A survey of Cr(VI) contamination of surface water in the proximity of ferrochromium smelters in South Africa

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ABSTRACT

South Africa holds approximately three-quarters of the world's viable chromite ore reserves and is one of the largest ferrochrome producers. It is impossible to completely exclude oxygen from all high-temperature ferrochrome production steps, which results in the unintentional possibility of generating small amounts of Cr(VI) species that are generally considered as carcinogenic. In this study, Cr(VI) levels present in surface water within the vicinity of ferrochrome smelters located in the Bushveld Igneous Complex were monitored for a period of 1 year. The results indicated that surface water in the proximity of ferrochrome smelters was mostly unaffected by Cr(VI) pollution. Two surface water sampling sites were consistently impacted by relatively low level Cr(VI) pollution (annual mean values of 4.4 and 6.3 µg/ℓ, respectively), with no values in excess of the 50 µg/ℓ drinking water limit recorded. However, at two other surface water sampling sites, maximum Cr(VI) concentrations of 198 and 220 µg/ℓ were measured. The median Cr(VI) concentrations for these two sites were 1.8 and 1.9 µg/ℓ, respectively, indicating that Cr(VI) pollution of the surface water at these sites was erratic and most likely due to surface run-off. Although drinking water pollution was not the main focus of this paper, results indicated that drinking water in the proximity of most FeCr smelters was not polluted by Cr(VI). However, the annual mean Cr(VI) concentration of drinking water that originated from a borehole at one drinking water sampling site was 45.3 µg/ℓ, with several months exceeding the 50 µg/ℓ limit. Significant steps have, however, already been taken to remedy the situation.

Keywords: Cr(VI); hexavalent chromium; surface water; drinking water; South Africa; ferrochromium industry

INTRODUCTION

Stainless steel is a vital alloy in modern-day living. New chromium units in stainless steel are obtained via the inclusion of ferrochromium (FeCr) – a crude alloy consisting mostly of chromium and iron (Murthy et al., 2011; Cramer et al., 2004). FeCr is mainly produced during the pyrometallurgical carbo-thermic reduction of chromite (the most common chromium-containing ore) in submerged arc furnaces (SAFs) and direct current arc furnaces (DCFs) (Beukes et al., 2010). South Africa holds approximately three-quarters of the world's viable chromite ore deposits (Murthy et al., 2011; Cramer, et al., 2004). Historically, South Africa has dominated the production of FeCr (Beukes et al., 2012), due to the abundant chromite resources and the relatively low cost of electricity (Basson et al., 2007). However, China has recently grown its FeCr production to similar levels (ICDA, 2012). This rise in Chinese FeCr production can be attributed to economic growth in China, as well as to electricity shortages and dramatic increases in the unit cost of electricity in South Africa (Kleynhans et al., 2012). Notwithstanding the afore-mentioned problems facing the South African FeCr industry, it is set to remain a dominant producer.

During the production of FeCr, it is impossible to completely exclude oxygen from all high-temperature process steps, with the corresponding unintentional possibility arising to generate small amounts of Cr(VI)-containing species (Beukes et al., 2010). Cr(VI) or hexavalent chromium is generally considered as carcinogenic, although there seems to be inadequate evidence to support the carcinogenicity of all Cr(VI) compounds (IARC, 1997).

Beukes et al. (2010) presented a relatively comprehensive review on the possible generation of Cr(VI) during the various production steps utilised in FeCr production. Although this review focused specifically on the South African FeCr industry, these production steps are applied internationally. These authors (Beukes et al., 2010) indicated that small amounts of Cr(VI) might form during various FeCr production steps, e.g., dry milling of chromite (Glastonbury et al., 2010; Beukes and Guest, 2001), oxidative sintering of chromite agglomerates, and during the furnace smelting operation, especially for open or semi-closed furnaces. This can lead to small amounts of Cr(VI) being present in the off-gas originating from the smelting process and other high-temperature process steps, and fumes formed during the tapping process and in the slag (Beukes et al., 2010). The major wastes associated with the FeCr industry are slag, as well as bag filter dust and venturi sludge originating from the off-gas. Based on volume, slag is the largest FeCr waste, since slag-to-metal production ratios vary from approximately 1.1 to 1.9. Current arising (newly-produced) FeCr slags are generally not considered as hazardous and are used as building agglomerate in many countries (Riekkola-Vanhanen, 1999). Recently, FeCr slag in South Africa has also been declassified for such use (Beukes et al., 2012). In contrast, bag filter dust and venturi scrubber sludge are regarded as hazardous wastes. These materials are mostly recycled back into the process, or treated to reduce Cr(VI) and subsequently disposed of in fit-for-purpose waste storage facilities, e.g., a slimes dam.

