

POTENTIAL LINK BETWEEN ATMOSPHERIC CHROMIUM POLLUTION AND HOME-BASED INDUSTRIES

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ABSTRACT

This paper explores the link between elevated atmospheric chromium levels and the growth of home-based industries in post-apartheid South Africa. Home industries and informal commercial operations have mushroomed in the new South Africa, and contributions of such activities to heavy metal atmospheric pollution is a novel consideration. A comparison of data from the apartheid era with our recently recorded results on heavy metal distribution revealed that atmospheric Cr levels were elevated, particularly in certain areas near schools, where such informal activities are flourishing. Six sites were selected for the investigation, and high volume air samplers were used to collect air particulates on 0.80 µm-pore size membrane filters. Sampling was conducted on a regular basis during office hours for about ten months. The collected filters were dried and prepared for subsequent acid digestion in 1M HNO₃ in a microwave digester. The resulting solutions were subjected to metal analysis by electrothermal atomic absorption (ETAA). The experimentally determined Cr levels fell in the range: 0.02 – 1 µg/m³, about a factor of 3 higher, in some cases, than the documented value (< 0.3 µg/m³). Elemental chromium in the atmosphere can produce species known to be carcinogenic to humans, and could pose a significant threat. Levels of other toxic metals (Ni, Cd, Pb) were within acceptable limits. The potential impact of our research and suggestions for remediation are discussed.

Keywords: atmospheric chromium, ETAA analysis, home industries, pollution, schools.

INTRODUCTION

Post-apartheid South Africa has seen a considerable growth in informal industrial activities such as small scale welding operations and domestic automobile repair agencies. In many cases, these activities are confined to residential areas, and contribute to dispersion of heavy metals in the atmosphere, thus leading to atmospheric pollution. Many of these commercial operations are mobile and move from one residential area to another for fixed periods in the year. In our study we found elevated levels of chromium (Cr) at selected sites, where home-based enterprises were ongoing. Several other toxic metals including Ni, Pb and Cd were measured in addition to Cr; however none of these metals were above their recommended limits.

The transport of such atmospheric pollutants depends on the height they reach in the atmosphere, their particle size and climatic factors (Alloway, 1993). Air pollutants tend to be transported by wind and mixed with the surrounding air until their concentration is relatively uniform. Dispersion in the horizontal plane is generally restricted and occurs more rapidly than vertical mixing. The extent to which air pollutants become diluted is governed by factors determining the degree of turbulence such as incoming solar radiation, wind speed, cloud cover and land topography (Fifield, 1996; Samara, 2005). These

factors were considered in establishing the level of pollution in this study.

Atmospheric heavy metal pollution could lead to fundamental disorders in children (Alloway, 1993). Such pollution might target specific but distinct sites within human cells, leading to alterations in gene expression among other health hazards. Species of chromium, in particular, are human carcinogens, and considered to be significant genotoxic agents (Bryant *et al.*, 2006; Baird, 1995). Investigations have indicated that chromium (VI) compounds can increase the risk of lung cancer. The World Health Organization (WHO) has determined that chromium (VI) is a human carcinogen (ATSDR, 2001). The recommended documented level for total atmospheric Cr is <0.3 µg.m⁻³ (WHO, 2004). Chromium is commonly associated with industrial pollution, and is usually released into the atmosphere from smelting and refining operations and incineration of waste materials (Srivastava, 2007). Clearly, the advent of several home industries and informal metal industries in the new South Africa could add to such pollution. Our research was prompted by the growth of various domestic industries in the greater Chatsworth-Durban area, Kwa-Zulu Natal (K-ZN), eastern South Africa. The principal objective of this work, therefore, was to determine if a link existed between the elevated distribution of Cr in the atmosphere (at the chosen sites) and the escalating growth of home-based industrial activities.

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MATERIALS AND METHODS

Sample Origin and Collection

All the sites selected were primary schools, at six different points from the central industrial area (Table 1). Apart from their proximity to informal and established industrial facilities these sites were also selected because of other factors, such as willingness by staff to assist in the research; the source of electricity and safety and maintenance of equipment. Gilian Envirocon high volume samplers were used for sampling. The samplers were set up on the school premises on each weekday morning, and programmed automatically. Sampling was conducted during office hours (when established and informal activities were usually operational), over a period of ten months.

