Seasonal First Flush phenomenon and environmental impacts of a number of heavy metals in stormwater discharges in the Witwatersrand Area

by

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Summary:

South Africa’s available freshwater resources are almost fully-utilised and under stress. Water will increasingly become the limiting resource in South Africa, and supply will become a major restriction for the future socio-economic development of the country, in terms of both the amount and quality of water available (Harris *et al.*, 1999). At present, many water resources contain large amounts of pollutants, such as dissolved metal elements (metals and metal compounds that occur in a dissolved state in water), particulate-bound metal elements (metals and metal compounds that are attached to particles such as sand), and suspended, colloidal and volatile fractions of these particulates (Sansalone *et al.*, 1996; Su & Mitchell, 2003).

Pollutants interfere with the normal life cycle functions of organisms living in or which are dependent on the water source. These pollutants originate from a variety of point and non-point sources. Among the most significant point sources are industrial waste disposal sites, municipal landfills, and leaking septic tanks. Non-point sources, on the other hand, include agricultural runoff, mine drainage, highway runoff, and runoff from lawns and natural areas. It is therefore necessary to monitor the levels of pollutants in the water to determine if the concentrations are within legal limits, and to implement strategies to mitigate the detrimental impacts of these pollutants on the environment (Miller, 2000).

The transport of anthropogenic pollutants by rainfall runoff from highways, in particular, has the potential to adversely impact the quality of adjacent receiving waters and soils (Su & Mitchell, 2003). These pollutants result from traffic activities (such as tire wear and brake wear), thus being dependent on the amount of traffic; and are accumulated on roadways before it is washed away by precipitation (McKenzie & Irwin, 1983; Sansalone *et al.*, 1996; Su & Mitchell, 2003). During the rising limb of the runoff hydrograph, often disproportionately large amounts of both the dissolved and particulate-bound fractions of these heavy metal pollutants are washed off the highway surface, causing peak concentrations of contaminants in rainfall runoff. This phenomenon is commonly referred to as the seasonal first flush, where the initial stage of a storm event contains a large percentage of total pollution (accumulated in the preceding dry season) in a relatively small percentage of runoff volume (Sansalone *et al.*, 1996; Lee *et al.*, 2004; Kim *et al.*, 2005). Such large concentrations of heavy metals introduced into the environment in a short amount of time can have immediate toxic effects, but, since heavy metal elements do not degrade in the environment, they can also accumulate and have long-term toxic effects caused by mass accumulation in plants, animals and humans (Sansalone *et al.*, 1996; Miller, 2000; Arthur, 2004; Kirkby & Römheld, 2004). However, a number of these heavy metals are also crucial in maintaining normal health in humans, animals and plants (Arthur, 2004; Kirkby & Römheld, 2004).

Therefore, the primary objectives of this study are to discuss the phenomenon of the seasonal first flush of highway runoff; describe possible environmental effects of too low and too high levels of heavy metals, with reference to relevant legislation concerning water pollution; describe possible best management practices (BMP's) to lessen the effects of too high levels of heavy metals; describe the study area and why it was chosen; identify shortcomings of the study; collect and analyse relevant data for the last five years (1999 – 2005) to determine if the first flush phenomenon is present for selected heavy metals (aluminium, cadmium, cobalt, chromium, copper, iron, manganese, nickel, lead, and zinc); identify the main heavy metals present in runoff in this area; propose improvements to future highway monitoring projects; and recommend mitigation strategies to reduce the environmental impacts of heavy metals.

It was found, using water quality data from Rand Water, that cadmium and copper were not detected at the selected study sites; however it is possible that some aluminium, chromium and lead were present in particulate form. Seasonal first flush was detected for cobalt, manganese, nickel, iron and zinc during most rainy seasons. It was also found that the concentrations of these metals were usually high above the regulation limits for irrigation, aquacultural purposes, aquatic ecosystem health, livestock watering and domestic use throughout the season. Therefore, the results of this study have shown that roads provide a significant contribution of heavy metals to nearby rivers, consequently justifying the need for further study. It is recommended that a monitoring system be designed to collect more accurate information so as to be able to research, plan and implement mitigation strategies, such as Best Management Practices (BMP's) to improve water quality and lessen the negative effect these metals have on the environment.

Opsomming:

Suid Afrika se beskikbare varswater hulpbronne is amper tenvolle aangewend en onder druk. Water is besig om die beperkende hulpbron in Suid Afrika te word met betrekking tot beide die hoeveelheid en kwaliteit beskikbaar asook die effektiewe verskaffing daarvan. Dit sal in die toekoms ‘n groot beperking plaas op sosio-ekonomiese ontwikkeling van die land (Harris *et al.*, 1999). Tans bevat baie water hulpbronne groot hoeveelhede besoedeling, soos opgelosde metaal elemente (metale en metaal verbindings wat voorkom in ‘n opgelosde toestand in water), deeltjie-gebinde metaal elemente (metale en metaal verbindings wat aangeheg is aan deeltjies), en gesuspendeerde, kollidale en vlugtig fraksies van hierdie deeltjies (Sansalone *et al.*, 1996; Su & Mitchell, 2003).

Besoedeling kan die normale lewenskringloopfunksies van organismes wat lewe in, of afhanklik is van, water beïnvloed. Hierdie besoedeling kan voortspruit vanuit ‘n verskeidenheid van punt en nie-punt bronne. Van die mees beduidende punt bronne is industriële en munisipale afvalwerwe en septiese tenks wat lek. Nie-punt bronne, aan die ander kant, sluit in agronomiese afloop, myndreinering, hoofwegafloop, en afloop vanaf grasperke en natuurlike areas. Dit is om hierdie rede nodig om die vlakke van besoedeling in die water te moniteer om te bepaal of hul konsentrasies binne wetlik perke is en om strategieë te implimenteer om die skadelik impakte van hierdie besoedeling op die omgewing te versag (Miller, 2000).

Die vervoer van mensgemaakte besoedeling deur reënvalafloop vanaf hoofweë, in besonder, het die potensiaal om ongunstige impakte op die kwaliteit van aangrensende water en grond te hê (Su & Mitchell, 2003). Hierdie besoedeling kom vanaf verkeersaktiwiteite (soos band en rem slytasie), en is dus afhanklik van die hoeveelheid verkeer en word opgebou op die padoppervlakte voor dit weg gewas word deur reënval (McKenzie & Irwin, 1983; Sansalone *et al.*, 1996; Su & Mitchell, 2003). Dikwels gedurende die begin van die hidrograaf word disproporsionele groot hoeveelhede van beide die opgelosde en deeltjie-gebinde fraksies van hierdie swaarmetaalbesoedeling

gewas vanaf die hoofwegoppervlak. Dit veroorsaak piek konsentrasies van besoedeling in stormwaterafloop. Hierdie verskynsel word gemeenskaplik na verwys as die seisoenale eerstespoel, waar die beginstadium van ‘n storm ‘n groot persentasie van die totale besoedeling bevat (opgebou in die voorafgaande droë seisoen) in ‘n relatief klein persentasie van afloopvolume (Sansalone *et al.*, 1996; Lee *et al.*, 2004; Kim *et al.*, 2005). Sodanige groot konsentrasies van swaarmetale wat ingevoer word in die omgewing in ‘n kort tyd kan onmiddellike toksiese effekte hê. Omdat swaar metale nie degradeer in die omgewing nie, kan hulle ook ophoop en langtermyn toksiese effekte veroorsaak deur massaversameling in plante, diere en mense (Sansalone *et al.*, 1996; Miller, 2000; Arthur, 2004; Kirkby & Römheld, 2004). ‘n Aantal van hierdie swaarmetale is egter ook noodsaaklik in die onderhoud van normale gesondheid in mense, diere en plante (Arthur, 2004; Kirkby & Römheld, 2004).

Die primêre doelwitte van hierdie studie is om die verskynsel van die seisoenale eerstespoel van hoofwegafloop te bespreek; die moontlik omgewingseffekte van te lae en te hoë vlakke van swaarmetale, in verband met toepaslik wetgewing rakende waterbesoedeling te beskryf; die moontlik beste hanteringspraktyke te beskryf om die effekte van te hoë vlakke van swaarmetale te verminder; die studiearea te beskryf en hoekom dit gekies was vir die studie; tekorte van die studie te identifiseer; toepaslik data vir die laaste vyf jaar (1999 – 2005) te kollekteer en te analiseer om te bepaal of die eerste spoel verskynsel teenwoordig is vir die gekose swaarmetale (aluminium, kadmium, kobalt, kroom, koper, yster, mangaan, niekel, lood, en sink); die hoof swaarmetale teenwoordig in afloop in hierdie area te identifiseer; verbeteringe tot toekomstige hoofwegmoniteringsprojekte te bespreek en om regstellende strategieë voor te stel om die impakte wat swaarmetale het op die omgewing te verminder.

Dit was gevind, deur gebruik te maak van water kwaliteit data vanaf Rand Water, dat kadmium en koper nie gevind was by die gekose studieareas nie; maar dit is moontlik dat aluminium, chroom en lood teenwoordig was in deeltjievorm. Seisoenale eerstespoel was gevind vir kobalt, mangaan, nikel, yster en sink gedurende meeste reënseisoene. Dit was ook gevind dat die konsentrasies van hierdie metale gewoonlik hoog bo die wetlike perke was regdeur die seisoen. Dus het die uitslae van hierdie studie gewys dat paaie ‘n beduidende bydrae van swaarmetale tot nabygeleë riviere maak en gevolglik is verdere studie geregverdig. Dit word aanbeveel dat ‘n moniteringsisteem ontwerp word om meer akkurate informasie te kollekteer om versagtingsstrategieë na te vors, te beplan en te implementeer, om beste hanteringspraktyke te ontwikkel om water kwaliteit te verbeter en dus negatiewe effeke wat hierdie metale op die omgewing het, te verminder.

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List of frequently used abbreviations:

Aluminium	Al
Average Annual Daily Traffic	AADT
Best Management Practice	BMP
Cadmium	Cd
Cobalt	Co
Chromium	Cr
Copper	Cu
Iron	Fe
Lead	Pb
Manganese	Mn
Nickel	Ni
Preceding Dry Days	PDD
Recommended Dietary Allowance	RDA
South African Department of Water Affairs and Forestry	SA-DWAF
Target Water Quality Range	TWQR
Zinc	Zn

Table of contents:

Page

List of figures:

List of tables

1. Introduction:

South Africa's available freshwater resources are already almost fully-utilised and under stress. At the projected population growth and economic development rates, it is unlikely that the projected demand on water resources in South Africa will be sustainable (Harris *et al.*, 1999). Water will increasingly become the limiting resource in South Africa, and supply will become a major restriction to the future socio-economic development of the country, in terms of both the amount and quality of water available. At present many water resources contain large amounts of pollutants, such as dissolved metal elements (DME) (metals and metal compounds that occur in a dissolved state in water), particulate-bound metal elements (PME) (metals and metal compounds that are attached to particles such as sand), and suspended, colloidal and volatile fractions of these particulates (Sansalone *et al.*, 1996; Su & Mitchell, 2003).

Pollutants interfere with the normal life cycle functions of organisms living in or dependent on the water source. These pollutants originate from a variety of point and non-point sources. Among the most significant point sources are industrial waste disposal sites, municipal landfills, leaking septic tanks, and occasional accidental spills of petroleum products and industrial liquids. Non-point sources, on the other hand, include agricultural runoff, mine drainage, highway runoff, and runoff from lawns and natural areas. If left unchecked, non-point source pollution can damage the quality of receiving surface and ground waters. The presence of pollutants in surface or ground water may interfere with the vital functions of the ecosystems and humans dependent on it (Miller, 2000).

It is therefore imperative that South Africa develop a water-efficient economy together with a social ethic of water conservation and ultimately a culture of sustainability of water resource use (Harris *et al.*, 1999). This can be achieved, in part, by monitoring the levels of pollutants in the water to determine if the concentrations are within legal limits, and implementing strategies to mitigate the detrimental impacts of these pollutants on the environment.

The transport of anthropogenic pollutants by rainfall runoff from highways, in particular, has the potential to adversely impact the quality of adjacent receiving waters and soils (Su & Mitchell, 2003). These pollutants result from traffic activities (such as tire wear and brake wear), thus being dependent on the amount of traffic; and are accumulated on roadways before it is washed away by precipitation (McKenzie & Irwin, 1983; Sansalone *et al.*, 1996; Su & Mitchell, 2003).

The poor condition of many roadways in South Africa enhances the tire wear of vehicles, which is a source of zinc and cadmium (Turer *et al.*, 2001). High levels of brake wear is caused in areas where there is a sharp decrease in the speed of vehicles (such as off-ramps on highways) and is a source of copper, lead, chromium and manganese (Sansalone *et al.*, 1996; Su & Mitchell, 2003). As South Africa's economy is still rising from a third-world state, many vehicles are old and not in good repair and thus engine wear and fluid leakage (sources of aluminium, copper, nickel and chromium) and vehicular component wear and detachment (sources of iron, aluminium, chromium and zinc) are also factors that must be taken into account (Sansalone *et al.*, 1996; Su & Mitchell, 2003; SA-NRA, 2004). These heavy metals, which are the subject of this study, are some of the most persistent pollutants found in highway runoff, as they do not degrade in the environment.

During the rising limb of the runoff hydrograph, often disproportionately large amounts of both the dissolved and particulate-bound fractions of these heavy metal pollutants are washed off the highway surface, causing peak concentrations of contaminants in storm water runoff (Sansalone *et al.*, 1996; Lee *et al.*, 2004; Kim *et al.*, 2005). This phenomenon is commonly referred to as the seasonal first flush, where the initial stage of a storm event contains a large percentage of total pollution (accumulated in the preceding dry season) in a relatively small percentage of runoff volume (Sansalone *et al.*, 1996; Su & Mitchell, 2003; Lee *et al.*, 2004; Kim *et al.*, 2005).

Such large concentrations of heavy metals introduced into the environment in a short amount of time can have immediate toxic effects, but, since heavy metal elements do not degrade in the environment, they can also accumulate and have long-term toxic effects caused by mass accumulation in plants, animals and humans (Sansalone *et al.*, 1996; Miller, 2000; Arthur, 2004; Kirkby & Römheld, 2004). However, a number of these heavy metals are also crucial in maintaining normal health in humans, animals and plants. Trace elements, which include iron, manganese, copper, zinc and nickel, are required by plants and animals in low concentrations for adequate growth and reproduction (Arthur, 2004; Kirkby & Römheld, 2004). At the same time, it is important to note that there is a thin line between essential and toxic concentrations.

Therefore, the primary objectives of this study are to discuss the phenomenon of the seasonal first flush of highway runoff; describe possible environmental effects of too low and too high levels of heavy metals, with reference to relevant legislation concerning water pollution; describe possible best management practices (BMP's) to lessen the effects of too high levels of heavy metals; describe the study area and why it was chosen; identify shortcomings of the study; collect and analyse relevant data for the last five years (1999 – 2005) to determine if the first flush phenomenon is present for selected heavy metals (aluminium, cadmium, cobalt, chromium, copper, iron, manganese, nickel, lead, and zinc); identify the main heavy metals present in runoff in this area; propose improvements to future highway monitoring projects; and recommend mitigation strategies to reduce the environmental impacts of heavy metals.

This study is important since the characterisation of heavy metals in highway runoff is necessary in order to develop effective control strategies (Best Management Practices) to immobilise toxic levels of heavy metals in the first flush runoff before it leaves the immediate vicinity of the roadway (Sansalone *et al.*, 1996; Su & Mitchell, 2003; Lee *et al.*, 2004; Kim *et al.*, 2005). It is essential that water used in farming and for human consumption is also effectively monitored for the presence of high levels of heavy metals.

However, heavy metal concentrations in highway storm water runoff are highly variable from site to site, storm event to storm event, and throughout a single storm event, making highway monitoring complex and time consuming (Su & Mitchell, 2003; Lee *et al.*, 2004; Kim *et al.*, 2005). It also appears that there is inadequate knowledge and data on heavy metal concentrations in South African waters. This has been attributed to relatively few studies that have been undertaken in South Africa dealing with levels of heavy metals, particularly their speciation in surface waters (Okonkwo & Mothiba, 2005).

Therefore, to be able to successfully undertake such a study, a number of objectives should be met - and these are outlined in the next section.

2. Problem statement:

At present, many water resources in South Africa are polluted by industrial effluents, domestic and commercial sewage, acid mine drainage, agricultural and highway runoff, and litter (Harris *et al.*, 1999). When these pollutants enter the receiving water body, they can cause toxic effects on the organisms that are dependent on the water (Su & Mitchell, 2003). It is essential that South Africa develop a strategy of sustainable water resource use through efficiency and conservation (Harris *et al.*, 1999). This can be achieved by monitoring the levels of pollutants in water, and implementing strategies to ensure that the concentrations remain within legal limits as well as mitigate the detrimental impacts of these pollutants on the environment.

This study focuses on heavy metal pollutants found in highway runoff and the biological effects of these metals on living organisms. This is important, since knowledge of the characteristics of highway runoff, such as the concentrations of pollutants and the physical and chemical processes that produce this runoff, is essential for decision makers and highway engineers to assess and mitigate the possible harmful impacts of highway runoff on receiving waters.

The main aim of this study is to determine if a seasonal first flush is present for heavy metals in highway rainfall runoff in the Witwatersrand area; and to compare the concentrations of these metals to the legal limits to determine if there is a problem with heavy metal pollution in this area.

Therefore, the primary objectives of this study are to:

- discuss the phenomenon of the seasonal first flush of highway runoff;
- describe possible environmental effects of too low and too high levels of heavy metals, with reference to relevant legislation concerning water pollution;
- describe possible best management practices (BMP's) to lessen the effects of too high levels of heavy metals;
- describe the study area and why it was chosen;

- identify shortcomings of the study;
- collect and analyse relevant data for the last five years (1999 – 2005) to determine if the first flush phenomenon is present for selected heavy metals (aluminium, cadmium, cobalt, chromium, copper, iron, manganese, nickel, lead, and zinc);
- identify the main heavy metals present in runoff in the Witwatersrand area;
- propose improvements to future highway monitoring projects; and
- recommend mitigation strategies to reduce the environmental impacts of heavy metals.

As this study focuses on heavy metal pollutants in the seasonal first flush of highway runoff, a more in-depth discussion of this phenomenon and the biological effects of these heavy metals in the environment are given in the next section.

3. The biological effects of heavy metals on living organisms in the environment:

3.1. Highway runoff and seasonal first flush:

Highway runoff is a complex mixture of dissolved and particulate-bound compounds as well as larger objects, such as organic material (e.g. leaves), soil and litter. It can include a variety of chemical compounds from vehicles, the highway, and other sources which accumulate on highway surfaces, roadside areas, and rights-of-way (Sansalone *et al.*, 1996; Bricker, 1999; Hunt *et al.*, 2002; Lee *et al.*, 2004; BEST, 2005). During rainfall runoff events, these compounds are washed to adjacent waters and may have adverse effects on ecosystems and biota if mitigating measures are not taken (Sansalone *et al.*, 1996; Buckler & Granato, 1999; Bricker, 1999; Breault & Granato, 2000; Hunt *et al.*, 2002; BEST, 2005). The term 'seasonal first flush' is used to refer to the initial rainfall event of a rainy season that contains a large percentage of pollution. Characterisation and treatment of the first flush runoff could minimise adverse water quality effects, while requiring less volume to be treated (Hunt *et al.*, 2002; Su & Mitchell, 2003; Kim *et al.*, 2005).

The roadway, bridges, safety structures, as well as fuel and vehicle exhausts and other materials may be a potential source of heavy metals in highway runoff that may be entrained in runoff and transported to receiving waters (Legret & Pagotto, 1999; Hunt *et al.*, 2002). The predominant build-up of pollutants is from vehicular traffic contributing particulates, metals, and organics resulting from tire, road, engine and brake wear, as well as exhaust emissions and fluid drippings (Sansalone *et al.*, 1996; Hunt *et al.*, 2002; Su & Mitchell, 2003; BEST, 2005). High concentrations of a large number of metals (such as aluminium, manganese, chromium, cobalt, iron, lead, nickel and zinc) have been found in brake dust and tire-wear particulate samples taken in New Zealand (Legret & Pagotto, 1999; Breault & Granato, 2000; Kennedy & Gadd, 2003).

However, heavy metal concentration, transport and fate are difficult to quantify, especially in highway runoff studies. Determination of accurate heavy metal data in runoff studies is made difficult by the complex physicochemical processes that influence the quality of highway runoff. Large variations in traffic volume, antecedent conditions, and precipitation characteristics that influence runoff quality and quantity between rainfall events, from season-to-season, from year-to-year and from site-to-site, may preclude quantitative interpretation of cause and effect relations. Furthermore, the logistics of rainfall runoff sampling are demanding (Sansalone *et al.*, 1996; Buckler & Granato, 1999; Breault & Granato, 2000; Hunt *et al.*, 2002; Su & Mitchell, 2003; BEST, 2005; Okonkwo & Mothiba, 2005). Nevertheless, highway runoff can have adverse effects on the environment if no measures are taken for the removal of excessive pollutants before the runoff reaches receiving waters. A thorough understanding of how heavy metals influence living organisms is essential when monitoring highway runoff and will therefore be discussed further.

3.2. Trace elements: an introduction to essentiality and toxicity:

Rainfall runoff from roadways often contains elevated amounts of metals in both particulate and dissolved forms (Sansalone *et al.*, 1996; BEST, 2005). Since metals do not degrade naturally, high concentrations in runoff can result in accumulation in the roadside waters and soil at levels that are toxic to organisms in surrounding environments. However, at low concentrations, many of these metals (called trace elements) are essential for health in plants and animals, including humans.

3.2.1. Trace element effects on plant, animal and human health:

Trace elements are essential for health in plants and animals including human beings. Many of them can cause health problems through over supply or under supply in the diet (Arthur, 2004; Takkar, 2004; Fraga, 2005; He *et al.*, 2005). Up to 20 trace elements have been considered as essential for optimal health in humans. The evidence for essentiality however, varies greatly from direct demonstration through to extrapolation from animal experiments carried out under very stringent conditions (WHO, 1996). Trace elements such as copper, zinc, manganese, iron, iodine, cobalt, molybdenum and selenium, which have well-defined biochemical functions, can be said to be essential. However, fluoride, arsenic, chromium, vanadium, silicon, nickel, lithium, lead and boron have all been suggested to be essential in animal studies, where they have reversed physiological impairment caused by ultra-pure diets. This evidence of essentiality is not absolute and there is some argument that the so-called 'ultra trace elements' may be displacing other trace elements from sites in enzymes and proteins that are causing physiological impairment (Arthur, 2004; Takkar, 2004; Fraga, 2005).

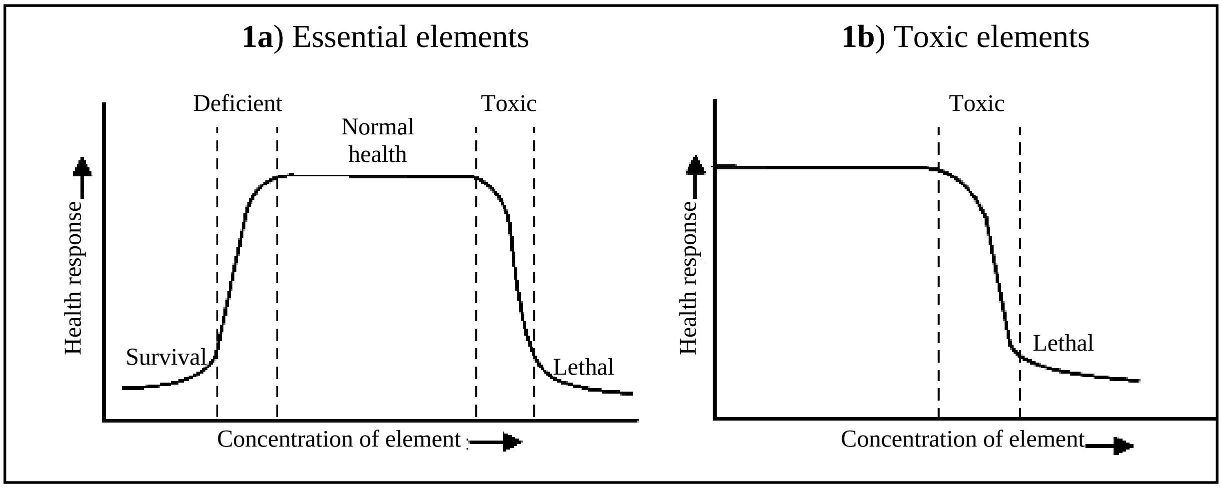
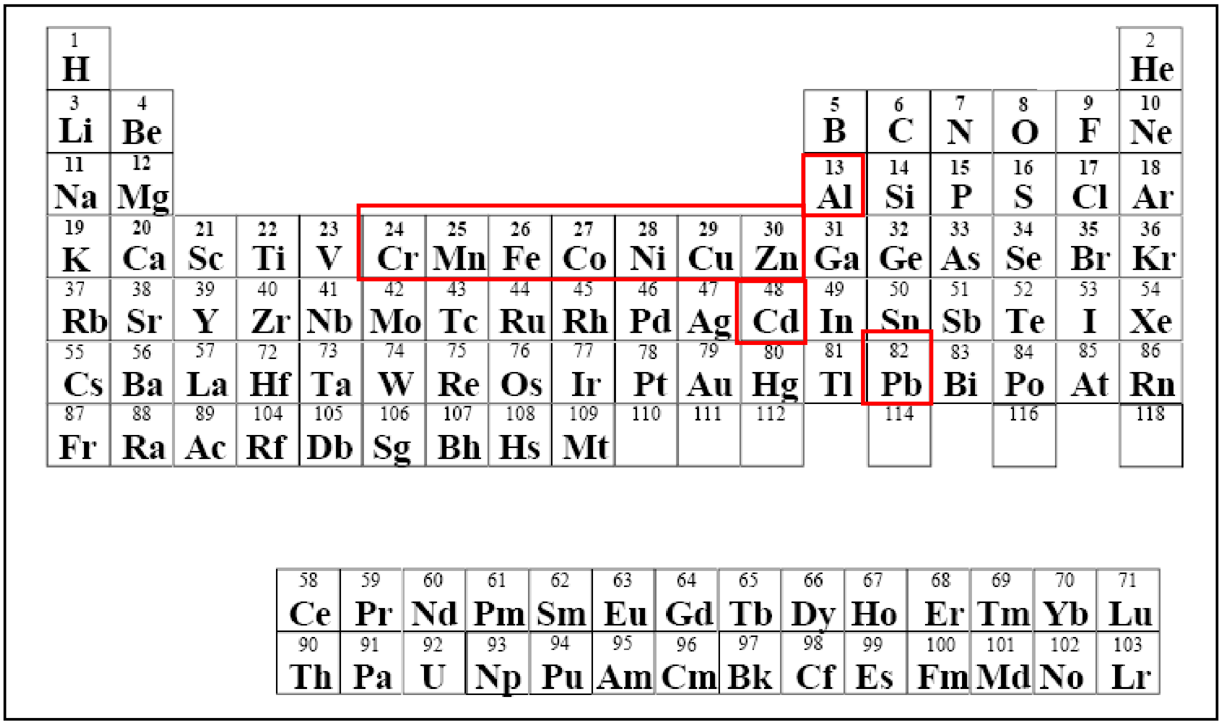


Figure 1: The relationship between health response and the concentrations of the elements, (a) essential elements, (b) toxic elements (Ansari *et al.*, 2004).

Whilst considering the essential functions of trace elements, it is important not to disregard their potential toxicity. As already mentioned, diets can provide too little as well as too much of the necessary trace elements. Toxicity will appear when dietary intake exceeds the optimal levels, as shown in figure 1a (Raven *et al.*, 2001; Ansari *et al.*, 2004; Hill, 2004). Some organisms can tolerate low levels of toxic elements, such as cadmium, but will quickly succumb to its lethal effects, as shown in figure 1b (Ansari *et al.*, 2004). In some cases these may be a small 'pharmacological' range where the element may have some direct, beneficial effects, for example, excess copper in pig diets promoting growth, before there are overt signs of toxicity (Ansari *et al.*, 2004). All essential elements may be toxic to some extent either directly or through interfering with the metabolism of other trace elements. Trace element toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs. Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes. Allergies are not uncommon and repeated long-term contact with some metals or their compounds may even cause cancer (Arthur, 2004; Fraga, 2005).

