Cr(VI) contamination of aqueous systems

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Water is the driving force of all nature

~Leonardo da Vinci~

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List of Abbreviations

AAS	Atomic adsorption spectrometry
ACGIH	American Conference of Governmental Industrial Hygienists
BIC	Bushveld Igneous Complex
Cr(III)	Trivalent chromium
Cr(VI)	Hexavalent chromium
DC	Direct current
DL	Detection Limit
DNA	Deoxyribonucleic acid
DPC	Diphenylcarbazide
DWAF	Department of Water Affairs and Forestry
EPA	US Environmental Protection Agency
ET-AAS	Electrothermal atomic absorption spectrometry
FAAS	Flame atomic absorption spectrometry
Fe(II)	Ferrous iron
FeCr	Ferrochrome
GF-AAS	Graphite furnace atomic absorption spectrometry
HPLC	High performance liquid chromatography
HPLC-ICP-MS	High performance liquid chromatography with inductively coupled plasma mass spectrometry
ICDA	International Chromium Development Association
ICP	Inductively coupled plasma
ICP-AES	Inductively coupled plasma – atomic emission spectrometry

ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
IC-UV-vis	Ion chromatography coupled to ultraviolet and visible light spectroscopy
LOD	Limit of detection
NWU	North-West University
PEEK	Polyetheretherketone
PGM	Platinum group metal
SEM	Scanning electron microscopy
SEM-EDS	Scanning electron microscopy incorporated with energy dispersive X-ray spectroscopy
SAF	Submerged arc furnace
TDS	Total dissolved solids
TLV	Threshold limit value
TWQR	Target water quality range
UG2	Upper group 2 ore
UV-vis	Ultraviolet and visible light spectroscopy
WHO	World Health Organisation

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Abstract

Hexavalent chromium, i.e. Cr(VI), is a potential pollutant species formed due to anthropogenic processes, e.g. leather tanning, Cr(VI) chemical production, stainless steel manufacturing and ferrochrome production. Cr(VI) is of concern since it is toxic to microorganisms, plants and animals, and carcinogenic for humans. Therefore, standard limits for the Cr(VI) contents in air, soil and water have been introduced by different health and legal organisations worldwide. Within the South African context, Cr(VI) water pollution specifically associated with ferrochrome production is of concern, since this is a large industry in South Africa with 14 ferrochrome smelters. Apart from Cr(VI) pollution, wastewater treatment processes applied at ferrochrome smelters could negatively affect water quality in general (e.g. chemical oxygen demand, hardness, pH levels and SO_4^{2-}) if run-off or leakage is allowed. In this study the focus was only the determination of Cr(VI) concentrations and conductivity levels (as a proxy for total dissolved solids).

Various analytical methods exist to determine Cr(VI) present in natural water. The method used during this study was ion chromatography coupled with an ultraviolet-visible absorbance detector. Diphenylcarbazide , a post-column colorant, was added to react with the Cr(VI) to form a species that can be detected at 540 nm wavelength. Experimentally the detection limit of this method was determined as 0.9 µg/L, which is slightly lower than the detection limit reported in literature, i.e. 1.0 µg/L. This improvement was achieved by reducing the baseline noise on the chromatographs.

Surface- and drinking water samples were collected within the vicinity of 12 ferrochrome smelters for the duration of one year. The water samples collected were analysed for Cr(VI) content, as well as the conductivity and the elemental analysis of the total dissolved solids fraction with scanning electron microscopy incorporated with energy dispersive X-ray spectroscopy. The results obtained for the surface water samples showed that Cr(VI) pollution was mostly not present, with the exception of four sites. Two of these sites had constant Cr(VI) pollution, but with levels lower than the drinking water limit, although such Cr(VI) contamination could still have an impact on the ecological system. The annual means for these two sites were 4.4 and 6.3 µg/L. The other two sampling sites also showed constant pollution, but with a few months in which the values exceeded the drinking water limit (198 and 220 µg/L). For the drinking water sampling sites, there were only three sites where Cr(VI) was detected constantly. Unfortunately, the origin of the water was unknown for two of these polluted sites (with levels lower than the prescribed drinking water limit). For the one site, where the drinking water limit was consistently exceeded, the water originated from a borehole. It was established that the pollution was a result of poor historical waste mismanagement at the nearby ferrochrome smelter.

The results obtained from the conductivity and elemental analysis of the total dissolved solids indicated that the surface- and drinking water tested was fit for human consumption. At two smelters where surface water contamination could have been suspected due to run-off, no pollution was detected. At four ferrochrome smelters, the surface water results indicated that these smelters contributed negatively to surface water quality, if conductivity was considered as the only evaluating criteria. Although the surface water quality was affected at these sites, the surface water was not appropriate for human consumption at only one of these sites when taking only conductivity into account. From the results, it could be concluded that deposition emanating from atmospheric emissions contributed less than run-off and/or seepage to the decrease in surface water quality in the proximity of the smelters.

The Cr(VI) pollution, conductivity and elemental composition of the total dissolved solids at the different sites were compared and four unique case studies were identified. Three case studies focused on the negative influence of the ferrochrome smelters on the surface water sampling sites, while the fourth case study was selected since the surface water was unpolluted, but the drinking water was contaminated. The surface water pollution was mainly attributed to run-off and/or seepage, while atmospheric deposition contributed less to the pollution at the specific measurement sites. At one of these sites, a high level of Cr(VI) pollution was recorded over a relatively short period. Circumstantial evidence indicated that this spike in Cr(VI) pollution had a significant impact on the population of diatoms. This linkage needs to be confirmed and investigated in greater detail in future.

Keywords: Hexavalent chromium (Cr(VI)), ferrochrome, South Africa, surface water, drinking water

Preface

Introduction

This thesis was submitted in article format, as allowed by the academic regulations of the North-West University (NWU). This entails that conventional chapters, i.e. experimental, and results and discussion chapters were excluded and reconstructed into written articles. These articles were all published in peer-reviewed ISI internationally-accredited journals. Separate chapters presenting background and motivation (Chapter 1), literature survey (Chapter 2) and project evaluation, conclusions and future perspectives (Chapter 6) were included in the thesis, even though some of this information was summarised in the three articles. Additionally, the formatting of the articles is according to the journals where they were published. Chapter 3 and Chapter 4 were published in Water SA, while Chapter 5 was published in Metallurgical and Materials Transactions B. The numbering of tables and figures of these chapters is therefore not consistent with the rest of the thesis.

Reasoning for selecting this thesis format

The pre-requisite for submitting a PhD thesis at the NWU is submitting one article to a peer-reviewed journal. In this study, the candidate opted to submit the thesis in article format, since it is the objective of the candidate to publish three papers from this PhD, not just the one submitted article as per the minimum requirements. Many PhD theses are accepted from which no or little material is published in scientific journals. By selecting the article format for this thesis, the candidate therefore forced herself to conduct research that is publishable.

Authors and their contributions

In this section, the authors of the three articles are presented separately, followed by a section stating each of the authors’ contributions.

Chapter 3 (containing article 1): *A survey of Cr(VI) contamination of surface water in the proximity of ferrochromium smelters in South Africa*

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Chapter 4 (containing article 2): *Conductivity as an indicator of surface water quality in the proximity of ferrochrome smelters in South Africa.*

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Chapter 5 (containing article 3): *Cr(VI) and Conductivity as Indicators of Surface Water Pollution from Ferrochrome Production in South Africa: Four case studies*

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The contributions of the various authors were as follows: the work was performed by the PhD candidate, Monique Marié Loock-Hattingh, with conceptual ideas and recommendations by Dr. J.P. Beukes (supervisor) and Dr. P.G. van Zyl (co-supervisor) on the experimental work, results and discussion, as well as on the three articles. Dr. L.R. Tiedt assisted with the scanning electron microscopy incorporated with energy dispersive X-ray spectroscopy (SEM-EDS) analysis, and also made conceptual contributions with regard to the diatom observations presented in article 3 (Chapter 5).

Status of articles

The guides for authors for these respective journals were available online at http://www.scielo.org.za/revistas/wsa/iinstruc.htm (Date of access: 22 September 2014) for Water

SA and http://www.springer.com/materials/special+types/journal/11663 (Date of access: 11 November 2014) for Metallurgical and Materials Transactions B. All three articles (Chapters 3-5) were accepted and published in the above mentioned scientific journals.

Declaration by co-authors

I, J.P. Beukes, hereby give my permission that Monique Marié Loock-Hattingh may submit the articles/manuscript for degree purposes.

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I, P.G. van Zyl, hereby give my permission that Monique Marié Loock-Hattingh may submit the articles/manuscript for degree purposes.

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I, L.R. Tiedt, hereby give my permission that Monique Marié Loock-Hattingh may submit the articles/manuscript for degree purposes.

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Chapter 1: Motivation and objectives

1.1 Introduction

An overview of the aim and objectives for the investigation of the hexavalent chromium (Cr(VI)) pollution of aqueous systems is provided in this chapter. In **§ 1.2**, background information, together with the motivation for this study, is presented, while the general aims and specific objectives are discussed in **§ 1.3**. This chapter is then concluded with a scope in **§ 1.4** that offers the layout of the respective chapters.

1.2 Background and motivation

Chromium (Cr) is a transition metal element that is naturally present in soils, rocks, volcanic dust, water, as well as fauna and flora. Cr occurs in the oxidation states of -2 to +6. However, from an environmental perspective, only the stable oxidation states of Cr metal/alloy (Cr(0)), trivalent Cr (Cr(III)) and Cr(VI) are of interest. Cr(III), present in chromite ore, is the most abundant naturally occurring oxidation state. Most Cr(III) and Cr(0) (e.g. in metals or alloys) compounds are not water-soluble. However, due to human activities (e.g. electroplating, leather tanning, metallurgical operations, as well as paint and dye production), Cr(III) can be converted to water-soluble Cr(VI)-containing compounds with different ionic Cr(VI) species, i.e. CrO_4^{-2}, $HCrO^{-4}$ and $Cr_2O_7^{-2}$ depending on the pH and concentration (Ashley *et al*., 2003). Therefore, waste containing Cr(VI) might leach into the soil, as well as surface or subsurface water systems (Chen *et al*., 2007; Erdem *et al*., 2005) and could even lead to drinking water contamination (Bartlett, 1991). Due to the aqueous solubility of most Cr(VI) compounds (Ashley *et al*., 2003), atmospheric pollution can also result in water contamination through dry and wet deposition of atmospheric particles containing Cr(VI) (Seigneur and Constantinou, 1995; Bartlett, 1991).

Cr(III) is not considered to be toxic and is in fact a vital micro nutrient (Ashley *et al*., 2003; Kotaś and Stasicka, 2000). In contrast, Cr(VI) can induce dermatitis and is generally considered carcinogenic, as well as mutagenic (Erdem *et al.*, 2005). The carcinogenicity of Cr(VI) is mainly associated with respiratory-induced ailments (Beaver *et al.*, 2009; Thomas *et al.*, 2002), which is especially important from an industrial occupational health perspective. If inhaled, it can also result in perforation of the nasal septum, bronchitis, asthma and pneumonitis (Kotaś and Stasicka, 2000). Drinking water standards for total Cr and Cr(VI) have been adopted by various countries and range between 3 and 100 µg/L (Ma and Garbers-Craig, 2006). The South African drinking water standard limits for total Cr and Cr(VI) are 100 and 50 µg/L, respectively. Although drinking water standards/guidelines/goals have been set for Cr(VI), there seems to be a conflict in literature pertaining to the toxicity and/or carcinogenicity thereof (Gatto *et al.*, 2010; Stern, 2010; Beaumont *et al.*, 2008). Cr(VI) that is present in soil water can also be absorbed by plants, with Cr(VI) concentrations as low as 0.5 mg/kg in the soil being toxic to plants (Fendorf, 1995). Inter-conversions of Cr species may also occur in the environment, thereby altering the toxicity thereof (Gómez and Callao, 2006).

Since the toxicity and/or carcinogenicity of Cr is determined by the oxidation state of Cr, the determination of the total Cr concentration in water samples will be insufficient for a health and/or environmental assessment. For this reason, the analytical techniques applied must be able to differentiate between oxidation states. A variety of analytical methods can be applied to analyse natural water to detect various oxidation states of Cr, e.g. atomic adsorption spectrometry (AAS), high performance liquid chromatography with inductively coupled plasma mass spectrometry (HPLC-ICP-MS), inductively coupled plasma mass spectrometry (ICP-MS), fluorimetry and ion chromatography coupled with ultraviolet and visible light spectroscopy (IC-UV-vis) (Chen *et al.*, 2007; Gómez and Callao, 2006; Shaw and Haddad, 2004). The most commonly used technique for Cr(VI) analysis in aqueous solutions is the UV-vis method with the addition of diphenylcarbazide (DPC).

The reason for the specific interest in the ferrochrome (FeCr) industry during this study was prompted by the abundance of Cr-related resources in South Africa. South Africa holds approximately 75% of the world's viable chromite ore deposits (Murthy *et al*., 2011; Cramer *et al*., 2004) and produced approximately 32% of the annual global high carbon FeCr (most common FeCr grade) in 2012 (ICDA, 2013). According to Beukes *et al*. (2012), there are 14 separate FeCr smelters in South Africa. Considering the size of the South African FeCr industry, it is evident that an assessment of possible Cr(VI) pollution of aqueous environments in the proximity of FeCr smelters in South Africa should be conducted. Although some studies have been conducted to determine Cr(VI) concentrations in localised areas near FeCr smelters in South Africa (e.g. Sedumedi *et al*., 2009; Mandiwana *et al*., 2007), a survey of all areas where FeCr industries are situated is lacking. In order to at least partially address this knowledge gap, the extent of Cr(VI) surface- and drinking water pollution, in the proximity of FeCr smelters located in the Bushveld Igneous Complex (BIC) was evaluated in this study.

The intention of the author with this particular study was not to implicate any specific FeCr smelter or associated company, but rather to obtain an overall picture of the extent of possible Cr(VI) (and conductivity, as a proxy of general water quality) water pollution near such smelters. Additionally, the candidate anticipates that the data presented in this thesis will be used to rectify possible problematic areas identified and thereby promote the sustainable development of the FeCr industry. The FeCr industry is vital for job creation and economic growth in South Africa due to its size. Of late (especially since 2008), the FeCr industry in South Africa has been under extreme pressure due to labour unrest, electricity shortages and rate increases, as well as the downturn in the world economy that led to a reduced demand for FeCr.

1.3 Aim and specific objectives

This PhD was conducted in the Chromium Technology group and submitted under the Chemical Resource Beneficiation Focus Area. Therefore, the candidate had to combine the environmental nature of this study with the more direct process related insights required in the research focus area. The overall aim was therefore not to conduct an in depth environmental assessment, but to do a first evaluation of certain surface water quality characteristic that could be directly linked to FeCr production processes. In order to meet this aim, the following specific objectives were formulated:

i. Identification of logistically feasible sampling sites consisting of surface- and drinking (municipal water) water sites in the proximity of FeCr smelters in the BIC.
ii. Sampling at these sites on a monthly basis for a full seasonal cycle, i.e. one year, in order to prevent seasonal bias of the results.
iii. Assess Cr(VI) and general water quality of surface- and drinking in the proximity of FeCr smelters. Although there are many important water quality characteristics (e.g. pH, temperature, dissolved oxygen, odour, total hardness, turbidity and organic carbon, as well as nutrients such as sulphates, phosphates and nitrates/nitrites), those considered in this study had to be limited, since a) this was the first study of its kind in South Africa and b) there had to be a direct link between the characteristics measured and the industrial processes. Considering the FeCr pyrometallurgical production and waste treatment processes, Cr(VI) concentrations and conductivity were chosen as characteristics to be monitored. Cr(VI) is a direct unintentional by-product of the FeCr pyrometallurgical processes and conductivity is a good indicator of other salts and/or compounds that could leach into surface/groundwater from FeCr processes and/or treatment/storage facilities.
iv. Recommendations for future investigations in this research field.

1.4 Scope of thesis

In order to achieve the afore-mentioned objectives, a scope was constructed for this study. The thesis is subdivided into six chapters (including this chapter, i.e. Chapter 1) and an Appendix.

In Chapter 1, the background pertaining to the study is presented together with the motivation. The specific objectives for this study are also clearly stated in this chapter.

In Chapter 2, a literature overview is presented on general information related to Cr and the importance thereof within the South African context. Subsequently, information on the natural and anthropogenic processes where Cr(VI) could be generated is presented, followed by more detailed information on possible Cr(VI)-containing waste generation during the FeCr production process. Hereafter, the relevance of Cr(VI) within the environment and health context, and the transportation and transformation thereof within the different phases are discussed. The different analytical detection methods that can be applied on environmental Cr(VI) samples are also discussed. This is followed by an overview of studies conducted on Cr(VI) research within South Africa, as well as the relevant background on water quality parameters. Finally, Chapter 2 is concluded with a summary.

Chapters 3 to 5 are presented in article format as stated in the preface. Each chapter focuses on a different section of the results and addresses a different objective(s) stated in **§ 1.3**, i.e.:

- Chapter 3: *A survey of Cr(VI) contamination of surface water in the proximity of ferrochromium smelters in South Africa* addresses a combination of objectives i, ii and iii.
- Chapter 4: *Conductivity as an indicator of surface water quality in the proximity of ferrochrome smelters in South Africa* addresses mainly objective iii.
- Chapter 5: *Cr(VI) and Conductivity as Indicators of Surface Water Pollution from Ferrochrome Production in South Africa: Four case studies* addresses mainly objective ii.

Chapter 6 presents a project evaluation, summarises the main conclusions and offers suggestions on future work that could emanate from this investigation.

Finally, in Appendix A additional information with regards to the analytical (e.g. calibrations curve, detection limit (DL)) and statistical methods applied are presented.

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Chapter 2: Literature review

2.1 Introduction

An overview of the relevant literature for the study is provided in this chapter. The chapter starts with general information **(§ 2.2**) on chromium (Cr) and the importance of the Cr industry to South Africa (**§ 2.3**). This is followed by a discussion of how the different Cr species are generated naturally and anthropogenically (**§ 2.4**), as well as the relevance of hexavalent Cr (Cr(VI)) in the environment (**§ 2.5**). Thereafter, the different transformations that Cr(VI) can undergo under environmental conditions are discussed (**§ 2.6**). **§ 2.7** provides an overview of the different analytical techniques that are currently employed to determine Cr(VI) in water samples, as well as the reasons for selecting the particular technique applied in this study. **§ 2.8** presents an overview of different studies that have been conducted on this subject. In section **§ 2.9**, the effect of other pollutants, resulting from wastewater treatment of ferrochrome (FeCr) smelters, on water quality is discussed. Finally, in **§ 2.10**, a brief summary is provided to conclude the chapter.

2.2 General information on chromium

2.2.1 Properties and history

Cr is a transition metal that is the 21st most abundant element in the crust of the earth, which appears as a grey-white, hard, yet brittle metal, with a crystalline structure. This metal is characterised by a high melting and boiling point of 1907 °C and 2671 °C, respectively. Cr metal also has relatively high densities of 7.15 and 6.3 g/cm^3 at room temperature and at melting point, respectively (Lide, 2009; Roza, 2008; IETEG, 2005). Cr is not found in its elemental form, but chromite ($FeO.Cr_2O_3$) is the only commercially available mineral of Cr (Niagru and Nieboer, 1988). This metal can present itself in different oxidation states that vary between Cr^{2-} and Cr^{6+} (Ashley *et al*., 2003). The oxidation states that are generally found within an aqueous solution are bivalent Cr (Cr(II)), trivalent Cr (Cr(III)) and Cr(VI). The most commonly naturally occurring oxidation states of Cr are Cr(III), which is the most stable, and Cr(VI), which is the most oxidised form (Jacobs and Testa, 2005; Fendorf, 1995). It has been shown that Cr(II) is unstable and that it readily oxidises to the Cr(III) oxidation state. The oxidation states Cr(IV) and Cr(V) may occur as intermediates in chemical reactions during the inter-conversions of Cr(III)/Cr(VI), but is characterised by limited stability (Cotton and Wilkinson, 1988). The other oxidation states of Cr, i.e. Cr^{2-}, Cr^{1-}, Cr^{0} and Cr^{1+}, are mainly observed in synthetic organic compounds. This wide variety of oxidation states of Cr ensures that the compounds are particularly colourful (Mohan and Pittman, 2006; Emsley, 2003). As an example, the presence of Cr in the mineral beryl contributes to the green colour of emeralds and also gives rubies there prominent red colour.

Crocoite was the first Cr-containing compound that was discovered in the Beresof gold mine in Siberia and analysed by Johann Gotlob Lechmann in 1766. Thereafter, Cr oxide was successfully produced by the French chemist Louis-Nicolas Vauquelin in 1797 by mixing crocoites with hydrochloric acid (Roza, 2008; Niagru and Nieboer, 1988). In 1821, a French scientist Pierre Berthier discovered that when Cr was alloyed with iron (Fe), a new corrosion resistant alloy was formed, but unfortunately it was too brittle for use (Roza, 2008). Further investigation by the French chemist, Henri Moissan resulted in an alloy he called FeCr. This discovery occurred in 1893 when Cr-containing ore and Fe were heated in a furnace in the presence of carbon. A number of scientists experimented with the ratios of these elements, until stainless steel, which is a vital modern alloy, was developed.

2.2.2 Consumption and uses

Cr has a wide variety of uses due to its versatility. This results in Cr being used for different industrial applications, e.g. FeCr, chromium metal, refractory bricks, chromite foundry sands and chromic acid. Global chromite consumption is divided into three main industrial uses, i.e. refractory, metallurgical and chemical applications (IETEG, 2005; Niagru and Nieboer, 1988). Approximately 95% of the annually mined chromite is consumed by the metallurgical industry and used for the production of different FeCr grades, e.g. high carbon FeCr (also sometime referred to as charge grade FeCr), medium carbon FeCr and low carbon FeCr (ICDA, 2010). FeCr is an alloy with a Cr content of 45 to 80%, depending on the specific composition of the chromite used and various amounts of Fe, C and other elements. This alloy is produced pyrometallurgically by means of the carbothermic reduction of chromite ore (Erdem *et al.*, 2005). The main uses for FeCr include the production of stainless steel, steel, other alloys and Cr-containing chemicals. Approximately 90% of all FeCr is consumed by the stainless steel industry (Murthy *et al.*, 2011; ICDA, 2010; Abubakre *et al.*, 2007; Niagru and Nieboer, 1988).

2.3 Importance of chromium in South Africa

2.3.1 Chromite ore deposits and reserves

As previously mentioned, chromite is the only Cr-containing ore form that is mined commercially (Roza, 2008; IETEG, 2005; Niagru and Nieboer, 1988). These commercially available chromite ore deposits are found in South Africa, China, Finland, Kazakhstan, Zimbabwe, Brazil, Russia, Turkey, Albania, Australia, Pakistan and Iran. Chromite deposits are, however, not only limited to these countries, but are also found in other countries, e.g. Greece and the USA (Papp, 2011; Papp, 2009; Papp, 2008; Niagru and Nieboer, 1988).

South Africa holds approximately three quarters of the world's viable chromite ore deposits (Beukes *et al.*, 2012; Murthy *et al.*, 2011; Cramer *et al.*, 2004; Riekkola-Vanhanen, 1999; Cowey, 1994). These deposits are mainly located in a geological phenomenon referred to as the Bushveld Igneous Complex (BIC). In **Fig. 2.1,** the extent of the BIC within a South African context is presented.