Table 1. Distances and Cr levels of selected sites from the central industrial area

Site	Distance from industrial area	Range of [Cr] $\mu\text{g}/\text{m}^3$
1	1.2 km east	0.02 – 1.6
2	3.5 km east	0.02 – 0.35
3	1.8 km north	0.10 – 0.50
4	2.9 km north	0.01 – 0.58
5	4.7 km northwest	0.01 – 0.18
6	5.9 km northwest	0.01 – 0.42

Preparation of standards and samples

'Working' reference standards in a range from 5-25 ng L^{-1} were prepared. The methods adopted for the preparation of air filter samples and spiked samples was a standard procedure that involved drying and storage of samples for a month. All glassware such as pipettes, beakers, teflon vessels and volumetric flasks were cleaned by soaking them in 50% nitric acid for 48 hours and thereafter rinsing them with deionized water. The glassware was further rinsed with 1M HNO_3 , prior to the preparation of samples. The sample filters and blank filters were weighed and then carefully transferred with a tweezer into teflon microwave vessels. The filters were 37 mm in diameter with a pore size of 0.8 microns to trap fine and coarse particles, allowing us to obtain a composite assessment of total atmospheric chromium. Thereafter 2 mL of 70% HNO_3 were added to each vessel. The vessels were sealed and put into the rotor of a microwave digester. A microwave heating programme was used to completely digest the samples.

Instrumentation

In ETAA measurements an aliquot of 50 μL was pipetted into the graphite tube. The temperature of the tube was then increased in a controlled manner (furnace programme) to dry, ash and atomize the sample, and finally to clean the tube of residual material for the next run. Most of the sample matrix was removed during the

ashing period. Atomization temperatures up to 3000°C could be achieved, thus enabling measurement of the most refractory elements. The data for this study were obtained using a Varian 1275 Atomic Absorption Spectrophotometer fitted with a graphite tube atomizer and an automatic sampler. Nitrogen was used as the purge gas. The recommended operating procedure for the analysis of Cr was: wavelength: 357.9 nm; slit width: 0.2 nm; lamp current: 7 mA. Each temperature step in the furnace programme was optimized, between 75°-2700°C.

Reproducibility and accuracy

Validation was attained in terms of linearity, accuracy and repeatability. Calibration of the instrument was checked on a regular basis during analysis, and throughout the investigation the procedure produced acceptable linearity. The repeatability of the system produced relative standard deviations (RSD) <6 %, and was evaluated by making five successive measurements ($n = 5$) on two individual samples that were randomly selected (Table 2). The accuracy of the system for the duration of the study was established with appropriate reference standards and produced a relative error within 7%. Blank determinations produced zero readings at the selected wavelength.

Table 2. Reproducibility of absorbance measurements using two samples

Measurement	Sample 1	Sample 2
1	0.28	0.41
2	0.29	0.44
3	0.27	0.39
4	0.30	0.44
5	0.31	0.46
Mean	0.29	0.43
Relative Std Deviation	4.9%	5.8%

RESULTS AND DISCUSSION

What are home-based industries?

Due to growing unemployment in the new South Africa there has been a significant increase in small scale industrial-type businesses within the residential environment. In general, home industries emerged out of the plight of unemployment and are a source of income for the poor and needy (Unpublished work, 2003; Rogerson, 2001). Since the advent of the new political dispensation in South Africa in 1994, the regulations governing the establishment of home industries have been more lenient, and as a result a large number of such industries have mushroomed in the area of interest. This encompasses businesses which are involved in electroplating, leather tanning, galvanizing operations, and wood treatment. Chromium is a significant component in all of these processes. As previously mentioned, many of these are mobile, returning to their original sites during fixed periods of the year.

Of serious concern is the possibility of chromium escaping into the atmosphere from solutions and aerosols from such informal electroplating and galvanizing industries that have grown around these residential areas. Included among these industries are roadside welding operations carried out for the benefit of motorists with leaking exhausts and other car problems. It is possible that the numerous welding operations adjacent to the schools may have made an appreciable contribution to the elevated levels of chromium found in the samples, during the first few months of the year (see below). Such welding operations, being mobile, would move to other sites as the year progressed. Another pollution problem involves the combustion of Cr containing materials such as magnetic tapes, plastics and timber by residents. Such activities could also contribute to the higher levels at the beginning of the year, especially after the major school holiday period.

