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Short communication

Regional atmospheric Cr(VI) pollution from the Bushveld Complex, South Africa



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ABSTRACT

Hexavalent chromium, Cr(VI), is a proven human carcinogen. Of interest in this paper was the regional atmospheric pollution of Cr(VI) from the ferrocromium and related industries located in the western Bushveld Complex (wBC) of South Africa. A significant fraction of the world's ferrocromium and platinum group metals is produced in this region. Particulate matter (PM), in two size fractions, i.e. PM_{2.5} ($\leq 2.5 \mu\text{m}$) and PM_{2.5-10} (2.5–10 μm), was sampled for a full calendar year at a regional background site, which is situated downwind of the wBC on the dominant anti-cyclonic recirculation route of air mass over the South African interior. Results indicated that Cr(VI) concentrations in air masses that had passed over the regional background were below the detection limit of the analytical technique applied, but that Cr(VI) in air masses that had passed over the wBC were elevated and had a median concentration of 4.6 ng/m³. The majority of Cr(VI) was found to be in the finer size fraction (PM_{2.5}), which could be explained by the nature of Cr(VI)-containing PM being emitted by the sources in the wBC and the atmospheric lifetimes of different PM size fractions. The results further indicated that it is possible that not only pyrometallurgical sources in the wBC, but also other combustion sources outside the wBC contributed to the observed atmospheric Cr(VI) concentrations.

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1. Introduction

Hexavalent chromium, i.e. Cr(VI), is a proven human carcinogen, particularly affecting the respiratory system (Beaver et al., 2009). Cr(VI) pollution is of international interest, since many countries are affected, e.g. the United States of America (Oze et al., 2004), New Caledonia (Oze et al., 2004), Mexico (Robles-Camacho and Armienta, 2000), India (Dubey et al., 2001) and South Africa (Loock et al., 2014).

Various anthropogenic (e.g. Loock et al., 2014; Du Preez et al., 2015; Mandiwana et al., 2007) and natural (e.g. Panichev et al., 2008; Oze et al., 2004, 2007; Steinpress et al., 2004; Robles-Camacho and Armienta, 2000) activities can lead to Cr(VI) pollution. Of particular interest in this paper is the regional atmospheric

pollution of Cr(VI) associated with the ferrocromium (FeCr) and related industries in South Africa. FeCr is a relatively crude alloy, consisting principally of Cr and iron (Fe). It is used mainly for the production of stainless steel that is a vital modern alloy. FeCr is mainly produced by the carbo-thermic reduction of chromite ore, mostly in submerged arch furnaces (SAFs) or direct current furnaces (DCFs) (Beukes et al., 2010). Chromite, a mineral with a spinel crystal structure, is the only commercially viable source of new Cr units. South Africa holds a significant portion of the world's viable chromite ore resources (Kleynhans et al., 2012 and references therein) and is the second largest FeCr-producing country (Beukes et al., 2012 and references therein). In South Africa, there are 14 separate FeCr-producing smelters, each with two to six large SAFs and/or DCFs (Beukes et al., 2012). Most of the afore-mentioned smelters are concentrated in or close to the Bushveld Complex (name of the geological structure), wherein the South African chromite deposits occur. The Bushveld Complex is the world's largest chromium and platinum group metals deposit, also with significant reserves of other metals such as vanadium (Xiao and

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Laplante, 2004; Moskalyk and Alfantazi, 2003). The production of FeCr is a reducing process, during which Cr(III) in the ore is reduced to Cr(0). However, small amounts of Cr(VI) are unintentionally generated by various processing steps applied by the FeCr industry (Du Preez et al., 2015; Beukes et al., 2010, 2012; Mandiwana et al., 2007; Beukes and Guest, 2001). South Africa is also one of the largest platinum group metals (PGMs) producers (Xiao and Laplante, 2004). Apart from the FeCr industry, the PGM mining and metallurgical refining industries in South Africa also consume significant volumes of chromite ore (Xiao and Laplante, 2004; Cramer et al., 2004). Considering that PGMs are primarily used in the manufacturing of automotive catalytic converters to improve air quality reinforces the notion that the Bushveld Complex is not only of national, but also of international importance.