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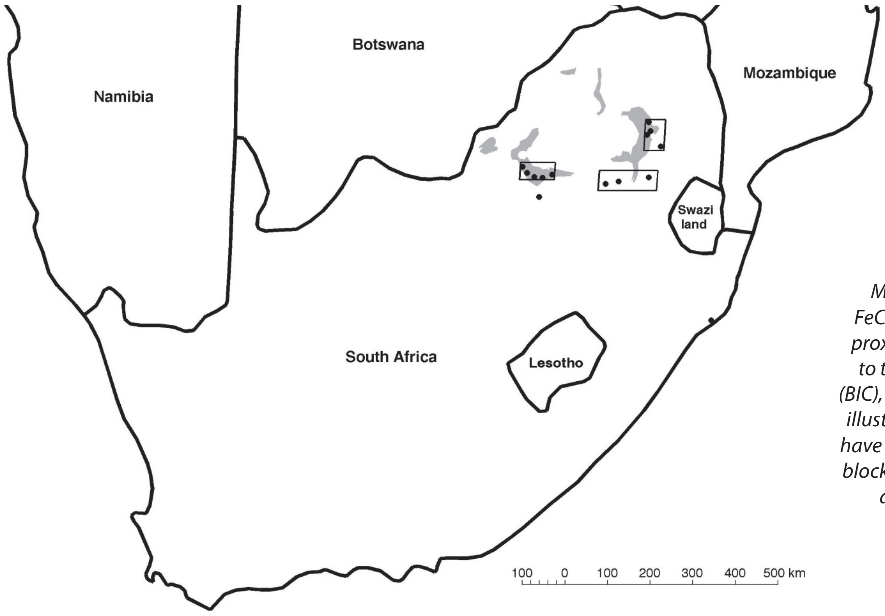

Figure 1
Map indicating the location of FeCr smelters with black dots. The proximity of most of these smelters to the Bushveld Igneous Complex (BIC), which is indicated in grey, is also illustrated. Additionally, three areas have been indicated with rectangular blocks. Enlarged maps of these three areas are presented in Fig. 2.

The Cr(VI) treatment processes applied by the South African FeCr producers were recently reviewed (Beukes et al., 2012) and are not discussed in further detail here.

Considering the size of the South African FeCr industry, it is obvious that an assessment of possible Cr(VI) pollution in the proximity of FeCr smelters should be conducted. However, limited studies have been conducted to determine environmental Cr(VI) contamination around such smelters. These studies have also focused on only one specific FeCr smelter (Sedumedi et al., 2009; Mandiwana et al., 2007). Cr(VI) pollution can manifest in air, soil and water (Bartlett, 1991). Due to the aqueous solubility of most Cr(VI) compounds (Ashley et al., 2003), soil and air contamination can eventually result in water contamination, due to Cr(VI) leaching from soils, as well as dry and wet deposition of atmospheric particles containing Cr(VI). The carcinogenicity of Cr(VI) is mainly associated with respiratory-induced ailments (Beaver et al., 2009; Thomas et al., 2002), which is especially important within an industrial occupational health context. However, in this paper, the focus was on Cr(VI) present in aqueous environments. Drinking water standards for total chromium and Cr(VI) have been adopted by various countries and range between 3 µg/ℓ and 100 µg/ℓ (Ma and Garbers-Craig, 2006). The South African drinking water standards for total chromium and Cr(VI) are 100 and 50 µg/ℓ, respectively. Although drinking water standards, guidelines and goals have been set for Cr(VI), there seems to be a conflict in literature pertaining to the toxicity or carcinogenicity of Cr(VI) in drinking water (Gatto et al., 2010; Stern, 2010; Beaumont et al., 2008).

In order to at least partially address the current knowledge gaps, i.e., the extent of Cr(VI) pollution in the proximity of FeCr smelters in South Africa, surface water close to FeCr smelters was evaluated over a period of 1 year. Although it was not the primary focus of this paper, drinking water was also considered to at least indicate problematic areas. It must be clearly stated that the intention of the authors with this paper was not to implicate any specific FeCr smelter or company, but rather to get a general picture of the extent of possible Cr(VI) pollution. Additionally, the authors hope that the data presented in this paper will be used to rectify possible problematic areas and thereby promote the sustainable development of the FeCr industry in South Africa. Due to the size of the FeCr industry in South Africa, this industry is vital for job creation and the growth of the economy.

EXPERIMENTAL

Reagents

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 sampling equipment and containers. Hanna pH buffers 7.01 and 10.01 were used to calibrate the pH meter prior to each sample collection campaign. Analytical grade (AR) ammonium sulphate (Merck) and 25% ammonium hydroxide (Associated Chemical Enterprises (ACE)) were used to prepare the buffer required for the sampling procedure. The afore-mentioned ammonium sulphate and ammonium hydroxide were also used to prepare the eluent utilised during Cr(VI) analysis. Diphenylcarbazide (Fluka), high pressure liquid chromatography (HPLC) grade methanol (Sigma Aldrich) and 98% analytical grade sulphuric acid (Rochelle Chemicals) were also used during the Cr(VI) analysis. Cr(VI) standard solutions for calibration of the analytical instrument were prepared from a Spectrascan chromate reference standard with a specified concentration of 1 009 ± 5 µg/mℓ CrO_4^{-2}. Cr(VI) solutions with known concentrations were also prepared form this reference standard, which were utilised to spike 1 of the 3 samples collected at each site.

