industrial areas and peri-urban site	PM10	2 to 5 (peri-urban site); 6 to 25 (industrial area)	< LOD (peri-urban site); 0.5-2.8 (industrial area)	[Catrambone et al., 2013]
San Nicolas, Argentina	suburban influenced by road transport	PM10	17.0±16.0 (winter) 11.0±6 (summer)		[Fujiwara et al., 2006]
Santiago, Chile	industrial zone and peripheral urban site	PM10	14.25 (industrial zone); 9.33 (peripheral urban site)		[Rubio et al., 2018]
Santiago, Chile	urban areas polluted by anthropogenic sources	PM10	240 (1997); 920 (2003)	5.0	[Richter at al., 2007]
Sihwa, Banwol, Ulsan, Yeosu, Onsan, Gumi, Deasan, Pohang, Korea	industrial areas and neighboring residential areas			0.09 -1.4	[Kang et al., 2016]
Singapore, Singapore	haze and non-haze	PM2.5	117 (haze); 34.8 (non-haze)		[Betha et al., 2014]
Sydney, Australia	residential industrial			0.14 0.2-1.3	[Li et al., 2002]
Telde, Gran Canaria, Spain	urban area	TSP	0.702		[Cancio et al., 2013]
Ulaanbaatar, Mongolia	urban area, anthropogenic sources	PM2.5 PM2.5-10	7.4-36.5 (av. 14.9) 3.5-12.0 (av. 8.83)		[Gunchin et al., 2021]
Upper Silesia, Poland	industrial zone near power plant	PM1	8.6		[Zajusz-Zubek et al., 2015]
Upper Silesia, Poland	power plant	PM2.5	7.8		[Zajusz-Zubek and Mainka, 2015]
Volos, Greece	harbor activities	PM10	4.48±2.36 (2014) 4.83±2.51 (2015)		[Manoli et al., 2017]
Welgegund, western Bushveld Complex, South Africa	industrial area	PM2.5 PM2.5-10		< LOD (0.84) 4.6	[Venter et al., 2016]
Xi'an, China	urban area	PM2.5	409.3 (winter) 269.8 (summer)		[Wu et al., 2021]

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Table S2. Weather conditions during particulate matter sampling.

Sample	Averaged values of temperature, humidity, precipitation, wind speed and direction*
	Spring
P1	15.6°C, 56%, 7 mm, 11.1 km/h (SW)
P2	14.1°C, 72%, 17 mm, 14.4 km/h (NE)
P3	14.3°C, 68%, 12 mm, 14.1 km/h (NW)
P4	17.3°C, 76%, 2 mm, 12.8 km/h (NW)
P5	21.0°C, 79%, 13 mm, 9.7 km/h (N)
P6	20.7°C, 78%, 17 mm, 12.6 km/h (N)
	Summer
P7	24.2°C, 76%, 18 mm, 15.6 km/h (W)
P8	22.0°C, 78%, 8 mm, 14.3 km/h (W)
P9	22.1°C, 75%, 16 mm, 12.5 km/h (SW)
P10	20.6°C, 77%, 5 mm, 11.1 km/h (NW)
P11	18.8°C, 80%, 2 mm, 12.3 km/h (SW)
P12	19.6°C, 72%, 3 mm, 12.5 km/h (NW)
	Autumn
P13	19.1°C, 81%, 3 mm, 15.7 km/h (SE)
P14	15.7°C, 82%, 14 mm, 13.4 km/h (SE)
P15	9,7°C, 87%, 5 mm, 15.3 km/h (SE)
P16	13.9°C, 88%, 1 mm, 11.5 km/h (S)
P17	8.0°C, 90%, 1 mm, 12.4 km/h (W)
P18	7.7°C, 89%, 10 mm, 10.6 km/h (S)
P19	2.4°C, 88%, 9 mm, 10.6 km/h (W)
P20	0.6°C, 83%, 3 mm, 23.9 km/h (SE)
P21	3.3°C, 91%, 12 mm, 11.6 km/h (W)
	Winter
P22	0.3°C, 89%, 9 mm, 11.2 km/h (SW)
P23	-8°C, 83%, 5 mm, 11.2 km/h (N)
P24	-4.1°C, 84%, 11 mm, 13.9 km/h (W)
P25	-8.1°C, 77%, 28 mm, 13.3 km/h (E)
P26	-1.9°C, 88%, 6 mm, 10.3 km/h (S)
P27	4.4°C, 80%, 10 mm, 14.6 km/h (NW)
P28	2.1°C, 76%, 17 mm, 13.7 km/h (SW)
P29	6.1°C, 79%, 17 mm, 18.6 km/h (W)

*Data comes from https://meteostat.net/en/#google_vignette and https://pl.weatherspark.com//

Table S3. Concentrations of total chromium, chromium(VI) and chromium(III) in PM10, PM2.5, PM1, and PM0.25 in Radom.