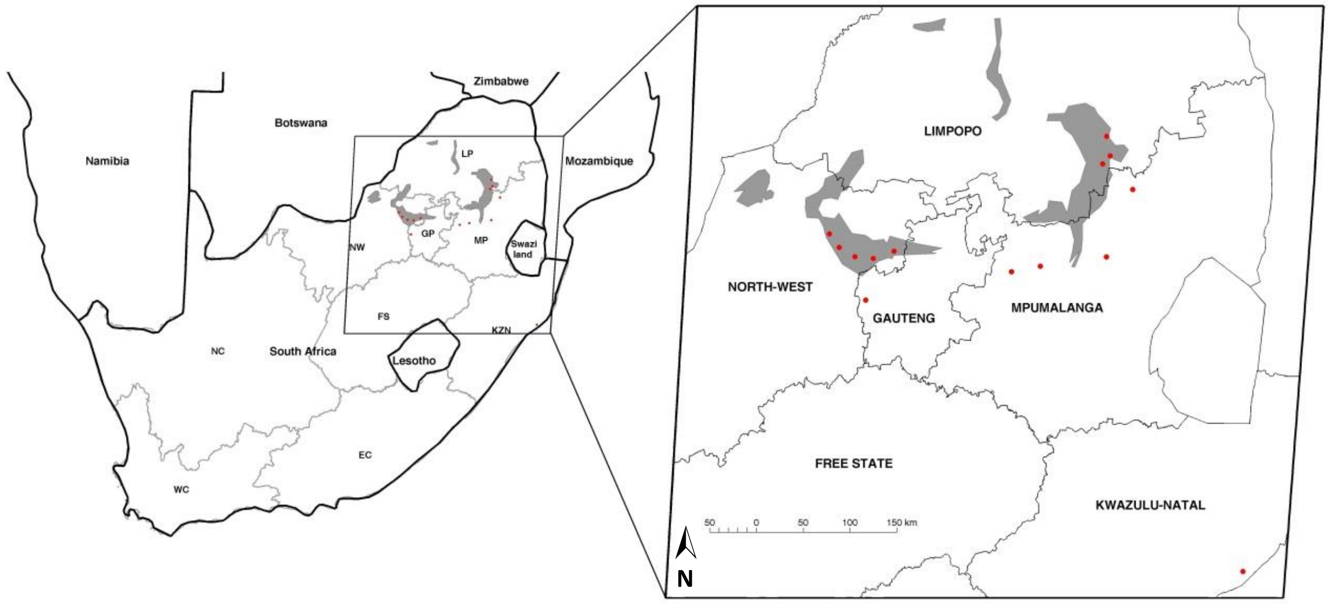

Figure 2.1 A graphical representation of the location of the BIC within the South African context is indicated by the grey areas, showing the different limbs in which the ore deposits are concentrated. The positions of the different FeCr smelters within the enlarged map area are indicated with red dots (Neizel, 2012).

The BIC extends for approximately 400 km from east to west and roughly for the same distance from north to south. As can be seen from **Fig. 2.1**, this area is located in the northern part of South Africa, known as the Highveld. In the BIC, there are major ore deposits located in the western and eastern limbs, with Cr-to-Fe ratios of 1.5 to 1.6 (Howatt, 1994), while the deposits located in the Zeerust and Potgietersrus areas have Cr-to-Fe ratios of 2 to 2.9. During 2009, the annual chromite production in South Africa was approximated to be 6.2 million tons (ICDA, 2010). Other mineral deposits are also found in the BIC, e.g. fluorspar, platinum group metals (PGMs), vanadium and tin. The FeCr industry also receives large amounts of Upper Group 2 (UG2) chromite. This form of chromite usually consists of lower Cr-to-Fe ratios (between 1.3 and 1.4) and is a lower grade ore mainly used in the PGM extraction process (Cramer *et al.*, 2004). In 2009, South Africa contributed approximately 37% of the world's chromite production, followed by Kazakhstan and India with a mere 16% each and Turkey with 8% (ICDA, 2010; Papp, 2008). A substantial fraction of chromite mined in South African is converted to FeCr locally.

2.3.2 Ferrochrome production in South Africa

During 1865, a German explorer first observed the occurrence of chromite in South Africa (Mintek, 1994). It was only during 1917 that a first attempt was made to exploit the ore deposits by sending chromite ore from the Lydenburg area to the British Munitions Board. Unfortunately, the Cr-to-Fe ratio was considered to be too low and the possible mining of the ore was turned down. In 1921, Cr mining finally started in South Africa and reached a production volume of 180 000 tons of chromite per year by the time of the Second World War (Mintek, 1994). The largest part of South Africa's chromite was exported up until the 1970s, when the local industries started to show more interest in FeCr and stainless steel manufacturing. South Africa started by converting less than 10% of the chromite into FeCr in 1970, which was increased to the conversion of more than 80% of chromite by 1995 (Wood, 1996). This resulted in South Africa globally becoming the largest producer of chromite and FeCr (Mintek, 1994). However, in recent years, the FeCr production in China has grown to similar levels (ICDA, 2012). The rise in China's production compared to FeCr production in South Africa can be attributed to their large economic growth, as well as the electricity shortages and the increase of the unit costs of electricity in South Africa (Kleynhans *et al*., 2012). **Table 2.1** indicates the production capacities of FeCr smelters located in South Africa.

Table 2.1 Production capacities of South African FeCr producers adapted from Beukes *et al*. (2012) and Jones (2011).

Plant	**Locality**	**Production capacity (t/a)**
ASA Metals Dilokong	Burgersfort	360 000
Assmang Chrome	Machadodorp	300 000
Ferrometals	Witbank	550 000
Hernic Ferrochrome	Brits	420 000
International Ferro-Metals	Rustenburg – Brits	267 000
Middelburg Ferrochrome	Middelburg	285 000
Mogale Alloys	Krugersdorp	130 000
Tata Ferrochrome	Richards Bay	135 000
Tubatse Ferrochrome	Steelpoort	360 000
Glencore Lydenburg	Lydenburg	400 000
Glencore-Merafe Boshoek	Rustenburg – Sun City	240 000
Glencore-Merafe Lion	Steelpoort	728 000
Glencore Rustenburg	Rustenburg	430 000
Glencore Wonderkop	Rustenburg - Brits	545 000
Total:		**4 766 000**

2.4 Cr(VI) generation

Cr(VI) can be introduced into the environment via natural and/or anthropogenic processes, affecting the air, soil, surface water, as well as groundwater. The largest amount of Cr(VI) present in the environment originates from anthropogenic sources, which is usually converted through natural chemical reductions to Cr(III) (Ashley *et al*., 2003).

2.4.1 Natural processes

Although Cr(VI) mainly originates from anthropogenic processes, recent literature reports naturally occurring Cr(VI) in surface- and groundwater (Oze *et al.*, 2007). Natural occurring aqueous Cr(VI) concentrations of 73 µg/L were reported in surface- and groundwater from California, Italy, New Caledonia and Mexico. These concentrations exceed the drinking water standard limit of the World Health Organisation (WHO), which is 50 µg/L (Oze *et al.*, 2007). The process of Cr(III) conversion to Cr(VI) is currently still a complicated mechanism to understand. Manganese (Mn) minerals present in Cr-rich rocks may serve as a catalyst for the potential oxidation to Cr(VI) (Fendorf, 1995). Additionally, if Cr(III) is found within ultramafic- and serpentinite-derived soils/sediments, it can be oxidised by natural processes leading to high levels of Cr(VI) in water systems (Oze *et al.*, 2007). The possible mechanism for Cr(VI) formation in the natural environment will be discussed in greater detail when Cr(III) to Cr(VI) inter-conversions are discussed in **§ 2.6**.

2.4.2 Anthropogenic processes

Various anthropogenic processes can result in the formation of small amounts of Cr(VI), e.g. FeCr production, stainless steel manufacturing, leather tanning, dye and pigment manufacturing and electroplating. Chemical manufacturing, and more specifically chromate production, results in the formation of significant amounts of Cr(VI) – in fact, the intended product is Cr(VI). Different industries that could potentially pollute the environment with Cr(VI) are discussed in the subsequent sections, with a specific focus on the FeCr industry to which this study was related.

2.4.2.1 Leather tanning and metal plating

The tanning of leather with Cr started in 1858. Cr(III) salts, e.g. Cr(III) sulphate, are used in the tanning of leather. This process depends on the likelihood of Cr(III) to form stable complexes with the proteins in the hide or synthetic polymers. This reaction results in the leather becoming resistant to bacterial attacks (Niagru and Nieboer, 1988).

Cr compounds are also used in the treatment of metal surfaces to improve the durability of the product and to prevent corrosion. There are diverse application techniques for the treatment of aluminium (Al), Fe, steel, brass, zinc (Zn) and magnesium (Mg) surfaces. Cr compounds have been applied as oil-, water- and wear-resistant coatings on different media. Common wear-resistant coatings can be found in decorative hardware, plumbing fixtures and appliances such as decorative plating. From an industrial perspective, it is also applied in hard plating, i.e. internal combustion engines, cylinder liners and piston rings for rolling equipment (Niagru and Nieboer, 1988). A study conducted showed that the Cr(III) contamination is higher than Cr(VI), but that electroplating factories have relatively high levels of airborne Cr(VI) (Kuo, 2003).

2.4.2.2 Cr(VI) chemical productions

Chromite ore is also used in the manufacturing of Cr compounds that are used as pigments and harsh dying. Commercially, more than 70 Cr compounds are used, but only a few are produced in large quantities, e.g. sodium chromate, potassium chromate, potassium dichromate, ammonium dichromate, chromic acid and the basic chromic sulphate used primarily for the leather tanning process (Niagru and Nieboer, 1988). The production process of Cr(VI) chemicals entails the intentional oxidising of the chromite ore by utilising an alkaline roasting proses (Antony *et al*., 2001). Within the South African market, there is a niche for Cr(VI) chemicals, but it is relatively small and not volume driven. The waste generated is much less than the FeCr industry, but the Cr(VI) content can be higher.

2.4.2.3 Ferrochrome industry

The mining of chromite ore for FeCr results in the generation of waste materials containing unrecovered chromite. The volume of mining waste material is substantial, but relatively inert (Gu and Wills, 1988) and almost all the Cr present is in the stable trivalent form.

The process used to produce FeCr is energy intensive and utilises fossil fuels and electricity. In **Fig. 2.2**, a general flow diagram of the possible process combinations, adapted form Riekkola-

Vanhanen (1999) by Beukes *et al.* (2010), is shown. Herein, the combinations of the most common process steps utilised by the South African FeCr industry are provided and discussed briefly.

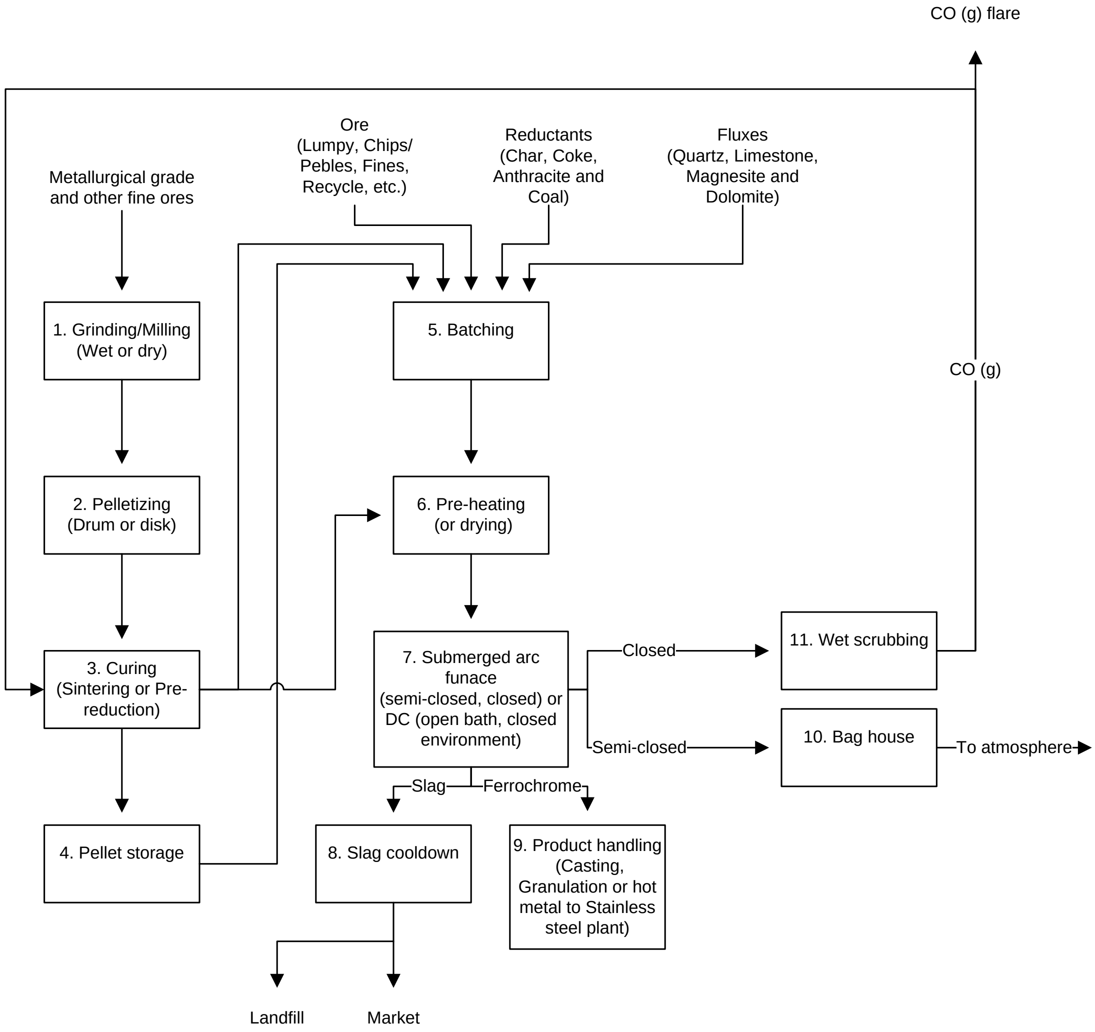

Figure 2.2 A flow diagram showing the most common process combinations for the production of FeCr in South Africa. The generalised diagram was adapted by Beukes *et al.* (2010) from Riekkola-Vanhanen (1999).

Rather than discussing the different processes at length, a brief overview is presented on the four most well-defined processes:

i. Conventional semi-closed submerged arc furnace (SAF) operations, with bag filter off-gas treatment. During this form of operation, coarse/lumpy ores are utilised. A small fraction of fine ores are also consumed in certain instances, but this increases the danger of blow-outs or bed turnovers (Riekkola-Vanhanen, 1999). Process steps 5, 7, 8, 9 and 10 indicated in

Fig. 2.2 are followed. Process steps 1 to 4 are also included if pelletised feed is used. Although this is the oldest process option, it still accounts for a significant fraction of overall FeCr production in South Africa (Beukes *et al*., 2010).

ii. Closed SAF operation, generally using oxidative sintered pelletised feed (Outotec, 2011). Process steps 1 to 5, 7 to 9 and 11 are included in the process. Step 6 can be included or excluded. This is the technology that has been employed most commonly in the South African FeCr industry for the last couple of decades.

iii. Closed SAF operation with pre-reduction pelletised feed (Niaker, 2007; Botha, 2003). Steps 1 to 5, 7 to 9 and 11 indicated in **Fig. 2.2** are used during this operation. Here, the feed is pelletised and differs from the oxidative sintered type, due to pre-reduction of pellets. Furthermore, these pellets are mostly hot when fed into the furnaces.

iv. Direct current (DC) arc furnace operations (Curr, 2009; Denton *et al*., 2004). Steps indicated in **Fig. 2.2** are steps 5 and 7 to 11. The feed used in this process can mainly consist of fine materials. The main difference of this process option compared to the other three processes is the use of a DC instead of an SAF during the smelting process.

The total exclusion of oxygen is impossible when utilising either one of the above-mentioned processes for the production of FeCr (Beukes *et al*., 2010). This results in the formation of small amounts of Cr(VI), although completely unintended.

According to Beukes *et al.* (2010), the waste products formed as a result of the FeCr industry are slag, bag filter dusts and scrubber sludge. Of these different wastes, bag filter dust originating from semi-open or open SAF operations is the most hazardous, since it contains relatively high levels of soluble Cr(VI) (Erdem *et al*., 2005; Gericke, 1995). Additionally, this waste is a fine dry material that is subject to wind dispersion if not contained and properly disposed of. If dispersion into the atmosphere occurs, it could lead to wet and dry deposition within the vicinity of the smelter or even farther away from the smelter. Scrubber sludge can also be classified as a fine waste material, but it does not contain high levels of Cr(VI), since it originates from closed SAF or DC arc furnaces. Furthermore, the sludge does not have the risk of wind dispersion. It does, however, contribute to the volume of fine waste materials that are usually disposed in fit-for-purpose slimes dams.

In subsequent paragraphs, some of the process steps presented in **Fig. 2.2** are discussed in more detail with regard to potential Cr(VI) formation.

Dry milling

The chromite ore is milled, since the agglomeration technique most widely used is pelletisation (in the form of drum- or disk pelletisation), which requires relatively fine materials. According to Beukes and Guest (2001), dry milling can result in the formation of Cr(VI). This is supported by information provided in a document compiled by the International Chromium Development Association (ICDA, 2007). Results indicated that Cr(VI) was generated during dry milling, while the Cr(VI) formation was limited when a wet milling process was used (Beukes *et al*., 2010). Glastonbury *et al*. (2010) also proved that Cr(VI) is formed during dry milling, although samples were prepared on laboratory scale. During dry milling experiments, no Cr(VI) was formed in an inert environment, indicating that the Cr(VI) was formed and not merely liberated from the chromite ore matrix (Glastonbury *et al*., 2010). Beukes and Guest (2001) suggested that Cr(VI) formation during dry milling occurs as a result of crystalline breakage that could lead to an increase in temperature where Cr(VI) could be formed, while the addition of water can limit or reduce this process. This form of Cr(VI) generation can result in air pollution due to the distribution of dust into the environment.

Furnace operation

The dust generated during the smelting of FeCr that is captured by bag filters or as sludge in wet venturis poses the biggest risk to the environment and human health. Different furnace operations, i.e. open, semi-closed and closed furnaces, result in different levels of Cr(VI) formation. In **Table 2.2**, Cr(VI) concentrations determined for the dust from closed and open furnaces are listed to illustrate these differences.

Table 2.2 Water-soluble Cr(VI) content of furnace dust from open and closed furnaces (Gericke, 1995).

Process		**ppm Cr(VI)**
Closed furnace:	acid slag practice	5
	basic slag practice	100
Open furnace:	acid slag practice	1 000
	basic slag practice	7 000

In open and semi-closed furnaces, Cr(III) is oxidised to Cr(VI) in the off-gas dust. In addition, as observed from the data presented in **Table 2.2**, there is another factor that can influence the Cr(VI) content in the off-gas, i.e. the chemical composition of the slag. Less Cr(VI) is generated with acidic than basic slag operations (**Table 2.2**).

It is generally assumed that closed FeCr furnaces generate less Cr(VI) than semi-closed and open furnaces do (Beukes and Guest, 2001; Gericke, 1995). However, this does not imply that they are inherently safer and could give a false sense of security. According to ICDA, Cr(VI) emissions from closed furnaces are not yet validated (Gediga and Russ, 2007). The possibility of Cr(VI) formation during the combustion of closed furnace off-gas was mentioned by Beukes and Guest (2001). Recently Du Preez *et al*. (2015) proved that Cr(VI) can be formed due to the combustion of closed furnace off-gas. Modelling scenarios presented by Visser (2005) indicate the atmospheric dispersion for open and closed furnaces of a South African FeCr producer.

Ferrochrome slag

Slag is a by-product or waste generated during the smelting of chromite ore that is discarded into dumps. The slag-to-metal production ratio varies between 1.1 and 1.9 for South African FeCr producers due to different production technologies (Beukes *et al*., 2010; Erdem *et al*., 2005). If the production volumes of the South African FeCr industry for 2013 are considered, i.e. 3 megatons of high carbon FeCr (ICDA, 2013), and an average slag-to-metal ratio of 1.5 is used, it implies that 4.5

megatons of slag was produced in that year alone. With the high volumes of slag being produced, it is necessary to consider possible Cr(VI) pollution from these slags.

FeCr slag consists mainly of Al, silicon (Si), calcium (Ca), Mg, Fe and Cr. Cr and Fe are present in the waste, since perfect FeCr recovery cannot be achieved. All of the afore-mentioned elements may occur in various oxide forms, as well as re-crystallised spinel within the slag. With consideration of the Cr(VI) within these slags, it is important to distinguish between historic slag dumps and current arising slag dumps (Beukes *et al.*, 2010). Before environmentally conscious practices were adopted, it was common to co-dispose bag filter dust with other wastes such as FeCr slag. Furthermore, these dumps were not lined and therefore aqueous soluble compounds could leach into the groundwater systems. Due to the environmental risks and the financial incentives related to these FeCr dumps, initiatives were launched in the reclamation of these dumps in South Africa (Mintek, 1994; Visser and Barett, 1992). During FeCr reclamation, Cr(VI) is treated with ferrous chloride of ferrous sulphate to reduce Cr(VI) to inert Cr(III) hydroxides (Beukes *et al.*, 2012).

Waste management

The waste generated during the FeCr production process can be managed in different ways, e.g. optimising the operation and thereby minimising the wastes generated, recycling of the waste into the furnaces, recovery processes, solidification and/or using the waste as raw materials and adding it to other products, e.g. fertilisers (Beukes *et al.*, 2012; Ma and Garbers-Craig, 2006). The treatment of these waste materials is performed by using reducing agents, e.g. Fe(II), to reduce Cr(VI) to Cr(III) (Beukes *et al.*, 2012). The FeCr smelters in South Africa primarily use ferrous chloride or ferrous sulphate as the reducing agent, since this process has received ample research attention (Qin *et al.*, 2005; He *et al.*, 2004; Buerge and Hugh, 1997; Fendorf and Li, 1996), which is considered to be a proven treatment strategy. Fe(II) is a reducing agent that forms insoluble Cr(III) hydroxide species and can be applied within the pH range relevant to the wastewater of the FeCr production process, e.g. 6.2-9.0. Most organic compounds can also be used for Cr(VI) reduction to a Cr(III) species. However, these compounds might form Cr(III)-complexes that are water-soluble and undesired (Beukes *et al*., 2012). Furthermore, these water-soluble Cr(III) species could seep through into the surface- and groundwater, resulting in environmental pollution. Other inorganic reducing species, e.g. S(IV), can only be used at pH levels lower than 5 (Beukes *et al*., 2000; Beukes *et al*., 1999).

Although the use of ferrous chemicals is highly effective for the reduction of Cr(VI) to Cr(III), a few disadvantages are associated with the use of these chemicals. One of the disadvantages is the impact of ferrous chemicals on the environment and general water quality (Beukes *et al*., 2012). For example, the use of chlorides and sulphates could lead to the increase of total dissolved solids (TDS) in the process- and wastewater. Fe(III) hydroxide is formed during the treatment process of Fe(II). The pH levels of the wastewater from the FeCr process subsequently create an environment where hydroxide precipitates leaving the chloride and sulphate in the solution, thereby increasing the TDS. The increase of TDS in the waste- and process water could lead to an increase in salination of surface- and groundwater if leakage occurs. Although it is not as hazardous as Cr(VI) pollution, salination could have an impact on the environment (Beukes *et al*., 2012). Other disadvantages of salination on the production of FeCr include the increased build-up of scale in pipes, since process water is recycled.