As this study focuses on heavy metal pollution of the seasonal first flush of highway runoff, this review will further expand on the biological effects of selected metals on plants, aquatic organisms, livestock and humans. The relevant legislation concerning water used for irrigation, aquacultural purposes, aquatic ecosystem health, livestock watering and domestic use for these metals will also be included. This information is used to determine if the concentration levels of the metals at the selected study sites could have adverse effects on the environment. The metals selected for this study are **aluminium, cadmium, cobalt, chromium, copper, iron, manganese, nickel, lead** and **zinc** as these are the most common metals originating from vehicles, as already mentioned. Figure 2 shows the periodic table of the elements and the positions of the above mentioned metals are outlined in red.



1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110	111	112		114		116		118

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Figure 2: Periodic table of the elements showing the positions of the selected metals.

3.3. Trace elements: biological effects on living organisms and relevant legislation for selected water use sectors:

It should be noted that the chemical speciation (and therefore also the bioavailability and possible toxicity) of heavy metals in the seasonal first flush and river water is dependent on pH (Hunter *et al.*, 1999).

3.3.1. Trace element aluminium (Al):

Aluminium (CAS number 7429-90-5) is a silvery-white, ductile and malleable metal and in compounds it is usually found as Al(III). Surface water concentrations of aluminium ions are minimal due to insolubility of aluminium hydroxide ($Al(OH)_3$) at neutral pH. In water with pH more acidic than 5.0, aluminium ions exists as the octahedral hexahydrate, $Al(H_2O)_6^{3+}$, often abbreviated as Al^{3+}. As water becomes less acidic, $Al(H_2O)_6^{3+}$ undergoes successive deprotonations to yield $Al(OH)^{2+}$ and $Al(OH)_2^{+}$. Neutral solutions give aluminium hydroxide ($Al(OH)_3$) precipitate, which redissolves in basic solutions, due to the formation of tetrahedral $Al(OH)_4^{-}$ (Brix & DeForest, 2000).

3.3.1.1. Effect of aluminium (Al) on plants:

Aluminium toxicity is an important growth-limiting factor for plants in most strongly acid soils ($pH < 5.0$). The most important symptom of aluminium toxicity in plants is the inhibition of root growth. Aluminium accumulates in the root tips at sites of cell division and cell elongation, causing the roots to become thick and brown and inefficient in absorbing water and nutrients (Kidd & Proctor, 2000; Mosser-Pietraszewska, 2001; Rout *et al.*, 2001; Wu *et al.*, 2005).

Long-term exposure of plants to aluminium also inhibits shoot growth by inducing magnesium (Mg), calcium (Ca) and phosphorus (P) deficiencies; drought stress; decreased photosynthetic activity leading to chlorosis and necrosis of leaves; total decrease in leaf number and size; and a decrease in shoot biomass (Kidd & Proctor, 2000; Mosser-Pietraszewska, 2001; Rout *et al.*, 2001; Wu *et al.*, 2005). Refer to Appendix A for detailed legislation concerning water quality for irrigation use.

3.3.1.2. Effect of aluminium (Al) on aquatic organisms:

Aluminium in acid habitats is toxic to fish, amphibians and phytoplankton (Brix & DeForest, 2000). Aluminium accumulates in fish organs like the brain, heart, kidney, skeleton and gills, whereas liver and muscles accumulate relatively low concentrations. However, it has profound effects on gills (Brix & DeForest, 2000):

- respiratory disturbances due to aluminium precipitation;
- osmoregulatory disturbances due to net loss in sodium, chloride and calcium ion uptake (Na^+, Cl^- and Ca^{2+}) caused by aluminium binding to the gill surface; and
- circulatory disturbances due to reduced blood plasma volume.

Accumulation of aluminium in aquatic macro-invertebrates, an important food source for many fish and some birds, may provide a route of entry of aluminium into the wider food chains (Brix & DeForest, 2000). Refer to Appendix A for detailed legislation concerning water quality in aquacultural use and aquatic ecosystem health.

3.3.1.3. Effect of aluminium (Al) on livestock:

Livestock may suffer from adverse chronic effects, such as neurotoxicity caused by high levels of aluminium in the water used for livestock watering. Refer to Appendix A for detailed legislation concerning water quality for livestock watering use.

3.3.1.4. Effect of aluminium (Al) on human health:

There is no known biological role for aluminium. In healthy individuals, most absorbed aluminium is excreted by the kidneys. When blood aluminium levels are high, bone appears to act as a sink, taking up aluminium and releasing it slowly over a long period (Wu *et al.*, 2005). The brain is vulnerable to many metals, including aluminium, but there is a blood-brain barrier which prevents most of the aluminium in blood from entering this organ. Aluminium is a known neurotoxic agent and interferes with a large number of neurochemical reactions. Symptoms of aluminium toxicity in humans include memory loss, learning difficulty, damage to the central nervous system, loss of coordination, disorientation, mental confusion, severe trembling, listlessness, colic, heartburn, flatulence and headaches (Wu *et al.*, 2005). Refer to Appendix A for detailed legislation concerning water quality for domestic use. A summary of the **Target Water Quality Range** (**TWQR**) for the different water use sectors (aquatic ecosystem health, domestic and agricultural use) is shown in table 1. The **Target Water Quality Ranges** (**TWQR**) for aquatic ecosystem health, domestic and agricultural use of the selected metals were obtained from the **South African Department of Water Affairs and Forestry** (**SA-DWAF**) and are reviewed in this study in order to attain the accepted water quality constituent values for further use in the Discussion of Results section.

Table 1: Summary of the TWQR for the different water sectors for aluminium (SA-DWAF: Field Guide, 1996).

	TWQR (mg/L)
Aquatic ecosystem health	<0.005
Domestic use (Human consumption)	0-0.15
Livestock watering	0-5
Irrigation	0-5
Aquaculture	<0.03

3.3.2. Trace element cadmium (Cd):

Cadmium (CAS number 7440-43-9) occurs naturally in the earth’s crust and is a relatively rare, soft, silver-white, transition metal closely related to zinc (Zn). Cadmium and its compounds have no known essential biological function nor do they have a definite odour or taste. In nature, two oxidation states are possible: 0 and +2.

The speciation of cadmium and fraction α of total concentration can be determined by equilibrium calculations using two extremes of major ion composition in global rivers (shown in figure 3). Using a compilation of global river water compositions, the 1% and 99% extremes of major ion composition were selected as representative of the likely range that would be encountered on a global scale (Hunter *et al.*, 1999). Therefore, the 1% level (in figure 3a) would represent a relatively ‘clean’ river and the 99% level (in figure 3b) would be a relatively ‘polluted’ river.

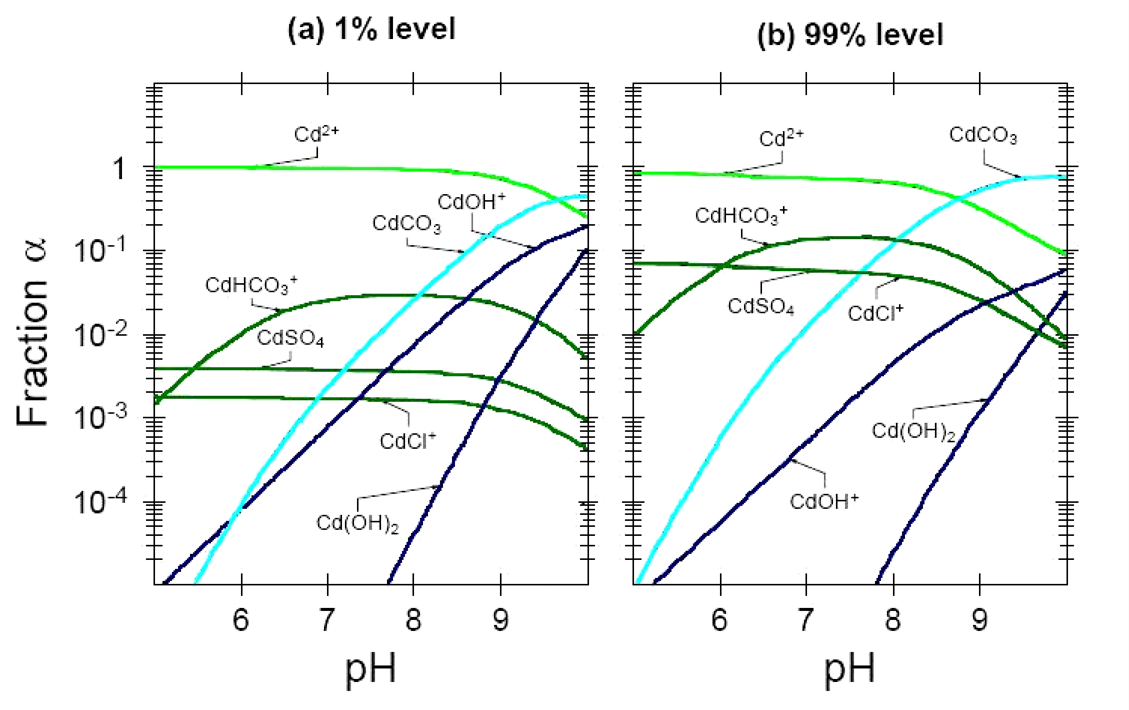


Figure 3: Calculated pH dependence of Cd(II) speciation in two reference river waters corresponding to the (a) 1% and (b) 99% percentile levels. The concentration of Cd^{2+} was set at 1 nmol/L. Vertical axis shows fraction α of total concentration present in the form of each complex (Hunter *et al.*, 1999).

Comparing figure 3a with 3b, it can be seen that the amount of ions present and the pH of the water influences the concentrations of different cadmium compounds. In figure 3b, representing the relatively more polluted river, the concentrations of $CdHCO_3^+$(aq), $CdSO_4$(aq) and $CdCl^+$(aq) (dark green lines) and $CdCO_3$(s) (light blue line) are higher than in the relatively clean river (shown in figure 3a). However, the concentrations of $CdOH^+$(aq) and $Cd(OH)_2$(s) (dark blue lines) are lower in 3b than in 3a. This shows that the level of pollutants in the river can have a noticeable influence on the speciation and thus the bioavailability and toxicity of cadmium (Hunter *et al.*, 1999). At low pH, the free Cd^{2+} aquo ion dominates (light green lines in figure 3a and 3b), with lesser amounts of $CdHCO_3^+$(aq), $CdSO_4$(aq) and $CdCl^+$(aq) present (dark green lines). Above pH 8.5, $CdCO_3$(s) becomes the dominant species (light blue lines), with smaller amounts of $CdOH^+$(aq) and $Cd(OH)_2$(s) present (dark blue lines). Therefore, as the pH rises, less free Cd^{2+} is present, and its bioavailability and toxicity thus decreases (Hunter *et al.*, 1999).

3.3.2.1. Effect of cadmium (Cd) on plants:

Cadmium plays no evident biological function in living organisms. The metal is concentrated primarily in the roots and to a lesser extent in the leaves of plants. Excess cadmium (in the form of the Cd^{2+} ion) causes a number of toxic symptoms in plants, such as (Prasad, 1995):

- growth retardation - Cell growth as well as whole plant growth is drastically inhibited due to cadmium toxicity;
- inhibition of photosynthesis by the depression of carbon assimilation;
- inhibition of enzymes - Complexes of cadmium with metallothioneins and phytochelatins can be formed;
- membrane damage by the generation of free radicals and efflux of cations;
- chlorosis;
- altered stomatal action, thus affecting transpiration; and
- decreased water stress tolerance, thus causing cell volume changes and resulting in turgor loss.

Refer to Appendix A for detailed legislation concerning water quality for irrigation use.

3.3.2.2. Effect of cadmium (Cd) on aquatic organisms:

Cadmium is extremely poisonous to a variety of species of aquatic organisms. Mammals, birds, fish, molluscs, crustaceans, lower animals, and higher plants bind cadmium to the protein metallothionein to make it unavailable for interaction, thus causing cadmium to bioaccumulate. Aquatic macrophytes (plants such as mosses, lichens and algae) can also accumulate cadmium and may act as a source of cadmium to grazing herbivores (Brix & DeForest, 2000; Ansari *et al.*, 2004). Asphyxiation, depression of the respiratory centre, hypocalcaemia, and gill injury are causal factors in the death of fish exposed to high levels of cadmium. Cadmium also causes behaviour, growth, and physiological problems in aquatic life (Brix & DeForest, 2000). Refer to Appendix A for detailed legislation concerning water quality for aquacultural use and aquatic ecosystem health.

3.3.2.3. Effect of cadmium (Cd) on livestock:

Livestock may suffer from adverse chronic effects such as anaemia, testicular degeneration, reduced feed intake and milk production, reduced growth, abortions and still births caused by high levels of cadmium in the water used for livestock watering. Animals eating or drinking cadmium also have higher blood pressure, iron-poor blood, liver disease, enlarged joints, scaly skin, liver and kidney damage, and nerve or brain damage. Refer to Appendix A for detailed legislation concerning water quality for livestock watering use.

3.3.2.4. Effect of cadmium (Cd) on human health:

Cadmium is not known to have any beneficial effects, but can cause a number of adverse health effects. The half-life of cadmium in the body is several decades as it is sequestered in metallothionein complexes; hence, it is important to avoid exposure (Hill, 2004). Cadmium competes with zinc (Zn) for binding sites and can therefore interfere with some of zinc's essential functions. Target organs in animals and humans are the liver, placenta, kidneys, lungs, brain, and bones. Symptoms of acute cadmium exposure are nausea, vomiting, abdominal pain, and breathing difficulty. Chronic exposure to cadmium can result in renal disease, fragile bones, anaemia, learning disorders, migraines, growth impairment, loss of taste and smell, poor appetite, and cardiovascular disease. There is sufficient evidence in humans for the carcinogenicity of cadmium and its compounds (Hill, 2004). Refer to Appendix A for detailed legislation concerning water quality for domestic use. A summary of the TWQR for the different water use sectors (aquatic ecosystem health, domestic and agricultural use) is shown in table 2.

Table 2: Summary of the TWQR for the different water sectors for cadmium (SA-DWAF: Field Guide, 1996).

	TWQR (µg/L)
Aquatic ecosystem health	<0.15
Domestic use (Human consumption)	0-5
Livestock watering	0-10
Irrigation	0-10
Aquaculture	0-0.2

3.3.3. Trace element cobalt (Co):

Cobalt (CAS number 7440-48-4) is widely distributed in the environment and is the thirty-third most abundant element in the earth's crust. Pure cobalt is a steel-grey, shiny, hard metal. Cobalt exists in water most commonly as Co(II) or Co(III) and with the use of equilibrium calculations, the speciation of cobalt can be determined (as shown in figure 4) (Hunter *et al.*, 1999). A comparison of figure 4a and 4b shows that the amount of ions present and the pH of the river water can influence the concentrations of different cobalt species. In the relatively more polluted river (figure 4b), the concentrations of $CoSO_4$(aq) and $CoCl^+$(aq) (dark green lines) and $CoCO_3$(s) (light blue line) are higher than in the relatively clean river (figure 4a). This shows that high levels of pollutants in rivers can cause higher concentrations of some cobalt species and therefore also influence the bioavailability and toxicity of cobalt (Hunter *et al.*, 1999). At low pH, the free Co^{2+} aquo ion dominates (light green lines in figure 4a and 4b), with lesser amounts of $CoSO_4$(aq) and $CoCl^+$(aq) present (dark green lines). Above pH 8, $Co(OH)_2$(s) and

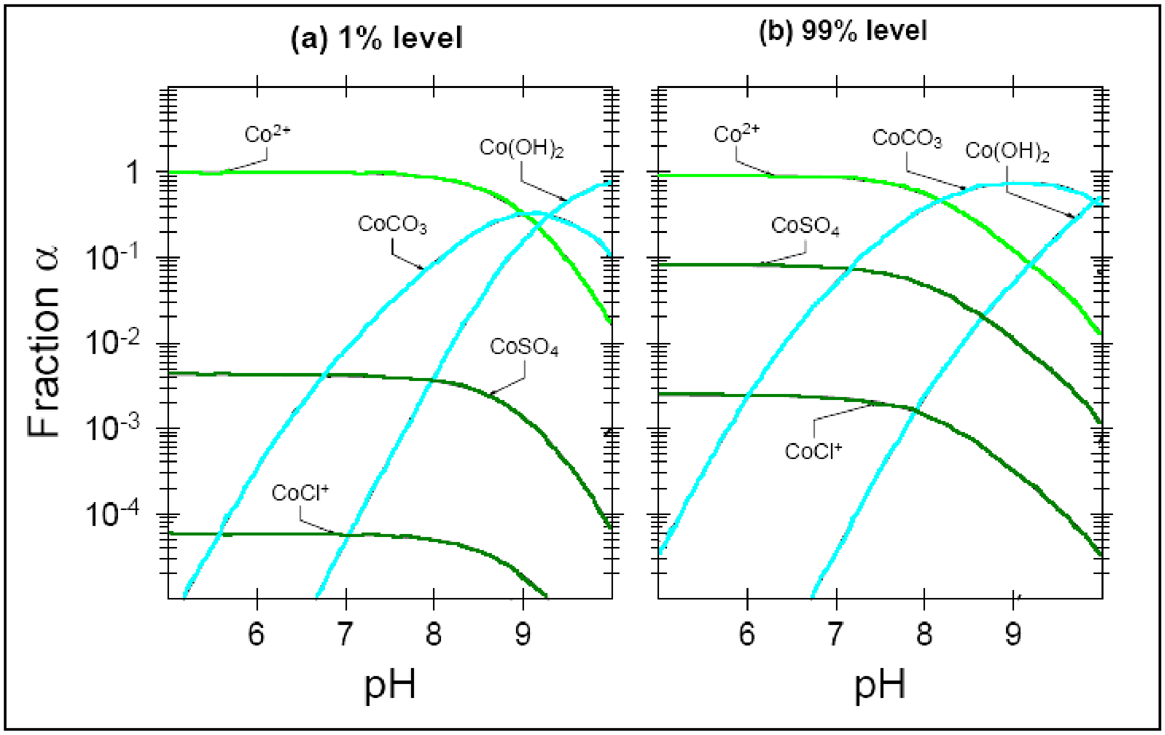


Figure 4: Calculated pH dependence of Co(II) speciation in two reference river waters corresponding to the (a) 1% and (b) 99% percentile levels. The concentration of Co^{2+} was set at 1 nmol/L. Vertical axis shows fraction α of total concentration present in the form of each complex (Hunter *et al.*, 1999).

$CoCO_3(s)$ become more prevalent (light blue lines). Therefore, as the pH rises, the amount of free Co^{2+} decreases and thus its bioavailability and toxicity also decreases (Hunter *et al.*, 1999).

3.3.3.1. Effect of cobalt (Co) on plants:

Cobalt is an essential nutrient for animals and plants; however it can also be accumulated in different plant parts. The observed gradient of accumulation is: root > stem + branches > leaf > fruit. Cobalt is required for nitrogen fixation in legumes and in root nodules of nonlegumes and deficient levels could result in nitrogen deficiency symptoms (El-Sheekh *et al.*, 2003; Kleizaite *et al.*, 2004; He *et al.*, 2005). Plant chlorosis and decreased chlorophyll concentration are indicators of exposure to toxic concentrations of cobalt. Cobalt can also cause oxidative cell damage (El-Sheekh *et al.*, 2003; Kleizaite *et al.*, 2004; He *et al.*, 2005). Refer to Appendix A for detailed legislation concerning water quality for irrigation use.

3.3.3.2. Effect of cobalt (Co) on aquatic organisms:

Cobalt is an essential element for the growth of many algal species, but in higher concentrations is toxic towards aquatic animals and plants. Molluscs, crustaceans, and other bottom feeders can accumulate high levels of cobalt, as it can be adsorbed to suspended particles and sediment (Brix & DeForest, 2000; Ansari *et al.*, 2004; Majmudar & Burleson, 2006).

3.3.3.3. Effect of cobalt (Co) on livestock:

Livestock may suffer from adverse chronic effects such as inappetence and weight loss caused by high levels of cobalt in the water used for livestock watering. Refer to Appendix A for detailed legislation concerning water quality for livestock watering use.

3.3.3.4. Effect of cobalt (Co) on human health:

In humans, cobalt is part of vitamin B_{12} and is essential in the body's synthesis of this essential vitamin. It is also necessary for normal functioning and maintenance of red blood cells as well as the nervous system and is necessary for metabolism of folic acid.

Cobalt is stored in the liver, kidneys, adrenal glands and bones and is poorly retained in body tissues. Excess cobalt is rapidly excreted, primarily in urine, although cobalt is secreted in the bile and hence reabsorption is possible. Exposure to cobalt over time can lead to several health effects in humans, including: heart function irregularities, elevated haemoglobin levels in the blood, hypothyroidism and goitre, and skin rashes. A summary of the TWQR for the different water use sectors (aquatic ecosystem health, domestic and agricultural use) for cobalt is shown in table 3.

Table 3: Summary of the TWQR for the different water sectors for cobalt (SA-DWAF: Field Guide, 1996).

	TWQR (mg/L)
Aquatic ecosystem health	Not available
Domestic use (Human consumption)	Not available
Livestock watering	0-1
Irrigation	0-0.05
Aquaculture	Not available

3.3.4. Trace element chromium (Cr):

Elemental chromium (CAS number 7440-47-3) is very stable, but is not usually found pure in nature. Chromium can exist in oxidation states ranging from -2 to +6, but is most frequently found in the environment in the trivalent (Cr^{3+}) and hexavalent (Cr^{6+}) oxidation states.

3.3.4.1. Effect of chromium (Cr) on plants:

Chromium is a toxic, nonessential element to plants. Toxicity of chromium to plants depends on its valence state: chromium(VI) (Cr^{6+}) is highly toxic and mobile whereas chromium(III) (Cr^{3+}) is less toxic. Since plants lack a specific transport system for chromium, it is taken up by carriers of essential ions such as iron (Fe) (Cooper, 2005; Shanker *et al.*, 2005). High levels of chromium affects all stages of plant growth and development: germination; root, shoot and leaf growth; as well as photosynthesis and enzyme metabolism. These toxic effects (summarised in table 4) can cause up to 50% reduction in crop yield (Shanker *et al.*, 2005). Refer to Appendix A for detailed legislation concerning water quality for irrigation use.

Table 4: Effects of chromium on plant growth and development and physiological processes (Shanker *et al.*, 2005).

Process	**Effects**
Germination	Reduced germination percentage and reduced bud sprouting
Root growth	Decrease in root length and dry weight, increase in root diameter and root hairs, proportional variations in cortical and pith tissue layers
Shoot growth	Reduction in plant height
Leaf growth	Reduction in leaf number, leaf area and biomass. Trifoliate leaves more affected than primary leaf in legumes; scorching of leaf tip, negative effect on leaf mesostructure
Yield and dry matter production	Up to 50% reduction in yield, reduced number of flowers per plant, reduced grain weight, increased seed deformity, reduced pod weight
Photosynthesis	Electron transport inhibition, Calvin cycle enzyme inactivation, reduced CO_2 fixation, chloroplast disorganisation
Water relations	Decreased water potential, increased transpiration rate, reduced diffusive resistance, wilting, reduction in tracheary vessel diameter
Mineral nutrition	Uptake of nitrogen, phosphorus, potassium, iron, magnesium, manganese, zinc, copper, calcium and boron affected
Enzymes and other compounds	Inhibition of assimilatory enzymes, increase activity of ROS scavenging enzymes, changes in glutathione pool, no production of phytochelatins

3.3.4.2. Effect of chromium (Cr) on aquatic organisms:

Both chromium (III) and (VI) are significant from the standpoint of potential impacts to aquatic organisms, however hexavalent chromium (Cr^{6+}) have potentially more negative effects (Brix & DeForest, 2000). Freshwater algae and invertebrates are more sensitive to chromium(VI) than fish and crustaceans are particularly sensitive to chromium(VI). Hexavalent chromium (Cr^{6+}) is easily absorbed by gut and body walls (such as shells, gills, and mantle) and at higher concentrations, Cr^{6+} is associated with abnormal enzyme activities, altered blood chemistry, lowered resistance to pathogens, behavioural modifications, disrupted feeding, and osmoregulatory upset (Brix & DeForest, 2000). Refer to Appendix A for detailed legislation concerning water quality for aquatic ecosystem health.

3.3.4.3. Effect of chromium (Cr) on livestock:

Livestock may suffer from adverse chronic effects such as diarrhoea and possible carcinogenic effects caused by high levels of chromium in the water used for livestock watering. Refer to Appendix A for detailed legislation concerning water quality for livestock watering.

3.3.4.4. Effect of chromium (Cr) on human health:

Small amounts of trivalent chromium (Cr^{3+}) are considered essential in animals and humans. It plays an important role in the maintenance of vascular integrity and, along with insulin, helps to maintain correct cholesterol, fatty acid, glucose, lipid, and protein metabolism. Lack of chromium can result in elevated serum cholesterol levels and could lead to cardiovascular problems. Hexavalent chromium (Cr^{6+}) compounds tend to be oxidisers and are associated with cancer risk and kidney damage (Arthur, 2004; Takkar, 2004; Fraga, 2005). The recommended dietary allowance (RDA) for chromium is shown in table 5.

Table 5: The recommended dietary allowance (RDA) of chromium (Arthur, 2004).

Life Stage		**Age**	**μg/day**
Infants		0-6 months	0.2
		7-12 months	5.5
Children		1-3 years	11
		4-8 years	15
	Male	9-13 years	25
	Female		21
Adolescents	Male	14-18 years	35
	Female		24
Adults	Male	19-50 years	35
	Female		25
	Male	51 years and older	30
	Female		20
Pregnancy		18 years and younger	29
		19 years and older	30
Breastfeeding		18 years and younger	44
		19 years and older	45

Refer to Appendix A for detailed legislation concerning water quality for domestic use. A summary of the TWQR for the different water use sectors (aquatic ecosystem health, domestic and agricultural use) is shown in table 6.

Table 6: Summary of the TWQR for the different water sectors for chromium(VI) (SA-DWAF: Field Guide, 1996).

	TWQR (mg/L)
Aquatic ecosystem health	<0.007 <0.012 – Chromium(III)
Domestic use (Human consumption)	0-0.05
Livestock watering	0-1
Irrigation	0-0.1
Aquaculture	<0.002

3.3.5. Trace element copper (Cu):

Copper (CAS number 7440-50-8) is a reddish metal and is widely distributed in nature. Copper exhibits oxidation states of +2 (the most common, forming Cu(II) compounds), and +1 (Cu(I), stable only in aqueous solution if part of a stable complex ion). Speciation equilibrium calculations can determine the abundance of kinetically labile complexes and of the free metal ion by taking into account the effects of the more abundant ligands in natural waters, particularly the major anions OH^-, Cl^-, SO_4^{2-} and CO_3^{2-}, as shown in figure 5 (Hunter *et al.*, 1999).

Comparing figure 5a with 5b, it can be seen that the amount of ions present and the pH of the river water can have an effect on the concentrations of different copper compounds. In figure 5b, which represents the relatively more polluted river, the concentrations of $CuSO_4$(aq), $CuCl^+$(aq) (dark green lines), $CuHCO_3^+$(aq) and $CuCO_3$(s) (dark blue lines) are higher than in the clean river shown in figure 5a. This demonstrates that high levels of pollutants in rivers can cause higher concentrations of some copper species and therefore also influence the bioavailability and toxicity of copper (Hunter *et al.*, 1999). At low pH, the free Cu^{2+} aquo ion dominates (light green lines in figure 5a and 5b), with lesser amounts of $CuSO_4$(aq) and $CuCl^+$(aq) present (dark green lines). Above pH 6.5, less than 50% of Cu(II) is present as the free Cu^{2+} ion, with more $CuHCO_3^+$(aq) and

$CuCO_3$(s) forming (dark blue lines). Above pH 8, $Cu(OH)_2$(s) starts to become the dominate species (light blue lines). Therefore, as the pH rises, the amount of free Cu^{2+} decreases and thus its bioavailability and toxicity decreases (Hunter *et al.*, 1999).