The western limb of the Bushveld Complex (wBC) is the most exploited, with 11 pyrometallurgical smelters occurring within an approximate 55 km radius (Venter et al., 2012; Hirsikko et al., 2012). Venter et al. (2012) indicated that air quality in the wBC is problematic, with ozone (O₃) and particulate matter (PM) with aerodynamic diameter less than 10 µm (PM₁₀) regularly exceeding the limits prescribed by the South African national ambient air quality standards (NAAQS). Hirsikko et al. (2012) indicated that high amounts of Aitken (20–100 nm in diameter) and accumulation (100–840 nm in diameter) mode particles in the morning and evening originate from household combustion for space heating and cooking from the numerous semi- and informal settlements that are in the wBC, while, during daytime, SO₂-based nucleation followed by condensational growth by vapours from anthropogenic and natural sources resulted in a large number of concentrations of nucleation (1–20 nm in diameter) and Aitken mode particles. Relatively recently, the wBC was also included in a declared air pollution hotspot in terms of the South African National Environmental Management Act (NEMA): Air Quality, termed the Waterberg Priority Area (www.environment.gov.za/sites/default/files/gazetted_notices/nemaqa_waterberg_declaration_g35435gen495.pdf, accessed 28 February 2016). The proclamation of such a priority area indicates that the South African government recognises that air quality standards in this area are regularly exceeded and that improvement in air quality is required.

Notwithstanding the national and international importance of the wBC, the known air quality issues therein and the potential for atmospheric Cr(VI) pollution from there, an assessment of regional atmospheric Cr(VI) pollution from the wBC has not yet been undertaken. In order to at least partially address this knowledge gap, sampling and Cr(VI) analyses were performed at the Welgegund atmospheric research station (www.welgegund.org).

2. Measurement site and methods

2.1. Sampling

In the atmosphere, Cr(VI) is associated with PM, since the vapour pressure of all Cr compounds at ambient conditions is negligible (Kimbrough et al., 1999; Seigneur and Constantinou, 1995). All inter-conversion reactions leading to possible Cr(VI) formation and reduction to Cr(III) are water phase reactions (Kimbrough et al., 1999; Seigneur and Constantinou, 1995). Wet deposition of atmospheric Cr(VI) was not specifically considered in this work, although it is likely that solubilised Cr(VI) will be reduced to Cr(III) (Kimbrough et al., 1999; Seigneur and Constantinou, 1995). Considering the afore-mentioned, only Cr(VI) occurring in PM was evaluated, since the dispersion of PM would be the principal mode of regional Cr(VI) distribution.

Starting at 00:00 am local South African time, daily 24-h PM_{2.5} (≤2.5 µm) and PM_{2.5–10} (2.5–10 µm) samples were automatically

collected on 47 mm PTFE filters (GIC Scientific) with a Dichotomous Partisol sampler (Rupprecht & Patashnick Co., Inc.) for a full calendar year, i.e. 1 June 2012–31 May 2013. The flows through the afore-mentioned size fractions were, 10.0 and 6.7 L/min, respectively, with the overall flow being 16.7 L/min. Sampling was conducted without a denuder, which implies that reactive gases that could lead to Cr(III) oxidation was not removed. Previously published results indicated that sampling without a denuder could lead to conversion of Cr(III) in excess of 10% (Mennen et al., 1998). The results reported in this paper should therefore be considered within the limitations of the sampling method applied. However, as will be indicated in subsequent sections, adequate preventative measures were applied during sampling extraction to prevent any inter-conversions between Cr(VI) and Cr(III).

Sampling was conducted at the Welgegund atmospheric research station (latitude 26°34'10"S, longitude 26°56'21"E, 1480 m AMSL), which is situated approximately 100 km west from Johannesburg on a commercial farm. Numerous authors have previously described this research station, its surroundings and the measurements conducted (Booyens et al., 2015; Jaars et al., 2014; Tiitta et al., 2014; Vakkari et al., 2014). For this investigation, Welgegund was a particularly good measurement site for two reasons. Firstly, Welgegund is situated approximately 105 km downwind of the nearest pyrometallurgical smelter in the wBC on the dominant anti-cyclonic recirculation route of air mass over the interior of South Africa (Garstang et al., 1996). This implies that the site is ideally positioned to determine the regional effect of air masses that had passed over the wBC. Secondly, Welgegund is considered to be a regionally representative background site with no direct impacts from pollution sources in close proximity.

