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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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Abstract. The paper assesses chromium occurrence in urban particulate matter: PM10, PM2.5, PM1, and PM0.25 over a calendar year. The seasonality of both pseudo-total chromium content and its valence speciation are studied. Airborne aerosol was sampled in the city of Radom (Poland) using a Hi-Flow MOUDI Model 130 cascade impactor from Copley. The pseudo-total chromium concentration (Cr_{tot}) was assayed with GF-AAS and the concentration of Cr(VI) with CCSV-DTPA techniques. Cr_{tot} concentrations in the particulate matter fractions investigated ranged from 0.08 to 4.09 ng/m^3. The results point to a seasonality of Cr_{tot} concentration changes in particulate matter. The concentration was maximum in winter (2.23±0.53 ng/m^3 on average), while Cr_{tot} in PM10 averaged 1.71±0.83 ng/m^3 in the whole measurement period. The average Cr(VI) concentration did not exceed 0.40 ng/m^3 and was maximum in winter, too (max. 1.354 ng/m^3). The Cr(VI) share in PM in the particular seasons varied a lot. It was minimum in summer (9.1% of Cr_{tot}) and maximum in winter (40% of Cr_{tot}). The carcinogenic risk for the urban residents based on the Cr(VI) concentration in PM10 was within the acceptable range (between $1\cdot10^{-6}$ and $1\cdot10^{-4}$) and amounted to between $1.11\cdot10^{-6}$ and $5.78\cdot10^{-6}$ for children and from $3.69\cdot10^{-6}$ to $1.92\cdot10^{-5}$ for adults. The non-carcinogenic health risk caused by the presence of Cr_{tot} was acceptable as well. The HQ values for both adults and children were lower than the safe level of 1 and ranged from $1.57\cdot10^{-2}$ to $3.92\cdot10^{-2}$.

1 Introduction

Air quality has continued to deteriorate lately, especially in urban and industrial areas. Particulate matter is a major pollutant whose substantial quantities are emitted into the air, affecting adversely both the climate and all parts of the environment (Fang et al., 2005; Wagner et al., 2008; Arhami et al., 2017). Particulate matter, considered one of the most dangerous environment pollutants (Park et al., 2009; Waheed et al., 2011; Izhar et al., 2016), has a complex and heterogeneous composition, dependent on the season, source of emissions, and weather conditions. Knowledge of the composition, concentration, and sources of particulate matter suspended in the air is of great importance to city and agglomeration residents, since breathing these particles in can increase mortality or morbidity due to respiratory and pulmonary conditions. The particulate matter's coarse fraction

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(2.5-10 µm) is assumed to be of natural origin, while the fine fraction (0.1–2.5 µm, especially the particles of less than 1 µm) comes from anthropogenic processes (Nocoń et al., 2018). The distribution of particulate matter particle sizes and its loading with different chemical compounds determine the aerosol's effect on human health and the environment. The particulate matter with grain diameters below 2.5 µm is particularly dangerous to living organisms as it penetrates alveoli pulmonis and thence potentially enters the bloodstream (Wagner et al., 2008; Pan et al., 2015). For this reason, this particulate matter fraction is the most common object of environmental studies (Feng at al., 2009; Rogula- Kozłowska et al., 2013a; Zajusz-Zubek and Mainka, 2015; Li et al., 2016; Sah et al., 2019; Xie et al., 2019; Anake et al., 2020; Wu et al., 2021; Wang et al., 2023;) (Table S1, Supplementary Material). Researchers frequently examine PM10 too (e.g. Richter et al., 2007; Catrambone et al., 2013; Huang et al., 2014a; Pandey et al., 2017; Rubio et al., 2018; Conca et al., 2020). The finer fractions, e.g. PM1, are investigated far more seldom (Rogula-Kozłowska et al., 2013b; Zajusz-Zubek et al., 2015; Zajusz-Zubek, 2017). Scientists rarely assay two (PM10 and PM2.5: Canepari et al., 2009; Dos Santos et al., 2009; Jan et al., 2018; Gunchin et al., 2021) or more grain fractions (PM1, PM2.5, and PM10: Samara and Voutsa, 2005; Rogula-Kozłowska et al., 2013b; Rogula-Kozłowska et al., 2015) in parallel.

A variety of toxic compounds, both organic and inorganic, are also transported along with the particulate matter. Special attention is paid to heavy metals (Wagner et al., 2008; Pan et al., 2015; Samara et al., 2016) that may contribute to oxidative DNA damage and cause carcinogenic lesions in effect (Somers, 2011; IARC, 2012; Arhami et al., 2017). Epidemiological research has shown a close connection between chromium(VI) exposure and lung cancer (IARC, 2012). Chromium air presence has been studied a lot given its harmfulness (Nriagu and Nieboer, 1988; Nusko and Heumann, 1997; Świetlik et al., 2011; Tirez et al., 2011; Torkmahalleh et al., 2013; Huang et al., 2014a, 2014b; Kang et al., 2016; Widziewicz et al., 2016; Molik et al., 2018; Nocoń et al., 2018). The element occurs in the air in two valence states: Cr(III) and Cr(VI), greatly varying in their physical and chemical properties and toxicity. Chromium (III) is a microelement necessary for living organisms, whereas chromium (VI) is toxic and classified as a carcinogen (Katz, 1991; Barceloux, 1999; Kotaś and Stasicka, 2000). Regionally, natural sources account for 30-40% of total chromium emissions (Pacyna, 1986; Kotaś and Stasicka, 2000). Authors report that fuel combustion in stationary sources is the chief source of Cr emissions in Europe and more than a half of all anthropogenic emissions (Pacyna et al., 2007). In Poland, the burning of fuels is responsible for 60% of all the Cr emissions to the environment (Ministry of Climate and Environment, 2020).