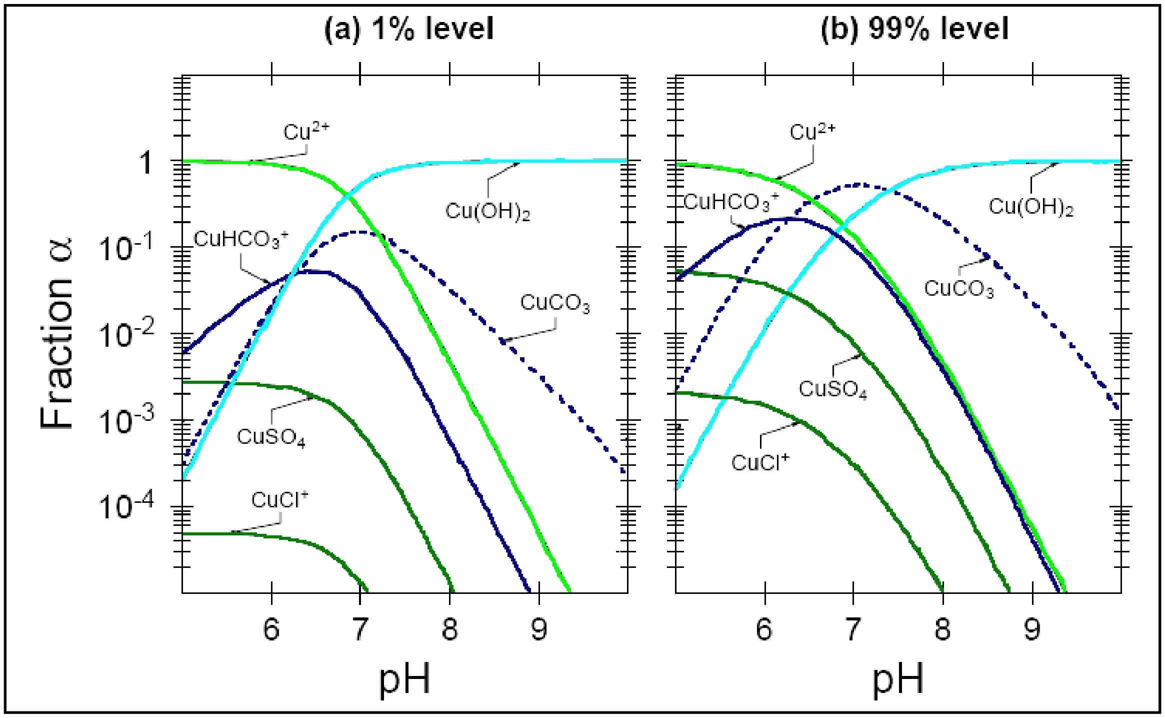


Figure 5: Calculated pH dependence of Cu(II) speciation in two reference river waters corresponding to the (a) 1% and (b) 99% percentile levels. The concentration of Cu^{2+} was set at 1 nmol/L. Vertical axis shows fraction α of total concentration present in the form of each complex (Hunter *et al.*, 1999).

3.3.5.1. Effect of copper (Cu) on plants:

Copper is an essential redox (reduction/oxidation)-active transition metal that is involved in many physiological processes in plants. It acts as a structural element in regulatory proteins and participates in photosynthetic electron transport, mitochondrial respiration, oxidative stress responses, cell wall metabolism and hormone signalling (Kirkby & Römheld, 2004; He *et al.*, 2005; Yruela, 2005). Copper deficiency reduces photosynthesis efficiency and leaves become twisted or malformed and show chlorosis (Kirkby & Römheld, 2004; Cooper, 2005; He *et al.*, 2005; Yruela, 2005). The redox properties that make copper an essential trace element also contribute to its inherent toxicity. Redox cycling between Cu^{2+} and Cu^{+} can catalyse the production of highly toxic hydroxyl radicals, with subsequent damage to DNA, lipids, proteins and other biomolecules. Excess copper can inhibit root growth and cause reduction in leaf size as well as interfere with important cellular processes such as photosynthesis, respiration and manganese (Mn) uptake (Kirkby & Römheld, 2004; He *et al.*, 2005; Yruela, 2005). Refer to Appendix A for detailed legislation concerning water quality for irrigation use.

3.3.5.2. Effect of copper (Cu) on aquatic organisms:

Copper is an essential element for plants and animals (e.g. as enzyme activators) (Ansari *et al.*, 2004). At too low levels of copper, reproductive effects on fish include blockage of spawning, reduced egg production per female, abnormalities in newly-hatched fry, and reduced survival of young (Brix & DeForest, 2000). High concentrations of copper in water can be toxic to many species of algae, crustaceans, annelids, cyprinids, and salmonids (Ansari *et al.*, 2004). Haematology of fish is altered, as is respiratory and cardiac physiology. Copper-induced histological alterations are found in the gill, kidney, and other tissues. Fish living or foraging in contaminated sediments may accumulate it directly from the sediments (Ansari *et al.*, 2004). Refer to Appendix A for detailed legislation concerning water quality for aquacultural use and aquatic ecosystem health.

3.3.5.3. Effect of copper (Cu) on livestock:

Adverse chronic effects in livestock such as diarrhoea and liver damage and acute effects such as haemolytic jaundice are caused by high levels of dissolved copper in water used for livestock watering. Refer to Appendix A for detailed legislation concerning water quality for livestock watering use.

3.3.5.4. Effect of copper (Cu) on human health:

Copper is at the active site of a number of enzymes that are involved in haemoglobin formation, carbohydrate metabolism, oxidant and antioxidant systems, adrenal hormone metabolism and connective tissue metabolism (Arthur, 2004; Takkar, 2004; Fraga, 2005). Copper deficiency can cause abnormal hair, losses of skin and hair pigment and severe problems with the nervous system. Too high levels of copper can cause it to accumulate in the liver, eyes, brain and kidneys from which health problems can occur (Arthur, 2004;

Takkar, 2004; Fraga, 2005). The recommended dietary allowance (RDA) for copper is shown in table 7.

Table 7: The recommended dietary allowance (RDA) for copper (Arthur, 2004).

Life Stage	**Age**	μg/day
Infants	0-6 months	200
	7-12 months	220
Children	1-3 years	340
	4-8 years	440
	9-13 years	700
Adolescents	14-18 years	890
Adults	19 years and older	900
Pregnancy	all ages	1000
Breastfeeding	all ages	1300

Refer to Appendix A for detailed legislation concerning water quality for domestic use. A summary of the TWQR for the different water use sectors (aquatic ecosystem health, domestic and agricultural use) is shown in table 8.

Table 8: Summary of the TWQR for the different water sectors for copper (SA-DWAF: Field Guide, 1996).

	TWQR (mg/L)
Aquatic ecosystem health	<0.0003
Domestic use (Human consumption)	0-1
Livestock watering	0-0.5 – Sheep and pre-weaned calves 0-1 – Cattle 0-5 – Horses, pigs & poultry
Irrigation	0-0.2
Aquaculture	0.005

3.3.6. Trace element iron (Fe):

Iron (CAS number 7439-89-6), is the second-most abundant metal in the Earth's crust and it is vital to all higher forms of life. Iron is found in three oxidation states, namely 0, II and III of which the III oxidation state is the most common. Water with low pH generally have high concentrations of dissolved ferrous ions (Fe^{2+}), while under alkaline conditions the ions oxidise and precipitate out of solution as ferric hydroxide ($Fe(OH)_3$) (Brix & DeForest, 2000).

3.3.6.1. Effect of iron (Fe) on plants:

Although iron is not a component of chlorophyll, it is a structural component of hemes (iron porphyrins) that are incorporated in the plant's cytochromes and enzymes, which are important in the synthesis of chlorophyll. A cytochrome is an iron-containing pigment associated with the electron transport system within the photosynthetic process. Iron is therefore essential for plant growth. To some extent, plants can detoxify excess iron by storing it in chlorophyll iron storage called ferritin, which may act as an iron reserve (Kirkby & Römheld, 2004; He *et al.*, 2005). Refer to Appendix A for detailed legislation concerning water quality for irrigation use.

3.3.6.2. Effect of iron (Fe) on aquatic organisms:

Iron is an essential element in the cellular respiratory process through its oxidation-reduction activity and electron transfer. Fish can absorb soluble iron (Fe^{2+}) from the water through the gills and it is stored in the liver, spleen, and kidneys (Brix & DeForest, 2000; Ansari *et al.*, 2004). Iron deficiency causes microcytic anaemia, suppressed hematocrit, haemoglobin, and plasma iron concentrations; and transferrin saturation. The major effects of iron toxicity include reduced growth, increased mortality, diarrhoea, and histopathological damage to liver cells. Direct precipitation of ferric hydroxide ($Fe(OH)_3$) onto the gills of fish or on incubating eggs interferes with the transport of oxygen (Brix & DeForest, 2000; Ansari *et al.*, 2004). Refer to Appendix A for detailed legislation concerning water quality for aquacultural use.

3.3.6.3. Effect of iron (Fe) on livestock:

Livestock may suffer from adverse chronic and acute effects such as diarrhoea, vomiting, acidosis and respiratory failure and liver and pancreas damage, caused by high levels of iron in the water used for livestock watering. Refer to Appendix A for detailed legislation concerning water quality for livestock watering use.

3.3.6.4. Effect of iron (Fe) on human health:

The major function for iron in the body is as a component of haemoglobin and myoglobin which take part in oxygen metabolism. Iron deficiency along with iodine (I) deficiency is the most widespread trace element related problem in humans. Iron deficiency can cause problems with neurological function that can manifest as impaired cognitive function, reduced attention span and other behavioural abnormalities (Arthur, 2004; Takkar, 2004; Fraga, 2005). If the amount of iron exceeds that which can be coped with by the normal storage methods in the liver, spleen and bone marrow, the free metal ions in the body could cause many damaging oxidative reactions to occur, since iron is very reactive due to its chemistry as a transition metal (Arthur, 2004; Takkar, 2004; Fraga, 2005). The daily recommended intakes for iron in humans are shown in table 9.

Table 9: Recommended dietary allowances (RDA's) for iron (Arthur, 2004).

Life Stage	Age	mg/day
Infants	0-6 months	6
Children	<10 years	10
Males	11-18 years	12
Males	>18 years	10
Females	11-50 years	15
Females	>50 years	10
Pregnancy		30
Lactation		15

Refer to Appendix A for detailed legislation concerning water quality for domestic use. A summary of the TWQR for the different water use sectors (aquatic ecosystem health, domestic and agricultural use) is shown in table 10.

Table 10: Summary of the TWQR for the different water sectors for iron (SA-DWAF: Field Guide, 1996).

	TWQR (mg/L)
Aquatic ecosystem health	Not available
Domestic use (Human consumption)	0-0.1
Livestock watering	0-10
Irrigation	0-5
Aquaculture	0.01

3.3.7. Trace element manganese (Mn):

Manganese (CAS number 7439-96-5) is a white-grey, brittle, and reactive metal. It is the 12th most abundant element and is widely distributed in soils, sediments, rocks, water, and biological materials. Manganese exists in the aquatic environment in two main forms: Mn^{2+} (Mn(II)) and Mn^{4+} (Mn(IV)). Transition between these two forms occurs via oxidation and reduction reactions that may be abiotic or microbially mediated. The environmental chemistry of manganese is largely governed by pH and redox conditions; Mn(II) dominates at lower pH and redox potential, with an increasing proportion of colloidal manganese oxyhydroxides forming above pH 5.5 (Brix & DeForest, 2000).

3.3.7.1. Effect of manganese (Mn) on plants:

Manganese is an essential trace element throughout all stages of plant development since it is important for vital plant functions. The main roles of manganese in plants are in the synthesis of chlorophyll, assimilation of nitrate, and activation of enzymes for fat biosynthesis. It also functions in the formation of riboflavin, ascorbic acid and carotene (Kirkby & Römheld, 2004; He *et al.*, 2005). The major symptom of manganese deficiency is a reduction in the efficiency of photosynthesis leading to a general decline in dry matter productivity and yield (Kirkby & Römheld, 2004; He *et al.*, 2005).

Manganese toxicity is a major factor for reduced production of crops grown in acid soils (Kirkby & Römheld, 2004; He *et al.*, 2005). Excess manganese can result in apoplastic deposition of oxidised manganese and phenolics. Manganese in the soil, present mainly as manganese ions (Mn^{2+}), is readily taken up by roots and transported to shoots. On older leaves, toxicity symptoms generally appear as small, distinct, dark-brown spots, necrotic lesions, and chlorosis of leaf edges and tips. In a typical sequence of symptom development, chlorotic (yellowed) areas appear on the leaves, the areas subsequently change to dark brown spots, the leaves desiccate (dry), and the leaves fall. The symptoms resemble those of calcium (Ca) deficiency (Kirkby & Römheld, 2004; He *et al.*, 2005). Refer to Appendix A for detailed legislation concerning water quality for irrigation use.

3.3.7.2. Effect of manganese (Mn) on aquatic organisms:

Manganese functions as an integral part of certain metallo-enzymes in carbohydrate, lipid, and protein metabolism. Manganese deficiency causes reduced growth and skeletal abnormalities in fish and can also cause poor hatchability and low manganese concentration in the eggs (Brix & DeForest, 2000). Entry of dissolved manganese into fish occurs mainly via gill transport and is accumulated in the liver. High concentrations of manganese interfere with the central nervous system by inhibiting the formation of the neurotransmitter dopamine (Brix & DeForest, 2000; Ansari *et al.*, 2004). High levels of manganese can induce iron (Fe) deficiency in some algae, notably blue-green algae, and this can lead to inhibition of chlorophyll synthesis. It can bioaccumulate in lower organisms (e.g., phytoplankton, algae, molluscs and some fish) but not in higher organisms (Brix & DeForest, 2000; Ansari *et al.*, 2004). Refer to Appendix A for detailed legislation concerning water quality for aquatic ecosystem health.

3.3.7.3. Effect of manganese (Mn) on livestock:

Signs of manganese deficiency in animals include impaired growth, impaired reproductive function, skeletal abnormalities, impaired glucose tolerance, and altered carbohydrate and lipid metabolism. Livestock may suffer from adverse chronic effects such as weight loss and anaemia caused by high levels of manganese in the water used for livestock watering. Refer to Appendix A for detailed legislation concerning water quality for livestock watering use.

3.3.7.4. Effect of manganese (Mn) on human health:

In humans, manganese is an essential trace element that plays a major role as an enzyme activator as well as in bone mineralisation, carbohydrate, amino acid, and cholesterol metabolism, metabolic regulation, and cellular protection from damaging free radical species. It is also necessary for the formation of connective tissue, and for growth, the embryonic development of the inner ear, and reproductive functions (Arthur, 2004; Takkar, 2004; Fraga, 2005).

Signs of manganese deficiency include impaired growth, impaired reproductive function, skeletal abnormalities, impaired glucose tolerance, and altered carbohydrate and lipid metabolism (Arthur, 2004; Takkar, 2004; Fraga, 2005). Manganese toxicity is an infrequent but serious human health hazard, resulting in severe and often irreversible disorders of the central nervous system (Arthur, 2004; Takkar, 2004; Fraga, 2005; Paschke *et al.*, 2005). The recommended dietary allowance (RDA) for manganese is given in table 11.

Table 11: The recommended dietary allowance (RDA) for manganese (Arthur, 2004).

Life Stage		**Age**	**mg/day**
Infants		0-6 months	0.003
		7-12 months	0.6
Children		1-3 years	1.2
		4-8 years	1.5
	Male	9-13 years	1.9
	Female		1.6
Adolescents	Male	14-18 years	2.2
	Female		1.6
Adults	Male	19 years and older	2.3
	Female		1.8
Pregnancy		All ages	2.0
Breastfeeding		All ages	2.6

Refer to Appendix A for detailed legislation concerning water quality for domestic use. A summary of the TWQR for the different water use sectors (aquatic ecosystem health, domestic and agricultural use) is shown in table 12.

Table 12: Summary of the TWQR for the different water sectors for manganese (SA-DWAF: Field Guide, 1996).

	TWQR (mg/L)
Aquatic ecosystem health	<0.18
Domestic use (Human consumption)	0-0.05
Livestock watering	0-10
Irrigation	0-0.02
Aquaculture	<0.1

3.3.8. Trace element nickel (Ni):

Nickel (CAS number 7440-02-0) is a hard, silvery metal, abundant in the earth's crust. Divalent nickel (Ni^{2+}) is the primary aqueous form, however, the specific speciation can be established by equilibrium calculations (as shown in figure 6). A comparison of figure 6a and 6b shows that the amount of ions present and the pH of the river water can influence the concentrations of different nickel compounds. In figure 6b (the relatively more polluted river), the concentrations of $NiHCO_3^+$(aq), $NiSO_4$(aq), $NiCl^+$(aq) (dark green lines) and $Ni(CO_3)_2^{2-}$(aq) (dark blue line) are higher than in figure 6a (the relatively clean river). This shows that high levels of pollutants in rivers can cause higher concentrations of some nickel species and therefore also influence the bioavailability and toxicity of nickel (Hunter *et al.*, 1999). At low pH, the free Ni^{2+} aquo ion dominates (light green lines in figure 6a and 6b), with lesser amounts of $NiHCO_3^+$(aq), $NiSO_4$(aq) and $NiCl^+$(aq) present (dark green lines). Above pH 6.5, $NiCO_3$(s) predominates (light

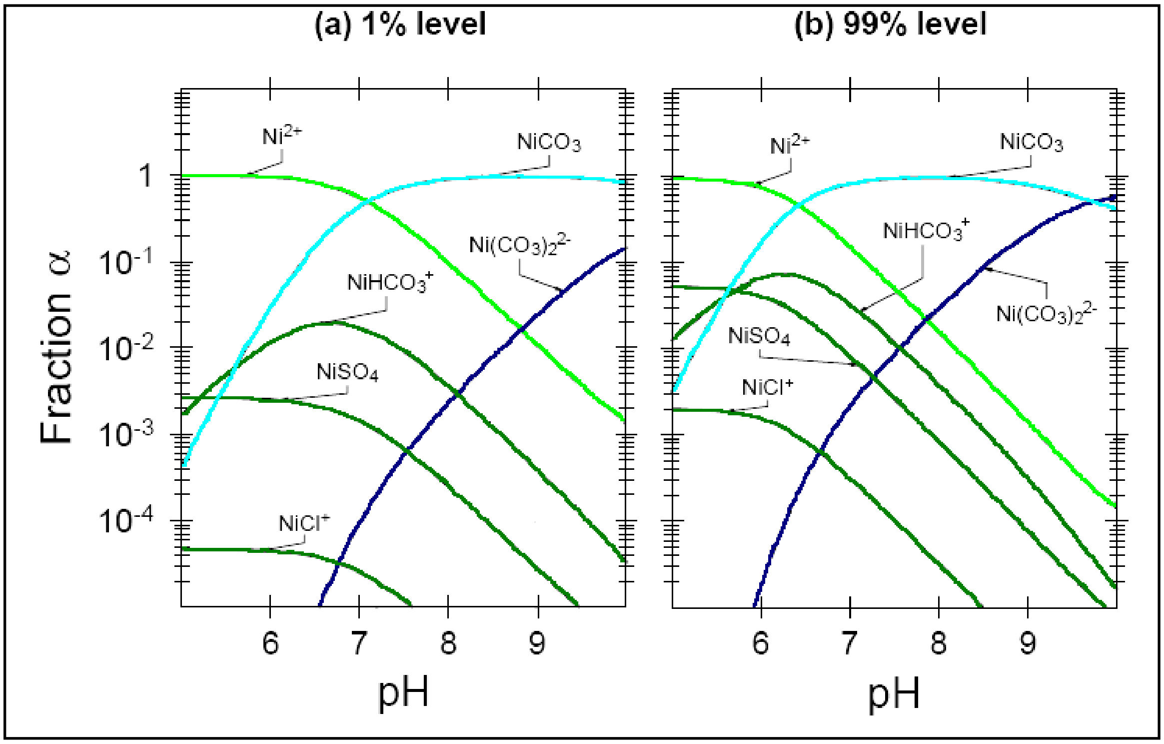


Figure 6: Calculated pH dependence of Ni(II) speciation in two reference river waters corresponding to the (a) 1% and (b) 99% percentile levels. The concentration of Ni^{2+} was set at 1 nmol/L. Vertical axis shows fraction α of total concentration present in the form of each complex (Hunter *et al.*, 1999).

blue lines), with smaller amounts of $Ni(CO_3)_2^{2-}(aq)$ present (dark blue lines). The free aquo ion, Ni^{2+}, can also adsorb to suspended organic matter. Therefore, as the pH rises, less free Ni^{2+} is present and so its bioavailability and toxicity also decreases (Hunter *et al.*, 1999).

3.3.8.1. Effect of nickel (Ni) on plants:

Nickel is necessary for healthy plant growth. It is an important component of urease, thus affecting nitrogen transformation reactions in certain legumes and microorganisms. Symptoms of nickel toxicity are iron (Fe) deficiency induced chlorosis, germination inhibition, foliar necrosis, abnormal flower shape, inhibited root growth (thus affecting nutrient absorption by the roots), and inhibited metabolism, photosynthesis and transpiration. Nickel can replace cobalt (Co) and other heavy metals located at active sites in metallo-enzymes and disrupt their functioning (Kirkby & Römheld, 2004; Cooper, 2005; He *et al.*, 2005). Refer to Appendix A for detailed legislation concerning water quality for irrigation use.

3.3.8.2. Effect of nickel (Ni) on aquatic organisms:

In natural waters, nickel occurs in the +2 valency state (Ni^{2+}) and is responsible for eliciting a toxic response in aquatic organisms (Brix & DeForest, 2000; Ansari *et al.*, 2004). The bioaccumulation and bioconcentration of nickel is moderate for mammals, birds, and fish, while the potential for bioaccumulation appears to be highest for molluscs, crustaceans, lower animals, mosses, lichens, algae, and higher plants (Brix & DeForest, 2000). However, little data is available regarding chronic toxicity of nickel in survival and reproduction of aquatic organisms (Ansari *et al.*, 2004).

3.3.8.3. Effect of nickel (Ni) on livestock:

Nickel deprivation has an effect on body weight, reproductive capability, viability of offspring, and induction of anaemia through reduced absorption of iron (Fe). Livestock may suffer from adverse chronic effects such as reduced growth and decreased body weight, increase in still births, decrease in birth weight of offspring and reduced reproductive capability caused by high levels of nickel in the water used for livestock watering. Refer to Appendix A for detailed legislation concerning water quality for livestock watering use.

3.3.8.4. Effect of nickel (Ni) on human health:

Although nickel-specific enzymes have yet to be identified in higher animals, nickel can activate or inhibit a number of enzymes that usually contain other elements. The production or action of some hormones responds to changes in nickel concentration. Within cells, nickel alters membrane properties and influences oxidation/reduction systems. Nickel has great affinity for cellular structures such as chromosomes and ion channels. Nickel deficiency has been linked to low blood glucose levels, abnormal bone growth, poor absorption of ferric iron (Fe^{3+}), and altered metabolism of calcium (Ca), vitamin B_{12} and energy nutrients.

High levels of nickel may upset the hormonal balance of the mother and can impair the development of the embryo. Acute toxicity following ingestion of high concentrations of nickel includes adverse effects on the gastrointestinal system, blood, and kidneys. Excessive nickel in tissues is pro-oxidant (damaging chromosomes and other cell components) and alters hormone and enzyme activities, movement of ions through membranes, and immune function. These effects can change glucose tolerance, blood pressure, response to stress, growth rate, bone development and resistance to infection. Under some conditions, large amounts of nickel may cause magnesium (Mg) deficiency or cause accumulation of iron (Fe) or zinc (Zn). A summary of the TWQR for nickel for the different water use sectors (aquatic ecosystem health, domestic and agricultural use) is shown in table 13.

Table 13: Summary of the TWQR for the different water sectors for nickel (SA-DWAF: Field Guide, 1996).

	TWQR (mg/L)
Aquatic ecosystem health	Not available
Domestic use (Human consumption)	Not available
Livestock watering	0-1
Irrigation	0-0.20

Aquaculture	Not available

3.3.9. Trace element lead (Pb):

Lead (CAS number 7439-92-1) is a naturally occurring, bluish-grey metal originating in the earth's crust. It is odourless, tasteless, and has no known physiological value. The vast majority of lead compounds are inorganic. The speciation of lead in water, as shown in figure 7, can be determined by equilibrium calculations. A comparison of figure 7a and 7b reveals that the amount of ions in the river as well as the pH can influence the concentrations of different lead compounds. In figure 7b, representing the relatively more polluted river, the concentrations of $PbHCO_3^+$(aq), $PbSO_4$(s), $PbCl^+$(aq) (dark green lines) and $Pb(CO_3)_2^{2-}$(aq) (dark blue line) are higher than in figure 7a, which shows the relatively clean river. However, the concentrations of $Pb(OH)^+$(aq) and $Pb(OH)_2$(s) (dark blue lines) are lower in figure 7b than in 7a. This shows that the level of pollutants in a river can have a noticeable influence on the concentration of different species of lead and therefore also the bioavailability and toxicity of lead (Hunter *et al.*, 1999). At low pH,

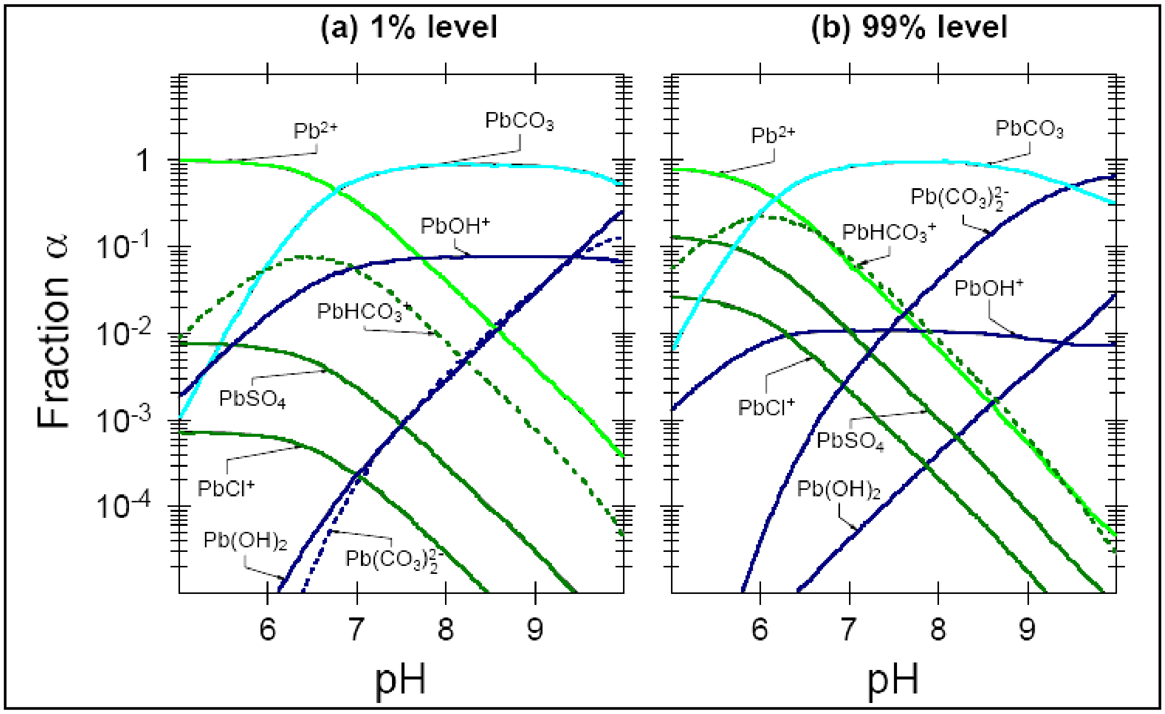


Figure 7: Calculated pH dependence of Pb(II) speciation in two reference river waters corresponding to the (a) 1% and (b) 99% percentile levels. The concentration of Pb^{2+} was set at 1 nmol/L. Vertical axis shows fraction α of total concentration present in the form of each complex (Hunter *et al.*, 1999).

the free Pb^{2+} aquo ion is dominant (light green lines in figure 7a and 7b), with lesser amounts of $PbHCO_3^+(aq)$, $PbSO_4(s)$ and $PbCl^+(aq)$ present (dark green lines). Above pH 6, $PbCO_3(s)$ becomes dominant (light blue lines), with smaller amounts of $Pb(OH)^+(aq)$, $Pb(CO_3)_2^{2-}(aq)$ and $Pb(OH)_2(s)$ present (dark blue lines). Soluble lead (Pb) is adsorbed strongly by suspended clay, humic substances and other suspended material (Brix & DeForest, 2000). Therefore, as the pH rises, less free Pb^{2+} is present and so its bioavailability and toxicity also decreases (Hunter *et al.*, 1999).

3.3.9.1. Effect of lead (Pb) on plants:

Although lead is not an essential element for plants, it is easily absorbed and accumulated in different plant parts (Sharma & Dubey, 2005). At elevated levels in plants, lead causes a number of toxicity symptoms in plants, as shown in figure 8. These include reductions in nutrient uptake, enzyme activity and ability to photosynthesise. Refer to Appendix A for detailed legislation concerning water quality for irrigation use.