Fig. 1 indicates the location of Welgegund within a regional southern African context and the extent of the Bushveld Complex ore deposits (greyscale areas on the southern African map). Additionally, in the zoomed-in map, the locations of large pyrometallurgical smelters in the wBC, the Johannesburg–Pretoria (Jhb-Pta) megacity (Lourens et al., 2012) and large atmospheric point sources (e.g. coal-fired power stations, petrochemical operations and pyrometallurgical smelters) in the interior of South Africa are indicated.

2.2. Cr(VI) extraction and analysis

Ultra-pure water (resistivity 18.2 MΩ cm⁻¹), produced by a Milli-Q water purification system, was used during all procedures requiring dilution, as well as to clean all glassware used. A buffer solution (Na₂CO₃–NaOH) to extract Cr(VI) from samples was prepared from sodium hydroxide (Promark chemicals) and sodium carbonate (Minema). Nitrogen (N₂) (99.999% pure, from AFROX) was used to purge all Cr(VI) extraction solutions and the headspace of extraction containers during leaching procedures. Diphenylcarbazide (DPC) (Fluka), high pressure liquid chromatography (HPLC) grade methanol (Sigma Aldrich) and 98% analytical grade sulphuric acid (Rochelle Chemicals) were used during the Cr(VI) analysis.

Total Cr(VI) was extracted from the filters into the aqueous phase with appropriate precautions taken to prevent any inter-conversions between Cr(VI) and Cr(III) (Ashley et al., 2003). Both water-soluble and water-insoluble Cr(VI) compounds were extracted by conducting hotplate digestion extraction with a buffer solution (Ashley et al., 2003). Ambient air in the hot alkaline extraction solution could potentially lead to the in situ formation of Cr(VI) in the presence of Cr(III). Therefore, in order to prevent the unwanted oxidation of Cr(III), the extraction solutions and the headspace of the extraction containers were purged with N₂ prior to, during, and after Cr(VI) extraction (Ashley et al., 2003; Du Preez

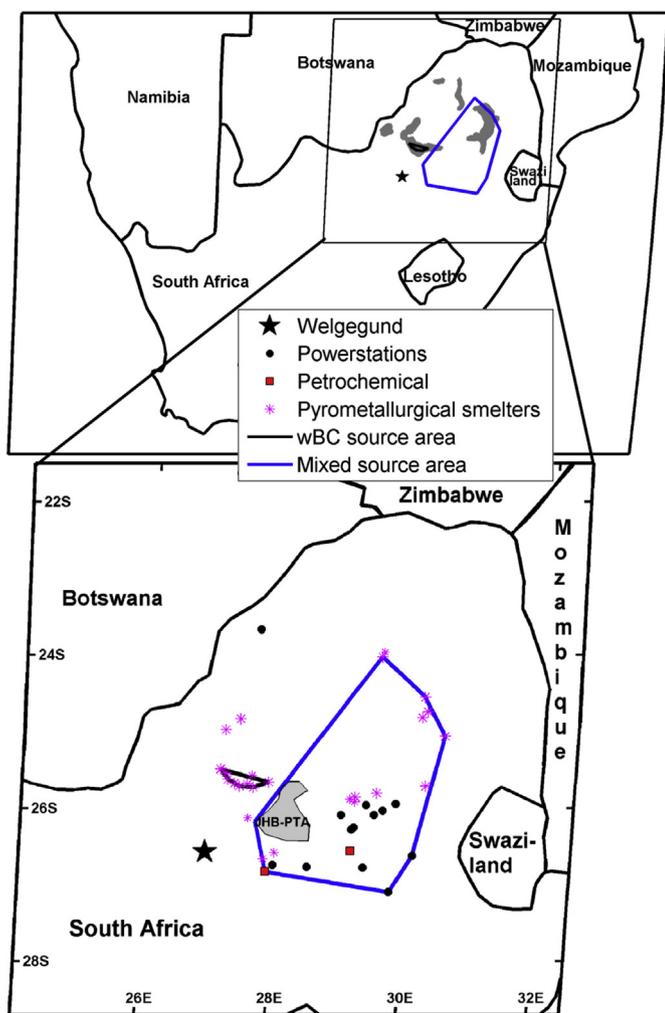


Fig. 1. The location of Welgegend within a regional southern African context and the extent of the Bushveld Complex ore deposits (greyscale areas in the southern African map). Additionally, in the zoomed-in map, the locations of large pyrometallurgical smelters in the wBC, the Johannesburg-Pretoria megacity (greyscale area in the zoomed-in map) and large atmospheric point sources in the interior of South Africa are indicated.

et al., 2015). Both samples and blanks were prepared, extracted and analysed with the same methods.