The natural air content of Cr_{tot} is estimated to range from 0.1 ng/m^3 to 1 ng/m^3. Nriagu et al. (1988) report an average atmospheric concentration of Cr starting from 1 ng/m^3 in rural areas to 10 ng/m^3 in polluted urban areas. Świetlik and Trojanowska (2022) review the average Cr in the urban air of diverse regions globally. Given the commonly encountered pollution levels worldwide, Cr_{tot} in the urban air averaged 13±2 ng/m^3, whereas Cr_{tot} in heavily polluted areas was many times higher, 350±70 ng/m^3 (Świetlik and Trojanowska, 2022). Average Cr(VI) concentration is far lower – 0.5 ng/m3 (Seinfeld and Pandis, 2006). It is normally higher close to industrial sources (Proctor et al., 2021). Acoording the US EPA National Air Toxics Assessment in 2017, the median, mean, and maximum Cr(VI) were 0.03 ng/m^3, 0.1 ng/m^3 and 3.18 ng/m^3, respectively (Proctor et al., 2021).

To assure legal protection against atmospheric chromium in Poland, reference values were set as follows: 20 μg/m^3 and 2.5 μg/m^3 for Cr(III) and Cr(VI) compounds and 4.6 μg/m^3 and 0.4 μg/m^3 for Cr(VI) over 1 h and 1 year, respectively (The Minister of the Environment Regulation, 2010).

Although chromium occurrence in urban air has been extensively studied and a range of publications have appeared recently (Catrambone et al., 2013; Widziewicz et al., 2016; Nocoń et al., 2018), investigations of total Cr occurrence and its valence speciation in particulate matter of different particle sizes are still unavailable. We have only examined Cr (III/VI) speciation in total suspended particulate (TSP) before (Świetlik et al., 2011). Our current study is designed to: (I) assess chromium occurrence and speciation in urban particulate matter fractions of varied particle sizes (PM10, PM2.5, PM1, PM0.25); (II) examine the fluctuations and seasonality of Cr concentrations over one year, and (III) estimate health risk caused by inhalation exposure to airborne Cr in two different exposure schemes: 1) the risk comes from the Cr_{tot} ambient concentrations; 2) the risk comes exclusively from Cr(VI) species. Radom is an interesting location for such research as the chromium environment pollution is a result not only of an aged urban structure relying on private hard coal heating, considerable road transit, and the operation of multiple metal working factories, but also tanneries clustered in the region for more than 70 years.

These are the results of the first-ever hexavalent chromium (Cr(VI)) measurements in the particulate matter of different sizes in the air of a medium-sized city in central Poland.

2 Experimental

2.1 Sampling area and the collection of PM samples

The airborne particulate matter was sampled in Radom, a medium-sized town (a population of 196 000, an area of 112 km^2) in central Poland, 100 km south of Warsaw. The local sources of chromium emissions are: road traffic, coal burning in homes, coal-fired municipal heating plants, and multiple metalworks. The sampling points of the suspended airborne particulate matter were located on the University of Radom premises. The area is adjacent to a housing estate with a prevalence of private houses heated with traditional coal furnaces, but not under an immediate impact of local sources of industrial emissions or streets with heavy traffic.

The airborne particulate matter was sampled in spring (variable weather: cool, sunny, wet; the heating campaign until the middle of April), summer (sunny, warm weather), autumn (variable weather: sunny, warm or cool, wet; heating campaign from the middle of October), and winter (cold, overcast and wet weather; heating campaign). A Hi-Flow MOUDI Model 130 cascade impactor from Copley was used, positioned at a height of 1.5 m above the ground level. It enabled the separation of four grain fractions of atmospheric dust: PM10, PM2.5, PM1 and PM0.25. The grain fractions of atmospheric particulate matter were sampled from February 2020 to April 2021 in 29 weekly cycles. A total of 116 samples were collected. The sampling time averaged 70 h. The air rate was maintained in the range of 0.35–0.5 m^3/min. The airborne particulate matter was collected on cellulose filters (POCH). The filters were weighed before and after sampling, the weight was 0.01 mg (Microbalance MX5 Mettler Toledo) in a temperature and relative humidity controlled environment (20±3°C and 50±10%, respectively). Then the filters were stored in a plastic CD-case. Before the analysis, the filters with the deposit were sectioned into four equal parts. The samples were only withdrawn when there was no precipitation.

2.2 The determination of the contents of the particular airborne particulate matter fractions

The concentrations of the particular particulate matter fractions were calculated by dividing the difference between filter weight prior to and following the exposure by the mean air flow at the time of atmospheric aerosol sampling.

2.3 The determination of pseudo-total chromium

In order to assay Cr_{tot} by means of GF-AAS, the particulate matter samples collected on filters were mineralised using microwave energy. A quarter deposited filter was placed in a 100 mL Teflon vessel with 5 mL 65% HNO_3 and 3 mL 30% H_2O_2. The samples were digested in a microwave oven (Milestone MLS 1200 Mega) according to the following program: 1) 6 min., 250 W; 2) 1 min., 0W; 3) 6 min., 400 W; 4) 6 min., 650 W; 5) 6 min., 250 W; 6) 5 min., ventilation. After the digestion, we filtered the solutions through a 0.45 µm Millex-HV syringe filter (Millipore), transferred them into a polypropylene volumetric flask, and diluted to 25.0 mL with deionized water.

A Perkin-Elmer 3100 AAS graphite furnace system equipped with HGA 600 and an AS-60 autosampler were used for the determination of pseudo-total chromium concentration. The standard chromium solution (J.T. Baker Inc.) at a concentration of 1000 µg/mL served to calibrate the device. LOD (instrumental) was found to be 0.2 µg/L of Cr or 0.03 ng/m^3 expressed as the concentration of Cr in the air. The quality of the chromium results was characterized with a recovery test of the CRM BCR-701 (river sediment). It was found to be 259±18 mg/kg Cr_{tot} (n = 3), while the certified value is 272±20 mg/kg, hence the recovery for extractable Cr was 95.2%.