3.3.9.2. Effect of lead (Pb) on aquatic organisms:

Lead is very toxic to aquatic organisms. Lead tends to bioaccumulate in fish, mussels, clams, algae, and macrophytes (Ansari *et al.*, 2004). In fish, lead deposits in active calcification areas such as scales, fin rays, and vertebrae to a much greater extent than in muscle tissue. Therefore, the availability in edible portions does not pose a human health danger. Benthic fish may accumulate lead directly from the sediments (Brix & DeForest, 2000; Ansari *et al.*, 2004). Fish exposed to high levels of lead exhibit a wide range of effects including muscular and neurological degeneration and destruction, growth inhibition, mortality, reproductive problems, and paralysis. Lead exposure can also lead to excess mucous formation which can coat the gills and impact respiration (Brix & DeForest, 2000; Ansari *et al.*, 2004). Refer to Appendix A for detailed legislation concerning water quality for aquacultural use and aquatic ecosystem health.

3.3.9.3. Effect of lead (Pb) on livestock:

In birds, lead has been implicated in decreases in eggshell thickness, growth, ovulation, and sperm formation. Chronic lead poisoning in sheep causes abortion, miscarriage and transitory sterility. Livestock may suffer from adverse chronic effects such as anorexia, emaciation, respiratory distress, excessive excitability, frothing from the mouth, muscular tremors, convulsions and hind limb incoordination caused by high levels of lead in the water used for livestock watering. Refer to Appendix A for detailed legislation concerning water quality for livestock watering use.

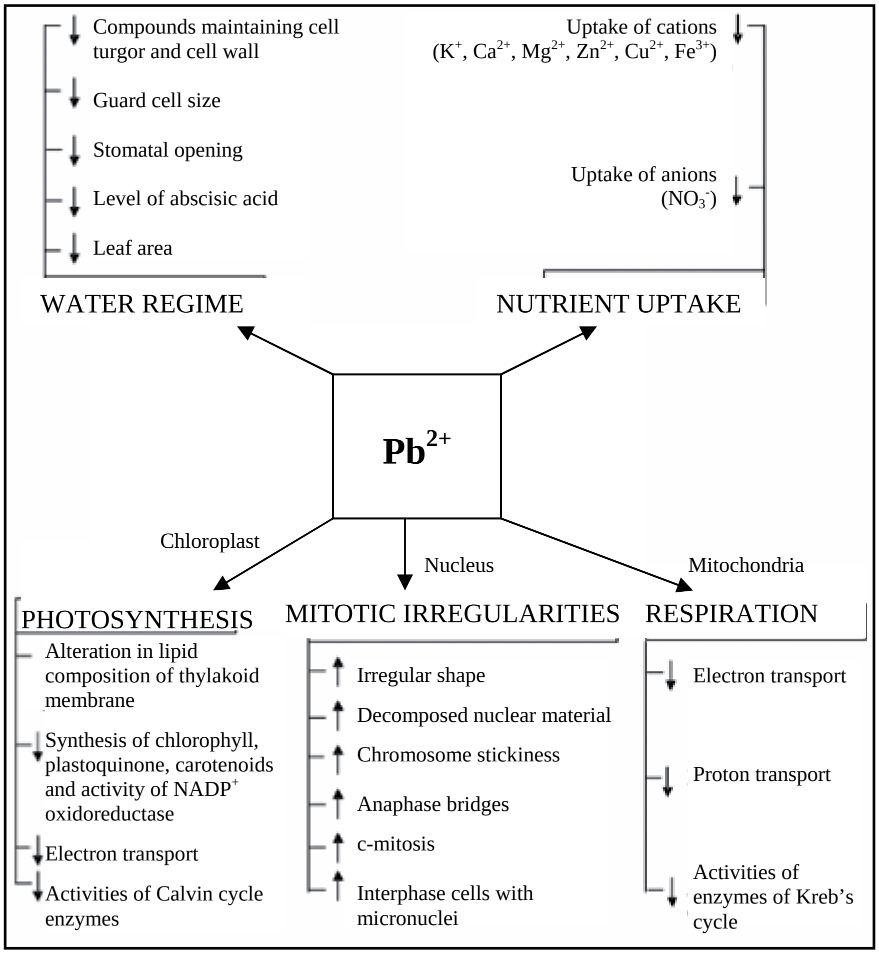


Figure 8: Effect of lead (Pb) on photosynthesis, mitotic irregularities, respiration, water regime and nutrient uptake. '↑' and '↓' signs represent enhanced and decreased activities respectively (Sharma & Dubey, 2005).

3.3.9.4. Effect of lead (Pb) on human health:

Lead serves no useful purpose in the human body, and its presence in the body can lead to toxic effects in every organ. Lead is cancer-causing and adversely affects the peripheral and central nervous systems, reproduction, liver and thyroid function, and disease resistance. Absorbed lead that is not excreted is exchanged primarily among three compartments: blood; soft tissue (liver, kidneys, lungs, brain, spleen, muscles, and heart); and mineralising tissues (bones and teeth), which typically contain the vast majority of the lead body burden. Initial symptoms of lead poisoning include: anorexia, insomnia, tremor, weakness, fatigue, nausea and vomiting, mood shifts such as aggression or depression, and impairment of memory. In the case of acute lead poisoning, possible health effects include mania, convulsions, delirium, fever, coma, and in some cases even death. Children exposed to lead may experience devastating consequences because of the effects of lead on the developing brain (Hill, 2004). Refer to Appendix A for detailed legislation concerning water quality for domestic use. A summary of the TWQR for the different water use sectors (aquatic ecosystem health, domestic and agricultural use) is shown in table 14.

Table 14: Summary of the TWQR for the different water sectors for lead (SA-DWAF: Field Guide, 1996).

	TWQR (mg/L)
Aquatic ecosystem health	<0.0002
Domestic use (Human consumption)	0-0.01
Livestock watering	0-0.1 – All other livestock 0-0.5 – Pigs
Irrigation	0-0.2
Aquaculture	0-0.01

3.3.10. Trace element zinc (Zn):

Zinc (CAS number 7440-66-6), a bluish-white shiny metal, is the 25th most abundant element and is widely distributed in nature. Speciation equilibrium calculations can determine the speciation of zinc in water, as shown in figure 9. Comparing figure 9a with 9b, it can be seen that the amount of ions present and the pH of the river water can influence the concentrations of different zinc compounds. In figure 9b, representing the relatively more polluted river, the concentrations of $ZnSO_4$(aq) and $ZnCl^+$(aq) (dark green lines) are higher than in figure 9a. However, the concentration of $Zn(OH)_2$(s) (light blue line) is lower in figure 9b than in 9a. This shows that the level of pollutants in a river can have a marked influence on the concentration of different species of zinc and

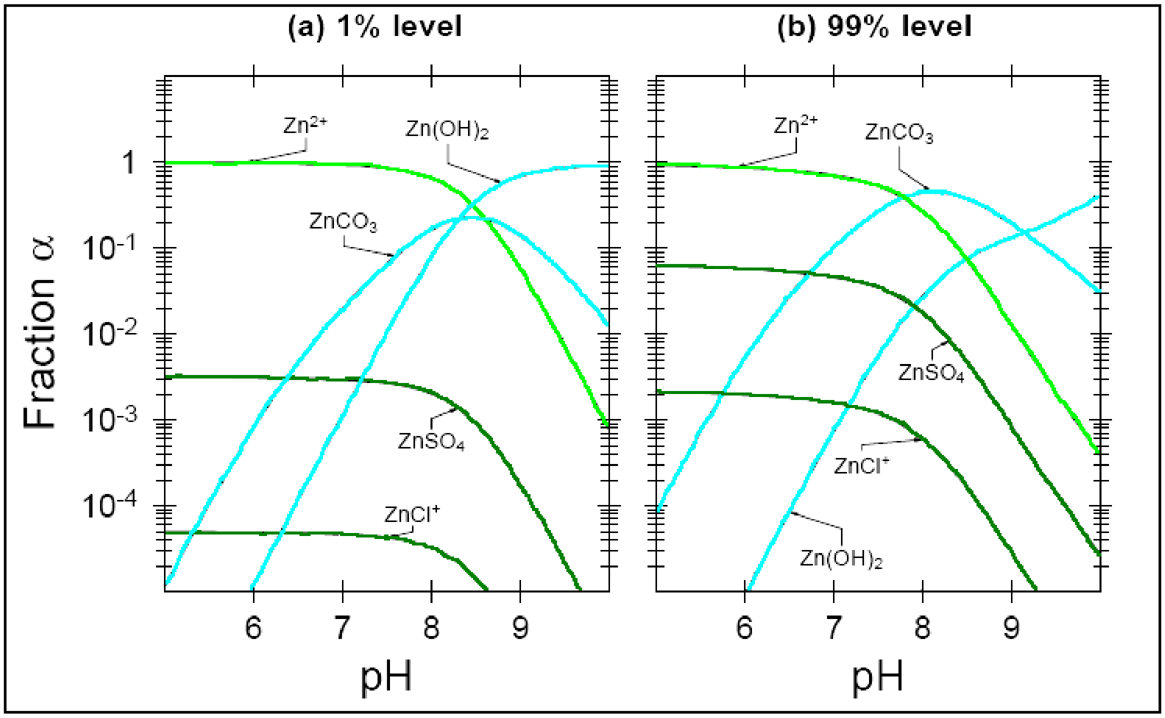


Figure 9: Calculated pH dependence of Zn(II) speciation in two reference river waters corresponding to the (a) 1% and (b) 99% percentile levels. The concentration of Zn^{2+} was set at 1 nmol/L. Vertical axis shows fraction α of total concentration present in the form of each complex (Hunter *et al.*, 1999).

therefore also the bioavailability and toxicity of zinc (Hunter *et al.*, 1999). At low pH, the free Zn^{2+} aquo ion dominates (light green lines in figure 9a and 9b), with lesser amounts of $ZnSO_4$(aq) and $ZnCl^+$(aq) present (dark green lines). Above pH 8, $Zn(OH)_2$(s) and $ZnCO_3$(s) predominates (light blue lines). Therefore, as the pH rises, the amount of free Zn^{2+} decreases and thus its bioavailability and toxicity decreases (Hunter *et al.*, 1999).

3.3.10.1. Effect of zinc (Zn) on plants:

Zinc is a vital trace element for a wide range of crops such as cereals, beans, tree fruits, and vegetables. It plays an important role in enzyme activation and is involved in protein synthesis and carbohydrate, nucleic acid and lipid metabolism. Zinc deficiency can cause losses of up to 30% of the crop yield, as well as reduce crop quality (Stoyanova & Doncheva, 2002; Kirkby & Römheld, 2004; Cooper, 2005; He *et al.*, 2005). However, when zinc is accumulated in excess in plant tissues, it causes alterations in vital growth processes such as photosynthesis and chlorophyll biosynthesis and membrane integrity. Excess zinc causes leaf chlorosis and root browning as well as significantly depressing the fresh mass of leaves, stems and roots (Stoyanova & Doncheva, 2002; Kirkby & Römheld, 2004; He *et al.*, 2005). Refer to Appendix A for detailed legislation concerning water quality for irrigation use.

3.3.10.2. Effect of zinc (Zn) on aquatic organisms:

Elevated concentrations of zinc in water are particularly toxic to many species of algae, crustaceans, and salmonids, causing disruptions to the internal ion balance. Fish living or foraging in sediments contaminated by zinc may accumulate zinc directly from the sediments (Brix & DeForest, 2000; Ansari *et al.*, 2004). Refer to Appendix A for detailed legislation concerning water quality for aquacultural use and aquatic ecosystem health.

3.3.10.3. Effect of zinc (Zn) on livestock:

Adverse chronic effects in livestock such as inappetence, anaemia, and diarrhoea are caused by high levels of dissolved zinc in water used for farming practices. Refer to Appendix A for detailed legislation concerning water used for livestock watering.

3.3.2.4. Effect of zinc (Zn) on human health:

In humans, some zinc in the diet is essential for normal growth and maturation, cell metabolism, development of reproductive organs, prevention of anaemia, functioning of the prostate gland, healing of wounds, enzyme activity, regulating zinc dependent enzymes, manufacture of proteins, and manufacture of nucleic acids (Arthur, 2004; Takkar, 2004; Fraga, 2005; Laker, 2005). The most frequently demonstrated effects of zinc deficiency in humans are dermatitis, emaciation, testicular atrophy, anorexia, impaired growth in children, immuno-suppression and infertility (Arthur, 2004; Takkar, 2004; Fraga, 2005). Prolonged excessive dietary intake of zinc can lead to deficiencies in iron (Fe) and copper (Cu), nausea, vomiting, fever, headache, tiredness, and abdominal pain (Arthur, 2004; Takkar, 2004; Fraga, 2005). The recommended dietary allowance (RDA) for zinc is shown in table 15.

Table 15: Recommended dietary allowances (RDA's) for zinc (Arthur, 2004).

Life Stage	**Age**	**mg/day**
Infants		5
Children	<10 years	10
Males	>10 years	15
Females	>10 years	12
Pregnancy		15
Lactation	0-6 months	19
	7-12 months	16

Refer to Appendix A for detailed legislation concerning water quality for domestic use. A summary of the TWQR for the different water use sectors (aquatic ecosystem health, domestic and agricultural use) is shown in table 16.

Table 16: Summary of the TWQR for the different water sectors for zinc (SA-DWAF: Field Guide, 1996).

	TWQR (mg/L)
Aquatic ecosystem health	<0.002
Domestic use (Human consumption)	0-3
Livestock watering	0-20
Irrigation	0-1
Aquaculture	<0.03

Where water acts as the primary conveyor of pollution such as heavy metals, preventative measures can reduce environmental impacts by preventing these pollutants from entering the hydrologic cycle (CGER, 1999).

3.4. Best Management Practices (BMP's) to mitigate pollution:

Best Management Practices (BMP's) are used as a qualitative tool for protecting the environment. They are designed to reduce the impact of accidental spills or the release of contaminants. Pollutant removal mechanisms employed by urban BMP's include settling and biological processes (VDCR, 1999; CGER, 2000).

Settling or sedimentation is limited to pollutants, such as heavy metals, that are attached to heavier sediment particles or suspended solids (called particulate pollutants) which drop out of the water column by way of gravitational settling. BMP's which utilise settling (dams and sediment forebays, for example) are usually suited for dual purposes, that is they can also provide storage volume for peak rate control, channel erosion, and/or flood control (VDCR, 1999; CGER, 2000).

Biological processes are the most effective removal mechanisms for soluble pollutants, such as heavy metals associated with highway rainfall runoff. A combination of shallow permanent pool depths and abundant vegetation help to create conditions which allow a natural food chain to develop. Marsh plants, algae and bacteria can then take up these soluble compounds. BMP's suited for this pollutant removal mechanism include enhanced detention and retention basins, and constructed wetlands (VDCR, 1999; CGER, 2000).

Many highway runoff BMP's will utilise a combination of settling and biological processes. In some cases, after a BMP has been in operation for a period of time, a layer of organic matter will develop within the BMP, thereby increasing its adsorption potential and enhancing the removal of soluble pollutants. BMP's which include plants and grasses also display increased pollutant removal efficiency over time as the biomass increases. As the vegetation thickens, it serves to slow the velocity of the runoff through the BMP. This allows for increased gravitational settling and filtering of pollutants, as well as decreased export of sediment and attached pollutants *via* erosion (VDCR, 1999; CGER, 2000).

Three of the BMP's that are most effective for the removal of dissolved heavy metals associated with highway rainfall runoff are discussed below.

3.4.1. Infiltration basins:

An infiltration basin is a vegetated, open impoundment where incoming rainfall runoff is stored until it gradually infiltrates into the soil strata. Infiltration effectively prevents pollutants in the captured runoff from reaching surface waters, as well as help recharge groundwater, thus helping to maintain low flows in stream systems. An infiltration basin provides for long-term water quality enhancement of rainfall runoff and is considered one of the most reliable and versatile BMP's available. The high removal rates of particulate and soluble pollutants are achieved through gravitational settling, biological uptake and decomposition (VDCR, 1999; CGER, 2000).

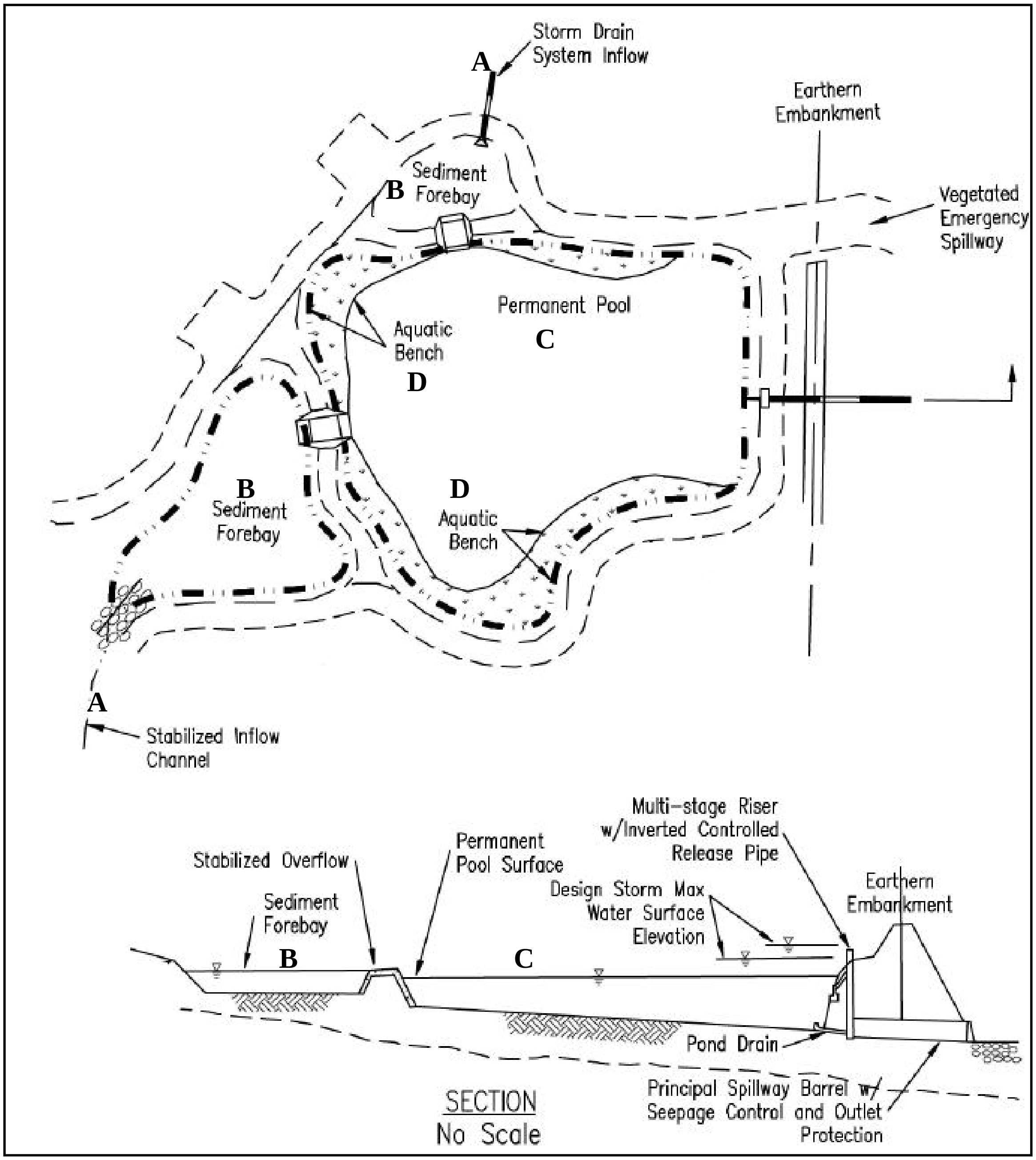


Figure 10: Schematic of an infiltration basin design (VDCR, 1999).

A conceptual schematic illustration of an infiltration basin is shown in figure 10. Infiltration basins should always be preceded by a pre-treatment facility, such as a sediment forebay (B in figure 10) where grease, oil, floatable organic materials, and settleable solids are removed from the runoff (entering from A) before it flows to the infiltration basin. Around the permanent pool (C) of the infiltration basin, an aquatic bench (D) is located. This bench provides suitable conditions for a variety of aquatic plants and associated algae, bacteria and other microorganisms that reduce organic matter and dissolved pollutants. In addition, aquatic bench vegetation provides an ideal habitat for wildlife, such as waterfowl and fish, and for predator insects that feed on mosquitoes and other nuisance insects. An aquatic bench also serves to stabilise and protect the shoreline from erosion resulting from fluctuating water levels.

Infiltration basins may be rejected as a viable BMP if groundwater quality is a concern, however, infiltration basins are relatively cost-effective practices since little infrastructure is needed when constructing them (VDCR, 1999).

3.4.2. Wet ponds and wetlands:

Wetlands provide physical, chemical, and biological water quality treatment of highway rainfall runoff. Physical treatment occurs as a result of decreasing flow velocities in the wetland, and is present in the form of evaporation, sedimentation, adsorption, and/or filtration. Chemical processes include chelation, precipitation, and chemical adsorption. Biological processes include decomposition, plant uptake and removal of nutrients, plus biological transformation and degradation. The large surface area of the bottom of the wetland encourages higher levels of adsorption, absorption, filtration, microbial transformation, and biological utilisation than might normally occur in more channelised water courses. Wetlands can also be constructed to remove heavy metals associated with highway rainfall runoff (VDCR, 1999; Beitia *et al.*, 2003).

3.4.2.1. Artificial wetlands:

Artificial wetlands offer natural aesthetic qualities, wildlife habitat, erosion control, and pollutant removal from highway rainfall runoff (VDCR, 1999; Beitia *et al.*, 2003). The wetland should be designed such that a minimum amount of maintenance is required. This can be done by utilising the natural surroundings, including the potential energy of a stream or a flooding river. The selection of vegetation should be limited to native plant species suitable for the pool depths expected within the different depth zones (shown in figure 11). Rainfall runoff (entering from A in figure 11) first flows into a sediment forebay (B) where settleable solids are removed before it flows to the permanent pool of the artificial wetland. Four depth zones are needed within the permanent pool: deep pool (C), low marsh (D), high marsh (E), and semi-wet (F). These different depth zones support a wide diversity of aquatic plants to maximise pollutant removal efficiency (VDCR, 1999).

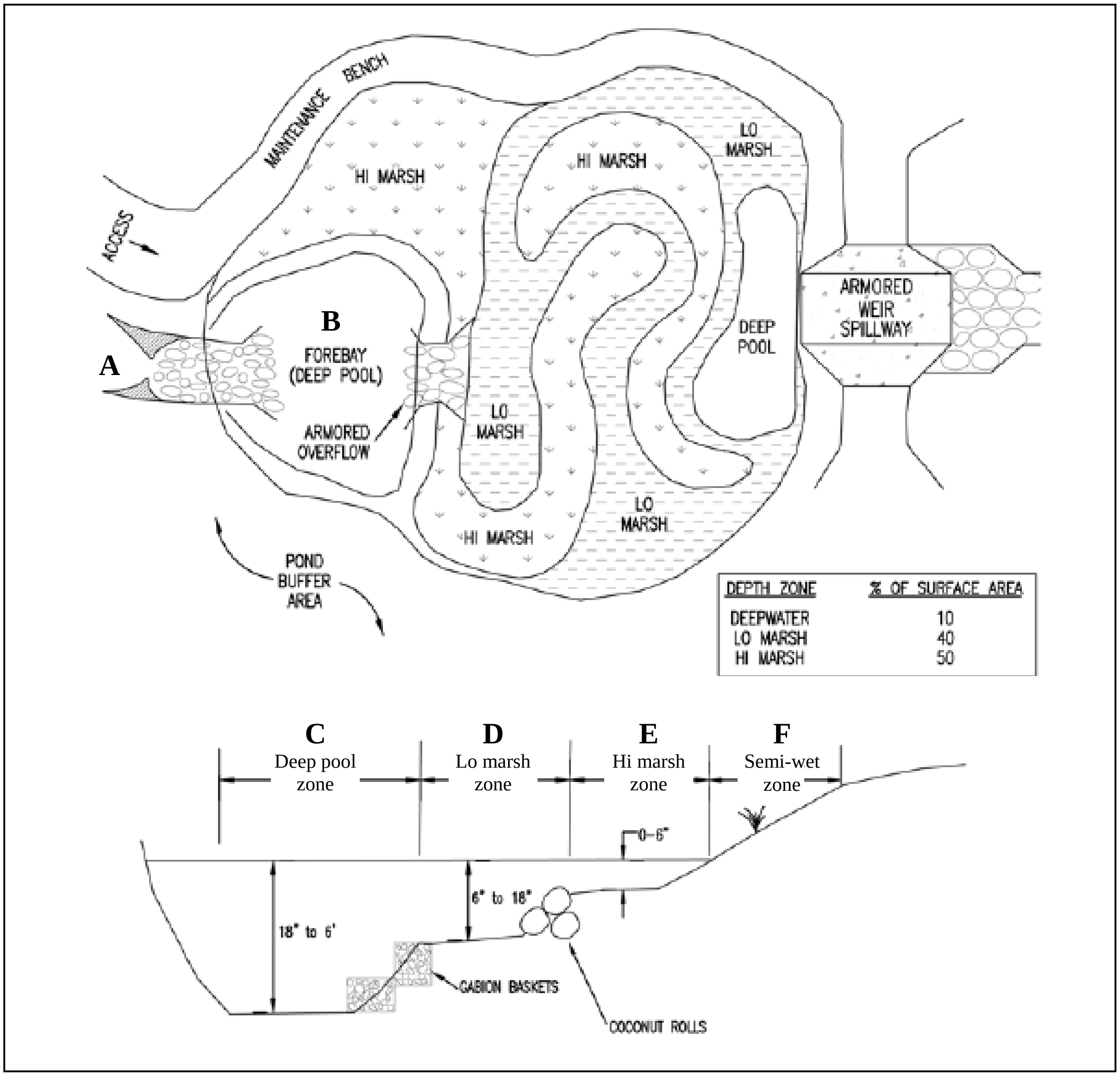


Figure 11: Plan and profile of an artificial wetland (VDCR, 1999).

It is necessary to recognise that a fully functional wetland cannot be established spontaneously. Time is required (one to two years) for vegetation to establish and for nutrient retention and wildlife enhancement to function efficiently. Also, the wetland should approximate a natural situation as much as possible, and unnatural attributes, such as a rectangular shape or a rigid channel, should be avoided. The wetland may be designed as either a stand-alone BMP, or as part of a larger non-point source treatment facility in conjunction with other devices, such as an infiltration basin (VDCR, 1999; Beitia *et al.*, 2003).

3.4.3. Biofiltration strips and swales:

Biofiltration strips and swales are designated treatment zones that receive rainfall runoff from the highway or other impervious surfaces, as shown in figure 12. They are sections of land vegetated with erosion resistant and flood tolerant grasses (such as Vetiver grass (*Vetiveria zizanioides*) (Dalton *et al.*, 1996)) over which rainfall runoff (from A in figure 12) flows as overland sheet flow before leaving a site or entering a storm sewer system. Check dams and trenches (B in figure 12) can also be used to slow the flow rate and create small, temporary ponding areas. Pollutants associated with highway rainfall runoff (such as heavy metals) are removed by filtration through and absorption by the vegetation; sedimentation; adsorption to soil particles; and infiltration through the soil (VDCR, 1999; Lantin & Alderete, 2002; Scharff *et al.*, 2003).

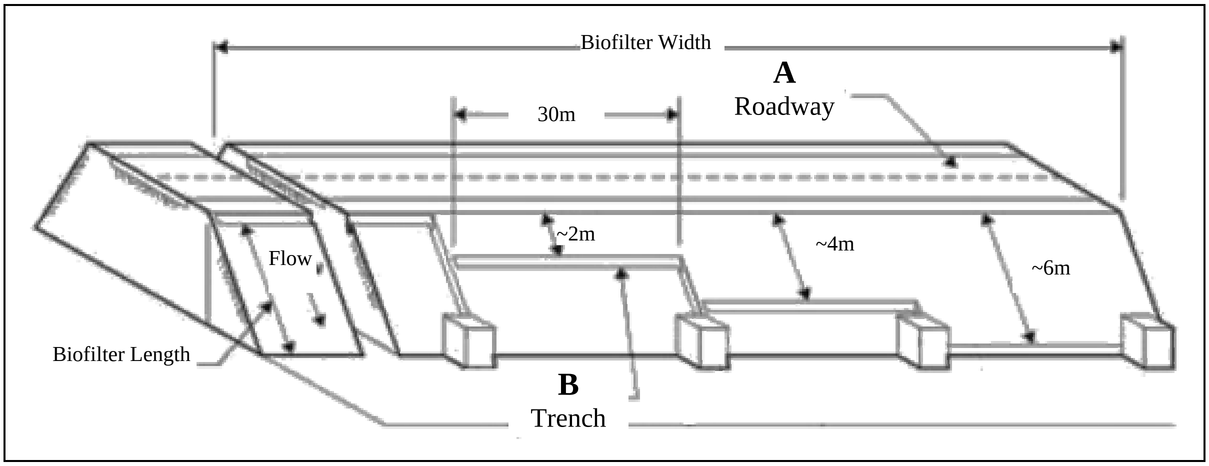


Figure 12: Schematic of a biofiltration strip and swale (Lantin & Alderete, 2002).