Various methods can be used to quantify Cr(VI) (Broadhurst and Maidza, 2006; Gómez and Calloa, 2006; Jacobs et al., 2004). The Cr(VI) analytical method applied in this study was adapted from Dionex Application updates 144 and 179 (2003 and 2011), as well as Thomas et al. (2002), as indicated by Loock et al. (2014). Cr(VI) analyses were conducted with an ion chromatograph (IC) (Thermo Scientific Dionex ICS-3000) with a post-column DPC colorant delivery system (AXP pump) coupled to an ultraviolet–visible (UV–vis) absorbance detector. The guard and analytical columns were Dionex IonPac AG7 4 × 50 mm and Dionex IonPac AS7 4 × 250 mm, respectively. A 1000 µl injection loop was used, as well as two 375 µl knitted reaction coils fitted in series. The post-column colorant reagent and eluent was prepared as previously described (Loock et al., 2014). An eluent flow rate of 1.00 ml/min was used, while the post-column colorant reagent was delivered at a flow rate of 0.5 ml/min.

Cr(VI) standard solutions for the calibration of the analytical instrument were prepared from a Spectrascan chromate reference standard with a specified concentration of $1009 \pm 5 \mu\text{g/ml CrO}_4^{2-}$.

According to literature, the Cr(VI) detection limit for this method was $1 \mu\text{g/l}$ (Dionex Application update 144, 2003). However, additional PEEK tubing was installed between the AXP pump and the back pressure tubing in order to reduce the pulse caused by the AXP pump that resulted in noise on the baseline of the chromatograms. This modification ensured a smoother baseline that improved the detection limit to $0.9 \mu\text{g/l}$, which was determined from the baseline amplitude and the calibration sensitivity (slope of the calibration curve over a Cr(VI) concentration range that gave linear response) according to the method described by Skoog et al. (2014) from a confidence factor that correlated with a 98.3% confidence level. By considering the volume of air sampled, the aforementioned detection limit in aqueous solution related to an atmospheric Cr(VI) detection limit of 0.84 ng/m^3 . The accuracy of the combined extraction and analysis method was verified by analysis of a Community Bureau of Reference (former reference materials programme of the European Commission) BCR N° 545 welding dust filter certified reference material (individual identification N° B7-36, purchased on 25 January 2013). After considering dilution factors, a value of 39.7 mg/g Cr(VI) was obtained, which was within the uncertainty of the reference material that was defined as the half width of the 95% confidence interval of the mean of 40.2 mg/g Cr(VI) and $39.5 \text{ mg/g total leachable Cr}$. Due to cost considerations, only one such certified reference material filter was analysed and precisions could not be calculated from it. Every filter obtained via sampling at the Welgegend research station in the study was analysed three times, with the mean used in further data processing. The standard deviation for each such set of three analyses was determined. As a measure of precision the average of all the aforementioned standard deviations were found to be 0.4 ng/m^3 .

2.3. Air mass histories and association with Cr(VI) analyses

Air mass history was determined by calculating back trajectories with the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) model (version 4.8), developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory (ARL) (Draxler and Hess, 2004). This model was run with meteorological data of the GDAS archive of the National Centre for Environmental Prediction (NCEP) of the United States National Weather Service and archived by the Air Resources Laboratory (ARL) (www.arl.noaa.gov/archives.php, accessed 11 November 2015). All back trajectories were calculated for 96 h, arriving every hour for the entire measurement period, at a height of 100 m. An arrival height of 100 m was chosen since the orography in HYSPPLIT is not very well defined, and therefore lower arrival heights could result in increased error margins on individually calculated trajectories.