2.4 The determination of chromium(VI)

The filters with the collected airborne particulate matter were extracted as per a modified US EPA 3060A standard by means of alkaline digestion (US EPA, 1996). The modification was necessary given the low chromium(VI) contents in the suspended particulate matter samples. For this purpose, a quarter of the exposed filter was placed in the Teflon vessel, 5 mL of 0.056 M Na_2CO_3/0.08 M NaOH was added and extracted in a microwave oven MLS 1200 Mega (3 min, 400W). The leachates were then centrifuged (MPW 342) and filtered through a 0.45 µm Millex-HV syringe filter (Millipore) into 10 mL test tubes.

Cr(VI) in the leachates was determined using the technique of catalytic cathodic stripping voltammetry with the adsorption of Cr(III)-DTPA complexes (CCSV-DTPA) [Li and Xue, 2001]. The voltammograms were recorded with a Trace Analyzer Model 394 connected to a hanging mercury drop working electrode Model 303A SMDE (EG&G Princeton Applied Research Electrochemical).

The supporting electrolyte (5 mL water, 500 µL saturated solution of KNO_3, 200 µL 0.1 M AcONa, 200 µL 0.1 M DTPA) and a 100 µL sample of Cr(VI) extract were transferred into an electrochemical cell, pH was adjusted to 6.00±0.05, and the solution was purged for 4 min with high purity argon. Deposition on a mercury drop was carried out for 60s at -0.95 V. Then the stirring was discontinued and an equilibration time of 10 s was allowed. The differential pulse scan was carried out from -0.95 V to -1.65 V, the pulse height was 50 mV and the rate 6 mV/s. The peak corresponding to the reduction of adsorbed Cr(III)-DTPA complex appeared at -1.20 V to -1.30 V. The chromium(VI) concentration was assayed using the technique of double spike-standard addition (2-10 µL, depending on the expected analyte concentration) with a concentration of 0.2 mg/L Cr(VI). LOD (instrumental) was found to be 2.9 µg/L or 0.010 ng/m^3 expressed as the concentration of Cr(VI) in the air. CMR061-030 (sandy loam) was used as the certified reference material to validate the analytical procedure. It was found to equal 239.3 mg/kg Cr(VI) (n =3), the certified value was 241.00±9.00 mg/kg, hence the recovery – 99.3%.

3 Results and discussion

3.1 The mass concentration of PM

The concentrations of the following particulate matter fractions were assayed: PM10, PM2.5, PM1, and PM0.25. The World Health Organization (WHO) claims that there is no evidence of a safe exposure level or threshold below which there are no adverse effects of exposure to particulate matter (WHO, 2013).

In Radom, the PM10 fraction ranged widely from 5.2 to 68.2 µg/m^3 (40±17 µg/m^3 on average). The PM2.5 concentrations were lower, from 3.1 to 59.2 µg/m^3 (33±15 µg/m^3 on average). The concentrations of finer particulate matters were in the following ranges: PM1 from 2.4 to 45.4 µg/m^3 (26±13 µg/m^3 on average), and PM0.25 – from 1.3 to 27.6 µg/m^3 (12.6±6.6 µg/m^3 on average) (Table 1). Comparable concentrations of urban PM2.5 are reported by other authors, e.g., Budapest (Hungary) 23 µg/m^3, Istanbul (Turkey) 40 µg/m^3 (Szigeti et al., 2013), Tehran (Iran) 33±11 µg/m^3 (Arhami et al., 2017), Katowice (Poland) 31 µg/m^3 (Rogula-Kozłowska et al., 2013a).

These concentrations were far lower than reported from our earlier study of TSP – from 36 to 282 µg/m^3, average 110 µg/m^3 (Świetlik et al., 2011).

Table 1. The concentrations of PM in the urban atmosphere.

	PM10 [µg/m^3]	PM2.5 [µg/m^3]	PM1 [µg/m^3]	PM0.25 [µg/m^3]
		Spring		
Min	5.2	3.1	2.4	1.3
Max	62.7	48.6	36.6	20.6
Mean	25	19	15	7.5
SD	21	17	13	7.2
		Summer		
Min	22.4	16.9	12.7	6.6
Max	43.3	33.1	22.9	12.0
Mean	28.6	22.1	16.3	8.3
SD	7.9	6.2	4.1	2.0
		Autumn		
Min	31.1	23.6	17.9	7.6
Max	68.2	59.2	45.1	27.6

Mean	53	44	34.3	15.9
SD	10	10	8.3	5.5
Winter				
Min	23.1	19.0	15.4	7.0
Max	60.9	51.8	45.4	24.2
Mean	45	39	32	15.8
SD	13	12	10	6.0

The average PM10 and PM2.5 concentrations in autumn (53±10 µg/m^3; 44±10 µg/m^3) and winter (45±13 µg/m^3; 39±12 µg/m^3) were in excess of the national (40 µg/m^3 and 20 µg/m^3, respectively) and European (40 µg/m^3 and 25 µg/m^3, respectively) air quality standards (The Minister of the Environment Regulation 2012; Directive 2008/50/EC). A relatively high share of PM2.5 respirable fraction relative to PM10 was found in the measurement period, 81% on average. Zajusz-Zubek and Mainka (2015) report a similar share of PM2.5 (88%) , although the particulate matter concentrations measured by them were somewhat lower: PM10 – 25.58 µg/m^3; PM2.5 – 22.93 µg/m^3 (PM1 concentration – 18.44 µg/m^3) (Zajusz-Zubek and Mainka, 2015). The literature states PM2.5 in most European locations constitutes 50 to 70% of PM10 (WHO, 2013).