Comparative studies – Apartheid and post-apartheid eras

Many of the metal plants in the central industrial area were established in the apartheid era and could represent significant sources of Cr emission. We, therefore, found that the area demarcated for investigation showed very little change in formal industrial activity between the apartheid and post-apartheid eras. The work done in the apartheid area by the National Nuclear Research Institute at Pelindaba (Unpublished data, 1978) in 1977/8 gives some indication of the concentrations of Cr in the various cities of South Africa, as shown in Table 3. At the start of the post-apartheid era, Albertyn (1994) also conducted similar research in 1993/4, and although no data is available for this particular period, it is known that the towns have become more prone to informal industrial activities and consequently the levels of these metals in the atmosphere could have increased dramatically. There is, therefore, a lack of updated information and our research could serve as a useful source of data. The mean Cr value for Chatsworth-Durban is roughly 1500 ng.m^{-3} . A comparison of the values obtained with that given for the apartheid era in 1977/8 (Table 3) suggests that these informal industrial activities could have contributed to the current elevated levels, as more than two decades have elapsed since the publication of those results.

Table 3. Comparison of ranges of Cr in the atmosphere in various cities in the Republic of South Africa in ng.m^{-3} in 1977/8 (apartheid era)

City	Cr (ng.m^{-3})
Richards Bay	4.4
Durban	34.0
Pretoria	32.0
Johannesburg	27.0
Cape Town	6.9

The average monthly concentrations of Cr in the atmosphere of the selected sites (Fig. 1) arose partly from industrial emissions and partly from contributions from secondary sources. As previously stated, the relatively higher levels of Cr in the atmosphere may be ascribed to the hectic startup of both formal and informal industrial activity at the beginning of the year. Due to the peripatetic nature of many of these home-based industries the emissions decreased as the months progressed, resulting in considerably lower concentrations towards the end of the year. This feature is corroborated in Figure 2 which delineates the Cr concentrations on a daily basis. Figure 2 shows that with the exception of the 3 days on which high Cr concentrations were recorded earlier in the year, the remaining levels were below $0.60 \text{ } \mu\text{g.m}^{-3}$ for all sites. It is interesting to note that in general, the Cr concentrations at the selected sites were high only for the first half of the year. Therefore, it is crucial that monitoring of Cr emissions is done throughout the year at suitably selected sites i.e. if a survey was carried out only for the latter half of the year, the result would have indicated a very low average value.

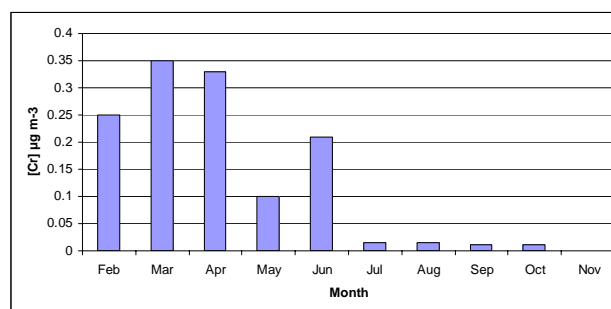


Fig. 1. Average monthly Cr concentrations in the Chatsworth area.

Table 4 gives an international comparison of the Cr ranges of other countries for urban areas according to Schroeder *et al.* (1987). An inspection of this table shows that our study in Chatsworth-Durban has an abnormally high range of chromium levels, although for most periods of the year the values were within acceptable limits.

Table 4. Comparison of ranges of Cr associated with particulate matter in the atmosphere at various international locations (Schroeder *et al.*, 1987) with that in Chatsworth-Durban (our study) in ng.m^{-3} .

Location	Cr (ng.m^{-3})
Canada	4 – 26
USA	2.2 - 124
Europe	3.7 - 227
Other	Traces - 277
Chatsworth (our study)	20 - 1630

