

Short communication

Chromium(III/VI) speciation in urban aerosol

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ARTICLE INFO

Article history:

Received 25 May 2010

Received in revised form

30 November 2010

Accepted 1 December 2010

Keywords:

Speciation

Hexavalent chromium

Trivalent chromium

Urban aerosol

Poland

ABSTRACT

Chromium(III/VI) speciation was measured in total suspended particulate (TSP) fraction of urban aerosol collected at five sites with different municipal structures. The results show that the highest airborne chromium (III) concentrations occurred at the industrial zone. In the other parts of city the differences between mean concentrations of total chromium were not statistically significant. The higher concentration of total Cr results, to a small extent, from higher dustiness of air. The industrial dust turned out to be almost fivefold richer in chromium(III). The level of chromium(VI) in air over the whole city was constant, which seems to exclude any presence of local sources of emission of this species of chromium. The mean Cr(VI) concentration of 6.0 ng m^{-3} is close to the Inhalation Reference Concentration of Cr(VI). In the industrial zone airborne chromium(VI) constitutes 11% of total chromium. However, in the city centre with the lowest concentration of airborne Cr(III), the share of Cr(VI) is 50%. The percentage of Cr(VI) remains at 30–40% in aerosol collected close to transit roads.

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1. Introduction

Chromium is emitted into the atmosphere from both anthropogenic and natural sources. On a regional scale the natural sources account for 30–40% of total emission (Pacyna, 1986). Chromium emission from anthropogenic sources in Europe in 2000 was estimated at 2711 Mg and it has been decreasing (Pacyna et al., 2007). In Poland anthropogenic emission of chromium decreased from 280 Mg year⁻¹ to 45 Mg year⁻¹ within the 1980–2005 period. Combustion processes are responsible for 73%, production processes for 23% and road transport for 4% of chromium emission (IOS, 2009).

Airborne chromium exists in two valence states: Cr(III) and Cr(VI) differing considerably in toxicity and behaviour in the environment. More toxic Cr(VI) is released into the atmosphere from industrial sources e.g. ferrochrome production plants, chrome-plating plants, power plants, incinerators, cement plants and welding processes (Werner et al., 2007).

Airborne total Cr concentration in non-polluted areas remains at a low level of 1–40 ng m⁻³ (Puxbaum, 1991) and the mean concentration of Cr(VI) is even lower – 0.5 ng m⁻³ (Seinfeld and Pandis, 2006). In urban areas, close to chromium emission sources in particular, Cr(VI) concentration can achieve much higher values, e.g. 20 ng m⁻³ close to a foundry (Krystek and Ritsema, 2007) and 20–70 ng m⁻³ around a ferrochrome smelter (Mandiwana et al., 2006). The mean concentrations of total chromium in the air in Poland were similar: in towns of Silesia (heavy industry region) – 30 ng m⁻³ (Nowak and Kwapuliński,

1991), in the central part of Poland (the city of Lodz) – 5 ng m⁻³ (Bem et al., 2003), in the vicinity of a power plant $2 \mu\text{g m}^{-3}$ (Nowak and Kwapuliński, 1991). There is no data on the occurrence of chromium (VI) in urban aerosol of Polish towns.

The aim of this study was to gain more insight into the variability of chromium(III/VI) speciation in atmospheric aerosol in various urban environments, such as an old city centre, a suburban area, ring roads and an industrial area.

Radom is an interesting place for carrying out such investigations because potential chromium pollution results not only from the old municipal structure employing individual coal heating, transit road traffic and metalworking activities but also from over 70 years of tanning industry activities concentrated in the area.

2. Experimental

2.1. Sampling area

Radom is a medium-sized city (a population of 225,000, 112 km² in area), situated in the central part of Poland, 100 km south of Warsaw. Local emission sources of chromium are vehicle traffic, coal combustion at homes, coal-fired municipal heating plants and a number of metalworking plants (ca. 2000 workers). The heating network supplies heating to 54% of heated surfaces while coal-fired boilers and domestic furnaces to 24% of heated surfaces. In the Radom area there are numerous spots which are strongly polluted by tannery waste and unreclaimed tannery sludge lagoons which deserve to be called *chromium hot spots* (Świetlik, 2001).

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2.2. Aerosol sampling

Sampling of airborne dust was carried out in winter (cold, overcast and wet weather; heating season), spring (variable weather; heating season until the middle of April) and summer (warm, sunny weather) in 2009 at five points in the city area, which represent several types of local anthropogenic emission: P-2 and P-3 domestic emission + vehicular emission (21 samples); P-1 and P-4 vehicular emission > domestic emission (36 samples), and P-5 industrial emission (14 samples).

The samples were collected only in precipitation-free periods (3–5 days), usually three successive samples were obtained during the sampling event. Sampling was not performed in parallel.

The airborne particulate matter was collected on quartz fiber circular filters (Type TFAQ 102, 4 inches, STAPLEX) using a high-volume air sampler (Model TFIA-2 STAPLEX, USA), which was positioned at a height of 1.5 m above the ground level and 7–10 m from the edge of the roadway.

The air was drawn through the filter at a mean flow rate of $0.6 \text{ m}^3 \text{ min}^{-1}$. Samples were collected over a period of 90 min. Before analysis the filters with the deposit were cut into four equal pieces.

2.3. Determination of total suspended particulates (TSP)

The mass concentration of TSP was calculated by dividing the difference of the filter mass after and before exposure by the product of the mean flow rate and sampling period.