Sampling site selection

Since the objective of this study was to assess the Cr(VI) contamination of surface water in the vicinity of FeCr smelters in South Africa, sampling site selection was critical. There are currently 14 separate FeCr smelters in South Africa (Beukes et al., 2012). Thirteen of these smelters are located within close proximity to the Bushveld Igneous Complex (BIC) where the chromite ore deposits in South Africa are found, while one smelter is located at the coast. The BIC stretches across the North West, Gauteng, Mpumalanga and Limpopo Provinces in South Africa. The locations of these FeCr smelters, as well as the extent of the BIC (presented by the grey regions), within a regional context are indicated in Fig. 1.

Ideally, sampling should have been conducted with the support of the local FeCr industry, government and private landowners to ensure full access to all the sites of interest. Information relating to the surface- and groundwater drainage patterns surrounding each FeCr smelter would also have been advantageous. However, certain limitations had to be considered during sampling site selection to make the study logistically feasible and scientifically credible. The following criteria were therefore used in order to identify surface water sampling sites:

- Sampling had to be logistically possible to enable monthly sampling campaigns.
- The study was conducted without prior notice to the FeCr industry and private landowners in the vicinity of the FeCr smelters. This ensured that the FeCr industry did not alter their operation in any manner to bias the results.
- The sites were selected to ensure easy access without trespassing on private property.
- Since South Africa has a relatively high crime rate (South African Police Service, 2012) and some of the smelters are located in relatively isolated rural settings, consideration had to be given to the safety aspects during monthly sampling.
- As far as possible, the directional flow of surface water drainage patterns was considered. This was achieved by examination of the drainage patterns by utilising Google Earth and by performing on-site inspections. In some instances, it might be possible that groundwater could contribute to surface water, e.g., springs. However, very limited information on groundwater drainage patterns around the relevant smelters was available in the public domain during the time of this study.
- The sampling sites were selected to also be able to capture possible spillages from the appropriate waste collection facilities (e.g. slimes dams) and surface run-off from the smelters, where possible.

Considering the above-mentioned criteria and constraints for sampling, surface water samples were collected in the proximity of 10 of the 14 FeCr smelters (Beukes et al., 2012) in South Africa. The smelter located near the coast (Fig. 1) was not considered due to logistical limitations, i.e., more than 600 km by road from the nearest smelter in the BIC. The smelter situated in the Johannesburg-Pretoria megacity (Lourens et al., 2012) was also not considered, since it would have been impossible to collect samples unnoticed in the proximity of this smelter for an extended period of time. Additionally, surface water samples were also not collected in the immediate surroundings of two more smelters, since no suitable surface water drainage structures (e.g. stream, rivers, cannels, erosion gutters) could be identified.

Although the focus of this paper was not on drinking water quality, drinking water samples were collected in parallel with surface water samples, since such data could in some instances give additional insight into surface water pollution issues. Sampling site selection for the drinking water sites was much less complicated, since samples were collected from restroom facilities accessible to the general public at filling stations as close as possible to the relevant smelters. It is assumed that drinking water obtained from such facilities would be representative of drinking water consumed by the population in the area close to that specific sampling site. Drinking water samples were collected in the proximity of 11 of the 14 FeCr smelters. Since surface water samples were not collected at the smelters located at the coast and in the Johannesburg-Pretoria megacity, drinking water samples were also not considered there. Additionally, drinking water samples were not collected close to another FeCr smelter, since the closest filling station was more than 25 km away. Collecting drinking water that far from the smelter is unlikely to be representative of the drinking water consumed by the community in the immediate vicinity of the smelter.