The data from highway monitoring sites can only be effectively analysed for significant information if there is a thorough knowledge of the relevant legislation as well as general understanding of the effects that heavy metals have on the environment, as discussed in this section. As a result, it is now possible to discuss in more detail the location of the study sites in the next section and to subsequently evaluate the results obtained from these monitoring sites.

4. Location of the study area:

4.1. Introduction:

South Africa's available freshwater resources are almost fully-utilised and under severe stress (Harris *et al.*, 1999). Water will increasingly become the limiting resource in South Africa, and supply will become a major restriction to the future development of the country, in terms of both the amount and quality of water available. At present many water resources contain large amounts of pollutants, such as dissolved metal elements (DME) (metals and metal compounds that is in a dissolved state in water), particulate-bound metal elements (PME) (metals and metal compounds that are insoluble or attached to particles such as sand), and suspended, colloidal and volatile fractions of these particulates (Sansalone *et al.*, 1996; Su & Mitchell, 2003). It is therefore important to monitor the levels of these heavy metals in the rivers and lakes of the country, especially in sites that are close to pollutant producing areas, such as mines, industrial sites, cities and towns, and roads.

Roads are the cornerstone of modern civilisation. They are used to transport goods to and from cities, thereby creating the basis of a thriving economy. Thousands of people use the highways in the Witwatersrand every day – but their vehicles and traffic activities produce large quantities of metals that can be washed into nearby rivers and lakes by rain. Examples of this are tire wear (source of iron, aluminium, zinc and cadmium), engine wear (source of aluminium, copper, cobalt, nickel and chromium) and brake wear (source of aluminium, manganese, cobalt, nickel, chromium, lead and zinc), as well as vehicular component wear and detachment (source of iron, aluminium, chromium and zinc), exhaust emissions (source of lead and manganese) and fluid drippings (source of copper, iron, lead, zinc and aluminium) (Sansalone *et al.*, 1996; Hunt *et al.*, 2002; Su & Mitchell, 2003; BEST, 2005).

High levels of many of these metals (also called trace elements or heavy metals) are harmful to the environment, as discussed in section 3 (Sansalone *et al.*, 1996; Bricker, 1999; Hunt *et al.*, 2002; BEST, 2005). Changing weather patterns, such as the existence of long dry or wet periods, can influence the quantity of metals in highway runoff (Hunt *et al.*, 2002; Lee *et al.*, 2004; BEST, 2005; Kim *et al.*, 2005). Typically, the peak concentrations of metals in rainfall runoff occur during the first rainfall event of the rainy season. This is known as the 'seasonal first flush' and it contains a large percentage of total pollution in a relatively small percentage of runoff volume (Hunt *et al.*, 2002; Su & Mitchell, 2003; Kim *et al.*, 2005). On the Witwatersrand in South Africa, the rainy season is during the spring and summer months (September to April), with a peak in December and January.

Therefore, the focus of this study is to determine if a seasonal first flush occurs at selected monitoring sites in the Witwatersrand area for a number of metals (**aluminium, cadmium, cobalt, chromium, copper, iron, manganese, nickel, lead** and **zinc**) and to determine if the concentrations of these metals could have a detrimental effect on the environment by comparison to the legal limits of the **Target Water Quality Ranges** (**TWQR**) for the different water use sectors (aquatic ecosystem health and domestic and agricultural use) as shown in section 3.

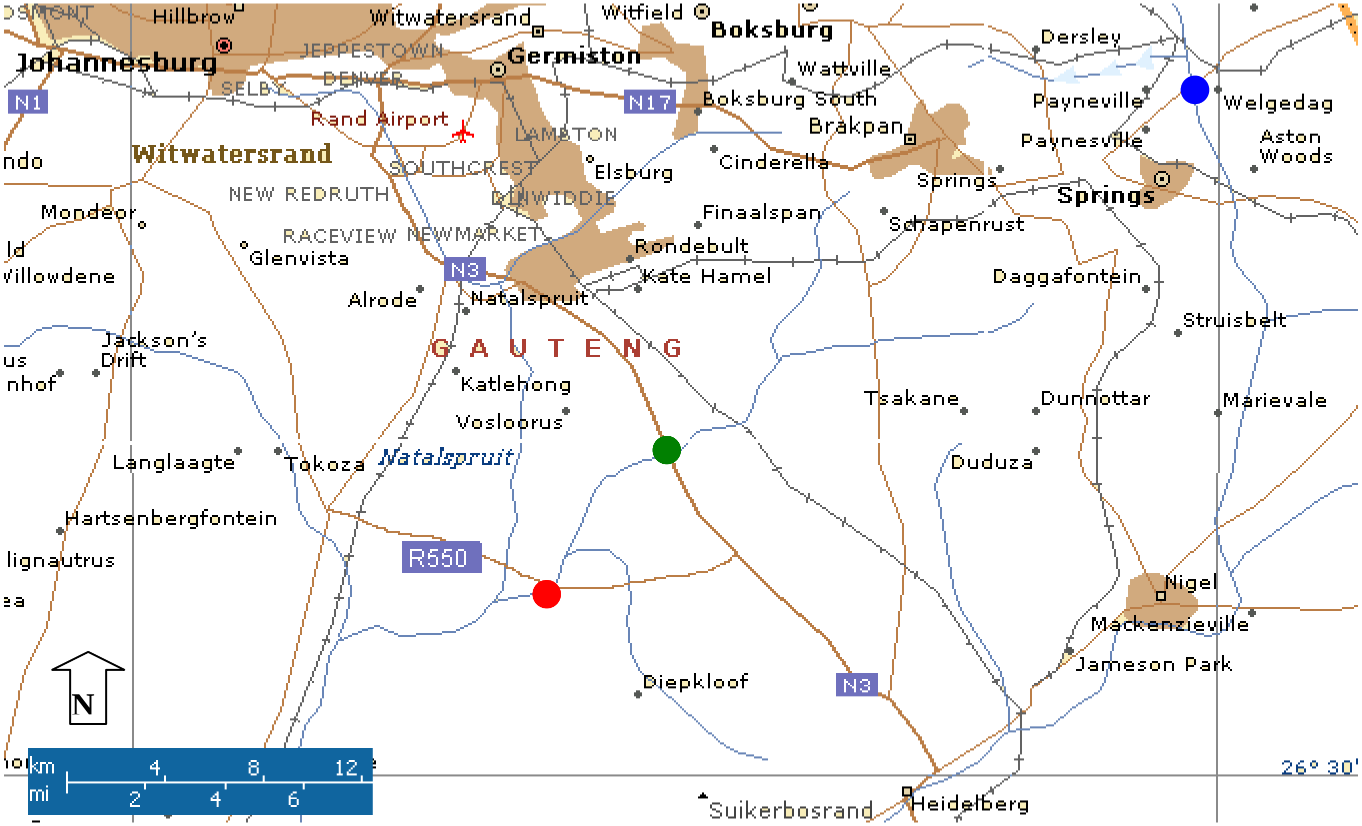
4.2. Location of the study sites in the Witwatersrand:

Rand Water has a water quality monitoring system spanning across Gauteng. Concentration levels of metals, non-metals (such as chloride) and organics (including algae and bacteria) are closely monitored. This ensures that the pollutants remain within legal limits and can be used to monitor the health of the aquatic environment. Many of the monitoring sites in the Witwatersrand area are of rivers and streams near roads. Three of these sites were selected as locations worthwhile for further study as these sites represent a range of different types of roads, ranging from the large N3 highway to smaller country roads (as shown in figure 13). The characteristics of each of the study sites are discussed below.

4.2.1. R4 - Rietspruit at N3 (Alberton-Heidelberg) (Green dot in Figure 13):

This site is located where the N3 highway between Alberton and Heidelberg passes over the Rietspruit River. This two-lane highway is a heavily-used, straight road, passing

Study Sites in the Witwatersrand Area



Study Sites

● **R4** –
Rietspruit at N3
(Alberton to
Heidelberg)

● **R5** –
Rietspruit at R550
(Hardman's Farm)

● **B5** –
Blesbokspruit at
Welgedacht Road
(Springs)

Figure 13: Study sites in the Witwatersrand area.

through open grassland with very few large trees or buildings. The **average annual daily traffic** (**AADT**) for 2003 was 28203 (SA-NRA, 2003), therefore, the amount of heavy metals that accumulate on the roadway should be quite large and the seasonal first flush ought to be easily detectable.

This site was chosen to determine if the large highway contributes a significant amount of heavy metals into the river because it flows past expanding formal and informal settlements, areas of spray irrigation and pastures, before flowing into a tributary of the Vaal River. To assess this, the concentrations of the selected heavy metals are compared to legal limits to determine if the metals could have a detrimental effect on the environment and human health. Refer to section 3 for a more detailed discussion of these environmental impacts.

4.2.2. R5 - Rietspruit at R550 (Hardman's Farm) (Red dot in Figure 13):

This site is located where the R550 road passes over the Rietspruit River, near Hardman's Farm. This single-lane highway is a straight road that passes through open grassland with very few large trees. There is no AADT data available for this road, however, it passes by a small community and Hardman's Farm, therefore it can be assumed that the road is in constant use and thus the seasonal first flush should also be detectable at this site.

This site was chosen to determine if the road contributes a significant amount of heavy metals into the river, as it passes by a large mielie farm and formal and informal settlements, before flowing into a tributary of the Vaal River. To determine this, the concentrations of the heavy metals are compared to legal limits to find out if the metals could have a detrimental effect on the environment and human health. A more detailed discussion of these environmental impacts can be found in section 3.

4.2.3. B5 - Blesbokspruit at Welgedacht Road (Springs) (Blue dot in Figure 13):

This site is located where Welgedacht Road in Springs passes over the Blesbokspruit River and wetland, which has been declared as a Ramsar site by the Convention on Wetlands, signed in Ramsar, Iran, in 1971 (AGA, 2004). A Ramsar wetland is viewed as a site that possesses international significance in terms of ecology, botany, zoology and hydrology (AGA, 2004). It should be noted that this wetland is currently on the Montreux Record as being a wetland degraded by excessive pollution (Peck, 2003). This site was therefore chosen to determine if the road contributes a significant amount of heavy metals into the wetland, which would subsequently increase the already high pollutant load and resulting environmental impacts. To discern this, the concentrations of the heavy metals are compared to legal limits to determine if the metals could have a harmful effect on the environment and human health (as detailed in section 3). In addition, maintaining good quality water in this river is even more important since the Blesbokspruit forms a component of one of the tributaries of the Vaal River, which provides water for drinking and irrigation to Gauteng. There is no ADDT data available for this road, however, this straight single-lane highway passes by the large Grootvlei Mines and is a main road in and out of Springs, and therefore it can be assumed that the road is in constant use and thus the seasonal first flush should be detectable at this site.

Since rainfall runoff from roads contain heavy metals caused by vehicular traffic, it is possible that the larger roads would cause larger concentrations of metals in the runoff, produced by the varying traffic densities. In spite of this, the seasonal first flush should still be detectable, since it is dependent on rain after a long period of dry weather. However, any effect on metal concentrations that can be attributed to traffic density will be noted in the section discussing the results.

A detailed discussion of the data used, how it was obtained, as well as the shortcomings encountered in this study will be given in the next section.

5. Data collection and methods of data manipulation:

5.1. Data collection:

5.1.1. Sources of data:

The purpose of this study is to investigate the seasonal first flush phenomenon of a number of heavy metals in rainfall runoff near selected roads in the Witwatersrand area (shown in figure 13). To accomplish this, a number of different sets of data were needed, as discussed below.

The first data set required were the concentrations of the selected heavy metals: **aluminium, cadmium, cobalt, chromium, copper, iron, manganese, nickel, lead** and **zinc** at the selected sites (figure 13). These metals were chosen as these are the most common metals originating from vehicles and traffic activities, as discussed in sections 3.1. and 4.1. Additional to this, the pH of the water was also needed, since the speciation and therefore the concentration of metals is dependent on the pH, as explained in section 3.3. Both of these data sets were obtained electronically from Rand Water for the period 1999 to 2005 in the form of Excel data sheets. The dates the samples were taken and the corresponding pH and concentration values were supplied. The basic method used to analyse the samples to determine the metal concentrations was also obtained, and will be described in more detail in section 5.1.2.

The first flush is dependent on rainfall and therefore daily precipitation data at or near the study sites were needed as the second data set. This was electronically obtained from the South African Weather Bureau for Heidelberg and Springs for the period 1999 - 2005 in the form of Excel data sheets. The Weather Bureau does not have monitoring sites closer to R4 and R5 than Heidelberg, however, no water monitoring site selected for study was more than 15 km from a weather monitoring station, therefore ensuring that the analysis for the rainfall runoff indicative of the first flush were as exact as possible.

5.1.2. Shortcomings of data:

As there is no official highway rainfall runoff monitoring system in South Africa (Okonkwo & Mothiba, 2005), there are a number of shortcomings to using this data, since accuracy in combining data from different sources can be lacking at times. Ideally, as in the USA, samples for water quality analysis of rainfall runoff should be taken multiple times during a rainfall event, therefore removing random fluctuations in the data and thus ensuring accurate and convincing evidence of the seasonal first flush (Sansalone *et al.*, 1996; Hunt *et al.*, 2002; Su & Mitchell, 2003). Unfortunately, such dedicated and precise data collection does not exist for this study. The water quality analyses done by Rand Water are done at preset dates with no relation to days when it rained. Therefore, it was frequently found that some rainfall events did not have corresponding water analysis data. Even if the water sample was collected a day later, runoff from the road would have long washed away and the water quality data would have no relevance to the study. Therefore, only rainfall events that have congruent water quality data were used in this study - nevertheless still providing enough information to detect 24 instances of a seasonal first flush between 1999 and 2005 for the selected metals. However, as only one analysis was done per rainfall event, slight fluctuations in the concentration data were found. These fluctuations were caused by differing site- and time-specific conditions when the samples were taken and analysed. It is important to be aware of this shortcoming and care should be taken not to accord too much significance to these fluctuations. Therefore, as the scope of this study is only to identify the presence of a seasonal first flush and whether the legal limits have been exceeded, and not an in-depth examination of each data-point, only the general trend presented by each metal will be discussed.

The largest shortcoming of using data from Rand Water is that it only represents the concentration of the dissolved fraction of the metal. According to their basic method of analysis, the samples collected at the monitoring sites were first filtered through a 45 μm filter to remove all particles before analysis were conducted using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS). Even though the dissolved state of metals are more bioavailable and potentially more harmful, the total concentration (dissolved and particulate fractions) of metals can help give a much clearer indication of the health of the environment, since many metals, such as **iron, chromium, lead** and **aluminium** occur in the natural environment almost exclusively bound to particles (Tuccillo, 2006).

However, in spite of all of these shortcomings, careful analysis of the available data still made meaningful conclusions possible concerning the presence of a seasonal first flush at the sites selected for study.

5.2. Methods of data analysis:

Rainfall and water quality data from the summer rainy season (September to April) over the last six years (1999 - 2005) were analysed for each of the study sites (shown in figure 13) to verify the existence of a seasonal first flush. It was determined by Lee *et al.* (2004) that the first flush can easily be detected by using metal concentrations (dissolved fraction) and normalised cumulative rainfall (calculated from daily rainfall) (Lee *et al.*, 2004) - refer to an example of this in figure 14. Normalised cumulative rainfall is usually used in this type of representation when rainfall volumes are not available. It should be noted that all water quality data used were at least 10% higher than the detection limit of the ICP-MS ensuring that the analysis of the runoff were as exact as possible.

The antecedent dry period (or **Preceding Dry Days - PDD**) is represented in figure 14a; the event total rainfall in figure 14b; and the concentration of zinc and other parameters according to the normalised cumulative rainfall in figure 14c. It can be seen that at the start of the rainy season, there had been almost 160 PDD (figure 14a) before it rained a small amount (figure 14b), resulting in a zinc concentration of approximately 0.90 mg/L (figure 14c). Later in the season (at normalised cumulative rainfall of 0.2, 0.4, and 0.6), amounts of rain higher than at the start of the season (figure 14b) did not equate to higher concentrations of zinc washed from the roadway, therefore providing evidence for a seasonal first flush in this specific example.

Therefore, the methods used for data analysis and presentation of results in this study were based on the study by Lee *et al.* (Lee *et al.*, 2004). Consequently, the daily rainfall records for Heidelberg and Springs were used to calculate the normalised cumulative rainfall and **Preceding Dry Days** (**PDD**). These terms, and how they are used, are further explained below.

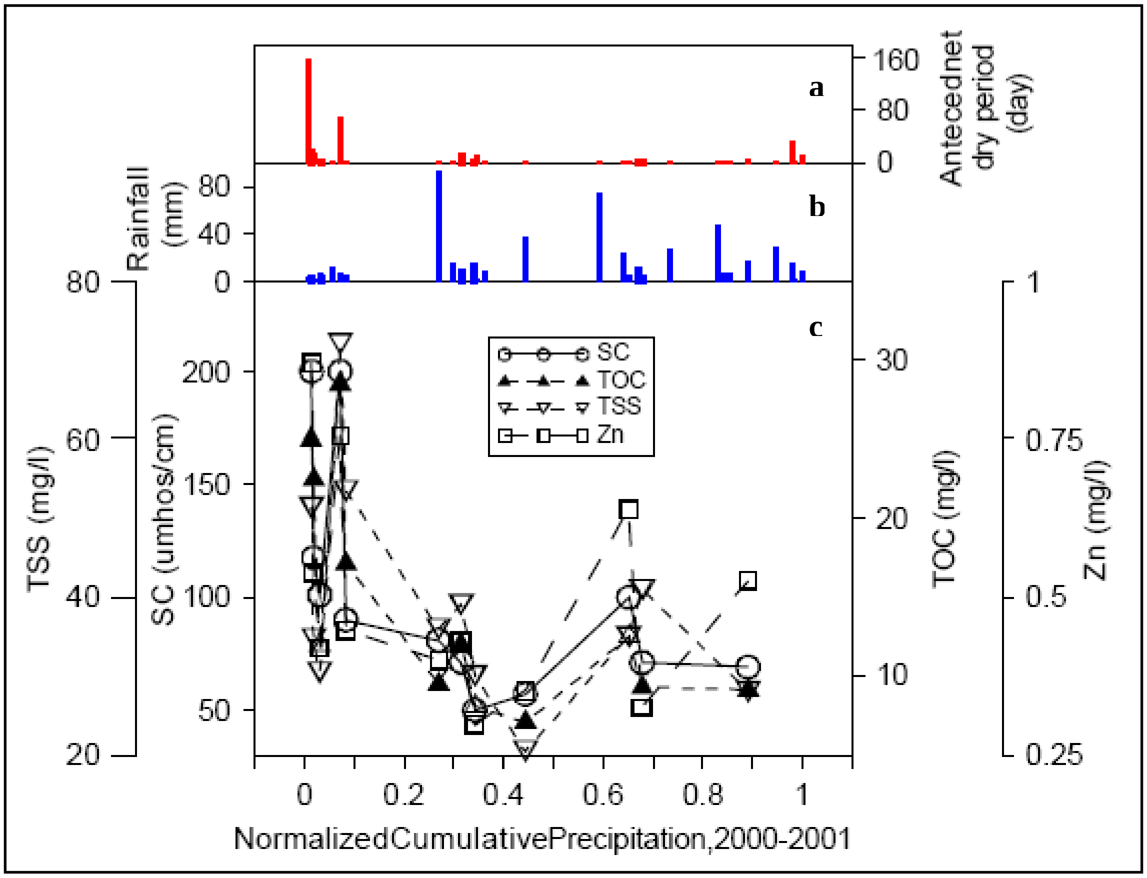


Figure 14: An example of how the data of a seasonal first flush can be presented (Lee *et al.*, 2004).

Normalised cumulative rainfall was calculated by adding the total rainfall for each event and dividing by the season total, as an example shows in table 17. A rainfall event for this study was chosen to be a collection of rainy days with no more than two PDD between them. The concentrations of the metals were then plotted against the normalised cumulative rainfall to obtain a graph showing how the metal concentrations are influenced by the amount of rainfall and the PDD throughout the season (represented by normalised cumulative rainfall). An example of this is given in figure 15, where it can be seen that the concentration of cobalt (Co), although showing slight fluctuations, decreases (from point c1 to c3) as the season progresses, even though the event total rainfall (point a1 to a3) increases. Therefore, this is a clear indication of the presence of a seasonal first

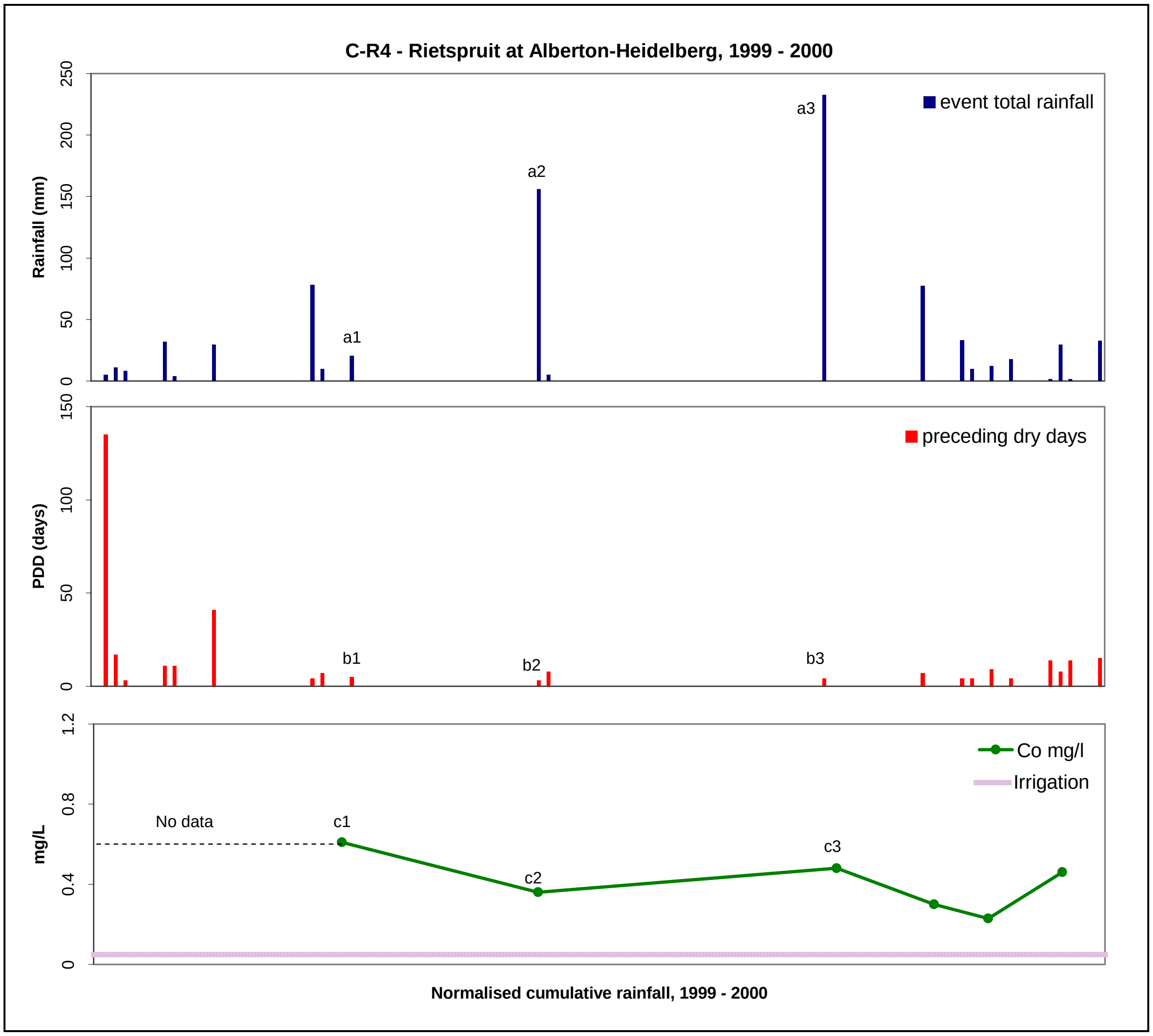


Figure 15: Example of graphs based on calculations in table 17 (Note: The TWQR legal limit for irrigation is indicated by the horizontal line on the graph.)

Table 17: Example of calculations used to obtain graphs in figure 15 for R4 study site (green dot in figure 13).

C-R4 - Rietspruit at Alberton-Heidelberg, rainy season 1999 - 2000				
Rainfall event	**Event total rainfall (mm)**	**Normalised cumulative rainfall**	**Preceding dry days (PDD)**	**Co (mg/l)**
2000-01-31 to 2000-02-02	point a1 = **20.5**	(Season total rainfall / Event total rainfall) + 0 = **0.25**	point b1 = **5**	point c1 = **0.61**
2000-02-06 to 2000-02-15	point a2 =**156**	(526 / 156) + 0.25 = **0.44**	point b2 = **3**	point c2 = **0.36**
2000-02-29 to 2000-03-06	point a3 = **232.5**	(526 / 232.5) + 0.44 = **0.73**	point b3 = **4**	point c3 = **0.48**
2000-03-14 to 2000-03-21	**77.5**	**0.83**	**7**	**0.3**
2000-04-04	**10**	**0.88**	**4**	**0.23**
2000-04-30 to 2000-05-03	**29.5**	**0.96**	**8**	**0.46**
Season total	**526**			

flush. However, not all the rainfall events had corresponding metal concentration data available and therefore some rainfall events and rainy seasons did not have enough relevant data available for meaningful analysis.

The results of the data analysis will be discussed in detail in the next section.

6. Discussion of Results:

6.1. Introduction:

Highway runoff can include a variety of heavy metals originating from vehicles (tire, engine and brake wear), the roadway, and other sources which accumulate on highway surfaces, roadside areas, and rights-of-way during long dry periods. During the initial rainfall events of a rainy season, higher concentrations of these metals are washed from road surfaces than in later events, during what is called a seasonal first flush, as discussed in section 3.1. Such high concentrations of metals flowing into rivers and lakes may be harmful to the aquatic environment as well as human health. Heavy metal toxicity can result in slowly progressing physical, muscular, and neurological degenerative processes and repeated long-term contact with some metals or their compounds may even cause cancer (Sansalone *et al.*, 1996; Bricker, 1999; Hunt *et al.*, 2002; Su & Mitchell, 2003; Arthur, 2004; BEST, 2005; Fraga, 2005). Refer to a detailed discussion of these effects in section 3.3.

The purpose of this study is to identify the presence of a seasonal first flush at selected monitoring sites (as shown in figure 13) for a number of metals as well as determining whether these metals are introduced into the environment at concentrations higher than the legal limits represented by the **Target Water Quality Ranges** (**TWQR**) for the different water use sectors of irrigation, domestic use, aquacultural purposes, aquatic ecosystem health and livestock watering (shown in table 18 and discussed in section 3.3.). The metals selected were **aluminium, cadmium, cobalt, chromium, copper, iron, manganese, nickel, lead** and **zinc** as these are the most common metals originating from vehicles and traffic activities (as explained in sections 3.1. and 4.1.).

Data of dissolved metal concentrations at the selected sites (shown in figure 13) and daily rainfall records were obtained from Rand Water and the South African Weather Bureau respectively, and analysed according to the methods discussed in section 5.2., which was based on the work of Lee *et al.* (Lee *at al.*, 2004). Generally, the proof of the seasonal first flush is presented graphically (Sansalone *et al.*, 1996; Su & Mitchell, 2003; Lee *at* *al.*, 2004; Kim *et al.*, 2005) and will also be presented as such in this study. More detailed data for each rainy season can be found in Appendix B.

Table 18: Legal limits (TWQR) for different water use sectors of selected heavy metals (SA-DWAF: Field Guide, 1996).