2.5 Relevance of Cr(VI) in the environment and related health impacts

As previously stated, Cr is commonly found within the environment in two main stable oxidation states, i.e. Cr(III) and Cr(VI), with Cr(III) being the dominant species. However, the environmental conditions, e.g. pH and oxidative properties, determine the ratio between the two dominant species (Kotaś and Stasicka, 2000). The trivalent oxidation state is considered to be non-carcinogenic and is an important trace element included in a balanced nutritional intake for a large range of organisms (Stern, 2010; Kim *et al*., 2007; Proctor *et al*., 2002; IARC, 1997; Fendorf, 1995; Yassi and Nieboer, 1988). This essential nutrient (in a correct amount within the human body) influences the sugar, protein and lipid metabolism (IETEG, 2005; Ashley *et al*., 2003). It is also sometimes used as a dietary supplement for health abnormalities (Hininger *et al*., 2007).

Cr(VI) is predominantly found in groundwater when the pH is above 7 and if the oxidising potentials are high (SWRCB, 2011). Due to these conditions, it could be that the Cr(VI) in groundwater, near certain contaminated areas, contributes to more than 75% of the total Cr present (Gonzalez *et al*., 2005). In contrast to Cr(III), Cr(VI) can be toxic for plants and animals, and carcinogenic for humans, as it is an oxidising agent. The toxicity of Cr(VI) to plants occurs at concentrations as low as 0.5 mg/L and 5 mg/kg in solution and soil, respectively (Fendorf, 1995). When Cr(VI) is constantly released into the environment, it leaches from the surface layer to the soil and groundwater. This can lead to a decrease in seed development and root growth (Peralta *et al*., 2001). The Department of Water Affairs and Forestry (DWAF, 1996a) provides toxicity levels that are applicable for soil, which range between 5 and 500 mg/kg for Cr(VI), and 50 and 5 000 mg/kg for Cr(III).

A potential link between the occupational exposures to chromates and an increased risk of lung cancer was first suggested by Lehmann in 1932 (Yassi and Nieboer, 1988). Numerous countries have conducted studies that confirmed that the risk of cancer increases when exposed to chromium-containing compounds. The carcinogenicity of Cr(VI) is mainly associated with respiratory induced ailments, e.g. pulmonary inflammation, chronic bronchitis and interstitial lung diseases (Beaver *et al*., 2009; Thomas *et al*., 2002), which is especially important from an industrial occupational health perspective. Governing agencies have established drinking water standards for Cr due to the carcinogenicity and toxicity thereof. However, there seems to be some discrepancy in literature on the level of harm that can be caused by the exposure and uptake of Cr(VI) by the human body. There also seems to be inadequate evidence to support the carcinogenicity of all Cr(VI) compounds (IARC, 1997). The current drinking water standard limit of 50 µg/L for Cr was based on the alleged capability of the gastric juices to reduce Cr(VI) to the non-toxic state, i.e. Cr(III) (WHO, 2008; DWAF, 1996a). Pharmacokinetic studies conducted suggested that the gastrointestinal tract possesses the capability of reducing up to 1 L of water containing 10 mg/L Cr(VI) (Finley *et al*., 1997). Recently, studies have been conducted that focused on the toxicokinetics and genotoxicity, which revealed that a fraction of the ingested dosage is absorbed. The absorbed Cr(VI) is then taken up by the surrounding cells and tissue, which results in deoxyribonucleic acid (DNA) damage. Additionally, it was found that there was an increased amount of oral and small intestine tumours in rats exposed to drinking water containing Cr(VI) (Gatto *et al*., 2010), and these tumours were increasingly found in human subjects (Sedman *et al*., 2006). Furthermore, during the reduction of the Cr(VI) to Cr(III) in the gastrointestinal tract, the small amount of Cr(VI) that could be absorbed can form free radicals in the biological systems, resulting in numerous DNA modifications (Flora, 2009). Additionally, the Target Water Quality Range (TWQR) for dissolved Cr(VI) in the aquatic ecosystems is 7 mg/L, but there is also a TWQR for dissolved Cr(III) i.e. 12 mg/L (DWAF, 1996b).

It is important to differentiate between Cr(III) and Cr(VI) species present in the environment due to the extreme differences on health impacts and toxicity (Fendorf, 1995). Cr(VI) compounds can be found in different concentrations and particle sizes within the occupational environment, while airborne Cr(VI) compounds also vary in toxicity and solubility. In **Table 2.3**, the threshold limit values (TLVs) for different Cr compounds encountered in air in the workplace accumulated by the American Conference of Governmental Industrial Hygienists (ACGIH) are presented.

Table 2.3 The TLVs for the different Cr compounds based on the toxicity data accumulated by ACGIH (Ashley *et al*., 2003).

Substance(s)	TLV (TWA)[a]	Comments
Calcium chromate, as Cr	0.001 mg/m^3	Suspected carcinogen
Chromite ore processing (chromate), as Cr	0.05 mg/m^3	Confirmed carcinogenicity
Chromium, and inorganic compounds, as Cr:		
Cr metal and Cr(III) compounds	0.5 mg/m^3	Allergens; no known carcinogenicity
Water soluble Cr(VI) compounds	0.05 mg/m^3	Confirmed carcinogens
Insoluble Cr(VI) compounds	0.01 mg/m^3	Confirmed carcinogens; allergens
Lead chromate, as Cr	0.012 mg/m^3	Suspected carcinogen
Strontium chromate, as Cr	0.0005 mg/m^3	Suspected carcinogen
Zinc chromate, as Cr	0.01 mg/m^3	Confirmed carcinogen

[a] 8-hour time-weighted average

2.6 Transportation, transformation and inter-conversion of chromium in soil, water and air

Cr is an inorganic element that can cause environmental problems, since inorganic compounds do not undergo significant degradation (Fendorf, 1995). As mentioned previously, Cr(III) present in the environment does not pose a problem However, if it is oxidised to Cr(VI), the risk of environmental pollution increases tremendously, as discussed in **§ 2.5**. In the event of Mn oxides being present in the environment, the potential for natural oxidation reaction exists. According to literature (Fendorf and Zasoski, 1992; Eary and Rai, 1987), Mn oxide is the only compound capable of initiating the oxidation of Cr(III) to Cr(VI) in the ambient environment. Precipitation and/or adsorption, organic complexation and surface coatings of Mn oxides are some of the processes through which the transformation of Cr(III) to Cr(VI) can occur. In order to understand the different risks posed by Cr species in the environment, the speciation reactions are considered in the subsequent paragraphs.

2.6.1 Speciation of Cr in the environment

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. This could subsequently lead to Cr(VI) leaching from soils, as well as dry and wet deposition of atmospheric particles containing Cr(VI).

2.6.1.1 Atmospheric chromium

Atmospheric Cr can be emitted into the atmosphere from anthropogenic- (60-70%) and natural (30-40%) sources (Seigneur and Constantinou, 1995). The predominant atmospheric Cr species are Cr(VI) and Cr(III). These two species can be present in the liquid or solid phase, but not in the gaseous phase. The reason for Cr species not being present in the gaseous phase can be attributed to its significantly low vapour pressure at ambient conditions (Seigneur and Constantinou, 1995).

Cr(VI) can be reduced to Cr(III) in the atmosphere, while Cr(III) could be oxidised to Cr(VI), thereby forming an atmospheric cycle presented in **Fig. 2.3**. The reduction of Cr(VI) can be induced by several chemicals (e.g. trivalent arsenic (As(III)), Fe(II), V and sulphur dioxide (SO_2)), but the oxidation of Cr(III) mainly occurs due to Mn oxides (Seigneur and Constantinou, 1995).

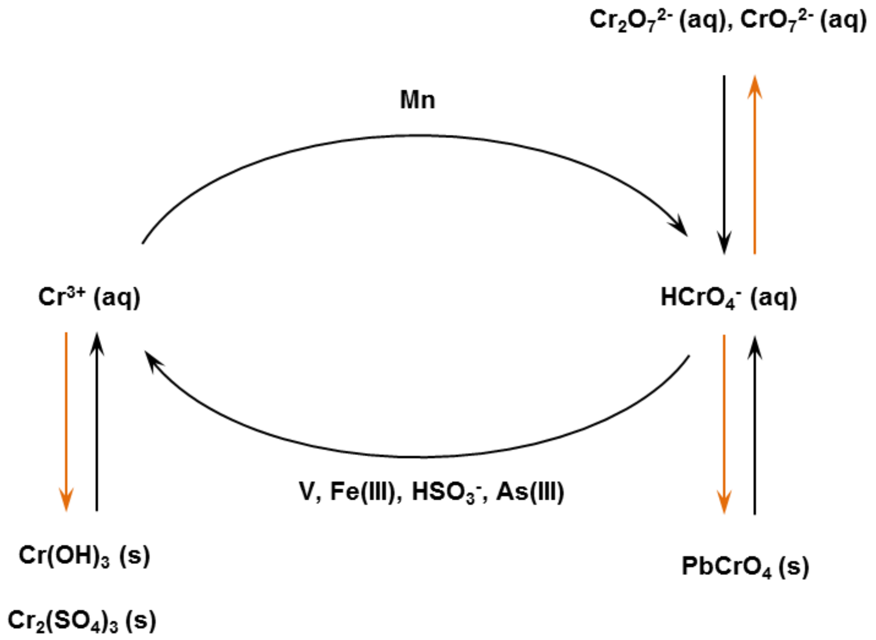

Figure 2.3 An illustration of the atmospheric Cr cycle, adapted from Seigneur and Constantinou (1995).

As indicated in **Fig. 2.3**, there are two reactions for Cr(III) precipitation, i.e. Cr sulphate ($Cr_2(SO_4)_3$) and Cr hydroxide ($Cr(OH)_3$) formation. The atmospheric pollutants are transferred to the soil and water by rain or fallout of the particles. The problem with this form of water and soil pollution, from the atmosphere, is that the pollution could have been carried far from the initial source by the wind (Kotaś and Stasicka, 2000).

2.6.1.2 Aqueous Cr

Cr(III) tends to form Cr(III) hydroxo-complexes in aqueous mediums, which is expected to be the dominant Cr(III) species in environmental water (Rai *et al*., 1987). These hydroxo-complexes were studied by investigating the solubility of $Cr(OH)_3$. In **Fig. 2.4**, an Eh-pH diagram is shown that provides the dominant aqueous species and the redox stability for Cr. These conditions are only valid for chemical equilibrium (Mohan and Pittman, 2006). Speciation of $Cr(OH)_3$ indicated that there were a few species formed of which the dominant species was $Cr(OH)^{2+}$. The presence of the latter was observed at pH values ranging between 3.8 and 6.3. $Cr(OH)_3$ was detected at pH values between 6.3 and 11.5, while $Cr(OH)_4$ was present at a pH above 11.5 (Rai *et al.*,1987). The total soluble Cr content in environmental water was not attributed to species such as $Cr_2(OH)_2^{4+}$ and $Cr_3(OH)_4^{5+}$ (Mohan and Pittman, 2006), while an evaluation of commonly found ligands in environmental samples (OH^-, SO_4^{2-}, NO_3^- and CO_3^{2-}) indicated that only OH^- significantly forms complexes with Cr(III) (Saleh *et al.*, 1989). The diagram in **Fig. 2.4** also illustrates the different oxidation states that are present at equilibrium with regard to the Eh and pH ranges, which indicates that Cr(III) is thermodynamically stable under reducing conditions. $Cr(OH)_3^0$ is a solid species and exists as an amorphous precipitate. Uncomplexed Cr(III) is predominantly present at a pH<3. At pH levels >3.5 hydrolysis of aqueous Cr(III) species are present ($CrOH^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3^0$ and $Cr(OH)_4^-$).

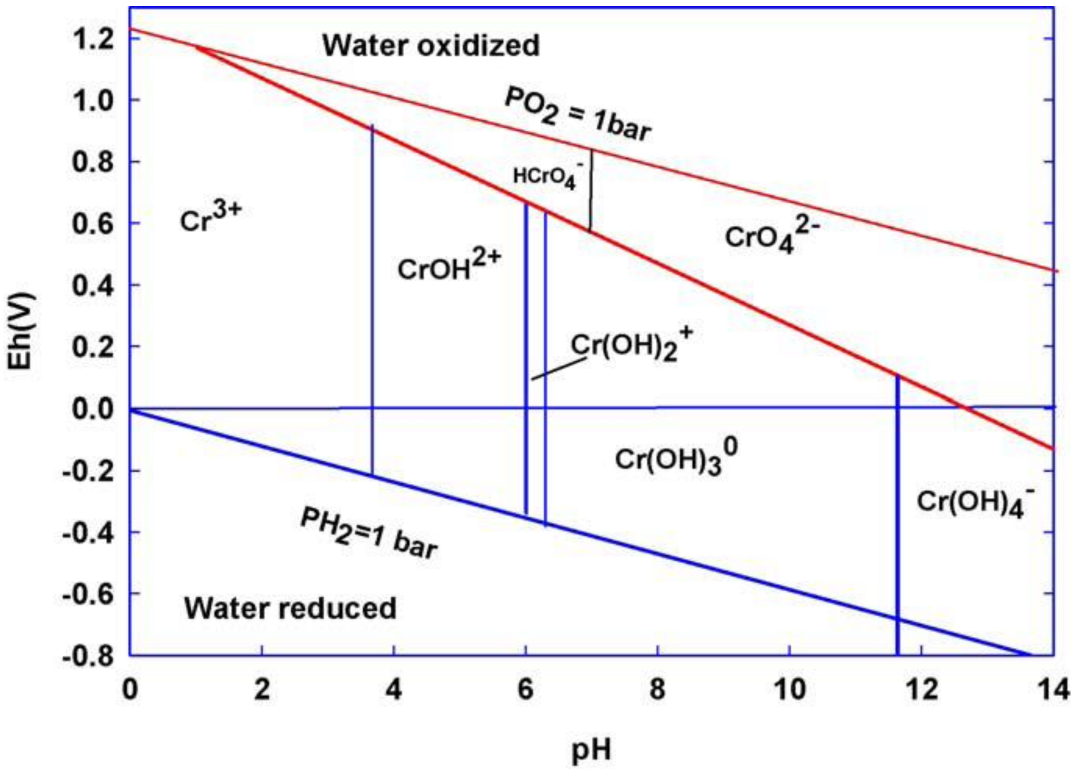

Figure 2.4 A phase diagram (Pourbaix diagram) illustrating the thermodynamic stability of the different aqueous species. These species are illustrated over a typical Eh range and pH values in the environment (Mohan and Pittman, 2006; Fendorf, 1995).

Different Cr(VI) species can be present in aqueous mediums, which are illustrated in the speciation diagram given in **Fig. 2.5**. At pH levels higher than 6, the Cr(VI) species present in the water are predominantly in the chromate form (Mohan and Pittman, 2006). The different Cr(VI) species present, according to **Fig. 2.5**, are chromic acid (H_2CrO_4), hydrogen chromate ions ($HCrO_4^-$) and chromate ions (CrO_4^{2-}), depending on the pH of the solution (Mohan and Pittman, 2006).

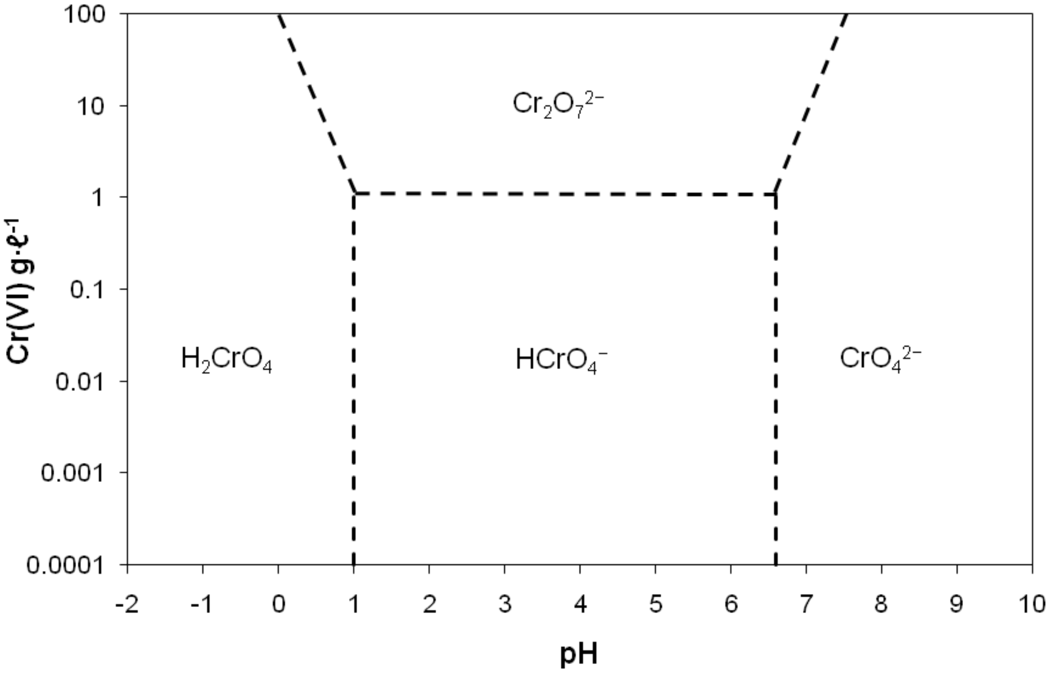

Figure 2.5 The relative distribution of different Cr(VI) species in aqueous solution as a function of pH and Cr(VI) concentration (Mohan and Pittman, 2006; Dionex, 1996).

2.6.1.3 Soil chromium

The presence of Cr(VI) within soil is mainly ascribed to human activity or the oxidation of Cr(III) pollution, while only a small concentration of Cr(VI) can be attributed to the natural processes (Bartlett, 1991). The Cr concentrations in soils resulting from human activity can mainly be divided into Cr-containing particles deposited from the atmosphere (wet and dry deposition), or leaching from sludge and other industrial waste. Two main Cr(III) components exist within soil, i.e. soluble species that can be oxidised or Cr(III) species that adsorb onto the soil particulates and therefore become immobile. The Cr species that are dominant with variations in the pH are $Cr(H_2O)_6^{3+}$ at pH<4 and its hydrolysed form, i.e. $CrOH^{2+}$ at pH<5.5. In a neutral to alkaline pH range, Cr(VI) exists as either the water-soluble (e.g. Na_2CrO_4) or moderately soluble form (e.g. $CaCrO_4$, $BaCrO_4$, $PbCrO_4$). The chromates, which are the most mobile Cr forms in soil, are dominant near pH levels of 6 (Kotaś and Stasicka, 2000). In **Fig. 2.6**, an illustration of the possible Cr cycle in soil and water is given to aid in the discussion of this section.

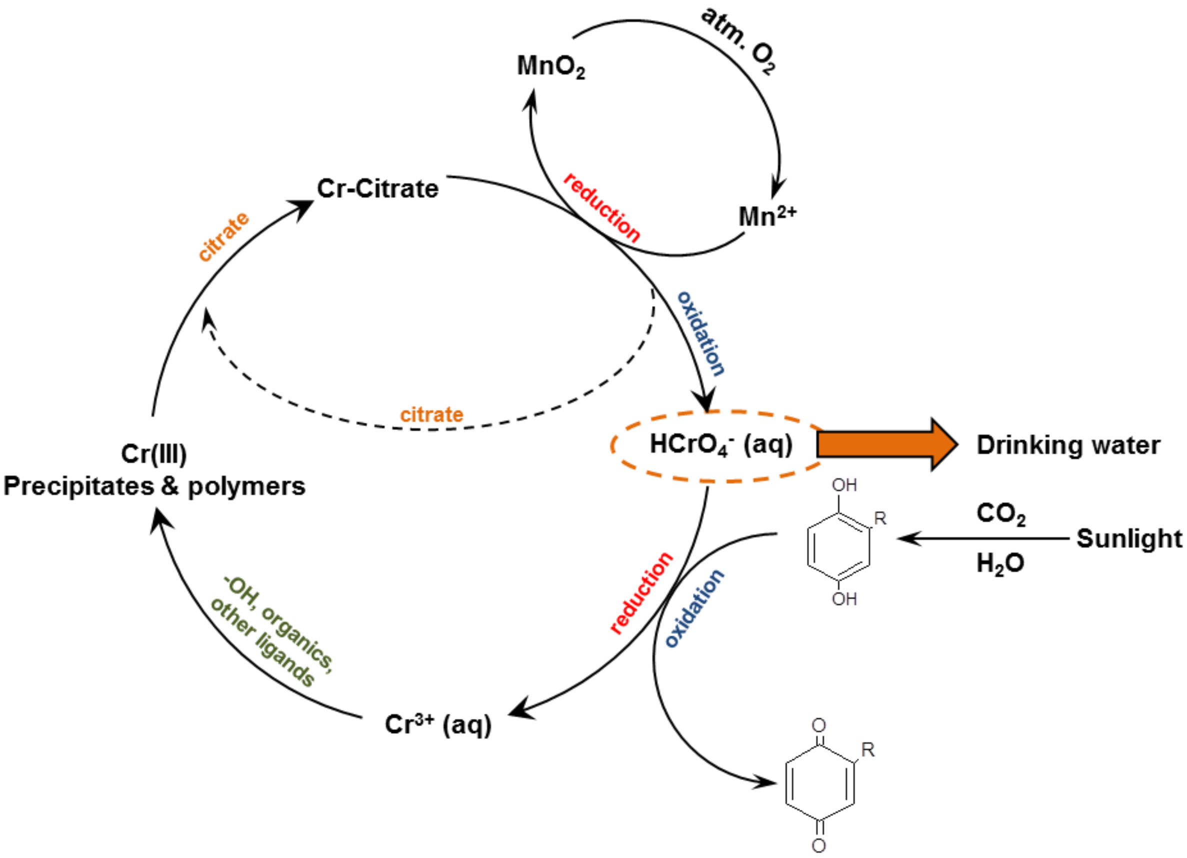

Figure 2.6 An illustration of the Cr cycle in soil and water, adapted from Bartlett (1991).

If Cr(III) is present in soil, there is a possibility of retention of the Cr onto soil minerals under most pH conditions. This also implies that the hydroxide species has low solubility and limits the Cr(III) concentrations present, which subsequently limits the mobility in soils and water. Under oxidising conditions, the Cr(VI) species are more thermodynamically stable with chromates and dichromates possibly being present. The Cr(VI) species are anionic and therefore more mobile in the soils, as well as being bioavailable. Reduction reactions of Cr(VI) within soil and water can be as a result of organic materials, sulphides and ferrous Fe (Fe(II)) being present. Furthermore, the reduction reactions in natural soils are slow and might even occur over a period of years (Bartlett, 1991). The oxidation reaction is not always direct, due to kinetic limitations. The dominant oxidant appears to be Mn oxide (Fendorf, 1995). The two main pathways to introduce soil contamination into the water systems are by surface run-off or leaching from the soil into groundwater (Kotaś and Stasicka, 2000).