In order to link sampled PM with air mass history, two source regions were defined. The first source region (indicated as the black polygon in the zoomed-in portion of Fig. 1, as well as Fig. 2a, b and c) comprised a relatively small area in the wBC wherein nine pyrometallurgical smelters occurred. The second source region (indicated as the blue polygon in the zoomed-in portion of Fig. 1, as well as Fig. 2a, b and c) encompassed the Jhb-Pta megacity, as well as the area where most of the very large atmospheric point sources (e.g. coal-fired power stations, petrochemical operations and other pyrometallurgical smelters) occur in the South African interior. Individually calculated hourly-arriving back trajectories for each 24-h sample period were then overlaid on a map that was divided into $0.2^\circ \times 0.2^\circ$ grid cells. On these maps, a colour code indicated the number of trajectories passing over each $0.2^\circ \times 0.2^\circ$ grid cell, with red being the highest number. These 24-h sampling period overlay back trajectory maps were then visualised and sorted into four categories:

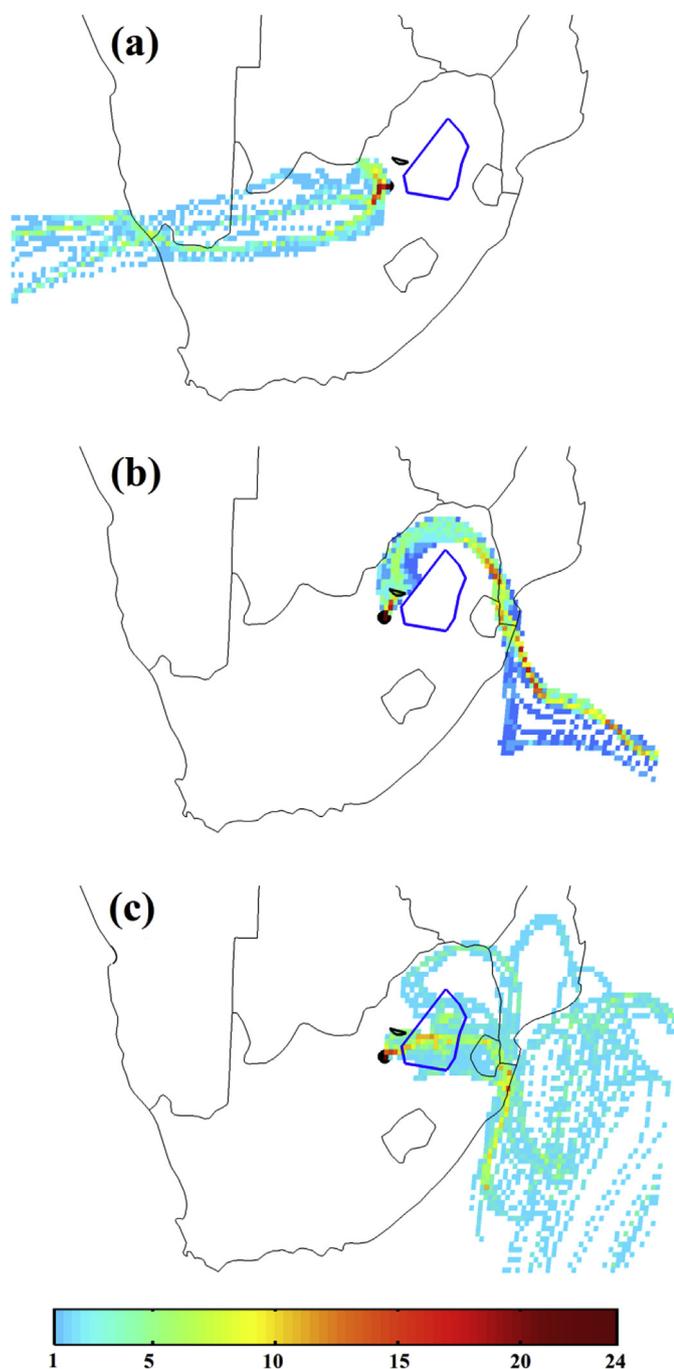


Fig. 2. Examples of air masses calculated for a specific 24-h sample that had passed over the regional background (a), air masses that had spent at least 2 h over the wBC source region (b) and air masses that had spent at least 2 h over the wBC source region, as well as five or more hours over the large mixed source region (c). The colour bar indicates the frequency of hourly-arriving back trajectories calculated for a day passing over $0.2^\circ \times 0.2^\circ$ grid cells.