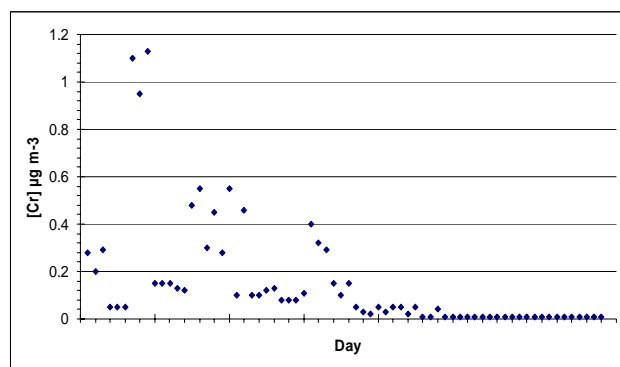
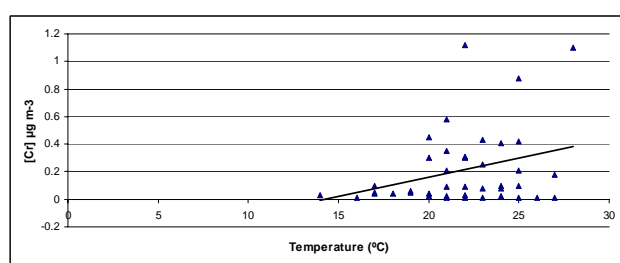
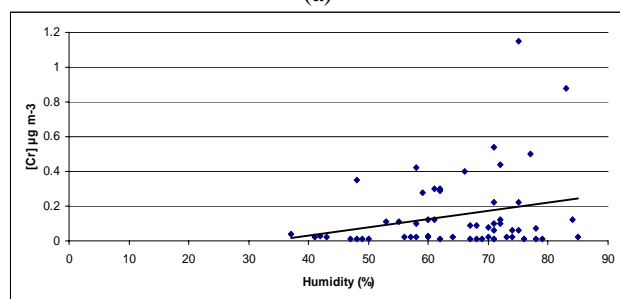


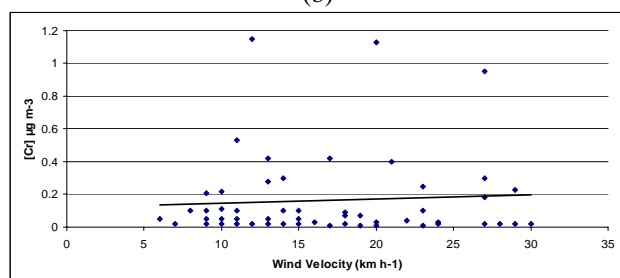
Fig. 2. Meteorological data associated with Cr concentrations.



(a)



(b)



(c)

Fig. 3. Cr concentrations for each day during the sampling period:

(a.) temperature; (b.) humidity; (c.) wind velocity

The role played by meteorological factors

Meteorological variables such as temperature, humidity and wind velocity were measured and their influence on the chromium concentration in the atmosphere was investigated. These relationships are illustrated in Figure 3. Figure 3 depicts the relationship between Cr

concentration and the variables temperature, humidity and wind velocity. Although the data points in Figure 3 delineate broad scatter, they suggest that temperature and humidity could lead to a more pronounced effect on pollutant level than wind velocity. In general, temperature and humidity (Figs. 3a and b) tend to show an inclining relationship with Cr concentration, whereas wind velocity (Fig. 3c) shows no particular correlation. However, no serious information could be gathered on the exact influence of these factors on pollutant level. Therefore, the role played by meteorological factors was not conclusive. In addition to the above factors, there would be an obvious contribution from automotive fuel but this component was overshadowed by the industrial and domestic emissions.

Home-based industries and Cr pollution – is there a link?

The answer to this question can be found in Table 1, where upper and lower Cr limits and distances from the industrial centre are shown. Sites 1, 3 and 5 in Table 1 could be considered control sites (where informal industrial activities were generally low). The remaining sites (2, 4 and 6), where domestic industries flourished, were further away from the central industrial area than their respective counterparts. Let's examine the results in Table 1 more closely. Sites 1 and 2 are both towards the east, 1.2 and 3.5 km, respectively, from the central industrial area. Site 1 registered a considerably higher upper Cr concentration – as expected. Site 2 (about three times further away) recorded an upper Cr level above the recommended limit, which could be due to either meteorological factors or informal commercial operations. We indicated above that the role played by meteorological factors was not conclusive; therefore, the data suggest that informal activities at Site 2 were probably responsible for the elevated Cr level. If we proceed further and inspect the data from sites 3 and 4 (1.8 and 2.9 km north of the industrial centre) we find that Site 4 has a higher upper Cr level. Here again, since meteorological factors were inconclusive, the Cr elevation could be attributed to home-based industries. The same pattern was observed for Sites 5 and 6, strongly suggesting that a link exists between such industrial activity and atmospheric Cr pollution. The substantial growth of home industries at the selected sites is thus a cause for concern and prompts the implementation of remedial measures.