Seasonality had a great influence on the concentrations of particulate matter suspended in urban air (Figure S1, Supplementary material). During the heating campaign, the concentrations of each fraction were nearly double those in summer, with a little greater PM10, PM2.5 and PM1 observed in autumn (by an average of 12%). Only PM0.25 concentrations were steady in autumn and winter and stood at 15.9±5.5 µg/m^3 and 15.8±6.0 µg/m^3, respectively (Table 1).

The high airborne particulate matter concentrations in the urban area investigated during the heating campaign suggest municipal emissions including coal burning in household furnaces were the chief source of particulate matter pollution.

The higher suspended particulate matter concentrations in the heating season have also been found by others, e.g., Rogula-Kozłowska et al. (2013a) reports PM2.5 concentrations in Zabrze and Katowice (Poland) usually ranging between 10 and 20 µg/m^3 and far greater in winter, from 50 to 110 µg/m^3 (Rogula-Kozłowska et al., 2013a). The higher suspended particulate matter concentrations in winter (pointing to a greater share of fuel combustion sources) have been noted by other authors, too (Krzemińska-Flowers et al., 2006; Widziewicz et al., 2016).

3.2 Chromium concentration

Given the environmental aspect of this study, the environmentally available chromium content Cr_{tot} (pseudo-total concentration of Cr) in the PM samples was assayed. All the results for Cr_{tot} concentrations in PM10, PM2.5, PM1 and PM0.25 are listed in Table S2 (Supplementary Material).

Cr_{tot} concentrations in the particulate matter fractions studied varied quite widely, from 0.08 to 4.09 ng/m^3. Like in the case of particulate matter concentrations, the results were several times lower than the chromium concentrations given in our previous work for the non-industrial zone (15 ng/m^3 on average), when we studied TSP (Świetlik et al., 2011). It should be pointed out particulate matter pollution has been substantially reduced in Poland in recent years owing to the application of state-of-the-art, efficient, and environment-friendly technological solutions. The continuing modernisation of the energy, heating, and industrial sectors, as well as an improved quality of fuel, have helped to cut the quantity of particulate matter pollution emitted into the air year by year.

The results indicate a marked impact of the heating season on Cr_{tot} concentrations in all the PM fractions (Figure 1).

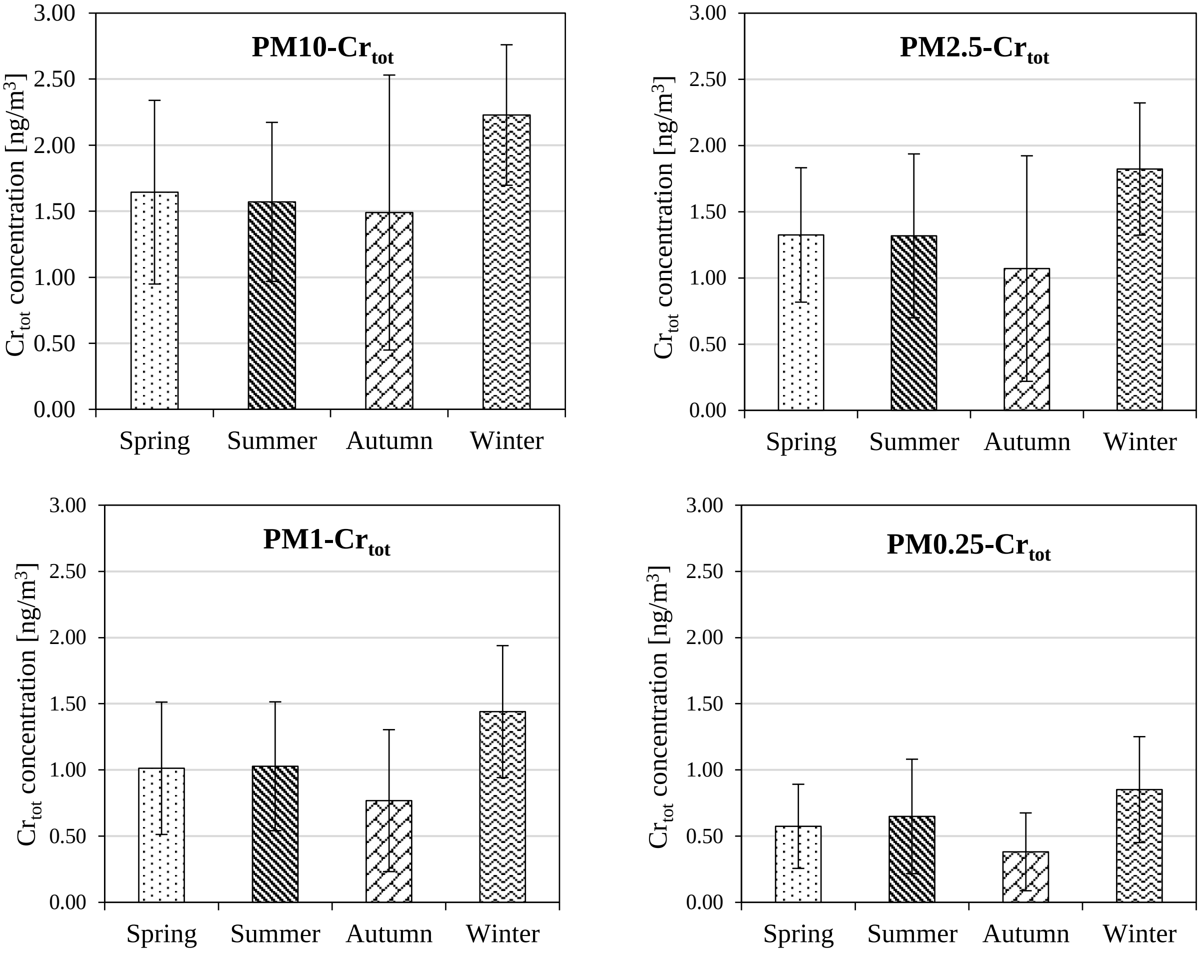

Figure 1. The concentrations of pseudo-total chromium in PM10, PM2.5, PM1 and PM0.25 depending on the seasons.