2.7 Cr (VI) analytical detection methods

A large number of analytical techniques are available to determine Cr due to the predominance and characteristic differences of the two most common oxidation states of this species. Available techniques focus on the determination of specifically Cr(VI), Cr(III) and/or the total Cr content. The analytical techniques available to determine Cr(VI) levels in different environments, e.g. water, soil and atmosphere, also vary. Analytical techniques can be categorised according to their method of detection, e.g. spectroscopic-, spectrophotometric-, chemiluminescence-, electrical methods and chromatographic systems (Gómez and Callao, 2006).

Spectroscopic methods: Spectroscopic methods that determine the total Cr content include flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GF-AAS), electrothermal atomic absorption spectrometry (ET-AAS) and inductively coupled plasma (ICP) tandems, i.e. inductively coupled plasma – atomic emission spectrometry (ICP-AES). It is possible to use these techniques to determine one or both of the Cr species, but this requires adequate pre-treatment for higher selectivity towards a particular species. The limits of detection (LODs) of these techniques vary from ng/L to µg/L, depending on the pre-treatment. The recommended technique for samples with high concentrations is FAAS, but when low levels are present, GF-AAS and ICP-AES have been shown to be more suitable (Gómez and Callao, 2006).

Spectrophotometric methods: A spectroscopic method that is more suitable to determine a particular, selective Cr species is ultraviolet-visible (UV-vis) spectrometry. In this method, reagents are used that form absorbing species with the Cr in order to enhance the selectivity of the species. The determination of Cr(VI) in aqueous solutions with diphenylcarbazide (DPC) is a commonly preferred method (Dionex Application update 179, 2011; Gómez and Callao, 2006).

Chemiluminescence methods: The determination of total Cr at ng/L levels is conducted by utilising these methods, e.g. fluorimetry (Gómez and Callao, 2006).

Electrical methods: The commonly used techniques are amperometry and voltammetry, which have LODs in the µg/L order. The LODs change to a detection limit of ng/L when selective absorbents are used (Gómez and Callao, 2006).

Chromatographic systems: Analytical systems mainly used are high pressure liquid chromatography (HPLC), gas chromatography (GC) and ionic chromatography (IC). The advantage of these systems lies in its ability of species separation and the reduction of reagent and sample volume needed (Gómez and Callao, 2006).

Although Cr(VI) can be present in different types of environments, the samples that are most frequently analysed are aqueous solutions (Gómez and Callao, 2006). Different aqueous samples that can be analysed include natural water, general wastewater, dye-plant wastewater, electroplating wastewater and tanning wastewater. In order to determine the Cr(VI) content in each of these samples, different techniques are implemented as each method poses different limits and challenges. During the analysis of natural water, a variety of analytical methods can be implemented to detect Cr(VI), i.e. atomic adsorption spectrometry (AAS), high performance liquid chromatography (HPLC) with ICP mass spectrometry (MS) (HPLC-ICP-MS), UV-vis spectrophotometry, ICP-MS, fluorimetry and IC-UV-vis detection (Gómez and Callao, 2006; Shaw and Haddad, 2004). In **Table 2.4,** a summary is provided of the different techniques employed to determine Cr(VI) in natural and wastewater, with the LODs of each method also indicated.

Table 2.4 A summary of the most relevant analytical techniques used to determine Cr(VI) in natural- and wastewater with the detection range associated with the particular method, adapted from Gómez and Callao (2006).

Matrix	**Cr content**	**Analyte**	**Detection technique**
Natural water	mg/L to ng/L	Cr(III) & Cr(VI)	AAS
Natural water	µg/L	Cr(III) & Cr(VI)	ICP-AES
Natural water	g/L - ng/L	Cr(III) & Cr(VI)	ICP-MS
Natural water	µg/L	Cr(III) & Cr(VI)	IC-ICP-MS
Natural water	µg/L	Cr(III) & Cr(VI)	ICP-OES
Natural water	g/L - µg/L	Cr(III) & Cr(VI)	Spectrophotometry
Natural water	µg/L	Cr(III) & Cr(VI)	Fluorimetry
Natural water	µg/L - ng/L	Cr(VI)	AAS
Natural water	few mg/L - µg/L	Cr(VI)	Spectrophotometry
Natural water	µg/L	Cr(VI)	IC-UV/vis detection
Natural water	µg/L	Cr(VI)	Fluorimetry
Natural water	µg/L	Cr(VI)	HPLC-ICP-MS
Wastewater	few mg/L - µg/L	Cr(III) & Cr(VI)	AAS
Wastewater	µg/L	Cr(III) & Cr(VI)	ICP-AES
Wastewater	mg/L	Cr(III) & Cr(VI)	Spectrophotometry
Wastewater	few mg/L	Cr(VI)	Spectrophotometry
Wastewater	µg/L	Cr(VI)	Fluorimetry
Wastewater	µg/L	Cr(VI)	IC-spectrophotometry

The method most commonly used to determine Cr(VI) in aqueous solutions is the UV-vis method, by using DPC. This method has the advantage that the reaction is specific to Cr(VI). However, this method also has the disadvantage of DPC reacting with other known metal species, i.e. Cu(II), Fe(III), Hg(II), Mo(VI) and V(V), which can cause an interference with the results obtained. The reaction between Cr(VI) and DPC results in a magenta-coloured solution that can be analysed at a wavelength of 540 nm. The formed carbazone inner complex salt of a chromos ion, i.e. Cr(II), illustrated in **Fig. 2.7**, can be measured spectrophotometrically with extremely high detection.

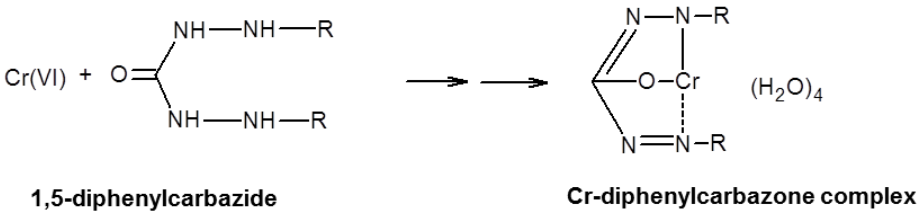

Figure 2.7 Illustration of the complex formed during the Cr(VI) reaction with DPC . This is the coloured carbazone complex that can be detected at 540 nm with UV/vis spectrophotometry (Ashley *et al.*, 2003).

Combining IC with the UV-vis and DPC analytical method is currently considered one of the most suitable methods applied to determine low levels of Cr(VI) concentrations (Thomas *et al.*, 2002). In this method, the different ionic species in the samples are separated on a column prior to reacting with the DPC and subsequent UV-vis analysis. IC also has the added advantage of using a guard column that removes most of the possible interfering compounds before the DPC is delivered through a post-column delivery system (Pettine and Capri, 2005; Ashley *et al.*, 2003). Another major problem to overcome when determining either one of the Cr species is the risk of inter-conversions taking place before analysis (Dionex Application 144, 2003).

Samples collected should be treated with a buffer solution, consisting of ammonium sulphate and -hydroxide, to adjust the pH of the water samples to 9.0-9.5. This pH range serves as an optimum range to store the water samples (Broadhurst and Maidza, 2006; Thomas *et al.*, 2002; US Environmental Protection Agency (EPA) method 218.6, 1994), since it prevents the reduction of the Cr(VI) by naturally occurring reducing agents (He *et al.*, 2004; Beukes *et al.*, 2000; Beukes *et al.*, 1999; Buerge and Hugh, 1997; Fendorf and Li, 1996). It also ensures the solubility of most of the

Cr(VI) (Ashley *et al*., 2003). Additionally, the samples must be cooled down to 4 °C and kept at this temperature during transportation (Dionex Application 179, 2011).

2.8 Cr(VI) studies conducted within South Africa

Considering the size of the FeCr industry within South Africa, as well as the potential environmental and health effects associated with Cr(VI) pollution, it is important to investigate Cr(VI) pollution from this industry. However, only a few studies available in the peer-reviewed public domain have been conducted on Cr(VI) pollution in the proximity of the South African FeCr smelters.

The review by Beukes *et al*. (2010) indicated where Cr(VI) can potentially be formed during FeCr production, as discussed in **§2.4**.

Mandiwana *et al*. (2007) investigated the amount of Cr(VI) generated during the production stages of FeCr. It was found that the Cr(VI) concentrations increased as the process progressed with the highest concentrations being detected within the dust and not the ore- or slag samples. The investigation also showed that Cr(VI) pollution decreased with an increase of distance away from the smelter within the soil. This was therefore considered not to be hazardous for animal consumption since the concentrations were low. Mandiwana *et al.* (2007) also reported that the chromite ores contained significant amounts of Cr(VI). However, Glastonbury *et al*. (2010) investigated this statement further and found that the increased levels were as a result of incorrect sample preparation.

Sedumedi *et al*. (2009) focused more on the environmental impact of one FeCr smelter on the surrounding area. The investigation focused on dust, soil, grass and tree bark in the area of a specific smelter. The dust collected from the smelter consisted of cyclone, fine and slimes dust and were found to exceed the acceptable concentrations of 20 µg/g (DWAF, 1998). The Cr(VI) concentrations of the environmental samples (i.e. grass, tree bark and soil) collected near the FeCr smelter were higher than samples collected from an uncontaminated area. Therefore, these authors stated that the smelter is the origin of environmental pollution regarding Cr(VI).

Glastonbury *et al*. (2010) investigated the possibility of Cr(VI) generation during the milling of ore according to a dry milling process. This study proved that the Cr(VI) content within the chromite samples is influenced by the sample preparation technique. It was indicated that there was a difference between pulverising the ore in an inert atmosphere and normal atmospheric conditions, with no Cr(VI) present in the samples when milled under inert conditions. Furthermore, it was suggested that it is unlikely that there was Cr(VI) present in South African chromite ores, as suggested by Mandiwana *et al*. (2007).

Beukes *et al*. (2012) provided insight into the waste management of the FeCr smelters in South Africa. Additionally, the paper provides a discussion of the interaction of Cr(VI) with Fe(II) present in the process and wastewater.

McIntyre (2013) conducted a study to identify and use biomarkers (microorganisms) to assist in evaluating the effect of Cr(VI) pollution in surface- and groundwater at a FeCr smelter, specifically at sites where historical waste was not managed properly. The study concluded that these biomarkers can assist researchers in the characterisation of the chemical environment and can indicate the presence of any Cr(VI) pollution, since these biomarkers are sensitive and specific to environmental changes. The total Cr content and the Cr(VI) concentrations of the samples collected were determined. The Cr(VI) values ranged between 0.1 and 3.9 mg/L, thereby exceeding the drinking water limit of 0.05 mg/L. The water samples collected were further used for the biomarker investigation with regard to Cr(VI) pollution. The microorganisms that were present in the samples were e.g. *Sediminibacterium salmoneum*, uncultured Cyanobacterium, uncultured Bacteroidetes bacterium and uncultured betaproteobacterium, have different metabolic activities and therefore behave differently under diverse environmental conditions. It was found that the microorganisms present in the water samples with higher Cr(VI) content, had the ability to either resist any effect of Cr(VI) or reduce the Cr(VI) concentrations, resulting in the ability to flourish in Cr(VI)-polluted water. Furthermore, these specific microorganisms could be used as biomarkers to determine locations of Cr(VI) pollution.

2.9 Additional water quality parameters associated with FeCr production

In addition to the potential Cr(VI) pollution generated during FeCr production, other water-soluble pollutants might also be generated, e.g. heavy metals (Fe and zinc (Sn)) (Riekkola-Vanhanen, 1999). During the course of the water treatment process, sulphate (SO_4^{2-}) and chloride (Cl^-) are also added (Beukes *et al.*, 2012). These salts are water soluble and that could have an impact on the aqueous systems and contribute to the salt content, as well as the conductivity of the natural water. Each of these salts is not considered in isolation, but the overall impact on water quality is considered within the context of TDS for further discussion. TDS in water refers to the total dissolved inorganic and/or organic materials and these compounds consist of salts and compounds that dissociate in water, thereby forming ions. Contributing factors in the increase of TDS values are from agricultural run-off, urban run-off, industrial wastewater, sewage, and natural sources such as leaves, silt, plankton and rocks. The most common dissolved species measured are sodium (Na^+), sulphate (SO_4^{2-}), chloride (Cl^-), calcium (Ca^{2+}), magnesium (Mg^{2+}) and bicarbonate (HCO_3^-). These dissolved salts and compounds are classified as secondary contamination to the environment with a suggested maximum limit of 500 mg/L (EPA, 1994). High TDS values in drinking water can cause gastrointestinal discomfort in some individuals, but pose no major health concerns. Therefore, drinking water regulations are seen as a voluntary guideline. The EPA levels for some of the salts are 250 µg/L, 10 µg/L and 250 µg/L for chloride-, nitrate- and sulphate, respectively. TDS levels were divided into preferable groups by the World Health Organization (WHO, 2008) by conducting a study using a panel of tasters. With TDS levels of less than 300 µg/L, the water was rated as excellent on grounds of the aesthetic factors. Levels of 300 to 600 µg/L were good, 600 to 900 µg/L was fair, 900 to 1 200 µg/L poor and values above 1 200 µg/L were labelled as unacceptable. The South African water guidelines give TWQR for each of these salts with regards to domestic use (DWAF, 1996c). The TWQR for sodium (Na^+), sulphate (SO_4^{2-}), chloride (Cl^-), calcium (Ca^{2+}), magnesium (Mg^{2+}) are 100 µg/L, 200 µg/L, 100 µg/L, 32 µg/L and 30 µg/L respectively (DWAF, 1996c). The TDS value stipulated in these guidelines for domestic used water is 450 µg/L.

A link between the TDS and conductivity of water exists, since TDS is the detection of the ionic species of the salts, and conductivity is the determination of the electrical conductivity measured in micro Siemens per centimetre (µS/cm). The different levels of conductivity can also be divided into groups to determine the limits and uses. Conductivity values of 0 to 800 µS/cm can be used for human consumption and irrigation. However, care must be taken during the irrigation of plants sensitive to high salt levels if the conductivity is higher than 300 µS/cm. Conductivity levels between 800 and 2 500 µS/cm are still suitable for human consumption, while irrigation at these levels should be managed to minimise plant damage. Both of these groups are suitable for consumption by livestock. The levels between 2 500 and 10 000 µS/cm are not recommended for human consumption, although levels of up to 3 000 µS/cm can be consumed. Salt tolerant crops can be irrigated with water with conductivity levels up to 6 000 µS/cm. Most livestock can consume drinking water with levels up to 10 000 µS/cm, but the drinking water of poultry and pigs should be limited to 6 000 µS/cm. Conductivity levels exceeding 10 000 µS/cm are not suitable for irrigation, human consumption, poultry, pigs and all lactating animals (Anderson and Cummings, 1999). Conductivity and TDS can therefore be used to determine the water quality by the levels detected.

2.10 Summary

In South Africa, FeCr is a large industry with 14 smelters located throughout the country, with the largest concentration of smelters present within the BIC. During the FeCr production process, there is the possibility of small amounts of Cr(VI) being generated, which is hazardous and carcinogenic. In general, Cr(VI) production is mainly caused by anthropogenic processes, but natural processes, e.g. MnO_2 catalyse oxidation of Cr(III), can also contribute to Cr(VI) pollution. Cr(VI) pollution is present within air, water and soil in the environment, which can form a cycle since, for example, atmospheric pollution could result in water and soil pollution due to the deposition of the pollution particles. There is a variety of instrumentation and methods available to detect Cr species with different oxidation states. Only a few studies have been conducted on possible Cr(VI) pollution within the context of the South African FeCr industry. These studies focused on very small areas surrounding single FeCr smelters, with no single study providing an overview of the current state of affairs. Apart from the potential Cr(VI) pollution, these smelters could also decrease the general water quality near these FeCr smelters. However, no such studies have been published for the South African FeCr industry. This study will therefore partially address the existing knowledge gaps on Cr(VI), with a specific focus on the levels thereof in general surface- and drinking water in the proximity of FeCr smelters.

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Chapter 3 Article 1:

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

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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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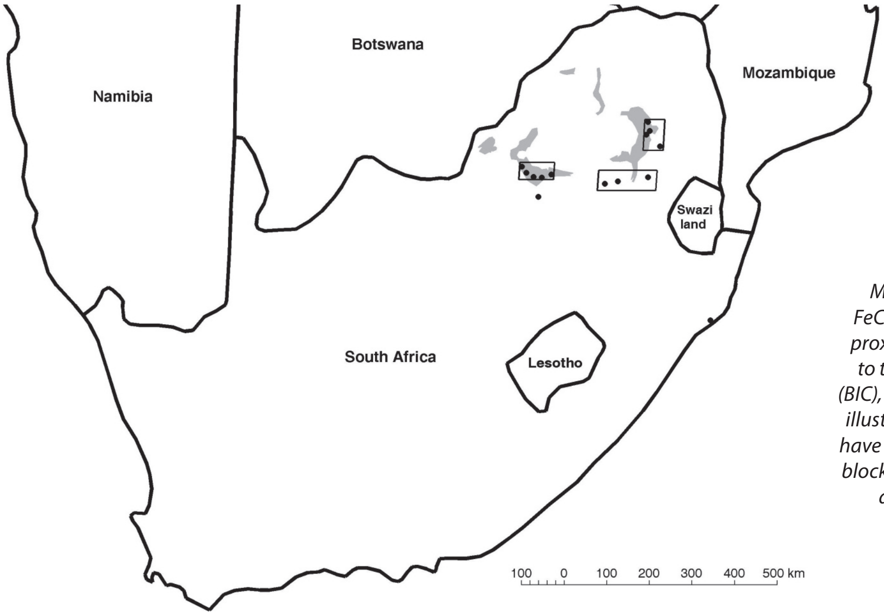

Figure 1
Map indicating the location of FeCr smelters with black dots. The proximity of most of these smelters to the Bushveld Igneous Complex (BIC), which is indicated in grey, is also illustrated. Additionally, three areas have been indicated with rectangular blocks. Enlarged maps of these three areas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

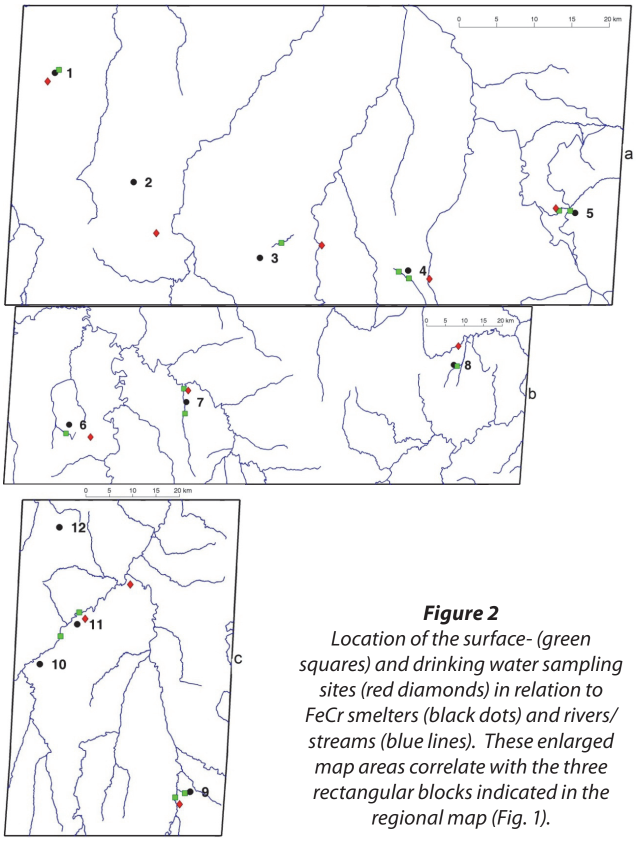

Figure 2
Location of the surface- (green squares) and drinking water sampling sites (red diamonds) in relation to FeCr smelters (black dots) and rivers/ streams (blue lines). These enlarged map areas correlate with the three rectangular blocks indicated in the regional map (Fig. 1).

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.

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

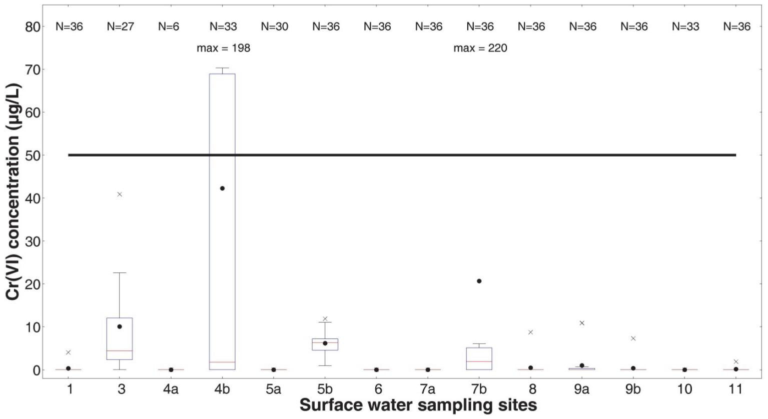

Figure 3
Statistical representation of the Cr(VI) concentrations obtained at each of the surface water sampling sites. The median Cr(VI) concentration is indicated by the short horizontal line, the mean by the dot, the maximum the cross, the top and bottom edges of the box the annual 25th and 75th percentiles, 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.

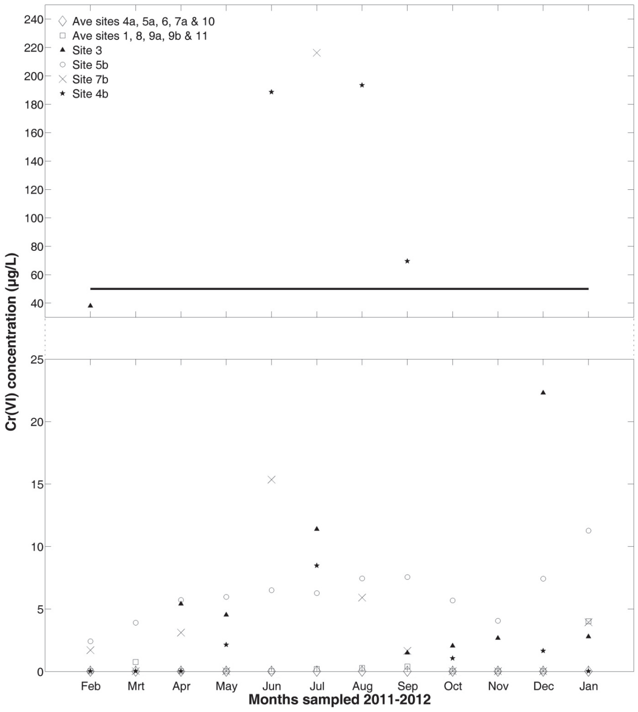

Figure 4
Temporal variation of the Cr(VI) concentrations in the surface water at sampling sites for February 2011 to January 2012.

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.