TWQR	Al (mg/L)	Cd (μg/L)	Co (mg/L)	Cr (mg/L)	Cu (mg/L)	Fe (mg/L)	Mn (mg/L)	Ni (mg/L)	Pb (mg/L)	Zn (mg/L)
Aquatic ecosystem health	0.005	0.15	N/A	0.007	0.0003	N/A	0.18	N/A	0.0002	0.002
Aquaculture	0.03	0.2	N/A	0.002	0.005	0.01	0.1	N/A	0.01	0.03
Domestic use	0.15	5	N/A	0.05	1	0.1	0.05	N/A	0.01	3
Irrigation	5	10	0.05	0.1	0.2	5	0.02	0.2	0.2	1
Livestock watering	5	10	1	1	5	10	10	1	0.5	20

For clarity, each study site is described as a separate segment, starting with the site next to the largest road – the N3 highway, and a comparative discussion of results and concluding remarks following thereafter.

6.2. Results and discussion of R4 - Rietspruit at N3 (Alberton-Heidelberg) (Green dot in Figure 13 and graphs in Figures 16, 17 and 18):

Water quality data for selected metals (**aluminium, cadmium, cobalt, chromium, copper, iron, manganese, nickel, lead** and **zinc**) were evaluated according to normalised cumulative rainfall and **preceding dry days** (**PDD**) for the rainy seasons 1999/2000, 2001/2002 and 2004/2005. Not all the rainfall events at this site had corresponding metal concentration data available and therefore some rainfall events and seasons did not have enough relevant data available for meaningful analysis.

6.2.1. R4 - Rainy season 1999 – 2000 (Figure 16):

Figure 16 shows the concentrations of cobalt (green), manganese (red), nickel (purple) and zinc (orange) according to the normalised cumulative rainfall (refer to Appendix B for more detailed data). Their safe legal limits for irrigation, domestic use, aquacultural

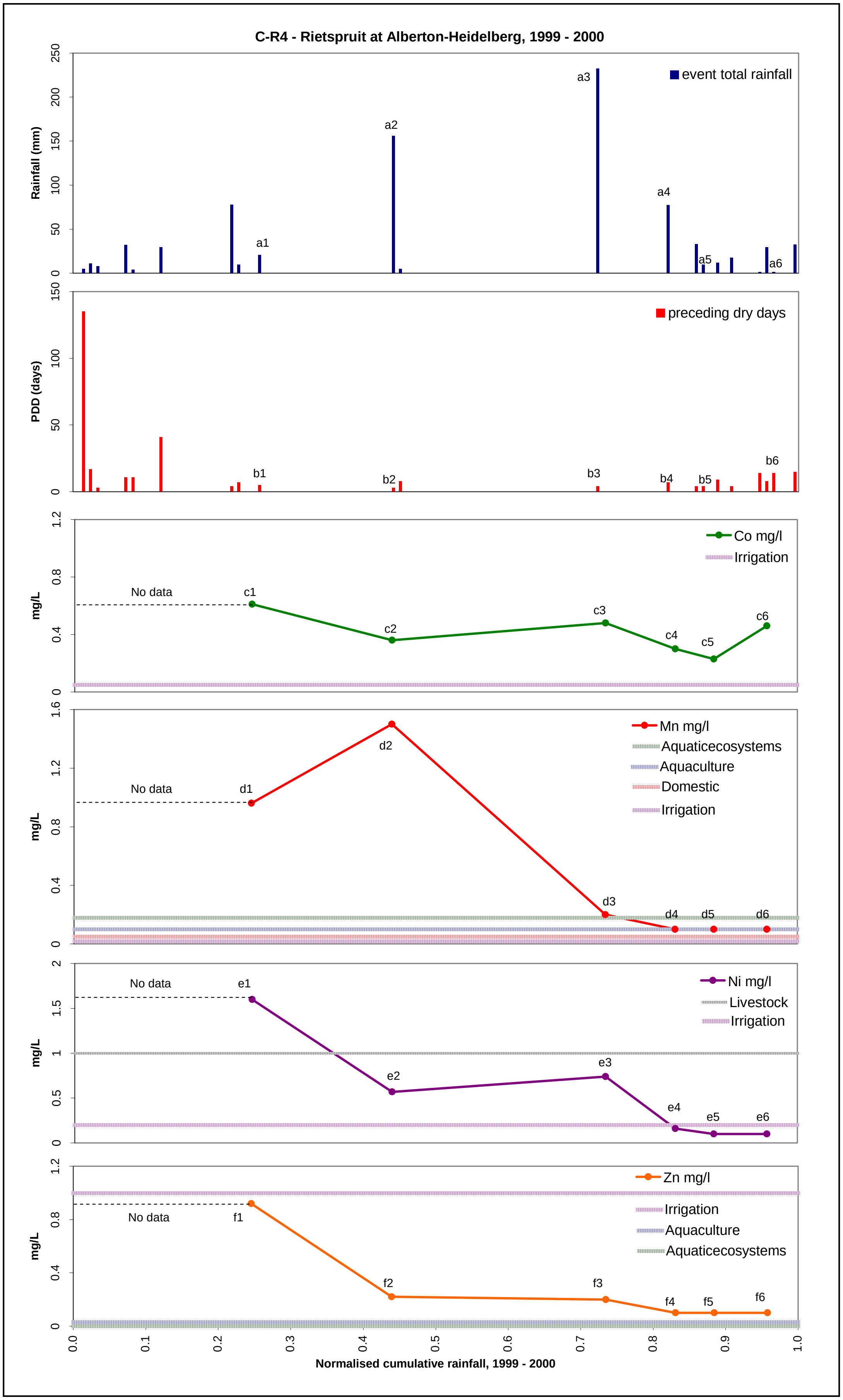


Figure 16: Concentrations versus normalised cumulative rainfall for 1999/2000 at R4 - Rietspruit at N3 (Alberton-Heidelberg) for cobalt, manganese, nickel and zinc (Note: The TWQR legal limits are indicated by the horizontal lines in the graphs).

purposes, aquatic ecosystem health and livestock watering are also shown (refer to table 18).

According to the available data, the other metals under investigation (**aluminium, cadmium, chromium, copper, iron** and **lead**) were not detected. As dissolved aluminium, chromium, iron and lead are predominately particulate-bound (Sansalone *et al.*, 1996; Tuccillo, 2006) or form insoluble compounds ($Fe(OH)_3(s)$ and $PbCO_3(s)$) (Hunter *et al.*, 1999; Brix & DeForest, 2000), they would be removed from the samples by the filtration process employed by Rand Water and thus not detected. Therefore, it is possible that some aluminium, chromium, iron and lead were present in the runoff as particulates. Cadmium and copper are mostly present in slightly alkaline waters as the free Cd^{2+} and Cu^{2+} ions respectively (Hunter *et al.*, 1999), and therefore, at this site (where the pH values ranged between 6.8 and 8.3 (slightly alkaline)) there was no cadmium or copper present in the runoff. In summary, **aluminium, chromium, iron** and **lead** could have been present in the runoff as particulates; and no **cadmium** or **copper** was present at all.

Figure 16 shows that the concentration of cobalt (green) was highest in the first relevant rainfall event (point c1) and showed a general decrease through the season (points c2 to c6), therefore implying the existence of a seasonal first flush for this metal. It can be seen that point c3 is slightly higher than c2, though still lower than point c1. This can be due to the fact that the rainfall event for point c3 (point a3 – 232.5 mm) was larger than that of point c2 (point a2 – 156 mm), and therefore more cobalt was washed from the road. Also, at the end of the season (point c6 – 0.46 mg/L), the concentration was almost the same as point c3 (0.48 mg/L) even though at point a3 it rained 232.5 mm and at point a6 only 1.5 mm. This might have been caused by the number of PDD of point b6 (14 days) compared to b3 (4 days). These results show that cobalt concentrations appear to be more influenced by number of PDD than the amount of rainfall. At point c1, the concentration of cobalt was more than 12 times the legal limit for irrigation (0.05 mg/L), and throughout the season, the concentration of cobalt washed into the river environment remained higher than that limit. High concentrations of cobalt in irrigation water can have a number of negative effects on plants, as discussed in section 3.3.3.1.

The concentration of manganese (red) also decreased as the season progressed (points d1 to d6), showing the presence of a seasonal first flush. However, the second relevant rainfall event (point a2) showed a much higher concentration (point d2) than the first (point d1). This might be due to the fact that the second relevant rainfall event (point a2 – 156 mm in total) was much larger than the first (point a1 - 20.5 mm), thus causing more manganese to be washed from the roadway. Later in the season, large rainfall events (like point a3 – 232.5 mm) did not cause such increases as much of the accumulated manganese had already been washed from the road. At the start of the season (point d1) the concentration of manganese was 19 times the legal limit for domestic use (0.05 mg/L); 48 times that for irrigation (0.02 mg/L); five times higher than the legal limit for aquatic ecosystem health (0.18 mg/L); and almost 10 times above the regulation level for aquacultural purposes (0.1 mg/L). In addition, the concentration of manganese introduced into the river remained higher than the legal limits for domestic use, irrigation, aquatic ecosystem health and aquaculture right through the season, only dropping below the limit for aquatic ecosystem health at point d4. High concentrations of manganese can have negative impacts on the environment and human health, as discussed in section 3.3.7.

The concentration of nickel (purple) was highest in the first relevant rainfall event (point e1) and decreased throughout the season (points e2 to e6 in figure 16), thus providing evidence of a seasonal first flush for this metal. As with cobalt, it can be seen that point e3 is slightly higher than e2, though still lower than point e1. This can be explained by the fact that the rainfall event for point e3 (point a3) was larger than that of point e2 (point a2), and therefore more nickel was washed from the road during this rainfall event. At the beginning of the season (point e1), the concentration of nickel was almost twice the legal limit for livestock watering (1 mg/L) and eight times higher than the limit for irrigation (0.2 mg/L). As the season progressed, the concentration decreased, dropping below the limit for livestock watering (points e2 and e3), and at the end of the season also dropping below the limit for irrigation (points e4 to e6). The negative impacts that high concentrations of nickel can have on plants and livestock are discussed in sections 3.3.8.1. and 3.3.8.3. respectively.

The concentration of zinc (orange) was highest in the first relevant rainfall event (point f1) and decreased all through the season (points f2 to f6 in figure 16), providing proof of the occurrence of a seasonal first flush for zinc. At the start of the season (point f1), the concentration of zinc was more than 30 times the regulation limit for aquaculture (0.03 mg/L) and 460 times the legal limit for aquatic ecosystem health (0.002 mg/L), and throughout the season, the concentration of zinc remained above these legal limits, as seen in figure 16. High concentrations of zinc introduced into the river can have detrimental effects on the aquatic environment, as discussed in section 3.3.10.2.

Manganese is expected to generally demonstrate a similar response to cobalt, nickel and zinc in the same solution (Sansalone *et al.*, 1996; Kirkby & Römheld, 2004; He *et al.*, 2005; Tuccillo, 2006), and it can be seen from figure 16 that this common pattern is evident for all four metals. This would mean that the metals all originate from the same source (the roadway) and were therefore subjected to the same physical (rainfall) and chemical (pH) conditions. This can be taken as evidence that the samples were not contaminated from other sources.

As discussed above and shown in figure 16, the N3 highway was a significant source of dissolved **cobalt, manganese, nickel** and **zinc** for the 1999/2000 season at this site and they were introduced into the environment at levels exceeding the safe legal limits of livestock watering, irrigation, aquatic ecosystem health, aquaculture and domestic use. However, since the water quality data used only represents the dissolved metal fractions, it is unknown how large the insoluble fraction was in the runoff. Still, it is possible to make some inferences with knowledge accessible in other studies. In slightly alkaline solutions, cobalt and manganese are mostly dissolved (Sansalone *et al.*, 1996; Hunter *et al.*, 1999), nickel partially adsorbs on organic matter (Brix & DeForest, 2000; Ansari *et al.*, 2004), and zinc forms a mixture of dissolved and insoluble compounds (Hunter *et al.*, 1999). Therefore, at this site, where the pH values ranged between 6.8 and 8.3 (slightly alkaline), it is possible that **nickel** and **zinc** were also present in the runoff as particles in unknown amounts. Consequently, water containing these particles could be ingested by animals and humans, possibly having further detrimental effects on their health than would be caused by the dissolved fractions alone.

In conclusion, a seasonal first flush was identified for **cobalt, manganese, nickel** and **zinc** for the 1999/2000 season. It was also found that the concentrations of the metals introduced into the Rietspruit River environment were much higher than the legal limits imposed for irrigation, domestic use, aquacultural purposes, livestock watering and aquatic ecosystem health, as shown in figure 16. Some additional **nickel** and **zinc** could also have been introduced in the form of particles. High concentrations of these metals can have damaging effects on the environment and human health, as discussed in sections 3.3.3. (cobalt), 3.3.7. (manganese), 3.3.8. (nickel), and 3.3.10. (zinc).

For ease of interpreting and explaining data, all subsequent graphs and discussions will be standardised according to the exact same format used in figure 16 and in this segment. The rainy season of 2001/2002 will be discussed next.

6.2.2. R4 - Rainy season 2001 – 2002 (Figure 17):

Figure 17 shows the concentrations of cobalt (green), manganese (red) and nickel (purple) according to the normalised cumulative rainfall (refer to Appendix B for more detailed data). Their safe legal limits for irrigation, domestic use, aquacultural purposes and aquatic ecosystem health are also shown (refer to table 18).

According to the available water quality data, the other metals under investigation (**aluminium, cadmium, chromium, copper, iron, lead** and **zinc**) were not detected. As was discussed in section 6.2.1., it is possible that some aluminium, chromium, iron and lead were present in the runoff as particulates and no cadmium or copper were present at all. Zinc forms a mixture of dissolved (Zn^{2+}) and insoluble ($ZnCO_3(s)$) compounds in slightly alkaline waters (Hunter *et al.*, 1999). Therefore, at this site (where the pH values

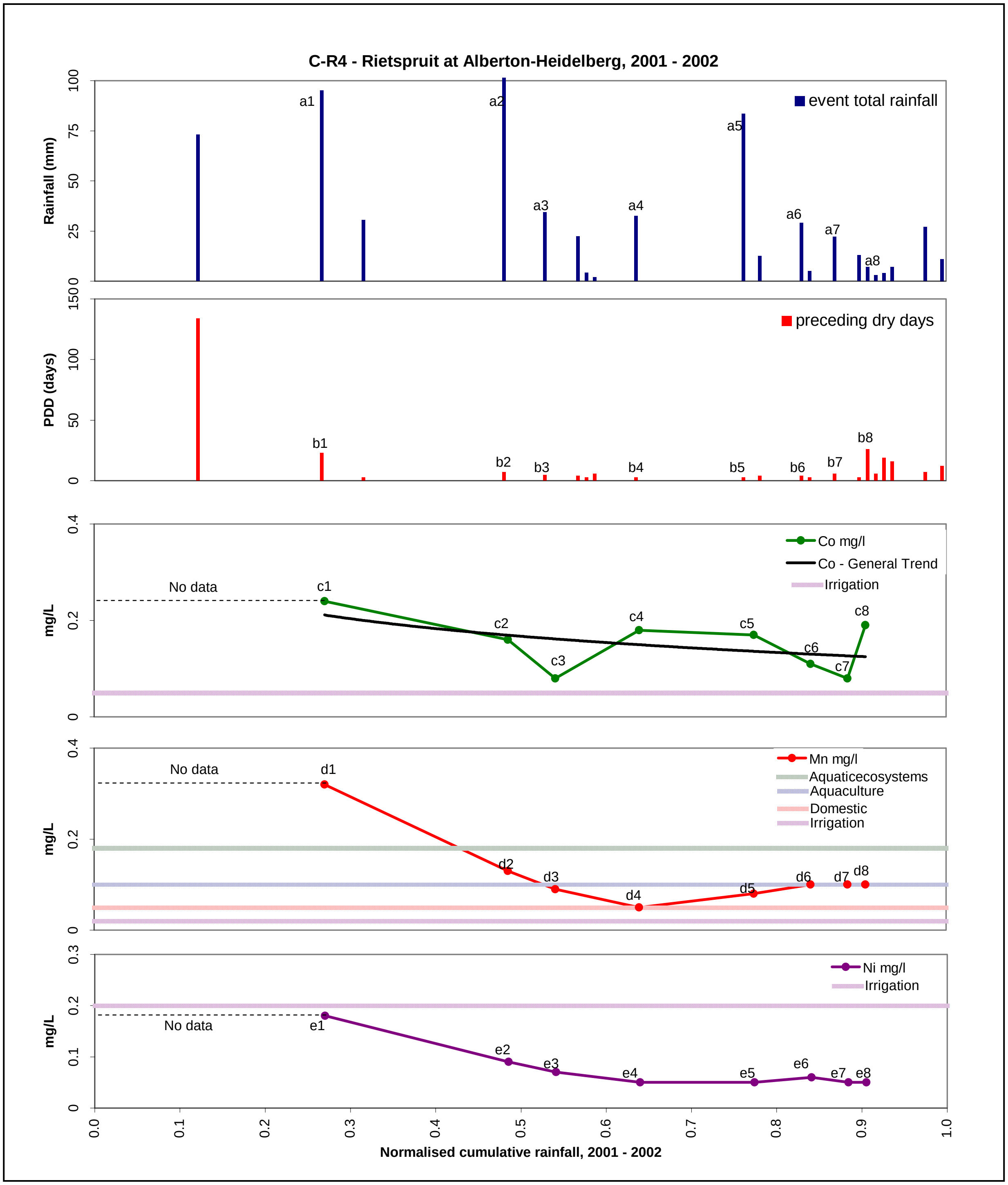


Figure 17: Concentrations versus normalised cumulative rainfall for 2001/2002 - Rietspruit at N3 (Alberton-Heidelberg) for cobalt, manganese and nickel (Note: The TWQR legal limits are indicated by the horizontal lines in the graphs).

ranged between 6.8 and 8.3 (slightly alkaline)), even though there was no soluble zinc found in the runoff, some insoluble zinc could have been present. However, it would have been removed from the samples by the filtration process employed by Rand Water and thus not detected. In summary, **aluminium, chromium, iron, lead** and **zinc** could have been present in the runoff as particulates; and no **cadmium** or **copper** were present at all.

The concentration of cobalt (green) was highest in the first relevant rainfall event (point c1) and showed a general decrease throughout the season, as shown in figure 17 (black line), therefore showing the presence of a seasonal first flush. It can be seen that point c8 appears higher than the other points, though still lower than point c1. This can be due to the fact that the PDD for point c8 (point b8 – 26 days) was larger than that of the other points and therefore more cobalt accumulated on the road before being washed away. These results show, as in section 6.2.1., that cobalt concentrations appear to be more influenced by PDD than the amount of rainfall. Throughout the season, the concentration of cobalt washed into the river environment was higher than the legal limit for irrigation (0.05 mg/L) and was almost five times this limit at point c1. High concentrations of cobalt in irrigation water could have a negative effect on plants, as discussed in section 3.3.3.1.

The concentration of manganese (red) also decreased as the season progressed (points d1 to d8), showing the presence of a seasonal first flush. At point d1, the concentration of manganese was more than six times the regulation limit for domestic use (0.05 mg/L); 16 times that for irrigation (0.02 mg/L); almost twice the legal concentration level for aquatic ecosystem health (0.18 mg/L); and three times the legal limit for aquaculture (0.1 mg/L). Right through the season, the concentration of manganese introduced into the river was higher than the legal limits for domestic use and irrigation, only dropping below the limit for aquatic ecosystem health at d2 and aquaculture at point d4. High concentrations of manganese can have a number of detrimental impacts on the environment and human health, as discussed in section 3.3.7.

The concentration of nickel (purple) was highest in the first relevant rainfall event (point e1) and decreased throughout the season (points e2 to e8 in figure 17). Throughout the season, the concentration of nickel was below the legal limits for irrigation (0.2 mg/L).

According to figure 17, there appears to be a common pattern evident for cobalt (green), manganese (red) and nickel (purple). This would mean, as discussed in section 6.2.1, that all of the metals most likely originate from the same source (in this case, the road) and were subjected to the same physical (rainfall) and chemical (pH) conditions, thus providing evidence that the samples were not contaminated from other sources.

It was found that the N3 highway was a significant source of dissolved **cobalt** and **manganese** throughout the 2001/2002 season at this site. These metals, as discussed above and shown in figure 17, were introduced into the environment at levels exceeding legal limits for irrigation, domestic use, aquacultural purposes and aquatic ecosystem health. However, the available water quality data only represents the dissolved metal fractions, and therefore the composition of the insoluble fraction in the runoff is unknown. Yet, as discussed in section 6.2.1. (by taking into account that the pH values at this site ranged between 6.8 and 8.3 (slightly alkaline)), it is possible to infer that an unknown amount of particulate-bound **nickel** was also present in the runoff. These particles could be ingested by animals and humans in drinking water, possibly having further negative effects on their health than would be caused by the dissolved fractions alone.

In conclusion, a seasonal first flush was identified for **cobalt, manganese** and **nickel** for the 2001/2002 season. As shown in figure 17, the concentrations of **cobalt** and **manganese** released into the Rietspruit River were higher than the legal limits for irrigation, domestic use, aquacultural purposes and aquatic ecosystem health. High concentrations of these metals can have a number of damaging effects on the environment, as discussed in sections 3.3.3. (cobalt), 3.3.7. (manganese), and 3.3.8. (nickel).

The rainy season of 2004/2005 will be discussed next.

6.2.3. R4 - Rainy season 2004 – 2005 (Figure 18):

Figure 18 shows the concentrations of cobalt (green), manganese (red), nickel (purple) and zinc (orange) according to the normalised cumulative rainfall (refer to Appendix B for more detailed data). According to the available water quality data, the other metals under investigation (**aluminium, cadmium, chromium, copper, iron** and **lead**) were not detected. As discussed in section 6.2.1., it is possible that some **aluminium, chromium, iron** and **lead** were present in the runoff as particulates and no **cadmium** or **copper** were present at all.

As shown in figure 18, the concentration of cobalt (green) were highest in the first relevant rainfall event (point c1) and displayed a general decline throughout the rest of the season (points c2 through c4), thus offering support for the presence of a seasonal first flush. At point c1, the concentration of cobalt was four times the legal limit for irrigation (0.05 mg/L) and throughout the season the concentration remained above this regulation level. High concentrations of cobalt in water used for irrigation could have a negative effect on plants, as discussed in section 3.3.3.1.

The concentration of manganese (red) also showed a general decrease as the season progressed, therefore providing evidence of the existence of a seasonal first flush for this metal. The concentration of manganese at point d1 was 10 times the level permitted by law for domestic use (0.05 mg/L); 25 times the level allowed for irrigation (0.02 mg/L); almost three times the legal limit for aquatic ecosystem health (0.18 mg/L); and five times the legal limit permitted for aquaculture (0.1 mg/L). All through the season, the concentration of manganese remained above the regulation limit for domestic use, aquaculture and irrigation, only dipping below the limit for aquatic ecosystem health at d2. High concentrations of manganese can have a number of harmful effects on the environment and human health, as discussed in section 3.3.7.

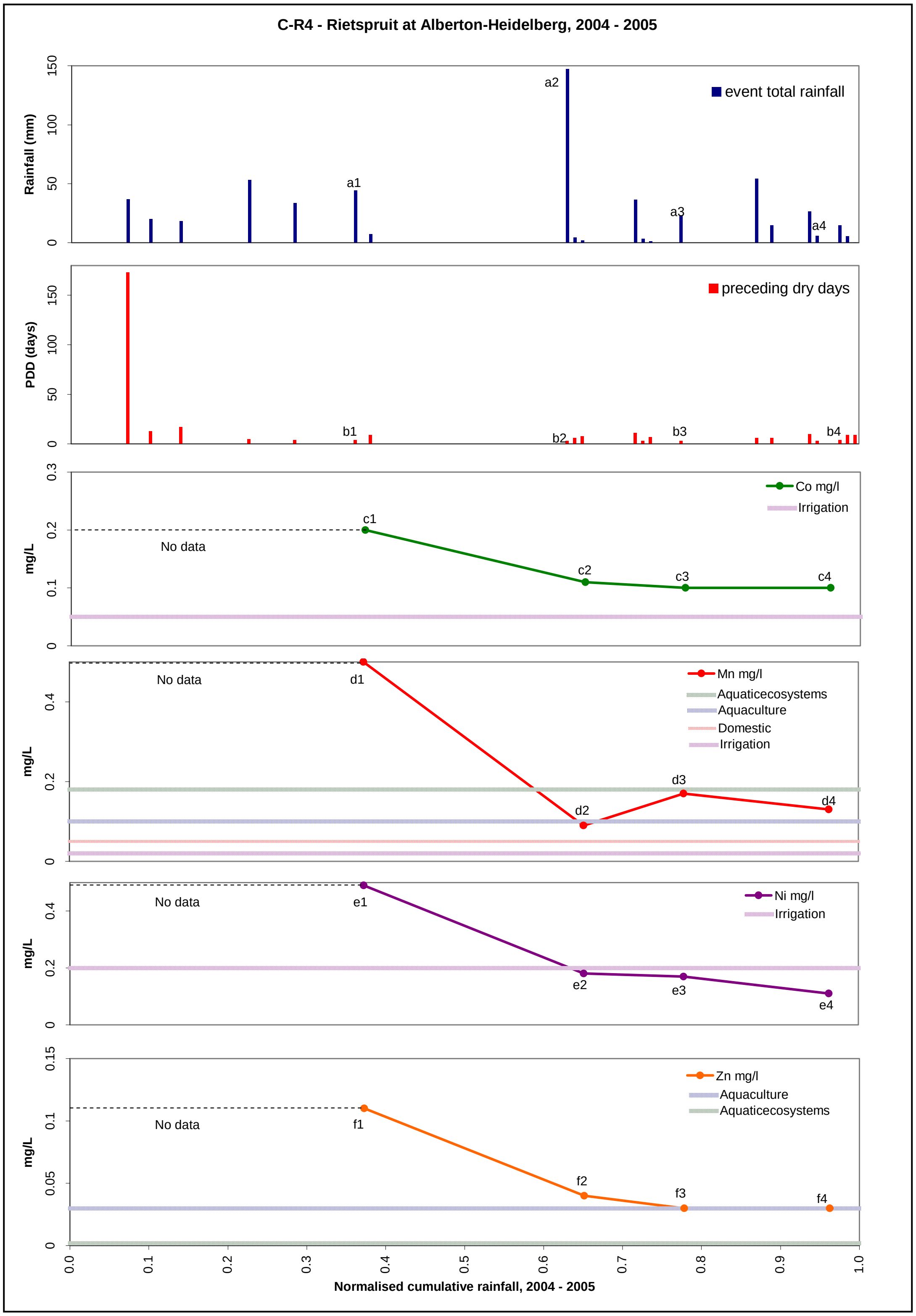


Figure 18: Concentrations versus normalised cumulative rainfall for 2004/2005 - Rietspruit at N3 (Alberton-Heidelberg) for cobalt, manganese, nickel and zinc (Note: The TWQR legal limits are indicated by the horizontal lines in the graphs).

Nickel concentrations (purple) displayed a decline through the season, in a clear indication of a seasonal first flush. In the beginning of the season (point e1), the concentration was more than twice the legal limit for irrigation (0.2 mg/L), however it dropped below that safe level at point e2. Irrigation water containing high concentrations of nickel can have a negative impact on plants, as discussed in section 3.3.8.1.

The recorded zinc concentrations (orange) also decreased throughout the season, showing an obvious seasonal first flush. At the start of the season (at point f1), the concentration of zinc was almost four times the legal regulation level for aquaculture (0.03 mg/L); and 55 times the legal limit for aquatic ecosystem health (0.002 mg/L). All through the season, the zinc concentrations remained above the legal regulations for aquaculture and aquatic ecosystem health. High concentrations of zinc in river water can have damaging effects on the aquatic environment, as discussed in section 3.3.10.2.

According to figure 18, there seems to be a common relationship between cobalt, manganese, nickel and zinc, as they seem to follow the same pattern. Therefore, as discussed in section 6.2.1., these metals are likely from the same source (the road) and experienced the same physical (rainfall) and chemical (pH) environment, thus eliminating the possibility of sample contamination from other sources.

The available data shows that, at this site, the N3 highway was a significant source of dissolved **cobalt, manganese, nickel** and **zinc** throughout the 2004/2005 season. These metals were introduced into the environment at levels exceeding safe legal limits for irrigation, aquatic ecosystem health, aquaculture and domestic use, as shown in figure 18. The existing water quality data, however, only characterises the dissolved metal fractions, therefore, the composition of the insoluble fraction in the runoff is unknown. However, as discussed in section 6.2.1. (by taking into account that the pH values ranged between 6.8 and 8.3 (slightly alkaline)), it is possible to infer that more **nickel** and **zinc** was present in the runoff than was detected. Animals and humans drinking this water could ingest these particles, possibly experiencing further negative effects on their health than would be caused by the dissolved fractions alone.