The maximum Cr_{tot} concentration relating to PM10 was found in winter (2.23±0.53 ng/m^3 on average), whereas it averaged 1.71±0.83 ng/m^3 in the entire measurement period. The PM2.5 fraction contains approximately 80% of the total chromium content (like in the case of particulate matter) . Municipal emissions, primarily stationary coal burning sources, and road traffic can be assumed to be responsible above all else for the quality of urban air.

Cr_{tot} concentrations in PM2.5, PM1 and PM0.25 were lower: 1.38±0.69 ng/m^3, 1.06±0.55 ng/m^3, 0.61±0.39 ng/m^3, respectively (Table S2). The mean chromium concentrations relating to PM2.5 in Radom were similar to those determined in other cities in Poland and globally during the whole measurement time: Zabrze 1.7±1.9 ng/m^3 (Rogula-Kozłowska et al. 2013a); Warsaw

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1.2±1.4 ng/m^3 (Majewski and Rogula-Kozłowska, 2016); Wrocław 1.6±0.8 ng/m^3 (Zwoździak et al., 2013); Łódź 2.82±0.34 ng/m^3 (PM3, Krzemińska-Flowers et al., 2006); Budapest (Hungary) 1.4 ng/m^3, Istanbul (Turkey) 2.8 ng/m^3 (Szigeti et al., 2013); Rome (Italy) 3.72 ng/m^3 (Canepari et al., 2009). Theconcentrations are far greater in industrial areas, e.g., Guangzhou (China) 7.693 ng/m^3 (Feng et al., 2009); Ewekoro (Nigeria) 11.4 ng/m^3 (Anake et al., 2020); Agra (India) 19.3 ng/m^3 (Sah et al., 2019); Nanjing (China) 26.61 ng/m^3 (Li et al., 2016).

In spring and summer, Cr_{tot} concentrations for the particular fractions were similar and averaged: PM10 – 1.64±0.70 and 1.57±0.60 ng/m^3, PM2.5 – 1.33±0.51 and 1.32±0.62 ng/m^3, PM1 – 1.01±0.50 and 1.03±0.49 ng/m^3, PM0.25 – 0.57±0.32 ng/m^3 and 0.65±0.43 ng/m^3, respectively (Table S2). They were maximum in winter: PM10 2.23±0.53 ng/m^3; PM2.5 1.82±0.50 ng/m^3; PM1 1.44±0.50 ng/m^3; PM0.25 0.85±0.40 ng/m^3 (Figure 1). The higher Cr_{tot} concentrations in winter are corroborated by other authors (Krzemińska-Flowers et al., 2006; Zwoździak et al., 2013; Widziewicz et al., 2016).

Based on the differences of Cr_{tot} concentrations in the particular fractions (PM10 and PM2.5; PM2.5 and PM1; PM1 and PM0.25), its concentrations in the fractions were calculated as follows: PM2.5-10, PM1-2.5, PM0.25-1 and PM0.25 (Table S3, Supplementary Material). Regardless of the season, Cr_{tot} content was always highest in the finest fraction, PM0.25 (Figure S2, Supplementary Material).

3.3 The speciation of chromium

Chromium speciation was also assayed in all the fractions of airborne particulate matter. Cr(VI), as a particularly harmful metal, is classified by the International Agency for Research on Cancer (IARC) as a Group 1 carcinogenic factor (IARC, 2023). Authors report most airborne Cr(VI) (60–70%) comes from anthropogenic sources (e.g. metallurgy, refractory production or chemical processing industries) (Kang et al., 2016; Wang et. al., 2020). Emissions associated with solid fuel combustion are of great significance as well (Nriagu and Pacyna, 1988). Combustion processes, mostly of anthropogenic origin, or gas to particle conversions of atmospheric substances produce small aerosol particles, whereas larger particles are formed by mechanical processes, such as wind erosion of soil or dust emission from public traffic (Nusko and Heumann, 1997). Cr(VI) presence in Radom's airborne aerosol may be chiefly a result of municipal (fuel burning in heating plants and household furnaces) and road traffic emissions. Industrial emissions are of lesser importance as the industrial sources are located far away from the sampling points.

Cr(VI) concentrations in the urban air of Radom were quite varied and ranged from undetectable levels (<LOD) to 1.354 ng/m^3 (Table S2). Average Cr(VI) concentrations did not exceed 0.400 ng/m^3 in the entire measurement period, though, and equalled: PM10 – 0.38 ng/m^3; PM2.5 – 0.32 ng/m^3, PM1 – 0.26 ng/m^3 and PM0.25 – 0.16 ng/m^3, respectively. Similar Cr(VI) concentrations in airborne particulate matter are reported by other authors: Wilmington (USA) 0.5-1.0 ng/m^3 (Khlystov and Ma, 2006), New Jersey (USA) 0.86-1.56 ng/m^3 (Huang et al., 2014b), Beijing (China) 0.006–0.266 ng/m^3 (PM2.5) (Wang et. al., 2023), although higher concentrations are also found, e.g., the Flemish region (Belgium) 1.2–5.2 ng/m^3 (Tirez et al., 2011).

Our investigation has shown 78-90% of total Cr(VI) content (depending on the season) was PM2.5 (83% on average). Like in the case of Cr$_{tot}$, a distinct effect of the heating campaign on Cr(VI) concentrations in PM could be noted. This was true of all the grain fractions (Figure 2).