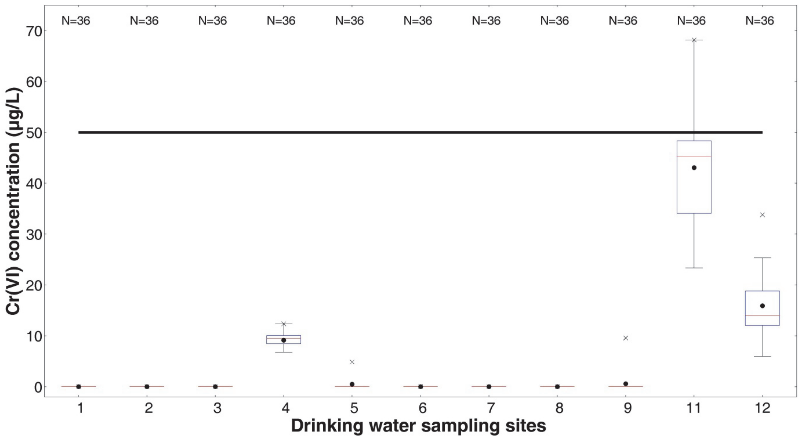

Figure 5
Statistical representation of the Cr(VI) concentrations obtained at each of the drinking water sampling sites. The median Cr(VI) concentration is indicated by the short horizontal line, the mean by the dot, the maximum by the cross, the top and bottom edges of the box the annual 25th and 75th percentiles, while the whiskers indicate $\pm 2.7\sigma$ *(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 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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Chapter 4 Article 2:

SHORT COMMUNICATION

Conductivity as an indicator of surface water quality in the proximity of ferrochrome smelters in South Africa

This article was accepted and published by Water SA.

Loock-Hattingh et al., 2014

Short Communication

Conductivity as an indicator of surface water quality in the proximity of ferrochrome smelters in South Africa

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ABSTRACT

South Africa is one of the leading ferrochrome (FeCr) producing countries. One of the main environmental and health-related issues associated with FeCr production is the possible generation of Cr(VI). However, Cr(VI) is not the only potential pollutant that has to be considered during FeCr production. Various water-soluble species are present in FeCr waste materials and in process water. Considering the size of the South African FeCr industry and its global importance, it is essential to assess the extent of potential surface water pollution in the proximity of FeCr smelters by such water-soluble species. In this study water conductivity was measured as a proxy of general water quality. Although deposition was not measured, comparison of surface water results indicated that atmospheric deposition of pollutants originating from FeCr smelting did not significantly impact surface water quality, but that surface run-off and/or groundwater leaching were the main contributors. At two FeCr smelters it was observed that these smelters did not impact surface water quality negatively. In contrast, surface water pollution originating from at least four FeCr smelters was apparent. However, only at one smelter did pollution result in surface water conductivity that indicated a water quality not fit for human consumption. No correlations could be made between potable water quality and possible pollution from FeCr smelters. Notwithstanding this limitation, it was found that potable water sampled at all sites complied with the conductivity criteria for human consumption.

Keywords: surface water, ferrochromium, South Africa, conductivity, elemental composition of total dissolved solids (TDS), potable water

INTRODUCTION

South Africa is one of the leading ferrochrome (FeCr) producing countries (ICDA, 2013; Beukes et al., 2012), since the country possesses approximately three quarters of the world's viable chromium ore (chromite) deposits (Murthy et al., 2011; Cramer et al., 2004). FeCr is mainly produced during pyrometallurgical carbo-thermic reduction of chromite in submerged arc furnaces (SAFs) and direct current arc furnaces (DCFs) (Beukes et al., 2010). One of the main environmental and health-related issues associated with FeCr production is the possible generation of Cr(VI). Since it is impossible to completely exclude oxygen from all high-temperature FeCr production steps, Cr(VI)-containing species can be unintentionally generated in small amounts (Beukes et al., 2010; Mandiwana et al., 2007). In a recent paper by Loock et al. (2014) the possible Cr(VI) contamination of surface water in the proximity of FeCr smelters in South Africa was investigated. These authors indicated that, in general, surface water was not consistently contaminated with Cr(VI) at all FeCr smelters, but that surface water quality near some FeCr smelters is of concern. Additionally, potable water was also collected close to the FeCr smelters to support the surface water results obtained. It was found that Cr(VI) levels in the potable water near one of the smelters were of concern.

Cr(VI) is, however, not the only potential pollutant of surface-, ground- and potable water that has to be considered in relation to FeCr production. As an example, Riekkola-Vanhanen (1999) indicated that FeCr furnace off-gas dust potentially contains many water-soluble heavy metals, while closed-furnace off-gas venturi water sludge specifically also contains cyanides. Water-soluble species such as sulphate (SO_4^{2-}) and chloride (Cl^-) are also added to process water during the treatment of Cr(VI)-containing wastes (Beukes et al., 2012). The presence of water-soluble species in FeCr production wastes and process water does not automatically imply that aqueous systems around such smelters will be polluted. FeCr waste materials, e.g., bag-filter dust, venturi sludge and slag, are mostly stored on fit-for-purpose waste facilities designed to prevent environmental pollution. Water draining from such waste facilities (e.g. slimes dams) and process water is usually kept in a closed loop. However, leakages from the afore-mentioned systems might occur. Additionally, historic groundwater contamination, which could migrate slowly, can also result in environmental aqueous systems being polluted.

Considering the above-mentioned context, it would be ideal to include all possible pollutant species in a study on the contamination of aqueous systems around FeCr smelters. Such investigations are likely to have been conducted for relatively new smelters for which environmental impact assessments (EIAs) were required, or for older FeCr smelters during the application for water use licences. However, this information is usually not available in the peer-reviewed literature. Considering the size of the South African FeCr industry and its global importance, it is essential to have such data available. In order to, at least partially, address this knowledge gap, conductivity of surface water was investigated in the proximity of most FeCr smelters in South Africa. The primary focus of this paper was to investigate surface water pollution, but potable water was also collected in the proximity of the selected FeCr

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smelters. The sampling sites selected correlated with those that Loock et al. (2014) introduced. Figure 1 illustrates a regional map indicating the extent of the chromite ore deposits in South Africa, as well as the locations of FeCr smelters that are shown in the enlarged sections of Fig. 1, i.e., 1a, 1b and 1c.

EXPERIMENTAL

Reagents

Ultra-pure water (resistivity 18.2 MΩ·cm^{-1}), produced by a Milli-Q water purification system, was used for cleaning equipment and sampling containers. Conductivity calibration solutions of 12 880 µS/cm and 1 413 µS/cm at 25°C (Hanna instruments) were used to calibrate the conductivity meter prior to each sample collection campaign.

Sampling site selection and sampling duration

The objective of this study was to assess the general water quality of surface water in the vicinity of FeCr smelters in South Africa. Currently South Africa has 14 different FeCr smelters (Beukes et al., 2012) – 13 located in or close to the chromite deposits in the Bushveld Igneous Complex (BIC) and one

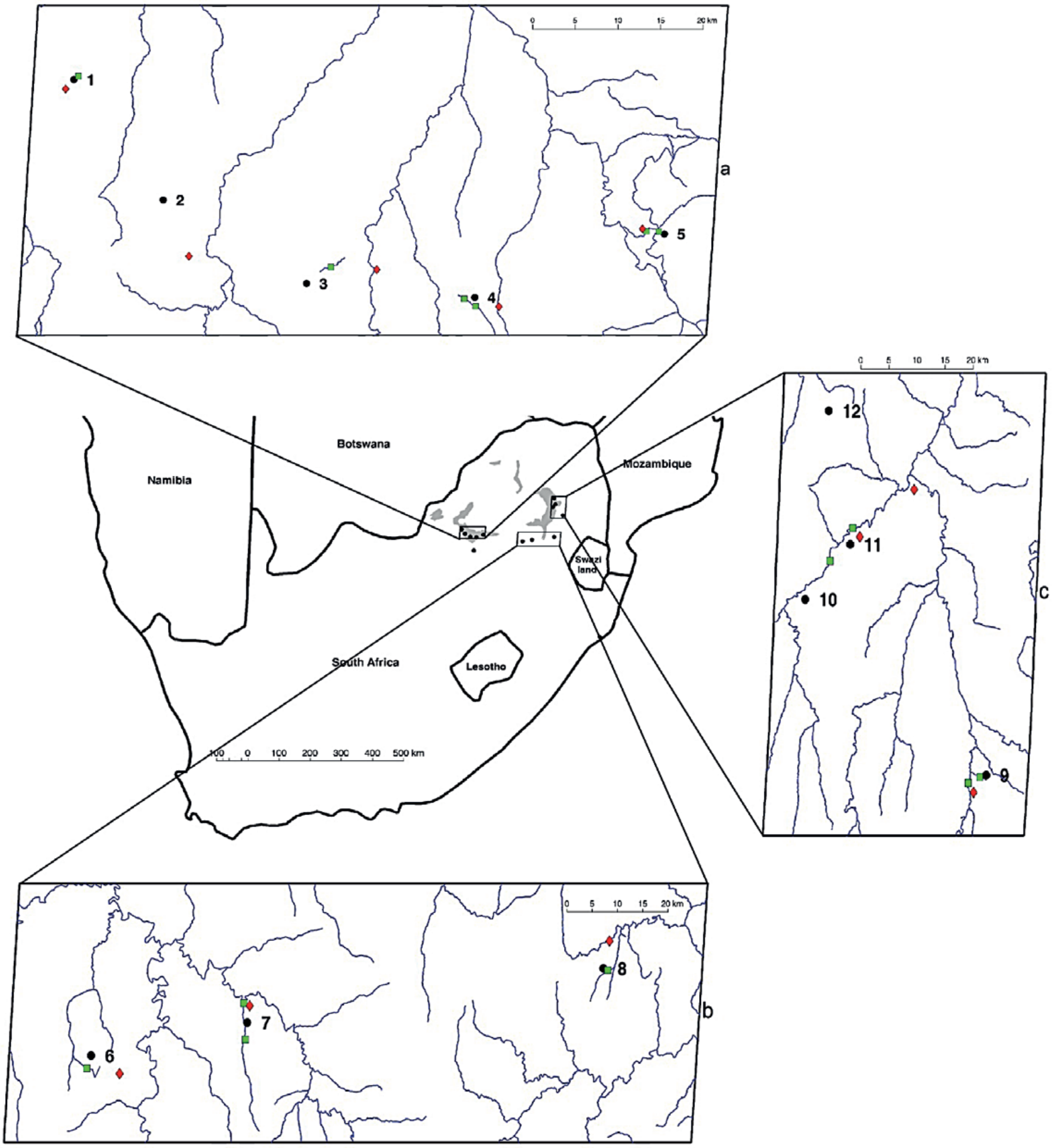

Figure 1

Location of the FeCr smelters (black dots) within the context of the South African Bushveld Igneous Complex (BIC) is illustrated in the regional map. The enlarged areas demonstrate the surface-(green squares) and potable water sampling sites (red diamonds) in relation to the FeCr smelters and rivers/streams (blue lines).

located close to the east coast (Fig. 1). Samples were collected at sites identified by Loock et al. (2014), who critically evaluated several criteria (personal safety during sampling collection, accessibility, logistical, drainage patterns, etc.) to identify the best suited sampling sites. Implementation of the afore-mentioned criteria resulted in the collection of surface- and potable water samples in the proximity of 10 and 11 FeCr smelters, respectively.

In order to relate the sampling site location to the results obtained, the various FeCr smelters were numbered 1 to 12, as shown in Figs. 1a, 1b and 1c. Surface and potable water sampling sites were numbered accordingly, i.e., correlating to the number of the closest FeCr smelter. At Smelters 4, 5, 7 and 9 (Fig. 1) two surface water sampling sites were located at each smelter, which were distinguished by indicating them as sampling sites ‘a’ and ‘b’.

The sampling sites were all located in the geographical area commonly referred to as the South African Highveld. Laakso et al. (2012), with references therein, 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 samples were collected only in a specific season. To limit seasonal bias, sampling was conducted monthly for almost a full year, i.e., March 2011 to January 2012.

Sampling and analytical procedures

The first step during sampling at any given site consisted of collecting a 1 ℓ sample in a Schott Duran glass bottle. The collected samples were then divided into several 100 mℓ portions. Some of these portions were used for Cr(VI) analysis, as discussed in Loock et al. (2014). 15 mℓ of one 100 mℓ sampled portion was then used for the determination of conductivity with a Hanna instrument HI 255 combined meter with a HI 76310 electrode. The remaining 85 mℓ was evaporated in an oven at 100°C so that scanning electron microscopy incorporated with energy dispersive X-ray spectroscopy (SEM-EDS) analysis could be done to identify the elemental composition of the total dissolved solids (TDS) portion. A FEI QUANTA FEQ 250 ESEM, integrated with an OXFORD INCA X-Sight 200 EDS system operating with a 15kV electron beam at a working distance of 10 mm was used. Sample preparations for the SEM-EDS analyses consisted of mounting the precipitate on buttons covered with carbon tape.

RESULTS AND DISCUSSION

Surface water

In Fig. 2 the mean, minimum and maximum conductivity values measured at the surface water sampling sites in the proximity of FeCr smelters (Fig. 1) for the entire sampling period are presented. As is evident from these data, there are significant differences in the conductivity values measured at the various sites. To facilitate the discussion of these results, it is necessary to consider possible conductivity ranges that suit specific applications. Various references indicate different conductivity ranges that are suitable for specific water use applications (e.g. Anderson et al., 1999; DWAF, 1996). Of these references, Anderson et al. (1999) gave one of the most comprehensive breakdowns in terms of conductivity ranges for defined water use applications. According to these guidelines (Anderson et al., 1999), conductivity values of 0 – 800 µS/cm can be used for human consumption and irrigation. However, if the conductivity is higher than 300 µS/cm, care must be taken during the irrigation of plants sensitive to higher salt levels. Conductivities between 800 and 2 500 µS/cm are still suitable for human consumption, while irrigation at these levels should be managed to minimise plant damage. Levels between 2 500 and 10 000 µS/cm are not recommended for human consumption. Salt-tolerant crops can be irrigated using water with conductivities of up to 6 000 µS/cm. Most livestock can consume water with levels of up to 10 000 µS/cm, but conductivity levels in the drinking water of poultry and pigs should be limited to 6 000 µS/cm. Considering the afore-mentioned conductivity criteria, the surface water conductivity results in Fig. 2 were divided into 4 categories, i.e., 0 – 300, 300 – 800, 800 – 2 500 µS/cm and above 2 500 µS/cm, respectively. These ranges are separated in Fig. 2 by the three lines indicated at 300, 800 and 2 500 µS/cm.

Surface water conductivity range: 0 – 300 µS/cm

According to the above-mentioned categorisation, the average conductivity at surface water sampling sites 1, 4a, 8 and 9b can be regarded as suitable for all water use applications (Anderson et al., 1999). The spread of conductivity levels at these sites was also relatively small (Fig. 2). The water sampled at surface water sampling site 1 drained directly out of the property of FeCr Smelter 1 (Fig. 1). Also, surface water sampling site 8 was positioned to capture possible seepage and run-off from Smelter 8. These two results therefore seem to indicate that Smelters 1 and 8 do not influence the surface water quality at sampling sites 1 and 8 to a significant extent. Sampling site 4a was positioned upstream from Smelter 4, while Site 9b was located on a separate branch of a perennial river not directly impacted by Smelter 9. Although atmospheric deposition was not specifically measured, comparison of the results for these two sites indicates that deposition of pollutant species released by Smelters 4 and 9 does not significantly impact the afore-mentioned sampling sites.

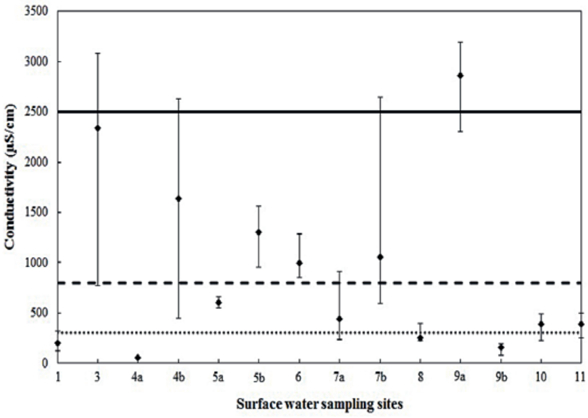

Figure 2

Mean conductivity values of the surface water sampling sites near the various FeCr smelters (Fig. 1). The error bars indicate the minimum and maximum values. The horizontal lines indicate the 300, 800 and 2 500 µS/cm values, which were used to categorise the data.

Surface water conductivity range 300 – 800 µS/cm

The average conductivity at surface water sampling sites 5a, 7a, 10 and 11 fell within the category that can be regarded as suitable for all water use applications, except for the irrigation of plants sensitive to higher salt levels (Anderson et al., 1999). The conductivity values of surface water sampling sites 5a, 10 and 11 had small spreads (Fig. 2), which indicated that seasonal cycles (e.g. rain) had little effect, nor did any large spillages from these smelters occur. Site 5a was located in a cement-lined waterway near Smelter 5. The lining of this waterway limited possible sources of water quality impacts to atmospheric deposition and/or upstream pollution. The acceptable status of the water according to the considered conductivity criteria applied indicated that atmospheric deposition from pollutant species from FeCr Smelter 5 did not significantly impact the water quality.

Since the surface water at Sites 10 and 11 was considered to be acceptable for all applications, except for the irrigation of plants sensitive to higher salt levels, it is likely that atmospheric deposition from Smelters 10 and 11 also did not impact water quality significantly. Sampling sites 10 and 11 were in a perennial river near Smelters 10 and 11, implying that groundwater seepage could also play a role. However, the satisfactory status of the surface water indicated that groundwater seepage and surface water run-off from Smelters 10 and 11 does not significantly impact on general surface water quality.

Sampling site 7a was in perennial stream, located upstream from Smelter 7. The larger spread of the conductivity values at Site 7a indicated possible seasonal variations. The seasonal variations observed in the conductivity levels at this site, as well as other sites for which seasonal cycles possibly occur, are presented in Fig. 3. The data (Fig. 3) indicate that the conductivity levels at surface water sampling site 7a are lower in the drier months of June–October and higher in the rainy season months, notwithstanding higher volumes of water in this stream during the rainy season. It is therefore highly likely that surface run-off and/or seepage upstream from Site 7a, and not Smelter 7, are responsible for the higher conductivity levels during the rainy season. Several opencast coal mines and large coal-fired power stations occur in this geographical area that could potentially serve as pollution sources (Lourens et al., 2011). The surface chemical composition (SEM-EDS) of the total dissolved solids (TDS) remaining after all samples were evaporated is presented in Fig. 4a, while Fig. 4b indicates the same data normalised excluding oxygen (O). Although TDS was not specifically measured in this study, there is usually a direct correlation between conductivity and TDS (e.g. Paul and Sen, 2012; Atekwana et al., 2004; McNeil and Cox, 2000). The elemental composition of the TDS at Site 7a shows relatively high levels of sulphur (S), which cannot be attributed to natural sources. Josipovic et al. (2009 and 2011) indicated that S wet and dry deposition on the Mpumalanga Highveld is higher than in any other region in South Africa, mainly due to the occurrence of numerous large atmospheric point sources in this region (e.g coal-fired power stations). It is therefore likely that the aforementioned atmospheric deposition will contribute to higher conductivity levels in the rainy season due to surface water run-off from the catchment area of Site 7a. Additionally, run-off and/or seepage from non-atmospheric pollutions sources (e.g. coal mines) upstream of surface water site 7a could also make a significant contribution in the rainy season.

Surface water conductivity range 800 – 2 500 µS/cm

Surface water sampling sites 3, 4b, 5b, 6 and 7b can be regarded as suitable for all consumptive water uses, but irrigation of plants should be managed to minimise damage (Anderson et al., 1999).

The conductivity values for surface water sampling sites 3, 4b and 7b had large spreads (Fig. 2) that could be due to seasonal cycles or spillages from the smelters. The conductivity data in Fig. 3 indicates no correlation to season cycles for any of these sites. Although seasonal cycles could therefore contribute to the spread of the conductivity data at these three sites, seasonal cycles cannot fully explain the large spreads. All of these sites, i.e., 3, 4b and 7b, are located downstream from the respected FeCr smelters and will capture any spillages and/or seepage. When comparing the conductivity values of surface water sampling sites 4a (upstream of Smelter 4) and 4b (downstream of Smelter 4), as well as 7a (upstream of Smelter 7) and 7b (downstream of Smelter 7), significant differences in the conductivity values are observed (Fig. 2). Additionally, if the elemental compositions of the TDS at Site 4b are compared to Site 4a (Fig. 4) an increase in the percentage of S and Cl can be observed, which can be associated with the wastewater of FeCr production (Beukes et al., 2012). As indicated earlier, surface water site 7a is already impacted upstream of the sampling site. Additionally, the elemental compositions of the TDS for this site did not differ significantly from those for Site 7b. Considering all the afore-mentioned discussions it can therefore be stated that it is likely that the higher and larger spread in conductivity values measured at Sites 3, 4b and 7b can be attributed to the impact of the respective smelters.

Surface water sampling sites 5b and 6 had smaller spreads in the conductivity values than Sites 3, 4b and 7b (Fig. 2), but these were still large enough to warrant exploration thereof. The conductivity values at both surface water sampling sites were variable, but did not indicate a significant correlation to seasonal cycles (Fig. 3). Both Site 5a and Site 5b are located close to FeCr Smelter 5 (Fig. 1), with the only difference between the two sampling sites being that 5a is a cement-lined waterway while 5b is an unlined river. As indicated earlier, Site 5a was minimally impacted by atmospheric deposition from FeCr Smelter 5. Therefore it is likely that Site 5b would also not be impacted in such a way. Surface water pollution at 5b (unlined river) can consequently only be as a result of run-off and/or

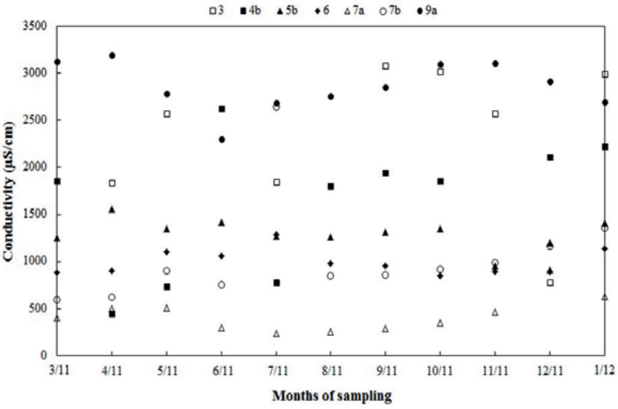

Figure 3

Seasonal variations observed in the conductivity levels at the different surface water sampling sites

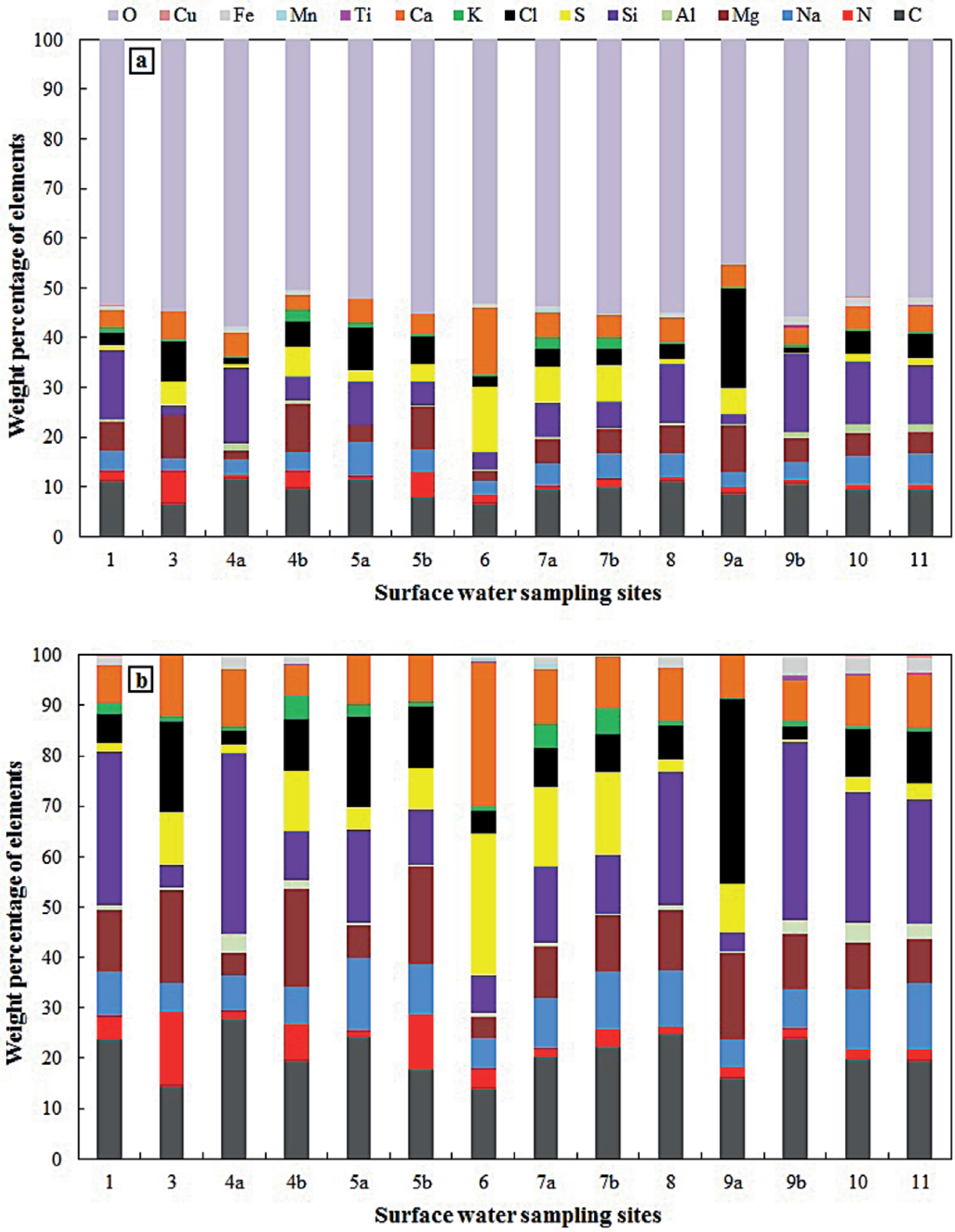

Figure 4

The surface chemical composition (SEM-EDS) of the solids remaining after surface water samples were evaporated, for all of the surface water sampling sites, are presented in Fig. 4a, while Fig. 4b indicates the same data normalised to exclude oxygen (O).

seepage. The difference between the conductivity values at Sites 5a and 5b (Fig. 3) demonstrates that there is a pollution source only affecting the river, thus implicating FeCr Smelter 5.