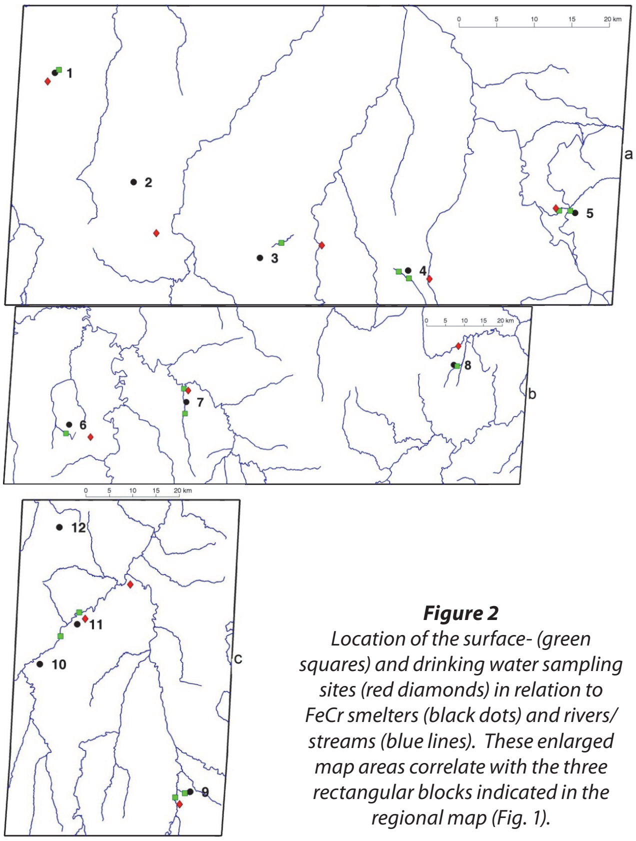

Figure 2
Location of the surface- (green squares) and drinking water sampling sites (red diamonds) in relation to FeCr smelters (black dots) and rivers/ streams (blue lines). These enlarged map areas correlate with the three rectangular blocks indicated in the regional map (Fig. 1).

In order to visualise the location of the surface- and drinking water sampling sites, as well as to indicate the proximity of these sites to the relevant smelters, these sampling sites are indicated on 3 maps in Fig. 2. In order to contextualise the location and the geographical extent of these three mapped areas, these areas were also indicated in Fig. 1 by the rectangular blocks.

In order to relate the sampling site location with the results obtained, the various FeCr smelters were numbered from 1 to 12 in Figs. 2(a), 2(b) and 2(c). Surface- and drinking water sampling sites were numbered accordingly, i.e., correlating to the number of the closest FeCr smelter. At the FeCr smelters numbered 4, 5, 7 and 9, two surface water sampling sites were located. These multiple collection points in the proximity of specific FeCr smelters were distinguished by indicating them as sampling sites ‘a’ and ‘b’. By adhering to the objectives of this paper, the authors refrained from referring to company, town/ city and river names that could be used to implicate any specific smelter.

Sampling duration

Most of the FeCr smelters are located in the geographical area commonly referred to as the South African Highveld. The Highveld covers an area of approximately 400 000 km^2, or roughly 30% of the surface area of South Africa. Laakso et al. (2012), with references therein, recently provided a concise description of the meteorological conditions over the South African Highveld. Almost all precipitation on the South African Highveld occurs during the wet season (middle October to April), with virtually no precipitation taking place during the dry season (May to middle October). These strong seasonal cycles could lead to bias if surface water samples were collected only in a specific season. In order to limit seasonal bias, sampling was conducted monthly for a full year, i.e., February 2011 to January 2012.

Sampling procedure

The first step during surface- and drinking water sampling at any given site consisted of collecting a 1 ℓ sample in a Schott Duran glass bottle. Thereafter, 100 ± 2 mℓ was transferred into a 100 mℓ glass sampling bottle. The pH of this 100 mℓ sample was measured with a portable Hanna Instrument (HI 991001) with an HI 1296 electrode. According to literature (Broadhurst and Maidza, 2006; Thomas et al., 2002; US Environmental Protection Agency (EPA) method 218.6, 1994), it is best practice to store aqueous Cr(VI)-containing environmental samples within a pH range of 9.0 to 9.5. Storage at these relatively high pH levels prevents the reduction of Cr(VI) by naturally occurring reducing agents, e.g., Fe(II) and S(VI) (He et al., 2004; Beukes et al., 2000; Beukes et al., 1999; Buerge and Hugh, 1997; Fendorf and Li, 1996) and also ensures that most of the Cr(VI) compounds are soluble (Ashley et al., 2003). This field pH measurement was therefore used to determine whether the pH of a specific sample should be raised by adding an ammonium sulphate–ammonium hydroxide buffer (Broadhurst and Maidza, 2006; Thomas et al., 2002; US EPA method 218.6, 1994). A fresh buffer solution was prepared prior to each sampling campaign. The buffer consisted of 3.3 g ammonium sulphate and 8.286 g ammonium hydroxide dissolved and diluted to 100 mℓ with Milli-Q water. If buffer addition was required, a calculated volume of buffer solution was added to the afore-mentioned 100 mℓ sample. Thereafter, the pH of this 100 mℓ sample was verified to ensure that the sample was within the targeted pH range. This first 100 mℓ sample was then discarded and not used further, since it could have been contaminated during the pH measurements.