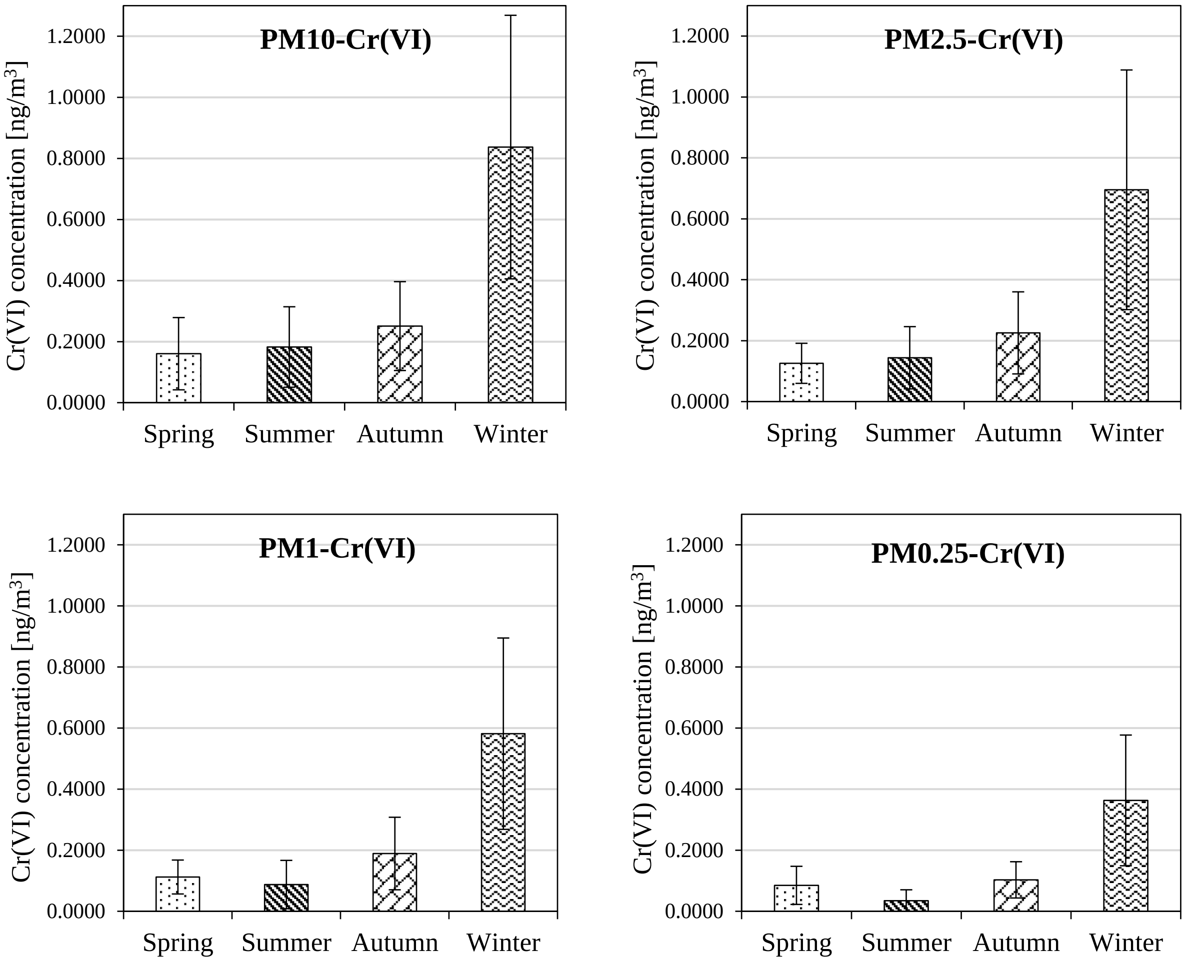

Figure 2. The concentrations of Cr(VI) in PM10, PM2.5, PM1 and PM0.25 depending on the seasons.

Cr(VI) concentrations were maximum in winter (the heating campaign) and averaged: PM10 – 0.84±0.43 ng/m^3, PM2.5 – 0.70±0.39 ng/m^3, PM1 – 0.58±0.31 ng/m^3, PM0.25 – 0.36±0.21 ng/m^3. Maximum Cr(VI) concentrations in PM10 reached 1.354 ng/m^3. For the sake of legal protection against airborne chromium(VI), a reference value of 0.4 µg/m^3 (for 1 year) was introduced in Poland (The Minister of the Environment Regulation, 2010). The World Health Organization (WHO) recommends the baseline limit of hexavalent chromium with an excess lifetime risk (RR values) of 1:10,000, 1:100,000 and 1:100,000 to be 2.5, 0.25, 0.0025 ng/m^3, respectively [WHO, 2000].

Regardless of the particulate matter fraction, chromium(VI) accounted for approximately 20% of Cr_{tot} content in the particulate matter (PM10 - 19.3%, PM2.5 – 19.9%, PM1 – 21.1%, PM0.25 – 22.4%) during the whole measurement period (Table 2). Cr(VI) share in the particular seasons varied, however. It was minimum in summer, averaging 9.1%, somewhat greater in spring (11.3%), to rise to 22.7% (from 18.1% to 26.9%) in the autumn. It was maximum in winter, constituting 40% of total chromium on average (from 37.6% to 42.6%). Our results are not different from those reported in the literature, e.g., Bell and Hipfner (1997) and Talebi (2003) claim that circa 20% airborne chromium was Cr(VI), Nusko and Heumann (1997) give approx. 30%. Tirez et al. (2011) reported that, in the case of PM2.5 from coal combustion, the share of Cr(VI) ranged from 6 to 43% of the total Cr (Tirez et al., 2011). Torkmahalleh et al. (2013) state the average Cr(VI) to total Cr ratios varied from 1 to 30%, whereas Kang et al. (2016) say the concentration of Cr(VI) measured accounted for 0.7 to 9.4 percent of the total chromium level, which is a low percentage compared to those in other urban areas around the world.