- 1) Air masses that had passed over the regional background mainly between north and south, to the west of Welgegund, but not over the two source regions defined in Fig. 1 (Fig. 2a as an example);
- 2) Air masses that had spent at least 2 h over the source region defined in the wBC (black polygon in Fig. 1) where nine pyrometallurgical smelters are (Fig. 2b as an example);
- 3) Air masses that had spent at least 2 h over the source region defined in the wBC (black polygon in Fig. 1), as well as five or

more hours over the large mixed source region defined in Fig. 1 (blue polygon) (Fig. 2c as an example). These samples were referred to as mixed overpass; and

- 4) Air masses that did not represent the regional background (category 1), but also did not qualify for category 2 or 3. Samples collected on these days were not considered further.

3. Results and discussions

According to the air mass history selection criteria applied (Section 2.3), 24 samples (each corresponding to 24 h of sampling) could be identified within the year of sampling for which the air history was classified as passing over the wBC source region (category 2, Fig. 2b). Additionally, 23 sample periods were identified for which the air mass history was classified as mixed (category 3, Fig. 2c), while the air mass history for 53 sample periods was classified as passing over the regional background (category 1, Fig. 2a).

Atmospheric Cr(VI) concentrations in the $PM_{2.5}$ and $PM_{2.5-10}$ samples associated with air masses that were classified as passing over the regional background were below the detection limit of the procedure applied. This does not imply that no Cr(VI) occurs in the PM associated with such air mass history, it merely indicates that the concentrations of Cr(VI) were low and could not be detected with the analytical technique applied.

In contrast to the above-mentioned, Cr(VI) in samples associated with air masses passing over the wBC source region (category 2, Fig. 2b) or the mixed region (category 3, Fig. 2c) was substantially higher. Fig. 3 presents the statistical distribution (median, 25 and 75th percentiles and ± 2.7 standard deviation) of Cr(VI) in both the $PM_{2.5}$ and $PM_{2.5-10}$ size fractions, as well as the combined PM_{10} fractions, which include both of the afore-mentioned fractions. From these results, it is evident that the majority of the Cr(VI) is present in the $PM_{2.5}$ fraction and to a lesser extent in the coarser $PM_{2.5-10}$ size fraction. Some of the Cr(VI) concentrations determined in the $PM_{2.5-10}$ size fraction were even below the detection limit. This concentration distribution is attributed to two reasons, i.e.: 1) Most of the pyrometallurgical processes potentially releasing PM-containing Cr(VI) will emit very fine PM. The Cr(VI)-containing particles in the off-gas from open and semi-closed SAFs, or from closed SAFs and DCFs, are removed with bag filters and wet venturi scrubbers, respectively (Beukes et al., 2012; Niemelä et al., 2004). These systems remove 99.9% of PM from the off-gas, but are not very effective in capturing PM_{10} (Niemelä et al., 2004). Additionally, Cr(III) in the PM_{10} that passes through the flare of the CO-rich off-gas

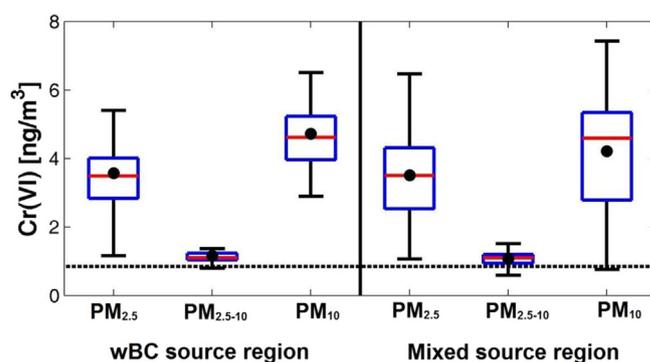


Fig. 3. Cr(VI) concentrations in $PM_{2.5}$ ($\leq 2.5 \mu m$), $PM_{2.5-10}$ ($2.5-10 \mu m$) and PM_{10} (sum of $PM_{2.5}$ and $PM_{2.5-10}$) associated with air masses that had passed over the wBC- and mixed source regions. The red line indicates the median, the black dot the mean, the blue rectangle the 25th and 75th percentiles, the whiskers ± 2.7 times the standard deviation and the horizontal black dashed line the detection limit.