During the next step of sampling, 3 additional 100 mℓ samples were transferred from the original 1 ℓ sample into 3 sampling bottles. The volumes of these three 100 mℓ samples were measured accurately with an A-grade 100 mℓ volumetric flask. If pH adjustment was required, the correct volume of buffer as determined by means of the above-mentioned procedure was added to all three of these 100 mℓ samples. One of these three 100 mℓ samples was also spiked with a predetermined amount of Cr(VI), which resulted in a controlled addition of 20 µg/ℓ Cr(VI) to the 100 mℓ sample. This was done to determine whether any Cr(III)-Cr(VI) interconversions occurred during transport and storage prior to analysis. The possible pH adjustments of all three 100 mℓ samples and the Cr(VI) spiking of one of the 100 mℓ samples resulted in a maximum dilution error of 1%, as previously specified (Dionex Application update 144, 2003 and Dionex Application update 179, 2011). The three 100 mℓ samples collected and prepared were then immediately placed in fit-for-purpose sample trays, which were stored in a 12/240 V temperature controlled 40 ℓ Engel chest fridge/freezer (model no: MT45F-G4-S) below 4°C up until analysis (Ashley et al., 2003; Dionex Application update 144, 2003; Dionex Application update 179, 2011).

Cr(VI) analytical method

The Cr(VI) analytical method utilised in this study was adapted from Dionex Application updates 144 and 179 (2003 and 2011), as well as Thomas et al. (2002). Cr(VI) analyses were conducted with an ion chromatograph (IC) with a post-column diphenylcarbazide colorant delivery system (AXP pump) coupled to an ultraviolet-visible (uv-vis) absorbance detector. A Thermo Scientific Dionex ICS-3000 was used, with a Dionex IonPac AG7 4 x 50 mm guard column and a Dionex IonPac AS7 4 x 250 mm analytical column. A 1 000 µℓ injection loop was used, as well as two 375 µℓ knitted reaction coils fitted in series. The post-column colorant reagent was prepared by adding 28 mℓ of sulphuric acid to 500 mℓ of Milli-Q water, which was left to cool down. Diphenylcarbazide (0.5 g) was then dissolved in 75 mℓ of methanol, which was ultrasonificated in order to dissolve all the diphenylcarbazide. This diphenylcarbazide solution was then diluted to 100 mℓ in a volumetric flask with methanol. This methanol mixture was added to the sulphuric acid solution, which was diluted with Milli-Q water to 1 ℓ. A residue, that is not described in any of the cited references, i.e., Dionex Application updates 144 and 179 (2003 and 2011) and Thomas et al. (2002), formed after these two solutions were mixed. In order to prevent blockages within the fine tubing of the IC, the prepared colorant solution was filtered through a 0.45 µm Whatman filter. Eluent was prepared by dissolving 66 g of ammonium sulphate and 15.08 mℓ of ammonium hydroxide with Milli-Q water and diluting to 2 ℓ.

An eluent flow-rate of 1.00 mℓ/min was utilised, while the post-column colorant reagent was delivered at a flow-rate of 0.5 mℓ/min. Additional PEEK tubing was also 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, which made the accurate determination of very low Cr(VI) concentrations possible. The detection limit for this analytical instrumental setup was 1 **µg/ℓ** (Dionex Application update 144, 2003).

RESULTS AND DISCUSSION

Surface water

In Fig. 3 the surface water Cr(VI) results are presented according to the sampling site numbers as described earlier. The number of samples (*N*) considered for each of the sampling sites in this statistical evaluation is indicated at the top edge of the graph. Surface water samples could not always be collected at all of the identified surface water sites. The streams or small rivers at sampling sites 3 and 4b were on occasion dry, most probably due to a lack of surface run-off water during the dryer periods of the year. Sampling site 4a was only sampled twice, since it also dried out in the arid months. Additionally, earth works for the construction of an additional lane to the regional highway prevented access during the wetter months after October 2011. At sampling site 5a, surface water was collected from a cement-lined irrigation waterway. During two sampling months, the waterway was dry due to sluice gates that were closed, preventing water from reaching the sampling point. Surface water was also not collected during 1 month

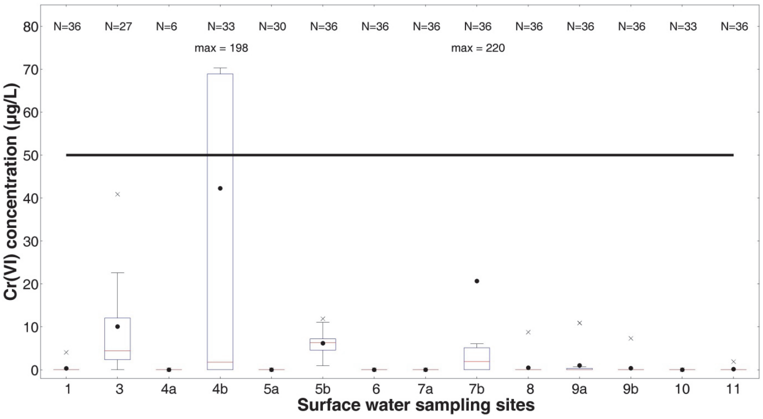

Figure 3
Statistical representation of the Cr(VI) concentrations obtained at each of the surface water sampling sites. The median Cr(VI) concentration is indicated by the short horizontal line, the mean by the dot, the maximum the cross, the top and bottom edges of the box the annual 25th and 75th percentiles, while the whiskers indicate ±2.7 σ (or 99.3% coverage if the data has a normal distribution (Matlab, 2013). The number of samples considered for each sampling site is also indicated at the top edge of the graph. The continuous horizontal line indicates the current South African Cr(VI) drinking water limit, i.e., 50 µg/ℓ.

at sampling site 10 due to safety reasons, which were always considered to be a priority.