In conclusion, a seasonal first flush was identified for **cobalt, manganese, nickel** and **zinc** for the 2004/2005 season. According to the available data, the concentrations of the metals introduced into the Rietspruit River were much higher than the legal limits required for irrigation, domestic use, aquacultural purposes and aquatic ecosystem health. High concentrations of these metals can have negative impacts on the environment, as discussed in sections 3.3.3. (cobalt), 3.3.7. (manganese), 3.3.8. (nickel), and 3.3.10. (zinc).

The examination of the study site on the N3 at the Rietspruit River provided evidence of a distinctive seasonal first flush in all rainy seasons studied. Seasonal first flush was detected for **cobalt, manganese, nickel** and **zinc** during the rainy seasons of 1999/2000 and 2004/2005 and for **cobalt, manganese** and **nickel** for the rainy season of 2001/2002. It was found that the metals all followed similar patterns throughout the season, therefore providing evidence that they came from the same source (the road). This site was chosen for study to determine if the large highway contributes a significant amount of heavy metals into the river because it flows past expanding formal and informal settlements, areas of spray irrigation and pastures, before flowing into a tributary of the Vaal River. It was determined that **cobalt, manganese, nickel** and **zinc** were introduced into the environment at concentrations higher than the legal limits for livestock watering, aquaculture, domestic use and especially irrigation and aquatic ecosystem health, as shown in figures 16, 17 and 18, and summarised in table 19. Therefore, since too large concentrations of **cobalt, manganese, nickel** and **zinc** can have potentially harmful effects on the aquatic environment, agriculture and human health (as described in section 3.3.), nearby settlements and farms could be negatively affected by the heavy metals washed from the N3 highway into the Rietspruit River.

The next site to be investigated was a smaller road than the N3 highway and the results are discussed below.

Table 19: Metals displaying seasonal first flush as well as approximate amount the metal concentrations, at the initial rainfall event, exceeded legal limits at the R4 monitoring site for the studied rainy seasons (**a** – No seasonal first flush; **b** – Legal Limit set by TWQR).

1999/2000	2001/2002	2004/2005
Co – irrigation – 12x [b]LL Mn – irrigation – 48x LL Mn – domestic – 19x LL Mn – aquaculture – 10x LL Mn – aquatic ecosystems – 5x LL Ni – irrigation – 8x LL Ni – livestock – 2x LL Zn – aquaculture – 30x LL Zn – aquatic ecosystems – 460x LL	Co – irrigation – 5x LL Mn – irrigation – 16x LL Mn – domestic – 6x LL Mn – aquaculture – 3x LL Mn – aquatic ecosystems – 2x LL Ni – below legal limits	Co – irrigation – 4x LL Mn – domestic – 10x LL Mn – irrigation – 25x LL Ni – irrigation – 2x LL Zn – aquaculture – 4x LL Zn – aquatic ecosystems – 55x LL

6.3. Results and discussion of R5 - Rietspruit at R550 (Hardman's Farm) (Red dot in Figure 13 and graphs in Figures 19, 20 and 21):

Water quality data for selected metals (**aluminium, cadmium, cobalt, chromium, copper, iron, manganese, nickel, lead** and **zinc**) were evaluated according to normalised cumulative rainfall and **preceding dry days** (**PDD**) for the rainy seasons 2001/2002, 2003/2004 and 2004/2005. Not all of the rainfall events have corresponding concentration data available and thus some rainfall events and some seasons did not have enough relevant data available for meaningful analysis.

6.3.1. R5 - Rainy season 2001 – 2002 (Figure 19):

In figure 19, the concentrations of cobalt (green), manganese (red) and nickel (purple) are shown according to the normalised cumulative rainfall (refer to Appendix B for more detailed data). The legal limits for irrigation, domestic use, aquacultural purposes and aquatic ecosystem health are also shown (refer to table 18). The available data shows that the other metals under investigation (**aluminium, cadmium, chromium, copper, iron, lead** and **zinc**) were not detected. Therefore, as discussed in sections 6.2.1. and 6.2.2. (also taking into account that the pH values at this site ranged between 7.8 and 8.8 (slightly alkaline)), some **aluminium, chromium, iron, lead** and **zinc** could possibly

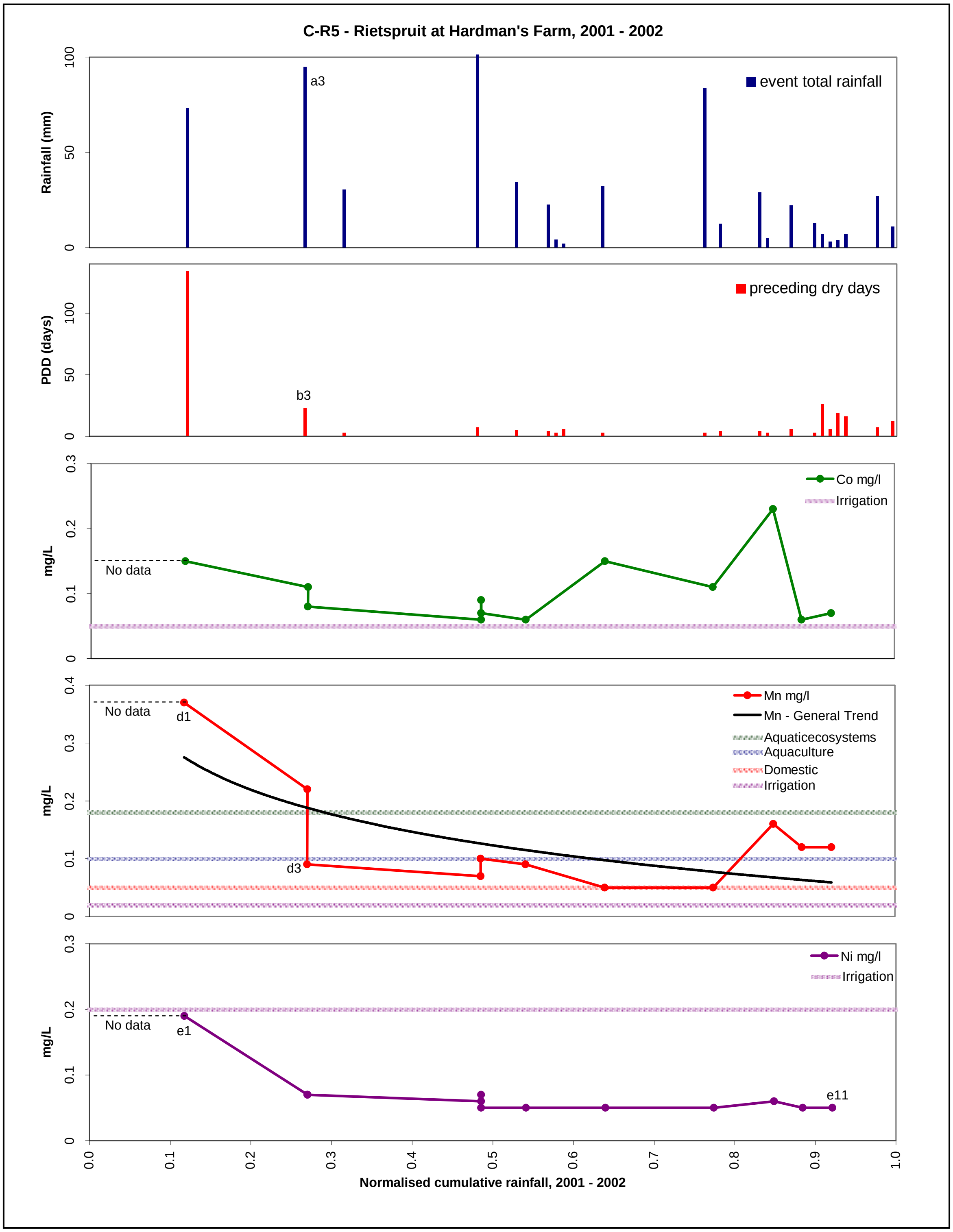


Figure 19: Concentrations versus normalised cumulative rainfall for 2001/2002 at R5 - Rietspruit at R550 (Hardman's Farm) for cobalt, manganese and nickel (Note: The TWQR legal limits are indicated by the horizontal lines in the graphs).

have been present in the runoff in the form of particles and no **cadmium** or **copper** were present at all.

In figure 19, the concentration of cobalt (green) did not seem to decrease, but it does seem to follow the same general pattern as manganese (red) and nickel (purple). Therefore, even though the evidence for a seasonal first flush for cobalt is inadequate, it is still possible to suggest that all three metals have the road as their source (refer to discussion in section 6.2.1.). The concentration levels of cobalt, however, remained above the limit for irrigation (0.05 mg/L) right through the season and was almost five times the legal limit at its highest concentration in the season (0.23 mg/L). High concentrations of cobalt in water used for irrigation can have harmful impacts on plants, as discussed in section 3.3.3.1.

As shown in figure 19, the concentration of manganese (red) was highest at the start of the season (at point d1), and decreased as the season progressed. This general trend can be more clearly seen by the black line, therefore providing support for the existence of a seasonal first flush. As shown in the red graph, the concentration of manganese at d1 was more than seven times the legal limit for domestic use (0.05 mg/L); more than 18 times the regulation level for irrigation (0.02 mg/L); twice the legal level for aquatic ecosystem health (0.18 mg/L); and almost eight times the legal limit for aquaculture (0.1 mg/L). In addition, the concentration of manganese remained above the legal limits for domestic use and irrigation throughout the season, however, at point d3, the concentration dropped below the regulatory levels for aquatic ecosystem health and aquaculture. High concentrations of manganese can have a number of detrimental effects on the environment and human health, as discussed in section 3.3.7. More detailed investigation of the data-points is not possible due to fluctuations in the concentration values. These slight fluctuations in the concentration data could be caused by differing site- and time-specific conditions when the samples were taken and analysed as well as the fact that only one analysis was done per rainfall event.

Furthermore, the nickel concentration (purple) was highest in the first relevant rainfall event (at point e1) and decreased throughout the rest of the season, suggesting the presence of a seasonal first flush for this metal. The concentration of nickel, in contrast to cobalt and manganese, remained below the legal limit for irrigation (0.2 mg/L) all through the season.

According to these results, the R550 was a significant source of dissolved **cobalt** and **manganese** during the 2001/2002 season at this site, as shown in figure 19. However, only the dissolved fractions of cobalt, manganese and nickel are represented in the water quality data and the composition of the insoluble fraction in the runoff is therefore unknown. Yet, as discussed in section 6.2.1. (by taking into consideration that the pH values at this site ranged between 7.8 and 8.8 (slightly alkaline)), it is possible to infer that more **nickel** was present in the runoff than was detected. Animals and humans could consume these particles in their drinking water, possibly experiencing more negative effects on their health than would be caused by the dissolved fractions alone.

In conclusion, a seasonal first flush was identified for **manganese** and **nickel** for the 2001/2002 season. As shown in figure 19, the concentrations of **cobalt** and **manganese** released into the Rietspruit River were higher than the legal limits for irrigation, domestic use, aquacultural purposes and aquatic ecosystem health. High concentrations of these metals can cause damage to the environment, as discussed in sections 3.3.3. (cobalt), 3.3.7. (manganese), and 3.3.8. (nickel).

The rainy season of 2003/2004 will be discussed next.

6.3.2. R5 - Rainy season 2003 – 2004 (Figure 20):

Figure 20 shows the concentrations of cobalt (green), manganese (red) and nickel (purple) according to the normalised cumulative rainfall (refer to Appendix B for more detailed data). Their safe legal limits for irrigation, domestic use, aquacultural purposes and aquatic ecosystem health are also shown (refer to table 18).

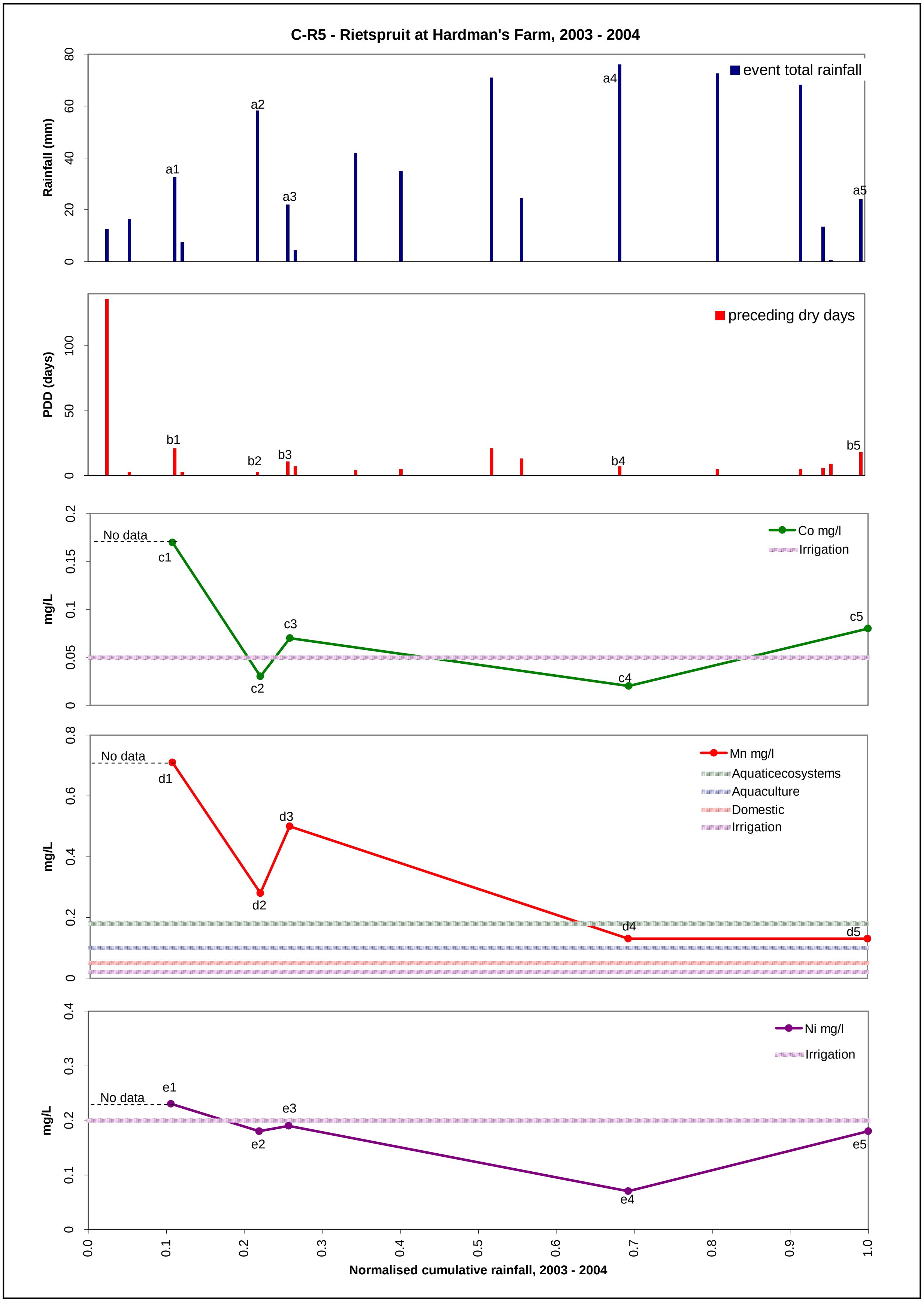


Figure 20: Concentrations versus normalised cumulative rainfall for 2003/2004 at R5 - Rietspruit at R550 (Hardman's Farm) for cobalt, manganese and nickel (Note: The TWQR legal limits are indicated by the horizontal lines in the graphs).

The other metals under investigation (**aluminium, cadmium, chromium, copper, iron, lead** and **zinc**) were not detected. As discussed earlier in sections 6.2.1. and 6.2.2., it is possible to conclude that some **aluminium, chromium, iron, lead** and **zinc** could have been present in the runoff in the form of particles and no **cadmium** or **copper** were present at all.

The concentration of cobalt (green), manganese (red) and nickel (purple) were highest in the first relevant rainfall event (points c1, d1 and e1, respectively) and showed a general decline throughout the season, as illustrated in figure 20. This pattern provides support for the presence of a seasonal first flush for cobalt, manganese and nickel. It also appears as if the concentrations of all three metals in the runoff are more influenced by the PDD than the amount of rainfall. For example, point c2 (0.03 mg/L cobalt) was measured as a result of a 58.2 mm rainfall event (point a2), with only 3 PDD (point b2), however, point c3 (0.07 mg/L cobalt) resulted from only a 22 mm rainfall event (point a3), but with 11 PDD (point b3). Yet, both of these points (c2 and c3) are lower than point c1 (0.17 mg/L cobalt), therefore supporting the statement that a seasonal first flush is present for this metal. This same statement can be made for manganese (red) as well as nickel (purple).

In the beginning of the season, the cobalt concentration (green) was more than three times above the legal limit for irrigation (0.05 mg/L). Throughout the rest of the season, the concentration remained close to the safe limit. High concentrations of cobalt in irrigation water can have harmful impacts on plants, as discussed in section 3.3.3.1. For manganese (red), the concentration at point d1 was more than seven times above the legal limit for aquaculture (0.1 mg/L); more than 14 times the safe limit for domestic use (0.05 mg/L); more than 35 times the safe level for irrigation (0.02 mg/L); and almost four times the legal limit for aquatic ecosystem health (0.18 mg/L). Also, the concentration of manganese remained above the regulatory safe levels for aquaculture, domestic use and irrigation throughout the season, only dropping below the limit for aquatic ecosystem health at d4. High concentrations of manganese in water can have a number of negative effects on the environment and human health, as discussed in section 3.3.7.

The concentration of nickel (purple) was only slightly above the limit for irrigation (0.2 mg/L) at the start of the season (point e1) with a value of 0.23 mg/L. Water used for irrigation containing high concentrations of nickel can have harmful effects on plants, as discussed in section 3.3.8.1.

According to figure 20, there is a common pattern evident for cobalt, manganese and nickel. Therefore, as discussed in section 6.2.1., it is likely that the metals originate from the same source (the road) and were subjected to the same physical (rainfall) and chemical (pH) surroundings

It was found that the R550 was a significant source of dissolved **cobalt** and **manganese** throughout the 2003/2004 season at this site. These metals were introduced into the environment at levels exceeding the legal limits of irrigation, aquatic ecosystem health, aquaculture, domestic use and irrigation, as illustrated in figure 20. Unfortunately, the water quality data that was used in this investigation only provided information on the dissolved metal fractions, the composition of the insoluble fraction in the runoff is unknown. However, as discussed in section 6.2.1. (by taking into consideration that the pH values at this site ranged between 7.8 and 8.8 (slightly alkaline)), it is still possible to surmise that more **nickel** was present in the runoff than was detected. Therefore, humans and animals drinking water contaminated by these particles could possibly experience further damaging effects on their health than would be caused by the dissolved fractions alone.

In conclusion, a seasonal first flush was identified for **cobalt, manganese** and **nickel** for the 2003/2004 season. The concentrations of **cobalt** and **manganese** released into the Rietspruit River were higher than the legal limits for irrigation, domestic use, aquacultural purposes and aquatic ecosystem health, as shown in figure 20. High concentrations of these metals can have detrimental impacts on the environment and human health, as discussed in sections 3.3.3. (cobalt), 3.3.7. (manganese), and 3.3.8. (nickel).

The rainy season of 2004/2005 will be discussed next.

6.3.3. R5 - Rainy season 2004 – 2005 (Figure 21):

In figure 21, the concentrations of cobalt (green), iron (blue), manganese (red) and nickel (purple) are shown according to the normalised cumulative rainfall for the 2004/2005 rainy season. The legal limits for irrigation, domestic use, aquacultural purposes and aquatic ecosystem health are also shown (refer to table 18). According to the water quality data, the other metals under investigation (**aluminium, cadmium, chromium, copper, lead** and **zinc**) were not detected in significant amounts. As previously discussed in sections 6.2.1. and 6.2.2., it is possible that some **aluminium, chromium, lead** and **zinc** could have been present in the runoff as particles and no **cadmium** or **copper** were present at all.

As shown in figure 21, the cobalt concentrations (green) did not show a large concentration peak which decreased as the season progressed. The same can be said for nickel (purple). Therefore, there is not enough evidence of a seasonal first flush for these two metals. However, the concentrations of iron (blue) and manganese (red) were highest in the first relevant rainfall event (points d1 and e1, respectively) and decreased continuously throughout the season. This pattern provides support for the presence of a seasonal first flush for iron and manganese.

The concentration of cobalt at points c3, c4 and c5 were above the legal safe limits for irrigation (0.05 mg/L) and was three times this limit at point c5. High concentrations of cobalt in irrigation water can have harmful effects on plants, as discussed in section 3.3.3.1. The iron concentration at d1 was 13 times the limit for aquaculture (0.01 mg/L) and stayed above this level throughout the season, however the concentration was only slightly above the safe limit for domestic use (0.1 mg/L), with a value of 0.13 mg/L, before dropping below this level at d2. High concentrations of iron in river water can have negative effects on the aquatic environment, as discussed in section 3.3.6.2. The manganese concentration (red) at e1 was more than nine times the regulation limit for aquatic ecosystem health (0.18 mg/L); 17 times the safe level for aquaculture (0.1 mg/L);

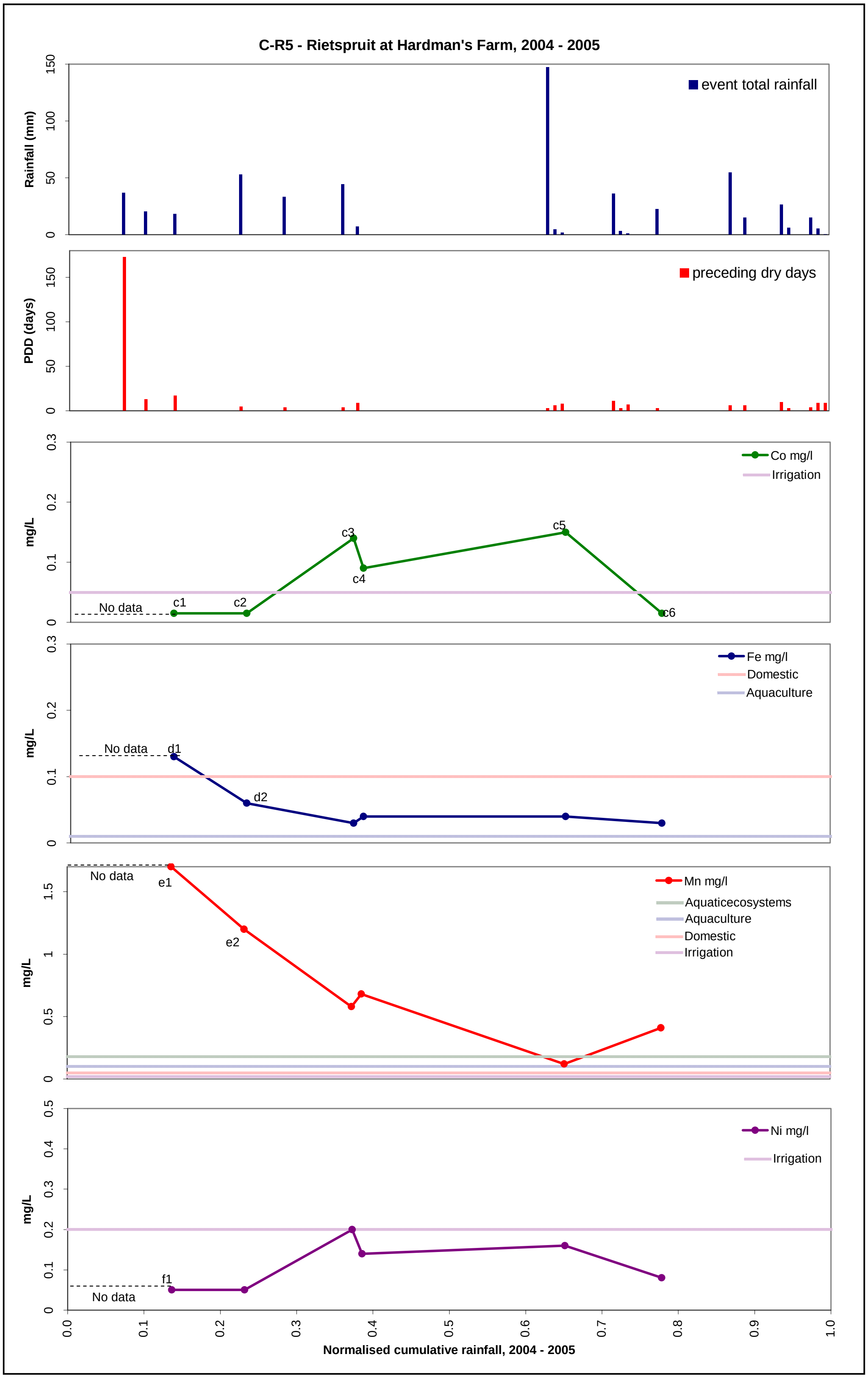


Figure 21: Concentrations versus normalised cumulative rainfall for 2004/2005 at R5 - Rietspruit at R550 (Hardman’s Farm) for cobalt, iron, manganese and nickel (Note: The TWQR legal limits are indicated by the horizontal lines in the graphs).

34 times the legal limit for domestic use (0.05 mg/L); and 85 times the legal safe limit for irrigation (0.02 mg/L). High concentrations of manganese persisted all the way through the season, remaining above the legal limits for the above water use sectors. These high concentrations can have a number of harmful impacts on the environment and human health, as discussed in section 3.3.7. The concentration of nickel (purple), however, remained below the legal level for irrigation (0.2 mg/L) during the season.

Manganese exhibits a similar response to nickel and cobalt (Sansalone *et al.*, 1996; Kirkby & Römheld, 2004; He *et al.*, 2005) and this is demonstrated in the results already discussed previously, where these metals displayed the same pattern throughout the season. However, in this case cobalt (green) and nickel (purple) have corresponding patterns and manganese (red) and iron (blue) are matched in their pattern. This association can be seen in the periodic table (figure 22), where manganese is next to iron (thus more similar in their physical and chemical properties (Arthur, 2004)) and cobalt is next to nickel (therefore also more similar in their properties than with manganese (Kirkby & Römheld, 2004; He *et al.*, 2005)). Even though all of these metals have much

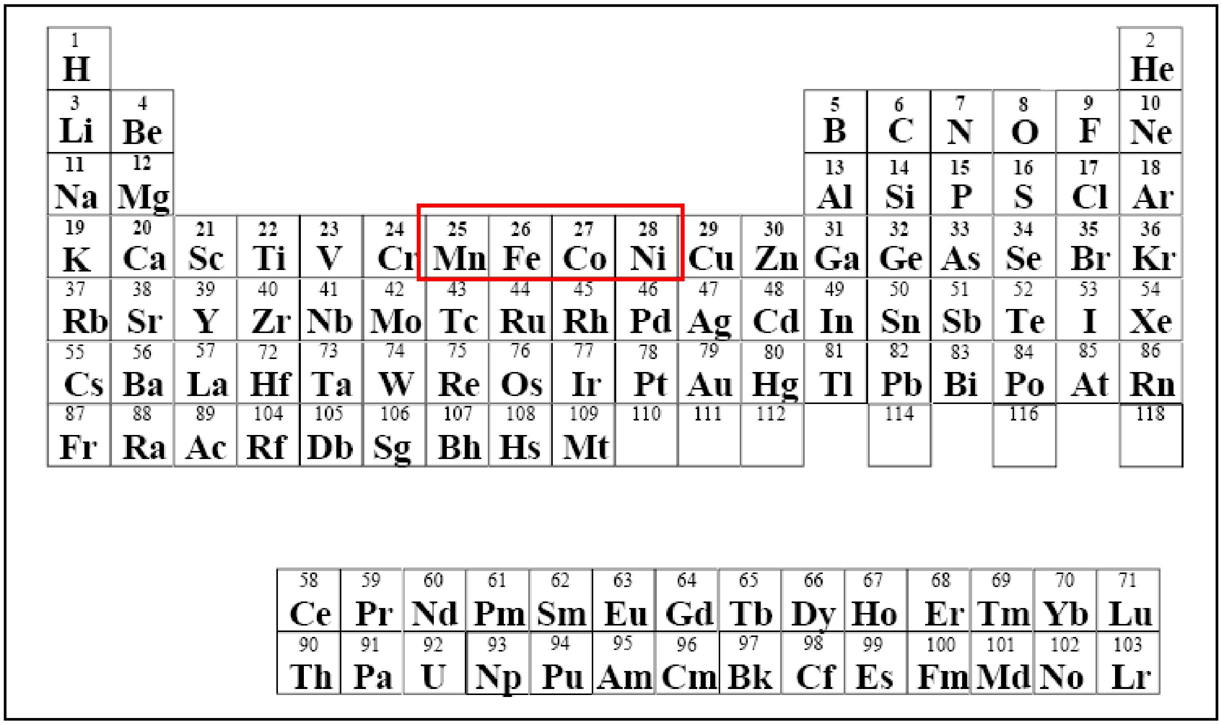


Figure 22: Periodic table of the elements showing the locations of manganese, iron, cobalt and nickel.

the same properties, when they are all present together, the differences in physical and chemical attributes can be demonstrated, as shown in figure 21. Therefore it is likely that all these metals come from the same source (the road) and were subjected to the same physical (rainfall) and chemical (pH) conditions, thus eliminating the possibility of sample contamination from other sources.