Table 2. The percentage share of chromium speciation.

Season	**PM10**		**PM2.5**		**PM1**		**PM0.25**	
	Share of Cr(VI) [%]	**Share of Cr(III) [%]**	**Share of Cr(VI) [%]**	**Share of Cr(III) [%]**	**Share of Cr(VI) [%]**	**Share of Cr(III) [%]**	**Share of Cr(VI) [%]**	**Share of Cr(III) [%]**
Spring	9.8	90.2	9.5	90.5	11.1	88.9	14.8	85.2
Summer	11.6	88.4	10.9	89.1	8.5	91.5	5.3	94.7
Autumn	18.1	81.9	21.1	78.9	24.6	75.4	26.9	73.1
Winter	37.6	62.4	38.1	61.9	40.4	59.6	42.6	57.4
Average value	19.3	80.7	19.9	80.1	21.1	78.9	22.4	77.6

Cr(III) averaged 79.3% of Cr_{tot} (Table 2). It was maximum in summer (90.9% on average) and a little lower in spring (88.7%). It was minimum in winter, 60.3% of the total chromium content (Figure S3, Supplementary Material).

Based on the difference of Cr(VI) concentrations assayed in PM10, PM2.5, PM1 and PM0.25, its concentrations in: $PM_{2.5-10}$, $PM_{1-2.5}$, $PM_{0.25-1}$ and $PM_{0.25}$ were calculated (Table S3). Like in the case of Cr_{tot}, regardless of the season, Cr(VI) concentrations were normally maximum in the finest fraction, PM0.25 (Figure S4, Supplementary Material). Some authors report that fine particulate matter particles, which can be carried over long distances, contain more Cr(VI) (Wang et al., 2023).

Attempts at correlating Cr_{tot} concentrations in PM10 with its values in finer fractions: PM2.5, PM1, and PM0.25, brought interesting results. The coefficients of determination (R^2) are relatively high: 0.9512 (for PM10-PM2.5), 0.8678 (for PM10-PM1), and 0.6283 (for PM10-PM0.25), mean R^2 = 0.8158 (Figure S5, Supplementary Material).

The correlation was even better for valence speciation. A clear dependence could be observed between the total Cr(VI) content in PM10 and Cr(VI) content in finer fractions: PM2.5, PM1, and PM0.25 (Figure S6, Supplementary Material). In this event, the coefficients of determination were greater than for Cr_{tot}: R^2=0.9852 (for PM10-PM2.5), 0.9715 (for PM10-PM1), and 0.9273 (and PM10-PM0.25), the average R^2 was 0.9613.

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3.4 The health risk of inhalation exposure to chromium

We estimated the health risk of respiratory exposure to chromium in the airborne particulate matter investigated. The model of risk assessment recommended by the U.S. Environmental Protection Agency (US EPA, 2009) was applied. The risk for both adults and children was estimated. The exposure concentration (*EC*) [µg/m^3] of non-carcinogenic and carcinogenic chromium was calculated according to Eq. (1):

$$\mathrm{EC} = \frac{\mathrm{C_{Cr}} \cdot \mathrm{ET} \cdot \mathrm{EF} \cdot \mathrm{ED}}{\mathrm{AT_n}} \quad (1)$$

where C_{Cr} is the average concentration of $\mathrm{Cr_{tot}}$ or Cr(VI) in atmospheric particulate matter [µg/m^3]; *ET* - exposure time [hours/day], *EF* - exposure frequency [days/year], *ED* - exposure duration [years], and AT_n is the averaging time of exposure [hours].

As recommended by the US EPA 2009 (Part F), a residential scenario could consist of inhalation exposure for up to 24 hours per day, up to 350 days per year for 6 to 30 years. The residential exposure parameters used in this study are listed in Table S4 (Supplementary material).

The non-carcinogenic health risk for chromium was evaluated by means of hazard quotient (*HQ*) using Eq. (2):

$$\mathrm{HQ} = \frac{\mathrm{EC}}{\mathrm{RfC_{Cr}} \cdot 1000} \quad (2)$$

where RfC_{Cr} is the inhalation reference concentration for Cr [mg/m^3]. Cancer risk (*CR*) was calculated using Eq. (3):

$$\mathrm{CR} = \mathrm{EC} \cdot \mathrm{IUR_{Cr}} \quad (3)$$

where IUR_{Cr} is the inhalation unit risk for Cr(VI) [(µg/m^3)$^{-1}$]. The values of RfC_{Cr} and IUR_{Cr} were cited from the Regional Screening Levels (RSL) Tables for US EPA Region 9 (US EPA 2022).

The acceptable carcinogenic risk ranges from $1 \cdot 10^{-6}$ (1 per 1 000 000) to $1 \cdot 10^{-4}$ (1 per 10 000) (US EPA, 1989). A carcinogenic risk value above the upper limit ($1 \cdot 10^{-4}$) suggests that chromium(VI) in atmospheric particulate matter is very likely to develop cancer through lifetime exposure, while values below the lower limit ($1 \cdot 10^{-6}$) indicate no significant cancer risk. *HQ* below one suggests no significant risk of non-carcinogenic effects. If *HQ* is equal to or more than 1, the non-carcinogenic effects are possible in the future.