In order to facilitate the discussions of the surface water results presented in Fig. 3, sites with similar Cr(VI) concentration levels and/or temporal variability of these concentration levels were grouped together into 6 groups, i.e., site(s) that had:

- No Cr(VI) concentrations above the detection limit of the analytical technique
- Cr(VI) concentrations below the detection limit for most of the time, with limited samples having concentrations above the detection limit
- Significant Cr(VI) concentrations that never exceeded the South African drinking water limit, which were also relatively variable over time
- Significant Cr(VI) concentrations that did not exceed the South African drinking water limit, but which were consistent in terms of temporal variability
- Significant Cr(VI) concentrations that exceeded the South African drinking water limit on one occasion, which were also relatively variable over time
- Significant C(VI) concentrations that exceeded the South African drinking water limit on several occasions, which exhibited relatively consistent temporal variation

The temporal variation of Cr(VI) concentrations in surface water of the sites grouped together is presented in Fig. 4. Due to the large variations in Cr(VI) concentrations, the y-axis of this figure is indicated on two separate scales, which are connected with a dashed line. The bottom part of this figure indicates values lower than 25 µg/ℓ, while the upper portion indicates values above 35 µg/ℓ.

It is evident from the surface water results presented in Figs. 3 and 4 that sampling sites 4a, 5a, 6, 7a and 10 always had Cr(VI) concentrations below the detection limit of the analytical technique employed. Although analyses indicated that the Cr(VI) concentrations were always below the detection limit, it cannot be stated that there is no Cr(VI) contamination of the surface water in these areas. The sampling site selection was influenced by several criteria and limitations, as previously stated. Additionally, the contamination of Cr(VI) could be reduced to Cr(III) by means of various naturally occurring (e.g. Fe(II), organic substances such as humus) and anthropogenically introduced compounds (e.g. S(IV), organic compounds originating form sewage) in the environment.

Surface water sampling sites 1, 8, 9a, 9b and 11 also had annual mean and median concentrations (Fig. 3) below the detection limit of the analytical technique employed. However, for these sites, there were certain months during which the Cr(VI) levels were above the detection limit. This is illustrated by the temporal variation of the average monthly concentrations for this group of sites in Fig. 4. For this group of sites, the highest maximum value was recorded for sampling site 9a, which had a monthly average Cr(VI) concentration of 9.9 µg/ℓ measured during January 2012. This indicates that the surface water at these sites might occasionally be influenced by a Cr(VI) source(s), although the maximum Cr(VI) levels measured were well below the South African drinking water limit.

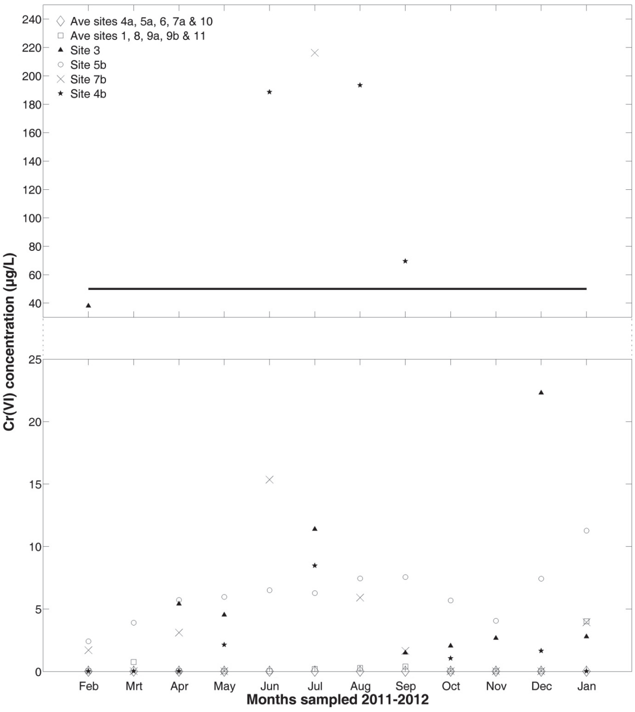

Figure 4
Temporal variation of the Cr(VI) concentrations in the surface water at sampling sites for February 2011 to January 2012.

Surface water sampling site 3 had an annual mean of 9.8 µg/ℓ and a median of 4.4 µg/ℓ (Fig. 3), which are well above the detection limit. Notwithstanding these relatively low annual mean and median values, the temporal variation (Fig. 4) indicates that there were several months during which the Cr(VI) concentrations were higher. The highest Cr(VI) concentration, i.e., 40.9 µg/ℓ, for this site was recorded during February 2011, which is not that far below the drinking water standard.