Sampling site 6 was located near FeCr Smelter 6, but not in a stream flowing directly to or from the smelter (Fig. 1). Additionally, several other large industries, as well as semi-formal and informal settlements, were located nearby. The authors also observed raw sewage running into the river on several occasions. Therefore it is impossible to relate the results in a systematic manner to FeCr Smelter 6.

Surface water conductivity above 2 500 µS/cm

According to the conductivity criteria applied, surface water at sampling site 9a is not recommended for human consumption (Anderson et al., 1999). The larger spread of conductivity values at Site 9a (Fig. 2) indicated that seasonal cycles and/or pollution from Smelter 9 might have an influence. The conductivity data for this site did not indicate a conclusive seasonal cycle (Fig. 3). However, comparison of conductivity levels between Site 9b (in a perennial river not directly impacted by Smelter 9) and Site 9a (in a stream running directly from the Smelter 9) indicated very clearly that the elevated levels of conductivity observed at 9a are a direct result of groundwater seepage and/or surface water run-off pollution from Smelter 9. The differences in the elemental composition of the TDS at sampling sites 9a and 9b (Fig. 4a and 4b) is also apparent.

Potable water

The mean, minimum and maximum conductivity values measured at the potable water sampling sites in the proximity of FeCr smelters (Fig. 1) during the entire sampling period are presented in Fig. 5. As for the investigations of surface water, the conductivity criteria suggested by Anderson et al. (1999) were applied. These category ranges are shown in Fig. 5 by the two lines indicated at 300 and 800 µS/cm.

In discussing the surface water sampling site results, the possible impacts of the various FeCr smelters could be explored, since the results could be contextualised using upstream and downstream measurements near certain smelters, as well as from streams running directly from smelters vs. streams not directly impacted. However, it is impossible to deliberate about the potable water conductivity results in a similar manner. Additionally, the source at a specific potable water site was not always known. As an example, groundwater that is commonly used as potable water in the Steelpoort valley has a high natural conductivity (Loock-Hattingh et al, 2015; Loock et al., 2014). Therefore, it would be preposterous to propose linkages between potable water conductivity and pollution originating from the various FeCr smelters. The only factual deduction that can be made from the data presented in Fig. 5 is that the potable water measured at all sites complied with the conductivity criteria proposed for human consumption (Anderson et al., 1999).

CONCLUSIONS

To the knowledge of the authors, this study is the first relatively comprehensive survey of surface water conductivity in the proximity of FeCr smelters in South Africa. In this study water conductivity was used as a proxy for general water quality, with application of the conductivity criteria suggested by Anderson et al. (1999). Obviously this approach has limitations, but the data compiled will help to close the current knowledge gap on the influence of FeCr production on water quality.

The results indicated that atmospheric deposition of pollutants originating from FeCr smelting did not significantly impact surface water quality. At certain FeCr smelters (e.g. Smelters 1 and 8) surface water sampling sites, which would have been impacted if surface run-off and/or seepage occurred from the relevant smelters, did not indicate any significant negative impacts. This proves that FeCr smelting does not automatically imply surface water pollution. In contrast, the surface water pollution originating from certain FeCr smelters was apparent, especially near smelters where upstream and downstream samples could be collected (Smelters 4, 5, 7 and 9). However, only at Smelter 9 did this pollution result in surface water conductivity not being fit for human consumption.

No correlations and/or deductions could be made between potable water quality and possible pollution from FeCr smelters. Notwithstanding this limitation, it was found that potable water sampled at all sites complied with the conductivity criteria for human consumption. Although groundwater quality in the proximity of ferrochrome smelters was not investigated, such an investigation should be considered as an important future perspective.

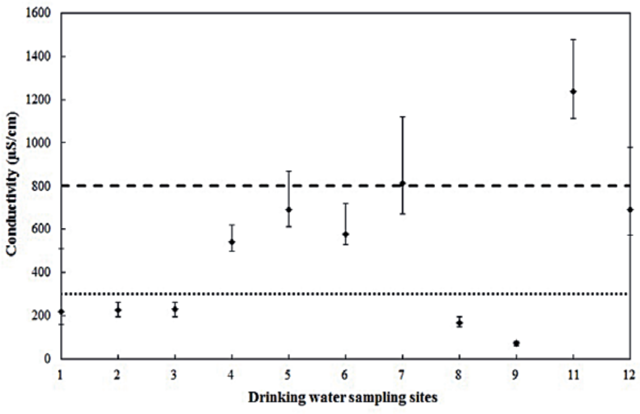

Figure 5

The mean conductivity values of the potable water sampling sites near the various FeCr smelters (Fig. 1). The error bars, indicate the minimum and maximum values. The horizontal lines indicates the 300 and 800 µS/cm values.

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Chapter 5 Article 3:

Cr(VI) and conductivity as indicators of surface water pollution from ferrochrome production in South Africa: Four case studies

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Cr(VI) and Conductivity as Indicators of Surface Water Pollution from Ferrochrome Production in South Africa: Four Case Studies

M.M. LOOCK-HATTINGH, J.P. BEUKES, P.G. VAN ZYL, and L.R. TIEDT

South Africa is one of the largest ferrochromium (FeCr) producers. Most FeCr is exported to developed countries. Therefore the impact of this industry is of national and international importance. Cr(VI) and conductivity of surface water in four case study areas, near five FeCr smelters were monitored for approximately 1 year. Results indicated that FeCr production in three case study areas had a negative influence on the Cr(VI) concentration and/or the conductivity of surface waters. In the remaining case study areas, drinking water, originating from groundwater, was severely polluted with Cr(VI). The main factors causing pollution were surface run-off and/or seepage, while atmospheric deposition did not seem to contribute significantly. The extinction of diatoms during a severe Cr(VI) surface water pollution event (concentrations up to 216 μg/L) in one of the case study areas was also observed, which clearly indicates the ecological impact of such surface water pollution events.

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I. INTRODUCTION

STAINLESS steel is a vital alloy in modern society. New chromium (Cr) units used to manufacture stainless steel which are obtained exclusively from ferrochromium (FeCr)—a crude alloy consisting mostly of Cr and iron (Fe), which is produced by smelting chromite ore. South Africa (SA) holds the majority of the world's viable chromite resources within the Bushveld Igneous Complex (BIC).[1,2] Due to the availability of ore and historically relative cheap electricity,[3] SA is globally one of the largest FeCr producers.[4,5] The production of FeCr entails various high temperature processes.[6] During these processes, oxygen cannot be completely excluded, which results in the formation of small amounts of Cr(VI)-containing species. Cr(VI) is generally regarded as carcinogenic, although it is mainly associated with respiratory ailments.[7] A substantial fraction of Cr(VI) compounds is water soluble[8] and could lead to water contamination when it leaches from waste materials and contaminated soils, as well as through the deposition of atmospheric Cr(VI)-containing particles.

In addition to Cr(VI), other water-soluble pollutant species might also be generated during FeCr production, *e.g.*, heavy metals.[9] Sulfate (SO_4^{2-}) and chloride (Cl^-) are also added to process water during the aqueous treatment of Cr(VI).[5] If released into the environment, the aforementioned water-soluble contaminants could have an impact on aqueous systems and on the wider ecosystem. Apart from the impacts on the ecosystem, the water-soluble contamination of aqueous systems also raises the total dissolved solid load, which is indicated by conductivity measurements. Anderson *et al.*[10] introduced various water conductivity guidelines that can be used to assess if water is safe for a specific use, *e.g.*, human and livestock consumption, as well as irrigation.

In this paper, four surface water case studies are presented in which Cr(VI) and conductivity levels were measured. The case study sampling sites were located in the proximity of five FeCr smelters. The results therefore indicate the potential impact of FeCr production in SA, which is an arid country,[11] on general surface water quality. Although it was not the focus of this paper, observations of diatom species number fluctuations are also presented to indicate the potential ecological impact of Cr(VI) surface water pollution.

II. EXPERIMENTAL

A. *Case Study Site Selection*

Currently, SA has 14 FeCr smelters,[5] with 13 located within, or close to the western or eastern limbs of the BIC (Figure 1). In order to assess FeCr production pollution of surface water, at least two types of sampling sites are needed to be located within the proximity of a specific smelter, *i.e.,* one site that would likely not be influenced and one that would probably be influenced by surface run-off and/or seepage if it occurred. For this purpose, four case study areas, which included five smelters, were selected. Since it was not the intention of

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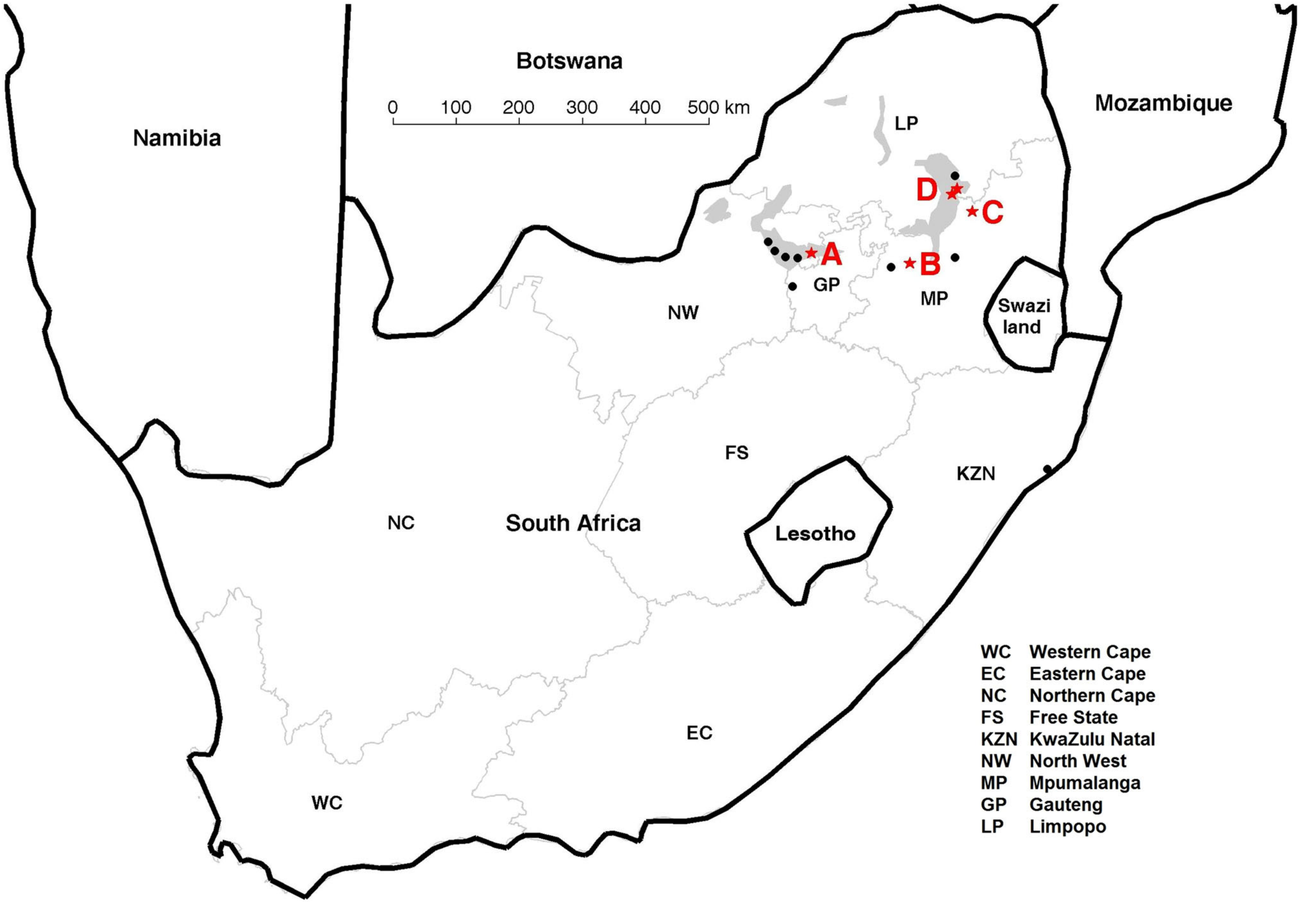

Fig. 1—Location of FeCr smelters (black dots) in South Africa, with the smelters associated with the four case studies indicated with stars. The gray-scale areas indicate the extent of the BIC. Provincial borders provide additional regional context.

the authors to implicate any specific company, the smelters discussed in this paper are referred to with symbols and/or numbers. FeCr smelter A is located in the western limb of the BIC, smelter B in-between the western and eastern limbs, smelter C near the eastern limb, and smelters D (later defined as D1 and D2) in the eastern limb of the BIC (Figure 1). These four case study locations are discussed in greater detail in the following paragraphs.

1. *Case study A*

In order to visualize the proximity of the surface water sampling sites to smelter A, the FeCr smelters with the relevant sampling sites are presented in Figure 2 on a Google Earth image. The two surface water sampling sites were 2.08 (s1) and 0.55 km (s2) from the smelter. Apart from the smelter, there is also a relatively large town nearby, while the immediate surroundings also include relatively intensive crop cultivation. Surface water sampling site s1 was in a perennial river, while s2 was located in a cement-lined waterway used for irrigation of crops.

2. *Case study B*

FeCr smelter B, with the relevant surface sampling sites, is presented in Figure 3. The two surface water sampling sites were 3.54 (s1) and 3.16 km (s2) from the smelter. Although not clear from Figure 3, there is also a steel smelter next to this FeCr smelter. As is evident from the Google Earth image, there is a small city nearby, with numerous residential areas close to the smelter. Agricultural activities close to the smelter are mainly associated with free-roaming livestock farming. Surface water sampling site s1 was located upstream from smelter B in perennial stream, while s2 was located downstream of the smelter in the same perennial stream.

3. *Case study C*

FeCr smelter C and its surroundings are indicated in Figure 4. The two surface water sampling sites were 1.25 (s1) and 3.53 km (s2) from the smelter. There is a town nearby, while agricultural activities close to the smelter are mainly associated with free-roaming livestock and game farming. Surface water sampling site s1 was located in a perennial stream that captured possible surface water run-off and/or seepage from smelter C, while s2 was located in a perennial river not directly impacted by the smelter. The perennial stream in which s1 was located, flowed into the perennial river downstream from where s2 was located.

4. *Case study D*

A composite map, indicating two FeCr smelters and their surroundings that combined formed case study

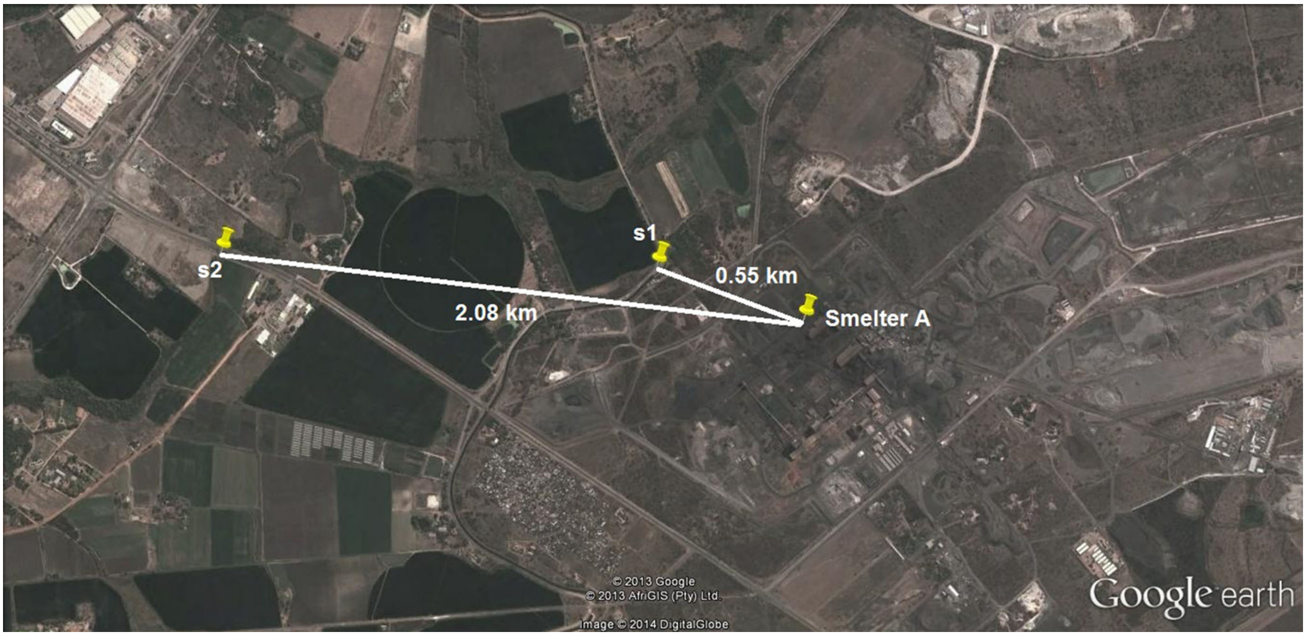

Fig. 2—Location of the surface water sampling sites s1 and s2 in relation to FeCr smelter A. The distance of each sampling site from the smelter is also indicated.

Fig. 3—Location of the surface water sampling sites s1 and s2 in relation to FeCr smelter B. The distance of each sampling site from the smelter is also illustrated.

location D, is indicated in Figure 5. Smelter D1 was located upstream of both the surface water sampling sites, with the smelter and its process water dams being 1.5 and 0.5 km, respectively from the perennial river in which the sampling sites were located. FeCr smelter D2 was downstream from the surface water sampling site s1 (4.36 km) and upstream of sampling site s2, which was 2.6 km from this smelter. Although drinking water was not considered in detail in this paper, it was also sampled at a single sampling site ("d" in Figure 5) that was 2.18 km from smelter D2. There is a small town close to smelter D2 and numerous semi- and informal settlements are also found in the area. This region is very arid with agricultural activities mainly associated with free-roaming livestock and game farming.

Fig. 4—Location of the surface water sampling sites s1 and s2 in relation to FeCr smelter C. The distance of each sampling site from the smelter is also indicated.

B. *Sampling Campaign Duration*

The FeCr smelters discussed in this study are located in the South African northern interior (Figure 1). Most of the precipitation for this area occurs during the wet season (middle October to April), with virtually no precipitation during the dry season (May to middle October).[12] Therefore, in order to limit seasonal bias, sampling was conducted monthly for approximately 1 year, *i.e.,* March 2011 to January 2012.

C. *Reagents*

Conductivity calibration solutions of 12,880 and 1413 μS/cm at 298 K (25 °C) (Hanna Instruments), as well as pH 7.01 and 10.01 buffer solutions (Hanna Instruments) were used to calibrate the pH and conductivity meters. Analytical grade ammonium sulfate (Merck) and 25 pct ammonium hydroxide (Associated Chemical Enterprises) were used to prepare the buffer solution required for sampling, as well as to prepare the eluent used during Cr(VI) analysis. Additionally, diphenylcarbazide (DPC) (Fluka), high pressure liquid chromatography (HPLC) grade methanol (Sigma Aldrich), and 98 pct analytical grade sulfuric acid (Rochelle Chemicals) were used for Cr(VI) analysis. Cr(VI) standard solutions for calibration were prepared from a Spectrascan chromate reference standard with a concentration of 1 009 ± 5 μm/mL CrO_4^{-2}. Ultra-pure water (resistivity 18.2 MΩ cm^{-1}) was used for cleaning and dilution purposes.

D. *Sampling Procedure and Storage*

At each sampling site, three samples were collected each month for Cr(VI) analysis. The sample collection and preservation procedures were the same as recently explained by Loock *et al.*[13] These procedures involved pH adjustment if required, as well as transportation/storage below 277 K (4 °C),[8,14,15] to prevent Cr(VI)–Cr(III) interconversions.[16–23] One of the aforementioned three samples was also spiked with a predetermined amount of Cr(VI) to confirm that not Cr(VI)–Cr(III) interconversions occurred.[14,15] All Cr(VI) results reported in this paper were calculated from the average of all three samples collected monthly at each site. A fourth, untreated sample was also collected that was used for conductivity and surface characterization analyses.

E. *Analytical Methods*

The Cr(VI) analytical method applied was adapted from Dionex Application updates 144 and 179,[14,15] as well as Thomas *et al.*,[17] as recently described by Loock *et al.*[13] In this method a Thermo Scientific Dionex IC (ICS-3000) with a post-column DPC colorant delivery system (AXP pump) coupled to an ultraviolet–visible (UV–Vis) detector was used. The detection limit for this analytical setup was 1 μg/L.[14]

15 mL of each of the untreated 100 mL samples were used to determine the conductivity with a Hanna Instruments conductivity meter (HI 255 meter with HI 76310 electrode). The remaining subsample (85 mL) was evaporated in an oven at 373 K (100 °C) to determine the elemental composition of the residue with scanning electron microscopy incorporated with energy dispersive X-ray spectroscopy (SEM-EDS). An FEI QUANTA FEQ 250 ESEM, integrated with an OXFORD INCA X-Sight 200 EDS system operating with a 15 kV electron beam at a working distance of 10 mm was used.