The estimated potential carcinogenic (CR) and non-carcinogenic (HQ) risk of inhalatory exposure to Cr present in PM10 for urban residents is shown in Table 3. Both were maximum in winter, when Cr concentrations become highest. In the light of the standard interpretation, however, regardless of the season, the carcinogenic risk to residents based on Cr(VI)concentration in PM10 was within the acceptable range (between $1 \cdot 10^{-6}$ and $1 \cdot 10^{-4}$) and amounted to between $1.11 \cdot 10^{-6}$ and $5.78 \cdot 10^{-6}$ for children and from $3.69 \cdot 10^{-6}$ to $1.92 \cdot 10^{-5}$ for adults. Even in the case of maximum Cr(VI) concentration in PM10 during the winter season, the estimated carcinogenic risk to the population of Radom was acceptable: $\mathrm{CR} = 9.24 \cdot 10^{-6}$ for children and $\mathrm{CR} = 3.12 \cdot 10^{-5}$ for adults.

Table 3. Carcinogenic and non-carcinogenic risk from chromium via inhalation exposure to the airborne particles of PM10.

Season	Carcinogenic risk - CR			Non-carcinogenic risk - HQ		
	Cr(VI) [ng/m^3]	Children	Adult	$\mathrm{Cr_{tot}}$ [ng/m^3]	Children	Adult
Average concentration of chromium in PM10 in each season						
Spring	0.1604	$1.11\cdot10^{-6}$	$3.69\cdot10^{-6}$	1.64	$1.57\cdot10^{-2}$	$1.57\cdot10^{-2}$
Summer	0.1823	$1.26\cdot10^{-6}$	$4.19\cdot10^{-6}$	1.57	$1.51\cdot10^{-2}$	$1.51\cdot10^{-2}$
Autumn	0.2508	$1.73\cdot10^{-6}$	$5.77\cdot10^{-6}$	1.38	$1.32\cdot10^{-2}$	$1.32\cdot10^{-2}$
Winter	0.8369	$5.78\cdot10^{-6}$	$1.92\cdot10^{-5}$	2.23	$2.14\cdot10^{-2}$	$2.14\cdot10^{-2}$
Av.		$2.47\cdot10^{-6}$	$8.21\cdot10^{-6}$		$1.64\cdot10^{-2}$	$1.64\cdot10^{-2}$
Maximum chromium concentration in PM10 throughout the measurement period						
	1.3544	$9.24\cdot10^{-6}$	$3.12\cdot10^{-5}$	4.09	$3.92\cdot10^{-2}$	$3.92\cdot10^{-2}$

The estimated non-carcinogenic inhalation risks from chromium for the residents of Radom posed no threat, either. The HQ values calculated on the basis of the total Cr concentration in PM10 were lower than the safe level (HQ = 1) and ranged from $1.32\cdot10^{-2}$ to $2.14\cdot10^{-2}$, indicating no non-carcinogenic risks from chromium. The non-carcinogenic health risk based on the maximum $\mathrm{Cr_{tot}}$ concentration in PM10 was acceptable, too, as it was not in excess of one (Table 3). These risk values are no different to those found in the literature, e.g., HQ in Italy was in the range $1.5\cdot10^{-2}$ – $5.4\cdot10^{-2}$ (Diana et al., 2023).

4 Conclusion

The mean concentrations of PM10 (40±17 µg/m^3) and PM2.5 (33±15 µg/m^3) in the city were above the national (40 µg/m^3 and 20 µg/m^3, respectively) and European (40 µg/m^3 and 25 µg/m^3, respectively). The total chromium content in PM10 ranged widely from 0.56 to 4.09 ng/m^3 and averaged 1.71±0.83 ng/m^3. The mean Cr(VI) concentration in PM10 was 0.38 ng/m^3 in the entire measurement period. Chromium(VI) accounted for ca. 20% of $\mathrm{Cr_{tot}}$ content in the particulate matter. The seasonality of $\mathrm{Cr_{tot}}$ and Cr(VI) concentration changes could be noted. The concentrations were maximum in the winter (heating) season: 2.23 ng/m^3 and 0.84 ng/m^3, respectively, most likely a result of a greater share of the air polluted by fuel combustion sources in the air emissions of this type of pollution. The share of Cr(VI) in PM in the individual seasons varied as well: it was minimum in summer (9.1% of $\mathrm{Cr_{tot}}$) and maximum in winter (40% of $\mathrm{Cr_{tot}}$).

Out of the airborne particulate matter fractions investigated ($\mathrm{PM_{2.5-10}}$, $\mathrm{PM_{1-2.5}}$, $\mathrm{PM_{0.25-1}}$, $\mathrm{PM_{0.25}}$), both $\mathrm{Cr_{tot}}$ and Cr(VI) concentrations were maximum in the finest fraction – PM0.25. Toxicity related to transitive metals is greater for fine than for coarse dust since, once they penetrate the respiratory system, the finest particulate matter particles reach pulmonary alveoli, where 60-80% of a transmitted element enters the blood (Rogula-Kozłowska, 2013b). The health risk to urban residents, both carcinogenic and non-carcinogenic, is estimated to be gravest in winter as $\mathrm{Cr_{tot}}$ and Cr(VI) concentrations reach their top values. Regardless of the season, however, these risk levels to the residents of Radom were within the acceptable risk range.

Research into the forms of atmospheric Cr is limited and atmospheric Cr(VI) needs to be further investigated.

Data availability

Data sets are available at https://doi.org/10.5281/zenodo.14808852 (Łożyńska, M., et al., 2025)

CRediT authorship contribution statement

M.Ł. - Data curation, Formal analysis, Methodology, Writing – original draft, Writing – review and editing, Conceptualization, Investigation, Validation; **M.T.** – Data curation, Methodology, Writing – original draft, Writing – review and editing, Conceptualization, Investigation, Validation; **A.M.** - Data curation, Methodology, Visualization, Investigation; **R.Ś.** – Conceptualization, Methodology, Project administration, Supervision.

Declaration of Competing Interest

The authors declare that they have no conflict of interest.

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