Toxicity and suggestions for remediation

As previously stated, the toxicity of chromium is dependent on its oxidation state (Langard and Norseth, 1986). Chromium can exist in more than one oxidation state; therefore, monitoring total Cr is useful from the perspective of obtaining a composite picture. Exposure to Cr (III) and Cr (VI) appear to be particularly hazardous (Menendez-Alonso *et al.*, 1999). It is interesting to note that Cr (III) is the form of chromium that is usually found

Table 5: Concentration ranges (ng.m⁻³) of other heavy metals at the selected sites

Site	Ni	Cu	Cd	Pb (x 10 ²)
1	5 – 54	18 - 75	3.1 – 5.6	0.70 – 8.3
2	6 – 14	20 - 233	1.6 - 18	0.20 – 5.9
3	7 - 17	16 - 65	14 - 25	0.40 – 3.1
4	8 - 27	12 - 63	1.2 – 2.7	0.40 – 7.5
5	10 - 23	20 - 49	0.5 – 2.0	1.0 – 5.0
6	5 - 16	7 - 32	0.8 – 3.6	0.40 – 4.2

in fruits and vegetables, among other food sources. In small quantities, this form of chromium is believed to be essential in the human body, stabilizing certain proteins, as well as being involved in metabolic reactions and glucose utilization in cells. (Mertz, 1969; Kirpnick *et al.*, 2006; Russo *et al.*, 2005; Bryant *et al.*, 2006). However, at elevated levels, Cr (III) can cause inhibition of DNA replication and DNA deletions, both of which are potentially mutagenic disorders. Additionally, in living cells, the oxidation of Cr (III) to Cr (V) and Cr (VI) can result in carcinogenic effects (Costa *et al.*, 2006). In particular, Cr (VI) is responsible for several deleterious effects including DNA cross-linking, single and double strand breaks, DNA deletions and genome rearrangements (Snow, 1994; Bryant *et al.*, 2006; Shrivastava *et al.*, 2005; Xie *et al.*, 2005). Recent studies have shown Cr (VI) is responsible for the development of lung cancer, and is associated with the induction of cancers in the gastrointestinal and central nervous systems as well (Costa, 2006).

The impact of our research results demonstrates that the observed distribution of Cr in the area of interest can pose a significant hazard. Therefore, it is important for local municipality bodies to consider adopting feasible remedial measures. Possible suggestions to remedy the current situation are: (i) regular monitoring of Cr levels in the designated areas; (ii) more stringent government regulations to confine informal industrial activities to appropriate industrial areas; (iii) environmental awareness programmes to enhance the current knowledge of the community; (iv) action by parent-teacher associations to curb the threat; (v) action by residents' associations to minimize domestic activities that contribute to such pollution.

Other Heavy Metals

Four additional heavy metals: nickel, copper, cadmium and lead were determined by applying the same analytical procedure described above. Table 5 presents the upper and lower concentration limits of these elements for the respective selected sites. The general sources of these anthropogenic heavy metal emissions are burning of fossil fuels, steel processing, metallurgy of non-ferrous metals, incinerators, cement production and the use of leaded petrol. According to the Agency for Toxic Substances and

Disease Registry (ATSDR) the maximum permissible emission limits for these metals in industrialized areas are: Ni: <1 mg.m⁻³; Cu: <1 mg.m⁻³; Cd: 200 µg.m⁻³; and Pb: 1.5 µg.m⁻³ (ATSDR, 1999; ATSDR, 2004; ATSDR, 2005). It is clear from Table 5 that our results do not exceed the acceptable limits for these metals.

CONCLUSIONS

Our work showed that a link exists between atmospheric Cr pollution and home-based industries. Our major concern was that the level of chromium in the atmosphere of Chatsworth-Durban found in the present investigation is more than a factor of 3 higher at some sites when matched with the US- documented data on acceptable atmospheric Cr levels. As a subject for future studies, sampling could be conducted on a regular basis at the beginning of the year and again towards the end of the year to gather more detailed information on the distribution of atmospheric concentrations of chromium. Contributory sources of Cr pollution such as home industries, such as informal metal-plating and other industries of this nature could be suppressed by the intervention of the local residents' association and parent-teacher associations. The carcinogenic nature of oxidized chromium prompts immediate measures to be taken to limit the atmospheric emissions to acceptable levels. In addition there is a need for establishing a database for ongoing monitoring of Cr in the area.

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