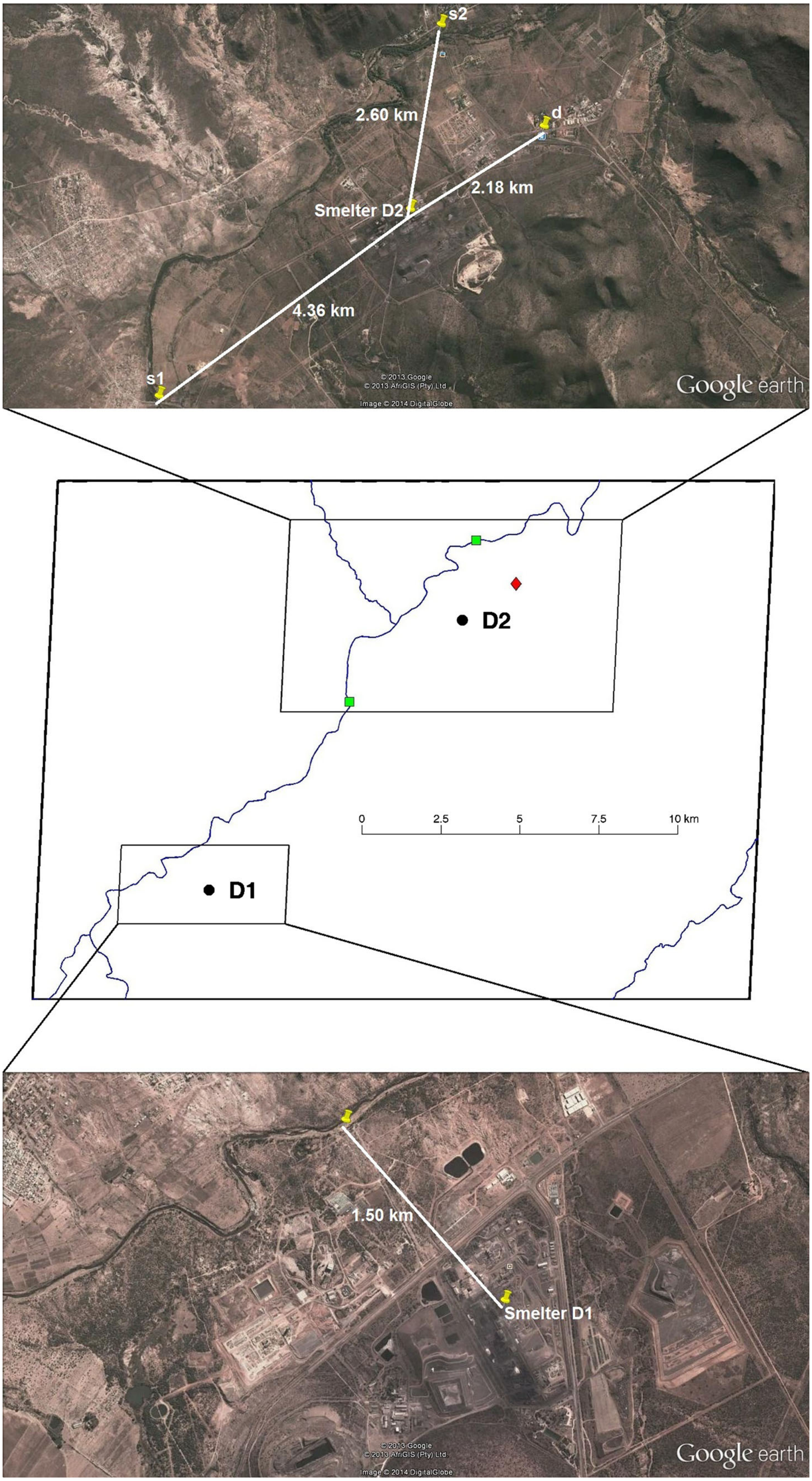

Fig. 5—Location of the surface (s1 and s2) and drinking water (d) sampling sites in relation to FeCr smelters D1 and D2. The distances of the sampling sites from smelter D2 are also indicated, as well as the distance of smelter D1 from the perennial river.

However, since the weight or the residues remaining after evaporation were not measured accurately, these results are only indicative (expressed as wt pct), not quantitative (*e.g.*, expressed as mg/L). Also, since SEM-EDS analysis of porous samples of light elements is at best semiquantitative, it should not be regarded as accurate below approximately 1 wt pct and are therefore reported to the first decimal. The sample preparations for the SEM-EDS analyses consisted of mounting the residue on sample buttons covered with carbon tape. After SEM-EDS analysis was completed, visual SEM analysis was also conducted on the mounted residue samples after they were gold vapor coated.

III. RESULTS AND DISCUSSION

A. *Case Study A*

The Cr(VI) and conductivity results obtained for the surface water sampling sites (s1 and s2) around smelter A are presented in Figure 6. No results are indicated for May and November 2011 at site s1, since water supply was cut off during those times. As is evident from the results, Cr(VI) concentrations detected for s1 were below the detection limit for the entire monitoring period. In contrast, Cr(VI) concentrations at s2 were significantly higher, although they remained below the drinking water limit of 50 μg/L with the highest value being 11.2 μg/L. The conductivity values indicated a similar tendency, *i.e.*, s1 having lower conductivity values than at s2. According to the conductivity guidelines introduced by Anderson *et al.*,[10] all samples could be considered suitable for human consumption. However, care should be taken when irrigating crops that are sensitive to higher salt levels.

The differences in the above-mentioned Cr(VI) and conductivity levels between sampling sites s1 and s2 can be related to the sampling site locations. Since site s1 is located in a cement-lined waterway, groundwater seepage from smelter A cannot influence it. It can only be impacted by upstream pollution sources other than smelter A or by atmospheric deposition of aerosol particulate emissions from smelter A. Site s2 can be affected in a similar manner by the deposition of aerosol particulate emissions from smelter A. However, since s2 has significantly higher Cr(VI) and conductivity values compared with s1, the results indicate that seepage into this river from smelter A is the most likely source of the increased contamination at s2.

It is generally accepted that water pH is a key factor controlling the leachability of especially metals. Cr(VI) compounds can be divided into water soluble (*e.g.*, K_2CrO_4), sparingly water soluble (*e.g.*, $SrCrO_4$), and water insoluble (*e.g.*, $PbCrO_4$). In contrast with most other heavy metals the solubility of Cr(VI) generally increases with increasing pH and an ultra-basic buffer such as a combination of 3 pct Na_2CO_3 and 2 pct NaOH solution will quantitatively extract even the water-insoluble Cr(VI) compounds.[8] A recent study proved that between pH 1 and 11 no significant increase in Cr(VI) leachability was observed for ferrochrome bag filter dust (BFD), originating from several South African FeCr producers.[24] BFD is the FeCr waste material that contains the most significant amounts of Cr(VI). For case study A, the surface water pH for all the samples collected over the entire monitoring period at both sampling sites ranged between 7.82 and 10.05. It is therefore unlikely that surface water pH played a significant role in the Cr(VI) surface water results presented (Figure 6).

In addition to Cr(VI) and other pollutants that originate from smelter A that can cause an increase in conductivity, the relatively intensive crop cultivation in the immediate area could also contribute to surface water pollution. SEM-EDS analyses were conducted on the residue obtained after evaporation of the samples to determine the relative occurrence of elements in the surface water. Due to the crop cultivation in the area and associated use of fertilizers, emphasis was

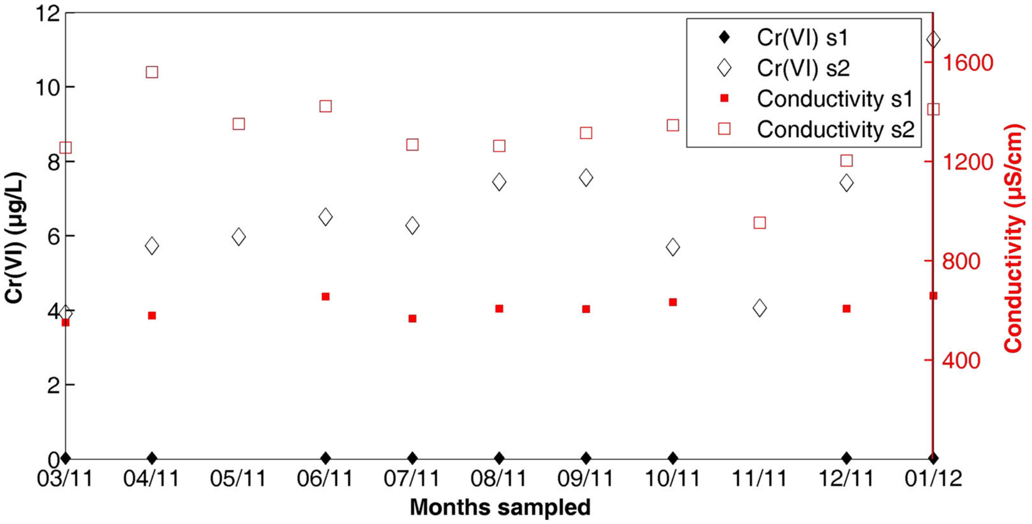

Fig. 6—Temporal Cr(VI) concentrations and conductivity levels of the surface water sampling sites near FeCr smelter A.

specifically placed on the presence of nitrogen (N). Average and standard deviation wt pct N for the entire monitoring period were found to be 0.6 ± 0.3 and 4.9 ± 1.7 for sampling sites s1 and s2 near FeCr smelter A, respectively. Calculation of Student's *t* test[25] proved that the two means were statistically significantly different, even with 99.9 pct probability. From this result, it is evident that N was significantly higher at s2 in the river, compared with s1 in the lined waterway, which demonstrates that leaching of fertilizer from the crop fields also makes a contribution to surface water pollution in the area.

B. *Case Study B*

In Figure 7, the Cr(VI) and conductivity results obtained for surface water sampling sites s1 and s2 are presented for case study site B. For both sampling sites s1 and s2, the Cr(VI) was in general below the detection limit of the analytical technique applied. However, in the period June to August 2011, Cr(VI) concentrations increased at surface water sampling site s2. These increased concentrations were well below the drinking water limit of 50 μg/L in June and August. However, in July, the Cr(VI) concentration at s2 was 216 μg/L. During the same period, the Cr(VI) concentration at sampling site s1 upstream of FeCr smelter B and sampling site s2, remained unchanged. This indicates that the Cr(VI) measured in this perennial stream at sampling site s2 originated due to surface run-off and/or seepage from FeCr smelter B and/or the adjacent steel smelter. Surface water pH ranged between 7.04 and 10.75 for case study B. As previously indicated, it is unlikely that surface water pH played a significant role in the leachability of Cr(VI) compounds within this pH range. Additionally, Cr(VI) values remained low throughout the entire sampling campaign at site s1, which indicates that the atmospheric deposition of Cr(VI)-containing aerosol particles did not contribute significantly to the Cr(VI) contamination of the surface water in the area.

The Mpumalanga Highveld (provincial boundaries in Figure 1) is well known as an industrialized area in SA,[26] with a large number of possible pollution sources. The South African government has declared the Mpumalanga Highveld and certain sections of the Gauteng Province as a national air pollution hotspot, termed as the Highveld Priority Area.[27] This declaration indicates that national government recognizes the need for improved air quality in this area. Lourens *et al.*[28] indicated that there is a nitrogen dioxide (NO_2) hotspot over this area with a tropospheric column density similar to that observed over south-east Asia. Josipovic *et al.*[29,30] also indicated the significance of atmospheric deposition of especially N- and sulfur-containing compounds in this region. Considering the aforementioned, it can be stated with a high degree of certainty that the surface water in the proximity of FeCr smelter B is impacted by atmospheric deposition and/or run-off and/or seepage from various industries located in the Mpumalanga Highveld. This is reflected by the conductivity values measured upstream from FeCr smelter B at site s1 (Figure 7) that cannot be considered to be low. Notwithstanding the general pollution of the perennial stream in which the surface water sampling sites were located, it is evident from the results presented (Figure 7) that the conductivity at s2, which is downstream of FeCr smelter B, is considerably higher than at s1. FeCr smelter B and/or the neighboring steel plant therefore significantly contribute(s) to the higher conductivity measured at s2. From Figure 7, it is clear that there is no direct correlation between conductivity and Cr(VI) levels at sampling site s2. However, it is evident that a considerable increase in Cr(VI) concentration and conductivity occurred in July 2011, which can most likely be attributed to a spillage event originating from smelter B and/or the adjacent steel plant. During this peak, the conductivity at s2 also exceeded the guideline that is considered suitable for human consumption.[10]

As previously mentioned, SEM-EDS analysis was conducted on the residue obtained after evaporation of the surface water samples. From these results, no

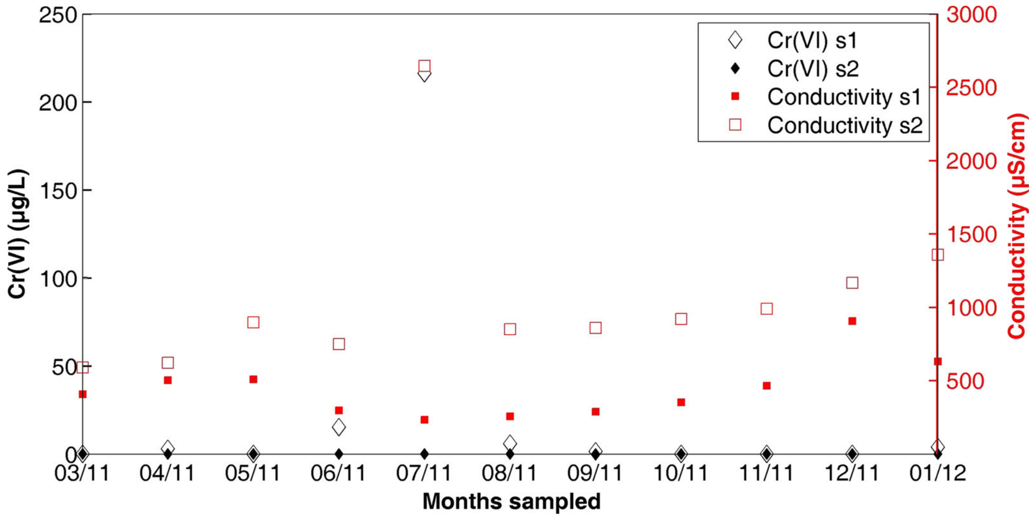

Fig. 7—Temporal Cr(VI) concentrations and conductivity values of the surface water sampling sites near FeCr smelter B.

statistically significant variation in composition was observed for the two sampling sites near smelter B, except for an inconsistency in the silicone (Si) content. At site s2, downstream of smelter B, a significant decline in Si content was observed during July 2011, which resulted in virtually no Si being detected in the residue. The occurrence of this very low Si content correlated with the Cr(VI) pollution event during July 2011 (Figure 7), which was attributed to a spillage event from the aforementioned smelter and/or adjacent steel plant.

The presence of Si in surface water can occur as a result of natural leaching of aluminosilicates and/or silicates from bedrock and soils.[31] Additionally, Si is found in the skeletal structures of diatoms occurring in surface waters.[32] The skeletal structures of diatoms might therefore form part of the Si content of the analyzed residue. In order to investigate this possibility, SEM micrographs were taken of the s1 and s2 residue samples collected prior to and after the pollution incident at smelter B in July 2011. These micrographs are presented in Figure 8. The micrographs of samples representing March 2011 indicate a large number of diatom skeletal structures (identifiable as similar shaped objects) in the residue of both surface water sampling sites near smelter B. The micrographs of the July 2011 samples indicate that diatoms were still present at s1, but no diatom structures could be found in the residue of site s2. These results seem to indicate that the occurrence of diatoms downstream of smelter B was detrimentally affected by the Cr(VI) pollution event. The diatom population seemed to have at least partially recovered after the Cr(VI) pollution event, which is indicated by the presence of diatom skeletal structures in the evaporated sample residue of samples collected at s2 during December 2011 (Figure 8).

C. *Case Study C*

In Figure 9, the Cr(VI) and conductivity data for surface water sampling sites in the vicinity of smelter C are presented. At both sampling sites, the Cr(VI) concentrations were below the detection limit of the analytical technique, with the exception of August and September 2011 at s1. However, even these detectable Cr(VI) values were well below the drinking water standard of 50 μg/L. Surface water pH, which ranged between 7.56 and 9.74 for case study C over the entire monitoring period, was unlikely to have influenced the reported surface water Cr(VI) results significantly.

In contrast to the Cr(VI) concentrations, significant differences could be observed between the conductivity values measured at sites s1 and s2. In general, the conductivity at site s1 was an order of magnitude higher than at s2. Since site s1 is located in a stream flowing directly from smelter C, it will capture any seepage and/or spillages. In contrast, s2 was located in a perennial river that is not directly influenced by seepage and/or run-off from smelter C. The aforementioned higher conductivity at s1 is therefore likely to be from surface run-off and/or seepage from the smelter. The level of conductivity at site s1 is also significant, since conductivity values of 2 500 μS/cm and above are not suitable for human consumption.[10,33]

SEM-EDS analysis of the residue obtained after evaporation of the surface water samples indicated a statistically significant difference (Student's *t* test with more than 99.9 pct probability) in the wt pct of chloride (Cl) between the two surface water sampling sites near smelter C. Ferrous chloride is currently the most commonly employed reducing agent for the aqueous treatment of Cr(VI) at FeCr smelters in SA.[5] Therefore, the significantly higher Cl content that was observed in the residue from s1 can most likely be attributed to run-off and/or seepage of process water from the aforementioned smelter.

D. *Case Study D*

The Cr(VI) and conductivity values for the surface water sampling sites s1 and s2 near smelters D1 and D2 (Figure 5) are presented in Figure 10. Due to personal security concerns no Cr(VI) samples could be collected for June 2011. As is evident from Figure 10, Cr(VI) concentrations at both surface water sampling sites were below the detection limit of the analytical technique, with the exception of July and September 2011 when low concentrations of Cr(VI), *i.e.,* approximately 1 μg/L, were detected at s2. As with the other case studies, surface water pH, which ranged between 8.34 and 9.38 for the entire monitoring period for both sampling sites, could not have influenced Cr(VI) leachability significantly. The conductivity levels at both sites were similar, *i.e.,* in the range between 230 and 500 μS/cm. The low Cr(VI) concentrations and the similarity in conductivity values for both the sites indicate that FeCr smelters D1 and D2 had little impact on the surface water quality in the perennial river sampled.

According to the above-mentioned discussion, the impact of FeCr production on surface water quality in the proximity of smelters D1 and D2 seems to be insignificant. However, Loock *et al.*[13] indicated that drinking water in this area is contaminated by Cr(VI). Therefore, although this case study focused specifically on possible surface water contamination from FeCr production, drinking water was additionally considered in case study D. In Figure 11, the Cr(VI) and conductivity values measured at drinking water sampling site D, as indicated in Figure 5, are presented. As is evident from these results, drinking water in the proximity of smelter D2 is significantly polluted by Cr(VI), with Cr(VI) values ranging from approximately 30 to 65 μg/L. Surface water sampled at sites s1 and s2 indicated no Cr(VI) contamination, indicating that groundwater might be used as drinking water at sampling site D. Since the general area around case study D is very arid, a substantial fraction of drinking water is obtained from groundwater. The conductivity of the drinking water at site D (Figure 11) was substantially higher than that of the surface water sampling sites (Figure 10), further strengthening the hypothesis that the drinking water sampled at site D originated from groundwater. Subsequently to this data being gathered, it was also confirmed by the users that the drinking water at site D indeed originate from groundwater.

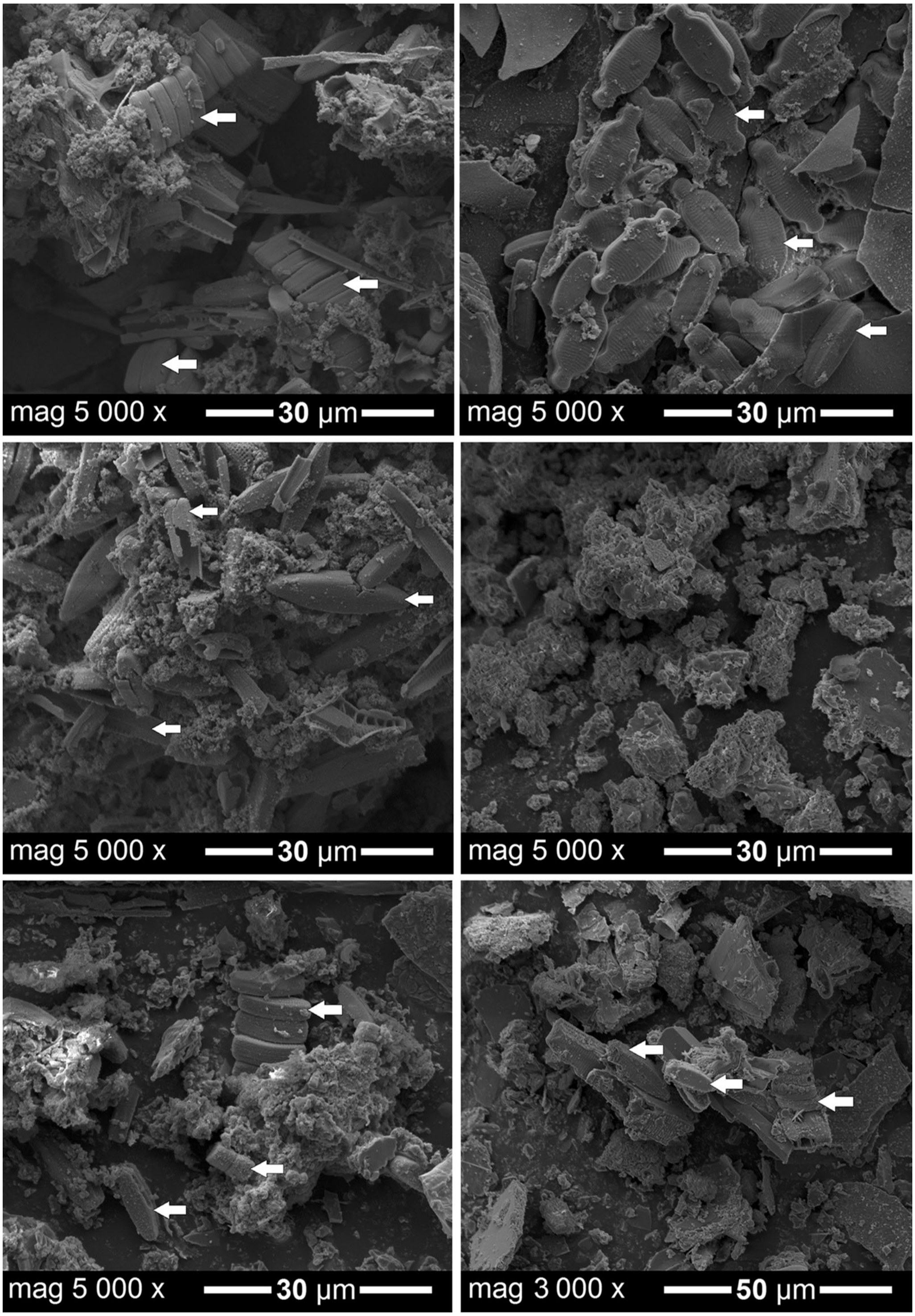

Fig. 8—SEM micrographs indicating the presence or absence of diatom skeletal structures in the residue obtained after the evaporation of water samples taken during March (top), July (middle), and December 2011 (bottom) for site s1 (left column) and site s2 (right column) near smelter B.