Sample	PM10			PM2.5			PM1			PM0.25		
	Cr_{tot} [ng/m^3]	Cr(VI) [ng/m^3]	Cr(III) [ng/m^3]	Cr_{tot} [ng/m^3]	Cr(VI) [ng/m^3]	Cr(III) [ng/m^3]	Cr_{tot} [ng/m^3]	Cr(VI) [ng/m^3]	Cr(III) [ng/m^3]	Cr_{tot} [ng/m^3]	Cr(VI) [ng/m^3]	Cr(III) [ng/m^3]
Spring												
P1	2.30	0.381	1.92	1.45	0.219	1.23	1.13	0.195	0.94	0.44	0.155	0.28
P2	2.62	0.140	2.48	2.17	0.133	2.04	1.87	0.116	1.75	1.07	0.092	0.98
P3	1.54	0.072	1.47	1.29	0.072	1.21	0.89	0.072	0.81	0.38	0.063	0.32
P4	1.13	0.052	1.08	1.00	0.052	0.95	0.81	0.045	0.77	0.44	< LOD	0.44
P5	1.50	0.185	1.32	1.38	0.185	1.20	1.03	0.156	0.88	0.86	0.156	0.70
P6	0.78	0.133	0.64	0.66	0.095	0.56	0.35	0.090	0.26	0.26	0.043	0.21
Av.	**1.64±0.70**	**0.16±0.12**	**1.48±0.64**	**1.33±0.51**	**0.126±0.066**	**1.20±0.48**	**1.01±0.50**	**0.112±0.056**	**0.90±0.48**	**0.57±0.32**	**0.085±0.062**	**0.49±0.30**
Summer												
P7	0.82	0.077	0.74	0.64	0.050	0.59	0.42	0.013	0.41	0.08	0.013	0.07
P8	2.28	0.295	1.99	2.22	0.271	1.95	1.71	0.216	1.49	1.22	0.100	1.12
P9	1.30	0.232	1.07	1.06	0.164	0.90	0.73	0.074	0.66	0.63	0.016	0.61
P10	2.19	0.352	1.83	1.81	0.241	1.57	1.36	0.096	1.26	0.79	0.040	0.75
P11	1.76	0.126	1.64	1.42	0.126	1.30	1.25	0.126	1.12	0.95	0.038	0.91
P12	1.07	0.013	1.06	0.75	0.013	0.74	0.70	< LOD	0.70	0.23	< LOD	0.23
Av.	**1.57±0.60**	**0.18±0.13**	**1.39±0.50**	**1.32±0.62**	**0.14±0.10**	**1.17±0.53**	**1.03±0.49**	**0.088±0.079**	**0.94±0.42**	**0.65±0.43**	**0.035±0.036**	**0.61±0.40**
Autumn												
P13	0.88	0.093	0.78	0.65	0.093	0.55	0.51	0.093	0.42	0.17	0.061	0.11
P14	4.09	0.420	3.67	3.18	0.371	2.81	2.02	0.332	1.68	0.94	0.193	0.75
P15	1.65	0.496	1.16	1.22	0.461	0.76	1.07	0.380	0.69	0.71	0.142	0.57
P16	0.75	0.209	0.54	0.71	0.209	0.51	0.42	0.147	0.28	0.28	0.116	0.17