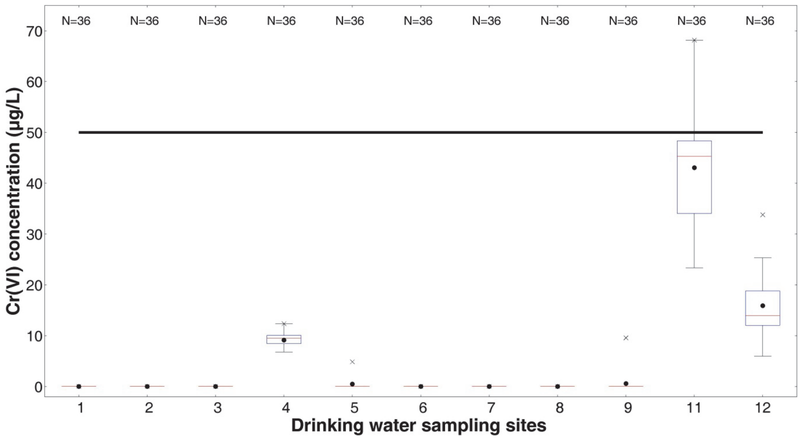

Figure 5
Statistical representation of the Cr(VI) concentrations obtained at each of the drinking water sampling sites. The median Cr(VI) concentration is indicated by the short horizontal line, the mean by the dot, the maximum by the cross, the top and bottom edges of the box the annual 25th and 75th percentiles, while the whiskers indicate ±2.7σ (or 99.3% coverage if the data has a normal distribution) (Matlab, 2013). The number of samples considered for each sampling sites are also indicated at the top edge of the graph. The continuous horizontal line indicates the current South African Cr(VI) drinking water limit, i.e. 50 µg/ℓ.

Surface water sampling site 5b was consistently impacted by Cr(VI) pollution, which is clearly indicated in Fig. 4 and by the relatively small statistical spread of the annual results presented in Fig. 3. The annual mean and median Cr(VI) concentrations for this site were 6.2 and 6.3 µg/ℓ, respectively. These relatively low mean and median values, together with the small statistical spread of the results, indicate that Cr(VI) pollution at this site is limited at present. However, if the consistent presence of Cr(VI) at surface water sampling site 5b (a river close to FeCr plant 5) is compared to the lack of any Cr(VI) at surface water sampling site 5a (a cement-lined irrigation waterway close to FeCr plant 5), it becomes apparent that these two sites are influenced in different ways although the sampling sites are just 1.25 km apart. Since site 5a is a lined cement waterway, groundwater leaching is unlikely to contribute to pollution of the surface water. However, surface water sampling site 5b can be impacted by groundwater leaching, since the river system is unlined. Therefore, although groundwater Cr(VI) concentrations were not evaluated in this study, it is likely that the origin of Cr(VI) at site 5b can be attributed to groundwater leaching.

Surface water sampling site 7b was not consistently impacted by Cr(VI) pollution, as indicated by the relatively large differences in the mean (20.7 µg/ℓ) and median (1.9 µg/ℓ) values, the relatively large spread of the results in Fig. 3 and the temporal behaviour presented in Fig. 4. For 5 months (March, May, October, November and December 2011), the Cr(VI) levels were below the detection limit (Fig. 4). For 6 months (February, April, June, August, September 2011 and January 2012), the Cr(VI) concentrations were above the detection limit (Fig. 4), although levels were relatively low with a maximum value of 16.9 µg/ℓ. During July 2011, the Cr(VI) concentrations escalated to a maximum value of 219.6 µg/ℓ, which should be considered as serious. These erratic Cr(VI) concentrations measured at site 7b indicate that there is a significant anthropogenic Cr(VI) source that influences the site on occasion. The anthropogenic nature of the Cr(VI) source is also supported by the observation that the Cr(VI) concentrations at surface sampling site 7a, which was upstream of FeCr smelter 7, were always below the detection limit.

Cr(VI) concentrations of surface water sampling site 4b were also erratic, with relatively large differences between the mean (42.3 µg/ℓ) and median (1.8 µg/ℓ) values. There was also a large statistical spread in the results (Fig. 3) and the temporal behaviour (Fig. 4) also indicated large variations. As previously mentioned, 1 month (November 2011) was not sampled at this site. For 4 months (February, March, April 2011 and January 2012), the Cr(VI) levels were below the detection limit (Fig. 4). For another 4 months (May, July, October and December 2011), the Cr(VI) concentrations were above the detection limit (Fig. 4) and relatively low, with a maximum value of 8.5 µg/ℓ. However, during June, August and September 2011, the Cr(VI) concentrations increased to monthly average values of 188.6, 193.4 and 69.5 µg/ℓ, respectively. Similar to surface water sampling site 7b, these erratic Cr(VI) concentrations at surface water sampling site 4b indicate that there is a significant anthropogenic Cr(VI) source that influences the site occasionally. This is also supported by the observation that the Cr(VI) concentrations at surface sampling site 4a (upstream of FeCr plant 4) were always below the detection limit.