originating from closed SAFs or DCFs being burned may be oxidised resulting in the formation of Cr(VI) (Du Preez et al., 2015). 2) Finer particles have longer atmospheric lifetimes than coarser particles. Therefore, even if coarser Cr(VI)-containing particles are released by mining and metallurgical activities in the wBC, these particles will be removed from the atmosphere relatively quickly, preventing their transport to the Welgegund research station. For instance, Beukes and Guest (2001) reported that the dry milling of chromite ore could lead to the generation of Cr(VI)-containing particles. However, the two most commonly applied FeCr production processes applied by the South African FeCr industry, i.e. pelletised oxidative sintering and pelletised pre-reduction, have ore milling size specifications of d_{90} (indicating the size for which 90% of particles are smaller) of 75 (Kleynhans et al., 2012) and 108 μm (Glastonbury et al., 2015), respectively. Such relatively coarse particles will not have a very long atmospheric lifetime and will therefore mostly only have a local influence within the wBC.

Apart from the above-mentioned deductions, the spread of Cr(VI) concentrations in air masses that had passed over the wBC source region (category 1, Fig. 2b) were much smaller than that of the mixed region. This smaller spread for the wBC source region is indicative of the similar types of sources within this area. Air masses that had passed over the mixed source region (category 3, Fig. 2c) occasionally had higher Cr(VI) concentrations than that of the wBC source region, indicating the existence of other potential sources of Cr(VI) in the mixed region. It is well known that relatively low grade coal with reasonably high ash content (Jeffrey, 2005) is consumed in South Africa for both industrial activities and for household space heating in semi- and informal settlements (Hersey et al., 2015; Venter et al., 2012). These sources could potentially also emit atmospheric Cr(VI) in the mixed source region.

It is also important to contextualise the atmospheric Cr(VI) concentrations reported here within a global context. As stated earlier, Cr(VI) concentrations of air masses that had passed mainly over the regional background (category 1, Fig. 2a) were below the detection limit of 0.84 ng/m^3 . The PM_{10} of air masses that had passed over both the wBC source region (category 2, Fig. 2b) and those that had passed over the mixed region (category 3, Fig. 2c) had median Cr(VI) concentrations of 4.6 ng/m^3 . This is higher than the average of 0.044 ng/m^3 for Washington DC (Tirez et al., 2011 and references therein) and the range reported for Vienna, i.e. 0.04–0.23 ng/m^3 (Hagendorfer and Uhl, 2007). However, the concentrations were in the same order as atmospheric Cr(VI) reported for a site in Northern Italy and at an industrial site in Tunis that had concentrations ranging between 0.68 and 3.68, and 5.4 and 7.8 ng/m^3 (Catrambone et al., 2013), respectively, as well as at two sites near a stainless steel production facility in Belgium that reported 90th percentiles of 3.5 and 14 ng/m^3 (Tirez et al., 2011).

4. Conclusions

As far as the authors could assess, this is the first scientific report on ambient atmospheric Cr(VI) concentrations for South Africa. Ambient Cr(VI) concentrations in air masses that had passed over the regional background were below the detection limit (0.84 ng/m^3). In contrast, air masses that had passed over the wBC and/or the mixed source regions had elevated Cr(VI) concentrations with an average of 4.6 ng/m^3 . The majority of Cr(VI) was found to be in the finer size fraction ($\text{PM}_{2.5}$), which could be explained by the nature of Cr(VI)-containing PM being emitted by the sources in the wBC source region and the atmospheric lifetimes of different PM size fractions. The results further indicated that not only pyrometallurgical sources in the wBC, but also other combustion sources outside the wBC could have contributed to the measured atmospheric Cr(VI). Current estimates of the atmospheric half-life

of Cr(VI) range from 16 h to 4.8 days (Kimbrough et al., 1999 and references therein). However, simultaneous measurements of atmospheric Cr(VI) concentrations in both the wBC and also at Welgegund could be carried out in future to quantify the range of atmospheric Cr(VI) half-life more precisely. Since numerous meteorological parameters are measured at Welgegund, multivariate data analysis methods could be applied to such a dataset to determine the effect of for instance relative humidity and temperature on the atmospheric half-life of Cr(VI). This would enable a better assessment and prediction of the regional dispersion of Cr(VI) from hotspots, such as the wBC in South Africa and similar areas internationally.

Conflict of interest

The authors of this study do not have any personal/financial conflicts of interest that could interfere with the objectivity of this work.

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