P17	0.56	0.236	0.32	0.41	0.206	0.21	0.35	0.181	0.17	0.16	0.074	0.09
P18	1.43	0.079	0.35	0.38	0.063	0.32	0.27	0.024	0.24	0.11	0.023	0.09
P19	1.47	0.196	1.27	0.88	0.200	0.68	0.65	0.196	0.45	0.44	0.117	0.33
P20	1.47	0.367	1.10	1.28	0.323	0.96	0.92	0.267	0.65	0.51	0.166	0.34
P21	1.16	0.162	1.00	0.92	0.109	0.81	0.71	0.081	0.632	0.10	0.032	0.07
Av.	**1.5±1.1**	**0.25±0.15**	**1.1±1.0**	**1.07±0.85**	**0.22±0.13**	**0.84±0.77**	**0.77±0.54**	**0.19±0.12**	**0.58±0.45**	**0.38±0.29**	**0.103±0.059**	**0.28±0.24**
						Winter						
P22	2.43	0.449	1.98	2.01	0.373	1.64	1.54	0.356	1.19	0.85	0.129	0.72
P23	1.63	0.447	1.18	1.35	0.282	1.07	0.69	0.267	0.42	0.43	0.186	0.24
P24	1.71	0.182	1.53	1.44	0.132	1.31	1.26	0.085	1.18	0.58	0.044	0.53
P25	2.29	1.354	0.94	1.70	1.169	0.53	1.22	0.948	0.27	0.81	0.651	0.16
P26	1.97	1.308	0.66	1.51	1.159	0.35	1.22	0.920	0.30	0.58	0.488	0.09
P27	2.15	1.084	1.06	1.62	0.873	0.74	1.37	0.741	0.63	0.65	0.465	0.19
P28	2.31	0.910	1.40	2.07	0.822	1.25	1.86	0.689	1.17	1.41	0.483	0.93
P29	3.34	0.961	2.38	2.88	0.753	2.13	2.36	0.646	1.72	1.51	0.459	1.05
Av.	**2.23±0.53**	**0.84±0.43**	**1.39±0.56**	**1.82±0.50**	**0.70±0.39**	**1.13±0.59**	**1.44±0.50**	**0.58±0.31**	**0.86±0.53**	**0.85±0.40**	**0.36±0.21**	**0.49±0.38**
mean	1.71	0.38	1.33	1.38	0.32	1.06	1.06	0.26	0.80	0.61	0.16	0.45
SD	0.83	0.38	0.71	0.69	0.32	0.61	0.55	0.27	0.47	0.39	0.18	0.34
max	4.09	1.354	3.67	3.18	1.169	2.81	2.36	0.948	1.75	1.51	0.651	1.12
min	0.56	0.013	0.32	0.38	0.013	0.21	0.27	< LOD	0.17	0.08	< LOD	0.07
median	1.63	0.23	1.16	1.35	0.21	0.95	1.03	0.16	0.69	0.58	0.10	0.33

Table S4. Concentrations of total chromium and speciation of chromium in $PM_{2.5-10}$; $PM_{1-2.5}$; $PM_{0.25-1}$ and $PM_{0.25}$ in Radom.

Sample	$PM_{2.5-10}$			$PM_{1-2.5}$			$PM_{0.25-1}$			$PM_{0.25}$		
	Cr_{tot} [ng/m^3]	Cr(VI) [ng/m^3]	Cr(III) [ng/m^3]	Cr_{tot} [ng/m^3]	Cr(VI) [ng/m^3]	Cr(III) [ng/m^3]	Cr_{tot} [ng/m^3]	Cr(VI) [ng/m^3]	Cr(III) [ng/m^3]	Cr_{tot} [ng/m^3]	Cr(VI) [ng/m^3]	Cr(III) [ng/m^3]
Spring												
P1	0.85	0.162	0.69	0.32	0.024	0.29	0.69	0.040	0.65	0.44	0.155	0.28
P2	0.44	0.007	0.44	0.30	0.017	0.29	0.80	0.024	0.77	1.07	0.092	0.98
P3	0.26	< LOD	0.26	0.40	< LOD	0.40	0.50	0.009	0.49	0.38	0.063	0.32
P4	0.13	< LOD	0.13	0.19	0.007	0.18	0.38	0.045	0.34	0.44	< LOD	0.44
P5	0.12	< LOD	0.12	0.35	0.029	0.32	0.17	< LOD	0.17	0.86	0.156	0.70
P6	0.12	0.039	0.08	0.31	0.005	0.31	0.09	0.047	0.04	0.26	0.043	0.21
Av.	**0.32±0.29**	**0.035±0.064**	**0.28±0.24**	**0.312±0.071**	**0.014±0.012**	**0.30±0.07**	**0.44±0.28**	**0.027±0.020**	**0.41±0.28**	**0.57±0.32**	**0.085±0.062**	**0.49±0.30**
Summer												
P7	0.17	0.027	0.15	0.22	0.037	0.19	0.34	< LOD	0.34	0.08	0.013	0.07
P8	0.06	0.024	0.04	0.51	0.055	0.46	0.49	0.115	0.37	1.22	0.100	1.12
P9	0.24	0.067	0.17	0.33	0.090	0.24	0.11	0.058	0.05	0.63	0.016	0.61
P10	0.38	0.111	0.26	0.46	0.145	0.31	0.57	0.056	0.51	0.79	0.040	0.75
P11	0.34	< LOD	0.34	0.17	< LOD	0.17	0.30	0.088	0.21	0.95	0.038	0.91
P12	0.32	< LOD	0.32	0.05	0.013	0.04	0.47	< LOD	0.47	0.23	< LOD	0.23
Av.	**0.25±0.12**	**0.038±0.043**	**0.21±0.12**	**0.29±0.18**	**0.057±0.054**	**0.23±0.14**	**0.38±0.17**	**0.053±0.046**	**0.33±0.17**	**0.65±0.43**	**0.035±0.036**	**0.61±0.40**
Autumn												
P13	0.23	< LOD	0.23	0.14	< LOD	0.14	0.34	0.032	0.30	0.17	0.061	0.11
P14	0.90	0.048	0.86	1.17	0.039	1.13	1.08	0.139	0.94	0.94	0.193	0.75
P15	0.43	0.035	0.40	0.15	0.081	0.07	0.36	0.238	0.12	0.71	0.142	0.57
P16	0.04	< LOD	0.04	0.29	0.062	0.23	0.14	0.031	0.11	0.28	0.116	0.17