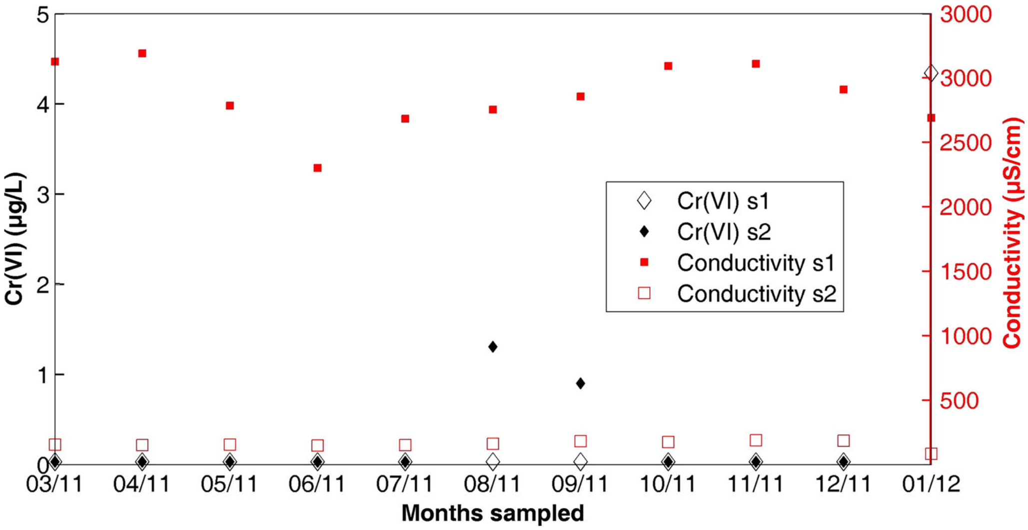

Fig. 9—Temporal Cr(VI) concentrations and conductivity values of the surface water sampling sites near FeCr smelter C.

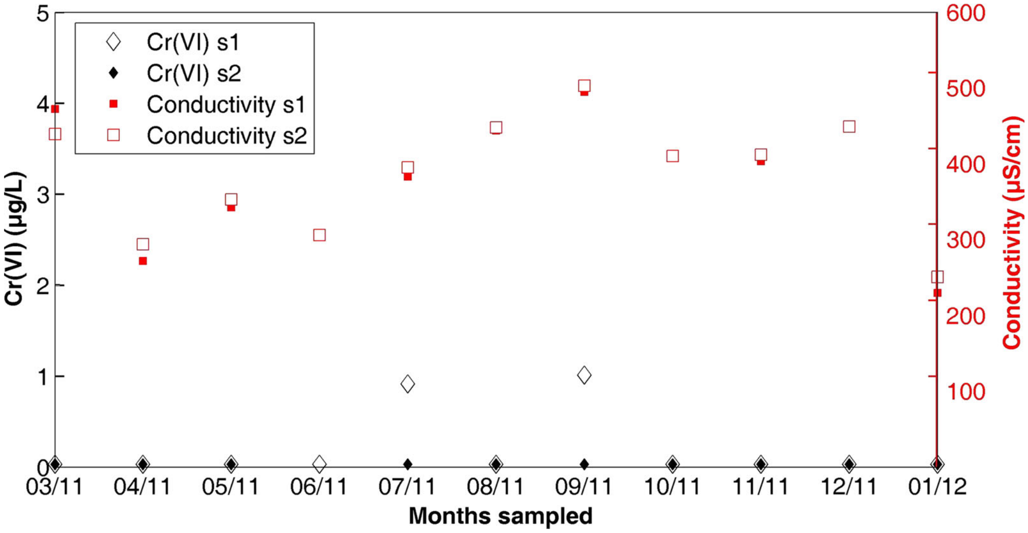

Fig. 10—Temporal Cr(VI) concentrations and conductivity values of the surface water sampling sites near FeCr smelters D1 and D2.

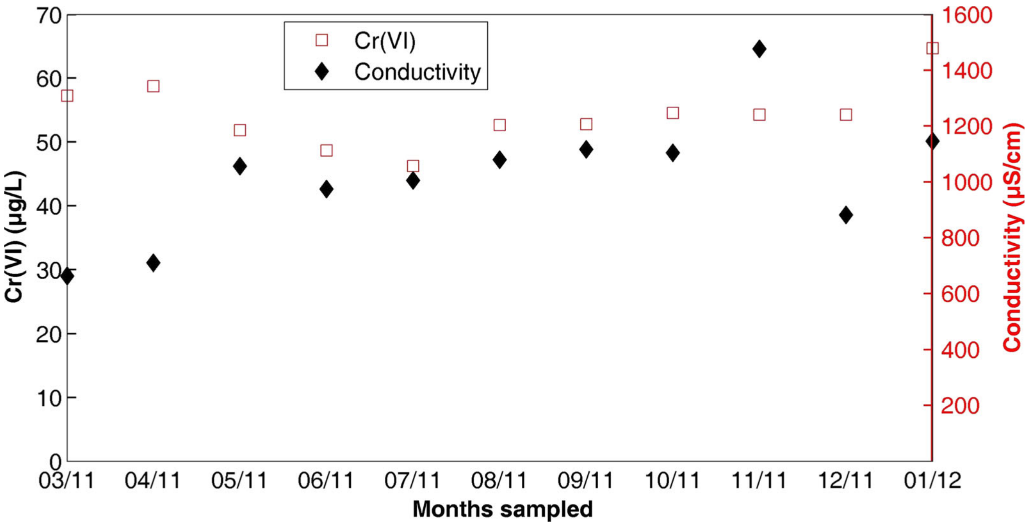

Fig. 11—Temporal Cr(VI) concentrations and conductivity values of the drinking water sampled near FeCr smelter D2.

IV. CONCLUSIONS

In this paper, four case studies were discussed relating to surface water pollution near FeCr smelters in SA. For case study areas A, B, and C, it was verified that FeCr production had a negative influence on Cr(VI) and/or the conductivity of surface water in the proximity of these smelters. Although surface water contamination could not be detected in case study D, drinking water originating from groundwater was polluted with Cr(VI). In general, the results seem to indicate that the main factors causing Cr(VI) pollution were surface run-off and/or seepage, while the atmospheric deposition of particulate matter emissions from FeCr production did not contribute significantly to surface water pollution. Although the Cr(VI) contamination of surface water can almost exclusively be attributed to FeCr production at the case study sites, other anthropogenic activities such as the use of fertilizer addition during crop cultivation can also make a noteworthy contribution to surface water pollution. The extinction of diatoms during a severe Cr(VI) surface water pollution event was also observed. According to the knowledge of the authors, this is the first documented case of such an observation reported in the peer-reviewed public domain.

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Chapter 6: Project evaluation, conclusions and recommendations

6.1 Introduction

In this chapter, the project evaluation and main conclusions are presented. Firstly, an evaluation of the quality control procedures applied are presented in **§ 6.2**. Thereafter, in **§ 6.3** the results are evaluated against the objectives previously stated (**§ 1.3)**. Weaknesses and/or limitations, as well as successes of the project are also discussed. Some future recommendations are provided in **§ 6.4**, while the chapter concludes with some final remarks in **§ 6.5**.

6.2 Quality control

Since very low Cr(VI) concentrations were assessed in this study, and due to possible Cr(VI) and Cr(III) inter-conversions, quality control procedures associated with Cr(VI) were critical. A synopsis of these is presented.

In order to ensure repeatability, three samples were collected every month at each of the sampling sites. One of the afore-mentioned samples were spiked with a known concentration of Cr(VI) to ensure that the above-mentioned inter-conversions did not occur during sample storage and/or transportation. Cr(VI) analyses were conducted with the aid of an IC fitted with a post-column DPC colorant delivery system coupled to an UV-vis absorbance detector. Standard solutions for calibration were prepared from a reference standard with a specified concentration. A 7 point calibration line, with varying concentrations ranging between 1 to 100 μg/L, yielded a linear correlation coefficient of $R^2 = 1.00$. Most samples analysed fell within the afore-mentioned linear dynamic concentration range and those that did not were diluted to within this range. The detection limit was calculated to be 0.9 μg/L, which was lower than the 1.0 μg/L stated in literature. This was achieved by the installation of additional PEEK tubing on the IC in order to reduce the pulse caused by the AXP pump. Some of the presented results were grouped together, according to concentration ranges. Student's t test (applied with 99.9 % probability) was applied to prove that the means of the concentrations were significantly different from a statistical point of view.

6.3 Project evaluation and main conclusions

In Chapter 1 (**§ 1.3**), several objectives were set. The successes, weaknesses and/or limitations of the project were evaluated against each of these objectives. Subsequently, each objective and its evaluation are presented:

i. Identification of logistically feasible sampling sites consisting of surface- and drinking (municipal water) water sites in the proximity of ferrochrome (FeCr) smelters in the Bushveld Igneous Complex (BIC).

Sampling sites were identified in the proximity of 12 FeCr smelters located in or close to the BIC. These sites were chosen based on several considerations (Chapter 3), which included accessibility, logistics, safety, occurrence of perennial surface water and drainage patterns. In total, 25 sampling sites were chosen, which consisted of 14 surface water sampling locations, as well as 11 drinking water sampling sites. At five of the FeCr smelters, two surface water sampling sites were identified, i.e. either upstream or downstream of the FeCr smelter, or in a non-impacted and impacted stream/river/waterway.

ii. Sampling at these sites on a monthly basis for a full seasonal cycle, i.e. one year, in order to prevent seasonal bias of the results.

Samples were collected at all of the above-mentioned sites once a month for a period of one year, i.e. February 2011 to January 2012. Due to unforeseen circumstances, surface water was not sampled at sampling site R1 near FeCr smelter 11 (referring to the numbers allocated in article 1, Chapter 3) for one month, due to safety-related concerns. Surface water near FeCr smelters 1 and 3, as well as sampling sites R1 near smelters 4 and 5 were not sampled for some months due to the streams/rivers/waterways being dry during the dry season. Overall, a 94.3% sample collection rate was maintained.

iii. Assess Cr(VI) and general water quality of surface- and drinking in the proximity of FeCr smelters. Although there are many characteristics (e.g. pH, temperature, dissolved oxygen, odour, total hardness, turbidity and organic carbon, as well as nutrients such as sulphates, phosphates and nitrates/nitrites) that are important from a water quality perspective, those considered in this study had to be limited, since a) this was the first study of its kind in South Africa and b) there had to be a directly link between the characteristics measured and the industrial processes. Considering the FeCr pyrometallurgical production and waste treatment processes, Cr(VI) and conductivity was chosen as characteristics to be monitored. Cr(VI) is a direct unintentional by-product of the FeCr pyrometallurgical processes and conductivity is a good indicator of other salts and/or compounds that leach into surface/groundwater from FeCr processes and/or treatment/storage facilities.

This study is the first relatively comprehensive survey of Cr(VI) pollution of surface water in the proximity of FeCr smelters in the BIC. 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 (numbers according to Article 1, Chapter 3) were, however, consistently impacted by Cr(VI) pollution, with annual mean values of 4.4 and 6.3 µg/L, respectively. In addition, 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 as a result of surface run-off due to poor wastewater management. From the four case studies conducted (Article 3, Chapter 5), it was evident that the main factors causing Cr(VI) surface water pollution were surface run-off and/or seepage, while the atmospheric deposition of particulate matter emissions from FeCr production did not contribute significantly at the specific sampling sites.

Although Cr(VI) drinking water pollution was not the main focus of this study, the results indicated that drinking water in the proximity of most FeCr smelters was unpolluted. However, the annual mean Cr(VI) concentration of drinking water at sampling site 11 (number according to Article 1, Chapter 3) 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. After the candidate pointed this out to the relevant FeCr producer (smelter 11), significant steps were taken to remedy the situation.

In this study water conductivity was used as a proxy for general water quality. The conductivity results confirmed the earlier deduction from Cr(VI) results that atmospheric deposition of pollutants originating from FeCr smelting did not significantly impact surface water quality at the specific sampling sites. At certain FeCr smelters (e.g. smelters 1 and 8, number according to Article 1, Chapter 3) surface water sampling sites, which would have been impacted if surface run-off and/or seepage occurred from the relevant smelters, did not indicate any significant negative impacts. This proves that FeCr smelting does not automatically imply surface water pollution. In contrast, the surface water pollution originating from certain FeCr smelters were apparent, especially near smelters where upstream and downstream type samples could be collected (smelters 4, 5, 7 and 9). The results also indicated that anthropogenic activities other than FeCr production, e.g. the use of fertilizer addition during crop cultivation, could also make a noteworthy contribution to surface water pollution.The Cr(VI) results presented (Chapters 3 and 5, i.e. Articles 1 and 3) were mostly compared with the drinking water standard, i.e. 50 µg/L. However, the afore-mentioned standard is does not consider ecosystem sustainability. As an example, the Target Water Quality Range (TWQR) of Cr(VI) to maintain aquatic ecosystems is 7 µg/L. Therefore, although the overall aim of this study was not to conduct an in depth environmental assessment, the quantitative results presented can be used by the wider research community to also assess other related Cr(VI) impacts.

vi Recommendations for future investigations in this research field.

The final objective regarding recommendations for future research is discussed in **§ 6.4**.

Although not part of a specific objective, one limitation of this study was that groundwater was not considered. However, it would have been impossible to include groundwater without the knowledge of the FeCr producer, landowners and the community, which could have led to biased results. Furthermore, since the origin of drinking water sampled during this study was not investigated, no direct link could be drawn between drinking- and surface water pollution from FeCr smelters.

6.3 Future perspectives and recommendations

The following proposed future work and/or recommendations can be made:

i. This study was conducted in isolation, without direct co-operation with the FeCr industry, government and private land owners. Although this was by design to prevent bias, it would be ideal to co-operate directly with the industry and the other stakeholders in future studies to determine the extent of the Cr(VI) pollution.

ii. An assessment of the groundwater in areas surrounding FeCr smelters should be undertaken in future.

iii. If possible, sediment and soil samples should also be gathered in conjunction with surface water samples. This would enable the determination of the total Cr, the stable oxidation state Cr (III and VI), manganese (Mn) oxides, as well as species that could serve as reducing agents for Cr(VI) (e.g. S(IV), Fe(II) and organics) in the soils/sediment. This would enable the estimation of the possibility of Cr(III)-Cr(VI) inter-conversions that could occur in a specific area.

iv. The effect of pollution originating from FeCr production should be considered in a wider context in future, e.g. ecotoxicological. In this study, a reduction in diatom numbers coincidental to relatively high Cr(VI) concentrations were observed (Article 3, Chapter 5). The extent of this study was too limited to proof that diatoms indeed died due to the afore-mentioned Cr(VI) pollution, however, it does give enough circumstantial evidence that this should be considered in greater detail in future studies. For such studies to succeed, cross-disciplinary cooperation between chemists, biologists, ecologists and toxicologists would be required.

v. Future investigations should also focus on the quantification of wet and dry Cr(VI) deposition near the FeCr smelters. The current study indicated that this contribution was minor, but this could not be quantified.

6.4 Final remarks

The results obtained from this PhD thesis present an insight into the overall impact of the FeCr industry throughout the BIC. The pollution was mainly due to run-off and/or seepage or could be attributed to historical waste mismanagement. Other aspects of the FeCr process, e.g. water treatment, also had an impact on the water quality. In addition, an environmental impact potentially related to micro-organisms was found.

The results obtained in this study were made available to the FeCr industry in South Africa. Certain FeCr smelters have already started to improve their waste management procedures, based on the results of this study.

Three articles (presented as Chapters 3,4 and 5) were published in ISI accredited peer reviewed journals from this.

Appendix: A

A.1 Introduction

In this thesis the experimental procedures/methodologies followed were discussed in the relevant articles (Chapters 3-5). However, no details were disclosed pertaining to the analytical calibration of the instrument used to quantify Cr(VI) and limited quality control information was given. Therefore, this Appendix was included to present some additional information (e.g. Cr(VI) calibration curve and detection limit (DL), and statistical methods) that supports the experimental information presented in the articles.

A.2 Cr(VI) analysis – calibration curve and detection limit

Cr(VI) analyses were conducted using an IC with a post-column DPC colorant delivery system coupled to an UV-vis absorbance detector. Cr(VI) solutions with known concentrations were prepared, from a certified reference standard that had a specified concentration, in order to perform a 7 point calibration. The IC instrument was calibrated before the analysis of each monthly sample batch. A typical calibration curve is presented in **Figure A.1**, with concentrations ranging between 1 and 100 μg/L Cr(VI).

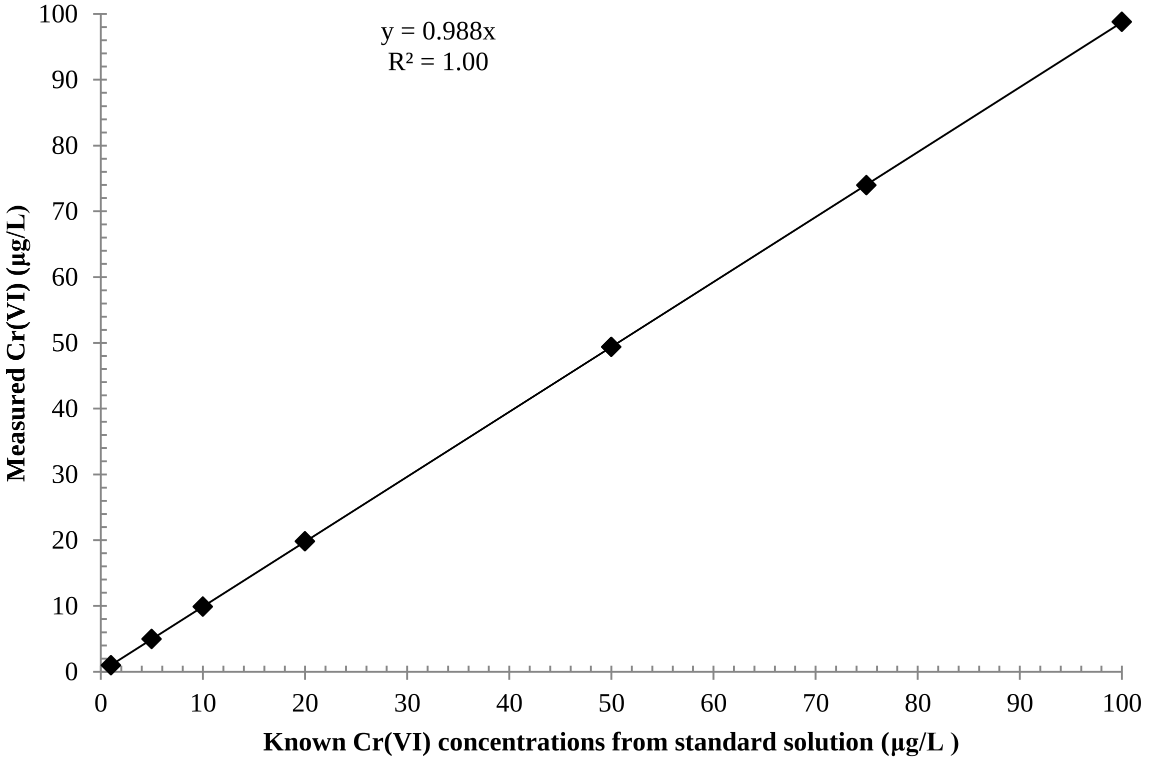

Figure A.1 An example calibration curve indicating measured Cr(VI) (y-axis) versus known Cr(VI) concentration (x-axis).

As is evident from **Figure A.1** the slope (m) of the example Cr(VI) calibration curve was close to 1 (i.e. 0.988) and the correlation coefficient R^2 also approximated 1 to the second decimal. Within the calibration range, i.e. up to 100 µg/L Cr(VI), the instrument response was therefore linear. Samples that fell outside this proven linear range (e.g. maximum Cr(VI) concentrations of 198 and 220 µg/L were measured at surface water sampling sites 4b and 7b, respectively, according to Chapter 3, Article 1, Figure 3) were diluted and re-analysed as to ensure Cr(VI) quantification of all samples were within the above-mentioned linear calibration range. Additionally, four calibration points were specifically included at Cr(VI) concentration ≤ 20 µg/L, since it was expected that most of the samples would be in this range. This approach was proven to be correct, e.g. as indicated by the Cr(VI) concentration ranges indicated in Chapter 3, Article 1, Figure 3.

The Cr(VI) IC method applied, was derived for procedures detailed in literature, for which the DL was specified as 1.0 µg/L (Dionex Application updates 144 and 179, 2003 and 2011; Thomas *et* *al*., 2002). As is common practice (e.g. Skoog *et al*., 2014) the experimental DL of a method can be determined by the equation below:

$$DL = \frac{ks_b}{m}$$ **Equation 1**

with, DL = detection limit, k = confidence factor, s_b = baseline amplitude and m = calibration sensitivity (slope of the calibration curve)

The factor k is usually chosen as 2 or 3. A value of 2 corresponds to a confidence level of 92.1%, while a k value of 3 corresponds to a 98.3% confidence level (Skoog *et al*., 2014). By application of the higher confidence level (98.3%), the experimental DL was calculated as:

DL = (3 X 0.3 ug/L)/0.988 = 0.9 ug/L (rounded to the first decimal)

The above-mentioned experimentally determined DL was singly better (lower) that the previously mentioned literature value, since additional PEEK tubing was installed in order to reduce the pulse caused by the AXP pump (see Chapter 3, Article 1, Section “Cr(VI) analytical method”). A reduction in the pulse of the pump resulted in a reduction of the baseline noise indicated on the chromatographs.

A.3 Statistical methods applied

Apart for using box and whisker plots that indicated median, mean, 25 and 75th percentiles, and ±2.7 σ (or 99.3% coverage if the data has a normal distribution) (Matlab, 2013), as well as other types of plots (e.g. indicating mean and range) to compare data statistically, Student’s t-test (Skoog *et al*., 2014) was also used to determine if the mean values of two datasets that were compared, were statistically significantly different from one another (e.g. Chapter 5, Article 3, Sections III A and C). Student’s t was calculated as indicated below:

$$t = \frac{\bar{x}_1 - \bar{x}_2}{s_{pooled}\sqrt{(N_1+N_2)/(N_1N_2)}}$$ **Equation 2**

with t = Student's t statistical parameter, $\bar{x}_1$ and $\bar{x}_2$ = mean values of the respective datasets, s_{pooled} = pooled standard deviation, N_1 and N_2 = number of data points in each dataset

By comparing the calculated t value to standard t values for certain degrees of freedom, various levels of probability could be assessed (Skoog *et al*., 2014). In all cases where Student's t were applied, a probability of were 99.9% used. This implies that differences between the means of the compared datasets were probable with a 99.9% confidence level.

A.4 References

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Nature never breaks her own laws

~Leonardo da Vinci~