Drinking water

In Fig. 5, the drinking water Cr(VI) results obtained are presented according to the sampling site numbers, as described earlier. No significant Cr(VI) concentrations were detected at any of the drinking water sampling sites, except at sites 4, 11 and 12.

Drinking water sampling site 4 was consistently impacted by Cr(VI) pollution, which is clearly indicated by the relatively small statistical spread in Fig. 5. The annual mean and median Cr(VI) concentrations for this site were 9.1 and 9.5 µg/ℓ, respectively. It is recommended that, as a precautionary step, the source of this Cr(VI) drinking water pollution should be investigated and addressed as an important future perspective. Since the origin of the drinking water was not investigated, no relationship between surface- and drinking water pollution can be suggested at smelter 4.

Considering the drinking water results presented in Fig. 5, it is evident that both sampling sites 11 and 12 are significantly impacted by Cr(VI) pollution. This was particularly significant at drinking water site 11. The annual mean and median values for this site were 43.1 and 45.3 µg/ℓ, respectively. Even the minimum value found for this site, i.e., 23.4 µg/ℓ, should be considered as relatively high within the context of possible long-term human consumption and exposure. The maximum concentration obtained during November 2011, i.e., 68.1 µg/ℓ, was well above the drinking water limit. The seriousness of the Cr(VI) drinking water pollution at this site is demonstrated by the proximity of a public primary school less than 1.1 km from site 11.

Due to the potential human health risks associated with Cr(VI) contaminated drinking water at site 11, the origin thereof was further investigated. Cr(VI) pollution in the drinking water at site 11 did not seem to be related to the

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major surface water source, i.e., a perennial river in the area, since the annual mean and median Cr(VI) concentrations in this river at surface sampling sites 10 and 11 were below the detection limit. However, further on-site investigation revealed that the drinking water at sampling site 11 was obtained from a borehole. This additional information indicated that groundwater in the proximity of smelter 11 was polluted with Cr(VI), while the major surface water source was not significantly affected. The management of FeCr smelter 11 was approached after all the data were gathered. They indicated that they and the appropriate authorities were aware of the afore-mentioned groundwater pollution and that it occurred due to historic mismanagement of waste, which had since been addressed. These improved waste management procedures also eliminated any possible surface water run-off, explaining the lack of Cr(VI) being observed at surface sampling sites 10 and 11. A comprehensive groundwater abstraction and cleaning system to the value > R100 m. had also been installed to clean the existing groundwater plume, after a geo-hydrological survey and model was compiled. Communities that were affected, according to the afore-mentioned model, were supplied with clean drinking water. However, the additional data supplied through this study indicated that groundwater at drinking water sampling site 11 was also impacted, although the model did not indicate it. Therefore, the groundwater abstraction scheme and supply of clean drinking water to affected communities were further expanded to include the affected area.

CONCLUSIONS

As far as the authors could assess, this study is the first relatively comprehensive survey of Cr(VI) pollution of surface water in the proximity of FeCr smelters in the BIC in South Africa published in the peer-reviewed public domain. The results indicated that surface water in the proximity of most FeCr smelters was unaffected by Cr(VI) pollution. Surface water sampling sites 3 and 5b were, however, consistently impacted by Cr(VI) pollution, with annual mean values of 4.4 and 6.3 µg/ℓ, respectively. No values in excess of the 50 µg/ℓ drinking water limit were recorded for these two sites. However, for surface water sampling sites 4b and 7b, maximum monthly Cr(VI) concentrations of 198 and 220 µg/ℓ were measured, respectively. The median Cr(VI) concentrations for these two sites were 1.8 and 1.9 µg/ℓ, indicating that Cr(VI) pollution of the surface water at these sites were erratic and most likely due to surface run-off due to poor wastewater management. Such pollution events of the surface water in the proximity of these FeCr smelters has to be prevented.

Although drinking water pollution was not the main focus of this paper, the results indicated that drinking water in the proximity of most FeCr smelters was not polluted by Cr(VI). However, the annual mean Cr(VI) concentration of drinking water at sampling site 11 was 45.3 µg/ℓ, with several months exceeding the 50 µg/ℓ limit. Further investigation proved that the drinking water at this site originated from a borehole, which was impacted by a Cr(VI) groundwater plume. Significant steps have, however, already been taken to remedy the situation in the proximity of smelter 11.

This paper only focused on the Cr(VI) pollution of surface water within the BIC, with limited information regarding drinking water. Groundwater was excluded due to the limitations of the project. In order to better quantify the extent of Cr(VI) pollution around affected sites, groundwater studies would be required and should therefore be considered as an important future perspective.

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