P17	0.15	0.030	0.12	0.06	0.024	0.03	0.19	0.107	0.09	0.16	0.074	0.09
P18	0.05	0.016	0.03	0.12	0.039	0.08	0.15	0.001	0.15	0.11	0.023	0.09
P19	0.59	< LOD	0.59	0.23	< LOD	0.23	0.21	0.078	0.13	0.44	0.117	0.33
P20	0.19	0.044	0.14	0.36	0.056	0.31	0.41	0.101	0.31	0.51	0.166	0.34
P21	0.24	0.053	0.18	0.21	0.028	0.18	0.61	0.049	0.56	0.10	0.032	0.07
Av.	**0.31±0.28**	**0.025±0.022**	**0.29±0.28**	**0.30±0.34**	**0.037±0.027**	**0.27±0.33**	**0.39±0.30**	**0.086±0.072**	**0.30±0.28**	**0.38±0.29**	**0.103±0.059**	**0.28±0.24**
						Winter						
P22	0.42	0.076	0.34	0.46	0.017	0.45	0.70	0.227	0.47	0.85	0.129	0.72
P23	0.28	0.165	0.11	0.66	0.015	0.65	0.26	0.081	0.18	0.43	0.186	0.24
P24	0.27	0.050	0.22	0.18	0.047	0.13	0.69	0.041	0.64	0.58	0.044	0.53
P25	0.60	0.185	0.41	0.47	0.221	0.25	0.41	0.300	0.12	0.81	0.651	0.16
P26	0.46	0.149	0.31	0.30	0.239	0.06	0.64	0.432	0.21	0.58	0.488	0.09
P27	0.53	0.212	0.32	0.25	0.132	0.11	0.72	0.276	0.44	0.65	0.465	0.19
P28	0.24	0.089	0.15	0.22	0.133	0.08	0.45	0.205	0.24	1.41	0.483	0.93
P29	0.46	0.207	0.25	0.52	0.107	0.41	0.85	0.188	0.66	1.51	0.459	1.05
Av.	**0.41±0.13**	**0.142±0.062**	**0.26±0.10**	**0.38±0.17**	**0.114±0.086**	**0.27±0.21**	**0.59±0.20**	**0.22±0.12**	**0.37±0.21**	**0.85±0.40**	**0.36±0.21**	**0.49±0.38**
mean	0.33	0.062	0.27	0.32	0.057	0.27	0.45	0.10	0.35	0.61	0.16	0.45
SD	0.22	0.069	0.19	0.22	0.064	0.22	0.25	0.11	0.24	0.39	0.18	0.34
max	0.90	0.212	0.86	1.17	0.239	1.13	1.08	0.432	0.94	1.51	0.651	1.12
min	0.04	< LOD	0.03	0.05	< LOD	0.03	0.09	< LOD	0.04	0.08	< LOD	0.07
median	0.27	0.039	0.23	0.30	0.037	0.23	0.41	0.06	0.31	0.58	0.10	0.33

Table S5. The values of parameters used in the health risk assessment.

Parameter	Acronym	Unit	Adult	Child	Reference
Exposure time	*ET*	hours/ day	24	24	[US EPA 2014]
Exposure frequency	*EF*	day/ year	350	350	[US EPA 2014]
Exposure duration	*ED*	year	20	6	[US EPA 2014]
Average exposure time*	AT_n				
	For carcinogens	hours	613 200	613 200	[US EPA 2014]
	For non-carcinogens	hours	175 200	52 560	[US EPA 2014]
Inhalation unit risk for Cr	*IUR*	$(\mu g/\ m^3)^{-1}$	$8.4 \cdot 10^{-2}$	$1.20 \cdot 10^{-2}$	[US EPA Region 9]
Reference concentration for Cr	*RfC*	$mg/\ m^{-3}$	$1.00 \cdot 10^{-4}$	$1.00 \cdot 10^{-4}$	[US EPA Region 9]

*The averaging time of exposure for carcinogens was calculated as AT_n = 70 years·365 days $year^{-1}$·24 h day^{-1}; while for non-carcinogens as AT_n = ED years·365 days $year^{-1}$·24 h day^{-1}.