2.4. Determination of pseudototal chromium

Microwave-assisted digestion (65% HNO_3 , GR Merck; 30% H_2O_2 , GR Lach-Ner) of the airborne particulate matter collected on the filters was applied prior to GF-AAS measurements (Perkin–Elmer 3100 AAS/HGA 600/AS-60). LOD (instrumental) was found to be $1.0 \mu\text{g L}^{-1}$ of Cr or 3.4 ng m^{-3} as the concentration of Cr in air. The total Cr concentrations in the air were calculated after the filter blank correction, mean 6.2 ng m^{-3} ($n = 3$).

2.5. Determination of chromium(VI)

The leaching of Cr(VI) from the aerosol samples was carried out similarly as described in the EPA 3060A method (USEPA, 1996). The concentration of the extraction solution was reduced five times in order to avoid solubilization of the quartz filter ($0.056 \text{ M Na}_2\text{CO}_3/0.080 \text{ M NaOH}$).

Determination of Cr(VI) was performed using the technique of catalytic cathodic stripping voltammetry with adsorption of Cr(III)-DTPA complexes (CCSV-DTPA) (Li and Xue, 2001). 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). LOD (instrumental) was found to be $2.9 \mu\text{g L}^{-1}$ or 1.0 ng m^{-3} as the concentration of Cr(VI) in air. The mean value of the blank filter extract 2.5 ng m^{-3} ($n = 4$) was subtracted from the value obtained.

2.6. Determination of chromium(III)

The concentration of Cr(III) was calculated as a difference of total Cr concentration and Cr(VI) concentration.

3. Results and discussion

All the results of the determination are given in Appendix A. The observed monthly levels of the chromium fractions during a six-month sampling period are displayed in Fig. 1.

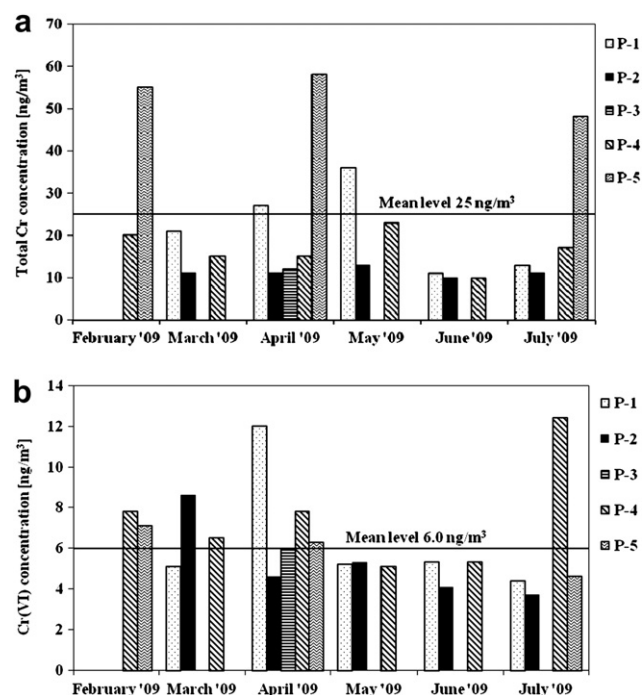


Fig. 1. Levels of chromium in atmospheric air of the city of Radom during a six-month sampling period: a – total Cr, b – Cr(VI); (sampling points: P-1, P-2, P-3, P-4, P-5).

The concentration of atmospheric total Cr in Radom varies within a relatively wide range, from 2.1 ng m^{-3} to 98 ng m^{-3} . The mean level of total Cr 25 ng m^{-3} does not differ significantly from the values recently published for several other cities: 27 ng m^{-3} Isfahan (Iran) (Talebi, 2003), 16.3 ng m^{-3} Frankfurt am Main (Germany) (Zereini et al., 2005), 7.1 ng m^{-3} Seville (Spain) (Fernández et al., 2000), and 2.7 ng m^{-3} Detroit (USA) (Utsunomiya et al., 2004).

A variation in total chromium concentration can be observed in various parts of Radom: low (12 ± 4) ng m^{-3} in the city centre (P-2 and P-3), higher (17 ± 8) ng m^{-3} in the vicinity of transit roads (P-1 and P-4) and high (53 ± 19) ng m^{-3} in the industrial area of the city (P-5). Taking into account the variability of the recorded total chromium concentrations determined by their standard deviation (after skipping outliers), one can assume that the differences between mean concentrations of total Cr in P-1, P-2, P-3 and P-4 are not statistically significant (Fig. 2). However, the level of total Cr in the air of the industrial area stands out. Production plants have a decisive influence on the level of the ambient air total chromium concentration in this part of Radom. Comparing the mean concentrations of total Cr in urban areas with various types of local anthropogenic emission, it can be estimated that in the industrial zone (P-5) the share of chromium originating from heating and vehicular traffic amounts to ca. $\frac{1}{3}$ total Cr.

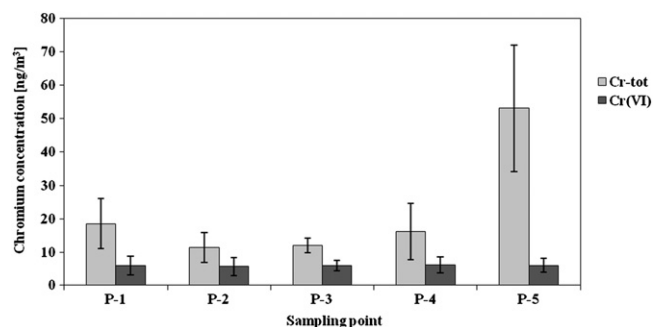


Fig. 2. Mean levels of total Cr and Cr(VI) in atmospheric aerosol in Radom (the ranges are illustrated by bars).

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