In slightly alkaline solutions, iron is mostly found as the insoluble ferric hydroxide ($Fe(OH)_3$) (Brix & DeForest, 2000; Tuccillo, 2006), but a small amount still remains in solution. It was found, as shown in figure 21 (blue line), that there was a noticeable amount of dissolved iron in the runoff throughout the season. Therefore, it can be presumed that there was an even larger amount of insoluble **iron** present in the runoff. In addition, as discussed in section 6.2.1. (by taking into consideration that the pH values at this site ranged between 7.8 and 8.8 (slightly alkaline)), it is also possible that more **nickel** (in particulate form) were present in the runoff than was detected. Water containing these particles can be consumed by animals and humans and their health could possibly be further negatively impacted than would be caused by the dissolved fractions alone.

In conclusion, a seasonal first flush was identified for **iron** and **manganese** for the 2004/2005 season at this site. According to the available data, the R550 was a significant source of **cobalt, manganese** and **iron** that was washed into the nearby Rietspruit River environment and their concentrations were above the regulation limits for aquatic ecosystem health, aquaculture, domestic use and irrigation. High concentrations of these metals can have a number of harmful impacts on the environment and human health, as discussed in sections 3.3.3. (cobalt), 3.3.6. (iron), 3.3.7. (manganese), and 3.3.8. (nickel).

The assessment of the study site on the R550 at the Rietspruit River identified distinctive seasonal first flush in all rainy seasons studied. Seasonal first flush was detected for **cobalt** during the rainy season of 2003/2004; **iron** for 2004/2005; **manganese** for 2001/2002, 2003/2004 and 2004/2005; and **nickel** for 2001/2002 and 2003/2004. It was found that the metals followed similar patterns throughout the season, therefore providing evidence that they have the same source (the road). This site was chosen for study to determine if the road contributes a significant amount of heavy metals into the river, as it passes by a large mielie farm and formal and informal settlements, before flowing into a tributary of the Vaal River. From these results it can be seen that there is a substantial problem at this site with high concentrations of dissolved **cobalt, manganese, nickel** and **zinc** (and to a lesser extent, **iron**) being introduced into the Rietspruit River environment, as shown in figures 19, 20 and 21, and summarised in table 20. These large concentrations of metals can have potentially harmful effects on the aquatic environment, plant, animal and human health and the nearby settlements and farms could be negatively influenced by the dissolved heavy metals washed from the R550 into the Rietspruit River. For a more detailed discussion of the effects of these metals on the environment, refer to section 3.3.

Table 20: Metals displaying seasonal first flush as well as approximate amount the metal concentrations, at the initial rainfall event, exceeded legal limits at the R5 monitoring site for the studied rainy seasons (**a** – No seasonal first flush; **b** – Legal Limit set by TWQR).

2001/2002	2003/2004	2004/2005
[a] Co – irrigation – 5x **[b]**LL	Co – irrigation – 3x LL	**[a]** Co – irrigation – 3x LL
Mn – domestic – 7x LL Mn – irrigation – 18x LL Mn – aquatic ecosystems – 2x LL Mn – aquaculture – 8x LL	Mn – irrigation – 35x LL Mn – domestic – 14x LL Mn – aquaculture – 7x LL Mn – aquatic ecosystems – 4x LL	Fe – aquaculture – 13x LL
		Mn – irrigation – 85x LL Mn – domestic – 34x LL Mn – aquaculture – 17x LL Mn – aquatic ecosystems – 9x LL
Ni – below legal limits	Ni – below legal limits	**[a]** Ni – below legal limits

The next site to be investigated was a road in Springs and the results are discussed next.

6.4. Results and discussion of B5 - Blesbokspruit at Welgedacht Road (Springs) (Blue dot in Figure 13 and graphs in Figures 23 and 24):

Water quality data for selected metals (**aluminium, cadmium, cobalt, chromium, copper, iron, manganese, nickel, lead** and **zinc**) were evaluated according to rainfall and **preceding dry days** (**PDD**) for the rainy seasons 1999/2000 and 2003/2004. Not all the rainfall events at this site have corresponding metal concentration data available and this resulted in some years not having enough relevant data available for meaningful analysis.

6.4.1. B5 - Rainy season 1999 – 2000 (Figure 23):

In figure 23, the concentrations of iron (blue) and manganese (red) are shown according to the normalised cumulative rainfall for the season (refer to Appendix B for more detailed data). The legal limits for irrigation, domestic use, aquaculture and aquatic ecosystem health are also presented (refer to table 18). According to the available water quality data, the other metals under investigation (**aluminium, cadmium, cobalt, chromium, copper, nickel, lead** and **zinc**) were not detected. As previously discussed in sections 6.2.1. and 6.2.2., it is possible that some aluminium, chromium, lead and zinc were present as particulates and no cadmium or copper were present in the runoff at all. Cobalt is mostly found as the free Co^{2+} ion in slightly alkaline waters (Hunter *et al.*, 1999) and therefore (since the pH values at this site ranged between 7.5 and 8.3 (slightly alkaline)) no cobalt was present in the runoff. Nickel occurs mostly as insoluble $NiCO_3(s)$, with lesser amounts of free Ni^{2+} ion (which can be adsorbed on organic matter (Brix & DeForest, 2000; Ansari *et al.*, 2004)) in slightly alkaline waters (Hunter *et al.*, 1999). Therefore, even though no dissolved nickel was found, it is possible that particulate-bound nickel was present in the runoff. In summary, **aluminium, chromium, nickel, lead** and **zinc** could have been present in the runoff as particulates; and no **cobalt**, **cadmium** or **copper** were present at all.

The first relevant rainfall event (point a1 – 26.2 mm) yielded the highest concentrations of iron (point c1 – 0.18 mg/L) and manganese (point d1 - 1.4 mg/L) and it dropped continuously throughout the season, even though there were very large rainfall events towards the end of the season (point a3 – 318.3 mm and a4 – 121.5 mm), as depicted in figure 23. The presence of a seasonal first flush can therefore be postulated for iron and manganese.

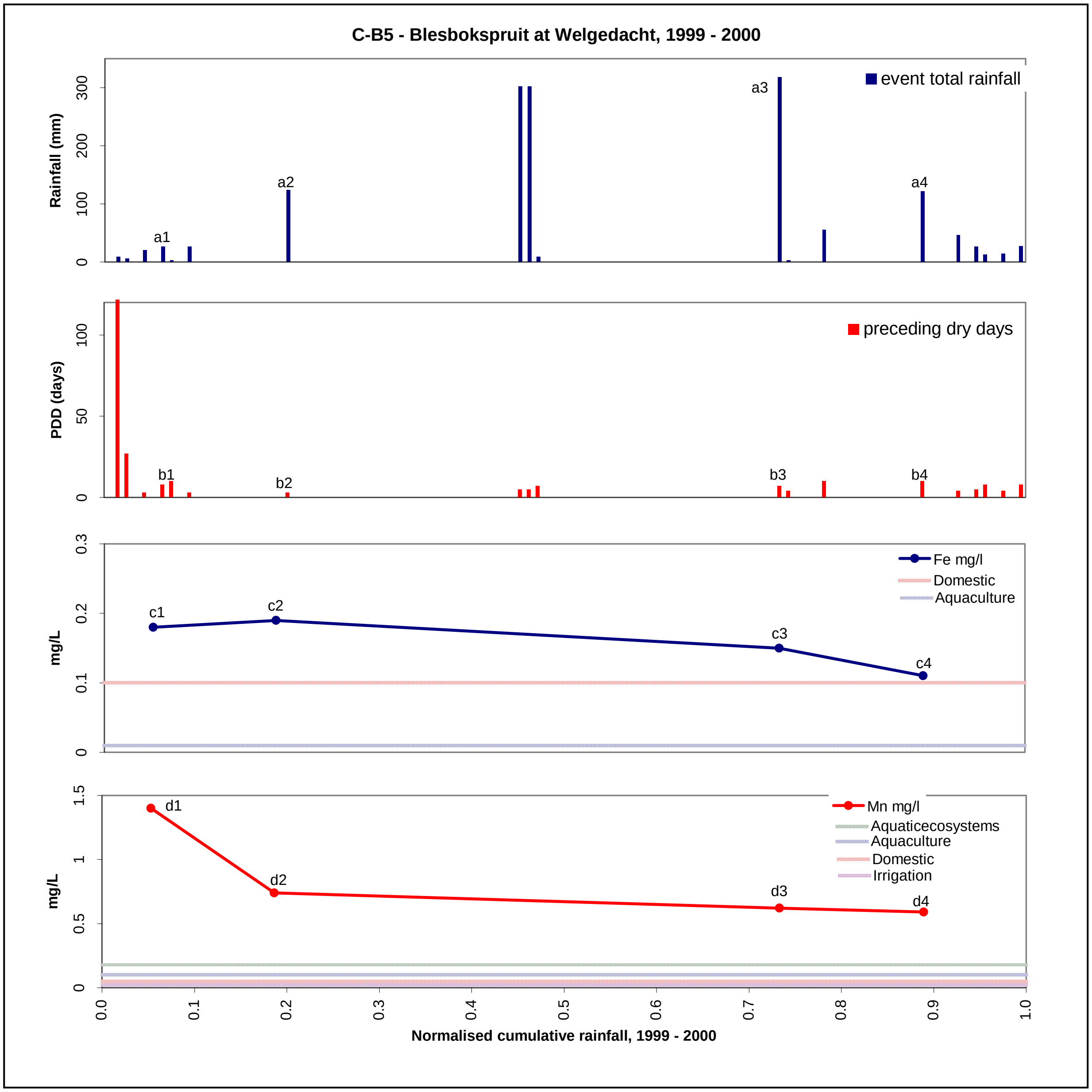


Figure 23: Concentrations versus normalised cumulative rainfall for 1999/2000 at B5 - Blesbokspruit at Welgedacht Road (Springs) for iron and manganese (Note: The TWQR legal limits are indicated by the horizontal lines in the graphs).

The concentration of iron remained above the legal safe limits for domestic use and aquaculture throughout the season, and at c1 was almost twice the legal safe limit for domestic use (0.1 mg/L); and 18 times the legal limit for aquaculture (0.01 mg/L). High concentrations of iron in water can have harmful impacts on the aquatic environment and human health, as discussed in sections 3.3.6.2. and 3.3.6.4. respectively. In addition, the concentration of manganese at d1 was almost eight times the regulation level for aquatic ecosystem health (0.18 mg/L); 14 times the safe legal level for aquaculture (0.1 mg/L);

28 times the regulation safe level for domestic use (0.05 mg/L); and 70 times the legal safe limit for irrigation (0.02 mg/L). High manganese concentration levels persisted throughout the season for the above mentioned water use sectors. These high concentrations can have a number of negative effects on the environment and human health, as discussed in section 3.3.7.

The similar response patterns of manganese and iron, as revealed at previous sites, cannot be seen in this instance. This is possibly due to the fact that there is not enough data available to make any more deductions beyond identifying the first flush.

It was found that the monitoring site on Welgedacht Road was a significant source of dissolved **iron** and **manganese** throughout the 1999/2000 season. These two metals were introduced into the Blesbokspruit wetland environment at concentration levels exceeding the legal limits of domestic use, aquaculture, aquatic ecosystem health and irrigation, as illustrated in figure 23. Unfortunately, the water quality data that was used in this investigation only provided information on the dissolved metal fractions, the composition of the insoluble fraction in the runoff is therefore unknown. However, as discussed in section 6.3.3., it is possible to surmise that a large amount of particulate bound (insoluble) **iron** was present in the runoff. Therefore, animals and humans consuming this contaminated water could possibly be caused further harm than would be produced by the dissolved fractions alone.

In conclusion, a seasonal first flush was identified for **iron** and **manganese** for the 1999/2000 season. The concentrations of these metals in the runoff that flowed into the Rietspruit River were above the legal limits set for irrigation, domestic use, aquacultural purposes and aquatic ecosystem health, as shown in figure 23. High concentrations of these metals can have detrimental effects on the environment, as discussed in sections 3.3.6. (iron) and 3.3.7. (manganese).

The rainy season of 2004/2005 will be discussed next.

6.4.2. B5 - Rainy season 2003 – 2004 (Figure 24):

Figure 24 shows the concentrations of aluminium (black), iron (blue), manganese (red), nickel (purple) and zinc (orange) according to the normalised cumulative rainfall for the season (refer to Appendix B for more detailed data). The legal limits for irrigation, domestic use, aquacultural purposes and aquatic ecosystems are also shown (refer to table 18). According to the available water quality data, the other metals under investigation (**cadmium, cobalt, chromium, copper** and **lead**) were not detected. As was previously discussed in sections 6.2.1. and 6.4.1., it is probable that some **chromium** and **lead** may have been present as particulates and no **cadmium**, **cobalt** or **copper** were present in the runoff at all.

A seasonal first flush could not be confirmed for aluminium, since the concentrations detected in the initial rainfall events are not higher than later in the season, as shown in figure 24 (black line). It is possible that the large concentration detected in the middle of the season (point c4) is from an outside source (possibly from the nearby Grootvlei Mines), since aluminium should show a similar response to iron (Sansalone *et al.*, 1996), which is not the case here. In spite of this, it is still apparent that the concentration of aluminium introduced into the wetland environment at c4 is 172 times the limit set for aquatic ecosystem health (0.005 mg/L); almost 29 times the legal safe level for aquacultural purposes (0.03 mg/L); and almost 6 times the legal limit for domestic use (0.15 mg/L). Such high concentrations of aluminium can have a number of detrimental impacts on the aquatic environment and human health, as discussed in sections 3.3.1.2. and 3.3.1.4. respectively.

In alkaline waters, aluminium is mostly present as $Al(OH)_4^-$ (Sansalone *et al.*, 1996; Brix & DeForest, 2000), which is then predominately bound to particulates. Therefore, at high concentrations of total aluminium, it is possible that some soluble $Al(OH)_4^-$ is present at detectable levels. This is confirmed by the available data (the pH values at this site ranged between 7.5 and 8.3 (slightly alkaline)), and shown in figure 24 as the black line, and as such, it is possible to conclude that a very large amount of particulate-bound **aluminium** was present in the runoff.

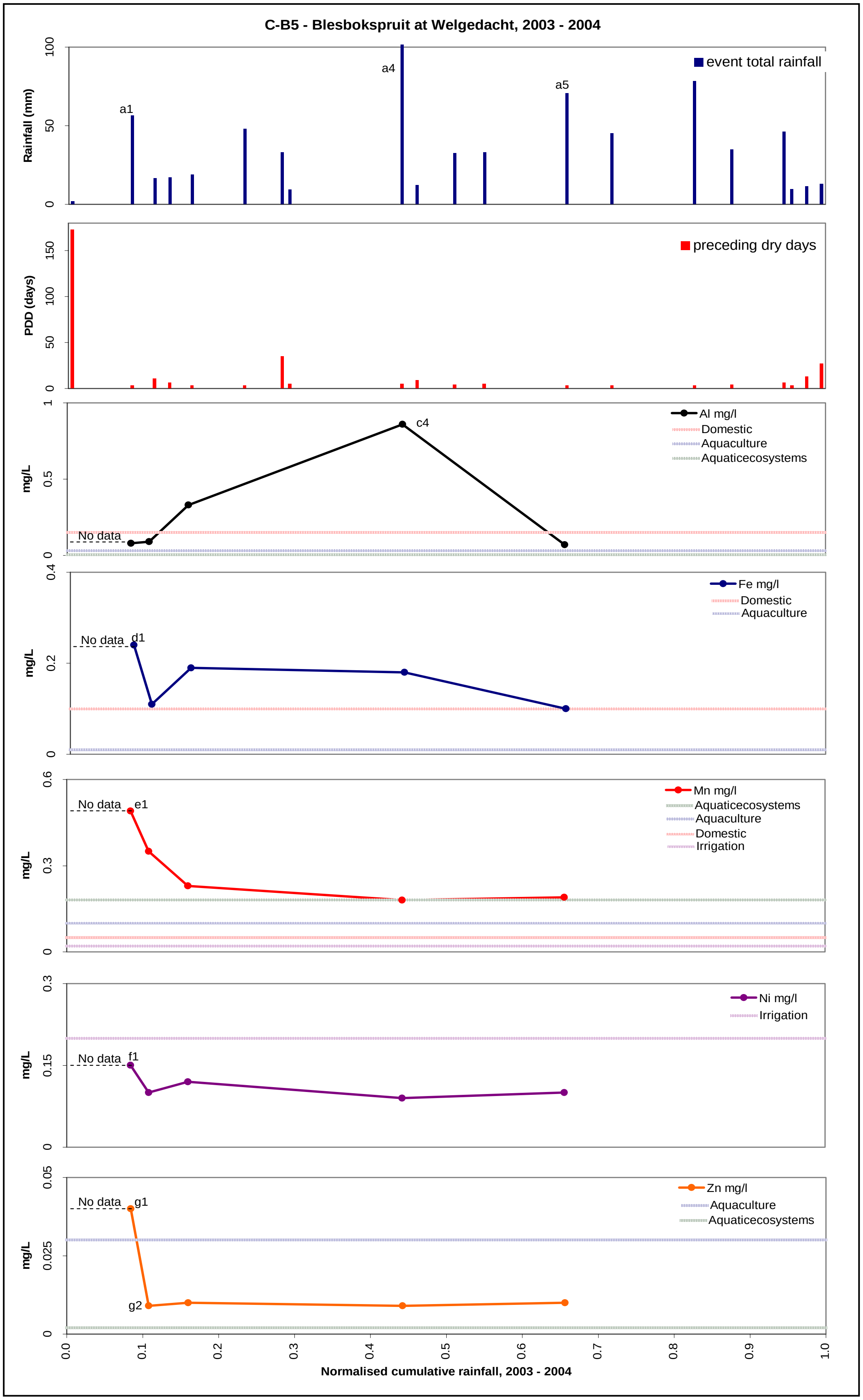


Figure 24: Concentrations versus normalised cumulative rainfall for 2003/2004 at B5 - Blesbokspruit at Welgedacht Road (Springs) for aluminium, iron, manganese, nickel and zinc (Note: The TWQR legal limits are indicated by the horizontal lines in the graphs).

The concentrations of iron (blue), manganese (red), nickel (purple) and zinc (orange) were at the season maximum (points d1, e1, f1 and g1 respectively) in the first relevant rainfall event (point a1 – 56.5 mm) and decreased continuously throughout the season, even though there were large rainfall events later in the season (points a4 – 105.5 mm and a5 – 70.8 mm), as shown in figure 24. This pattern provides support for the presence of a seasonal first flush for iron, manganese nickel and zinc.

At d1, the concentration of iron was more than twice the legal safe level for domestic use (0.1 mg/L); and eight times the legal limit for aquaculture (0.03 mg/L). Also, throughout the season, the concentration of iron was above the safe levels for these water use sectors, as shown in figure 24. High concentrations of iron can have a number of negative impacts on the aquatic environment and human health, as discussed in sections 3.3.6.2. and 3.3.6.4. respectively. The concentration of manganese at e1 was almost three times the legal level for aquatic ecosystem health (0.18 mg/L); almost five times the regulation safe level for aquaculture (0.1 mg/L); almost 10 times the legal limit for domestic use (0.05 mg/L); and almost 25 times the regulation safe limit for irrigation (0.02 mg/L). For the duration of the season, the concentration of manganese stayed above the safe limits set for these water use sectors. Concentrations of manganese above these legal limits can have negative effects on the environment as well as human health, as discussed in section 3.3.7. Nickel concentrations, however, were below the legal limit for irrigation (0.2 mg/L) throughout the season. On the other hand, the zinc concentration at g1 was 20 times the legal limit for aquatic ecosystem health (0.002 mg/L). The zinc concentration was only slightly above the safe level set for aquaculture (0.03 mg/L) with a value of 0.04 mg/L before it dropped below this level at point g2. High concentrations of zinc can negatively impact the aquatic environment, as discussed in section 3.3.10.2.

Iron, manganese, nickel and zinc generally seem to exhibit a similar pattern, as shown in figure 24, as is expected (Sansalone *et al.*, 1996; Kirkby & Römheld, 2004; He *et al.*, 2005). Therefore, as discussed in section 6.2.1., it is likely that the metals originate from the same source (the road) and were subjected to the same physical (rainfall) and chemical (pH) surroundings, thus reducing the possibility of contamination from other sources.

It was found that this road in Springs was a significant source of dissolved **aluminium, iron, manganese** and **zinc** throughout the 2003/2004 season at this monitoring site. These metals were introduced into the environment at levels exceeding legal limits for domestic use, irrigation, aquatic ecosystem health and aquaculture, as illustrated in figure 24. The water quality data that was used for this study only provided information on the dissolved metal fractions and so the composition of the insoluble fraction present in the runoff is not known. However, as discussed in sections 6.2.1. and 6.3.3., it is still possible to surmise that more **iron** and **zinc** was present in the runoff than was detected. Water containing these particles can be ingested by animals and humans and their health could possibly be further negatively impacted than would be caused by the dissolved fractions alone.

In conclusion, a seasonal first flush was identified for **iron, manganese, nickel** and **zinc** for the 2003/2004 season. The concentrations of **aluminium, iron, manganese** and **zinc** released into the Rietspruit River and wetland were higher than set legal limits for domestic use, aquaculture, aquatic ecosystem health and irrigation, as shown in figure 24. High concentrations of these metals can have damaging effects on the environment as well as human health, as discussed in sections 3.3.1. (aluminium), 3.3.6. (iron), 3.3.7. (manganese), and 3.3.10. (zinc).

The results of the investigation of the study site on the Welgedacht Road identified seasonal first flush in all rainy seasons studied. Seasonal first flush was detected for **iron** during the rainy season of 1999/2000 and 2003/2004; **manganese** for 1999/2000 and 2003/2004; **nickel** for 2003/2004; and **zinc** for 2003/2004. It was also found that these metals followed similar patterns throughout the season, therefore providing evidence that they have the same source (i.e. the road). This site was chosen for study to determine if the road contributes a significant amount of heavy metals into the wetland, since wetlands are areas where water is the primary factor controlling the environment and the associated plant and animal life. The Blesbokspruit wetland forms a component of one of the tributaries of the Vaal River, which provides water for drinking and irrigation to Gauteng, and has been declared as a Ramsar site (AGA, 2004). It was revealed that **aluminium, iron, manganese,** and **zinc** (and to a lesser extent, **nickel**) were introduced into the Rietspruit River environment at concentrations higher than the legal limits for domestic use, aquaculture, aquatic ecosystem health and irrigation, as shown in figures 23 and 24, and summarised in table 21, during the evaluated rainy seasons. Therefore, the aquatic plant and animal life in the wetland would have been impacted the most by these high concentrations of metals. For a more detailed discussion of these impacts, refer to section 3.3.

Table 21: Metals displaying seasonal first flush as well as approximate amount the metal concentrations, at the initial rainfall event, exceeded legal limits at the B5 monitoring site for the studied rainy seasons (**a** – No seasonal first flush; **b** – Legal Limit set by TWQR).

1999/2000	2003/2004
Fe – domestic 2x [b]LL Fe – aquaculture – 18x LL Mn – irrigation – 70x LL Mn – domestic – 28x LL Mn – aquaculture – 14x LL Mn – aquatic ecosystems – 8x LL	[a] Al – domestic – 6x LL [a] Al – aquaculture – 29x LL [a] Al – aquatic ecosystems – 172x LL Fe – domestic – 2x LL Fe – aquaculture – 8x LL Mn – irrigation – 25x LL Mn – domestic – 10x LL Mn – aquaculture – 5x LL Mn – aquatic ecosystems – 3x LL Ni – below legal limits Zn – aquatic ecosystems – 20x LL

Comparing the results of all the monitoring sites, the following can be noted. The monitoring site R4 consistently exhibited seasonal first flush for **cobalt, manganese, nickel** and **zinc**. It is possible that, since this site is on a large and frequently used road (N3 highway), tire wear, engine wear and brake wear of a large number of vehicles can be the source of these metals. The consistency shown for the seasonal first flush at site R4 is not present for the other two sites. It is possibly due to sporadic traffic densities and changing conditions of the roads at these sites (since they are smaller than the N3) and therefore build-up of metals is not consistent. However, it is more probable that there is just not enough information available for a more detailed analysis. It is not possible to compare the concentrations of metals across the different seasons or different sites, since concentration is dependent on the amount (and volume) of rainfall, which is not the same for different years.

In the following section, a summary of the results is given and conclusions are made based thereon.

7. Conclusions:

The primary objectives of this study were to:

- discuss the phenomenon of the seasonal first flush of highway runoff;
- describe possible environmental effects of too low and too high levels of heavy metals, with reference to relevant legislation concerning water pollution;
- describe possible best management practices (BMP's) to lessen the effects of too high levels of heavy metals;
- describe the study area and why it was chosen;
- identify shortcomings of the study;
- collect and analyse relevant data for the last five years (1999 – 2005) to determine if the first flush phenomenon is present for selected heavy metals (aluminium, cadmium, cobalt, chromium, copper, iron, manganese, nickel, lead, and zinc);
- identify the main heavy metals present in runoff in the Witwatersrand area;
- propose improvements to future highway monitoring projects; and
- recommend mitigation strategies to reduce the environmental impacts of heavy metals.

As discussed in section 3.1., highway runoff is a mixture of chemical compounds (such as heavy metals) from vehicles which accumulate on highway surfaces (Sansalone *et al.*, 1996; Bricker, 1999; Hunt *et al.*, 2002; Lee *et al.*, 2004; BEST, 2005). During rainfall events, these heavy metals are washed from road surfaces to adjacent waters and may have adverse effects on ecosystems and biota if mitigating measures are not taken (Sansalone *et al.*, 1996; Buckler & Granato, 1999; Bricker, 1999; Breault & Granato, 2000; Hunt *et al.*, 2002; BEST, 2005). The term 'seasonal first flush' is used to refer to the initial rainfall event of a rainy season that contains a large percentage of pollution.

Highway runoff can have adverse effects on the environment if no measures are taken for the removal of excessive pollutants (such as heavy metals) before the runoff reaches receiving waters. A thorough understanding of how heavy metals influence living organisms is essential when monitoring highway runoff and was discussed in section 3.3. It was found that the selected metals (aluminium, cadmium, cobalt, chromium, copper, iron, manganese, nickel, lead and zinc) could have serious health effects on plants, aquatic organisms, livestock and humans. **Target Water Quality Ranges** (**TWQR**) from the **South African Department of Water Affairs and Forestry** (**SA-DWAF**) were used to attain the accepted water quality constituent values for aquatic ecosystem health, and domestic and agricultural use so as to evaluate the concentration values obtained at the selected study sites.

A number of **Best Management Practices** (**BMP**'s) were described (section 3.4.) that can be used to reduce the impact of contaminants associated with highway rainfall runoff, such as heavy metals, on the environment. Three of the BMP's that are most effective for the removal of heavy metals were discussed: infiltration basins; artificial wetlands; and biofiltration strips and swales.

South Africa's available freshwater resources are almost fully-utilised and under severe stress (Harris *et al.*, 1999) and at present many water resources contain large amounts of pollutants, such as heavy metals (Sansalone *et al.*, 1996; Su & Mitchell, 2003). It is therefore important to monitor the levels of these heavy metals in the rivers and lakes of the country, especially in sites that are close to pollutant producing areas, such as roads. Rand Water has a water quality monitoring system spanning across Gauteng. Therefore, three water monitoring sites in the Witwatersrand, maintained by Rand Water, were selected as locations worthwhile for further study as these sites represent a range of different types of roads, ranging from the large N3 highway to smaller country roads. The characteristics of each of the study sites were discussed in section 4.2.:

- R4 - Rietspruit at N3 (Alberton-Heidelberg) – on the large N3 highway;
- R5 - Rietspruit at R550 (Hardman's Farm) – near a farm and settlement; and
- B5 - Blesbokspruit at Welgedacht Road (Springs) – passing through a wetland.

Relevant data from the last five years (1999 – 2005) were collected and analysed, as discussed in section 5. The first data set required were the concentrations of the selected heavy metals at the selected sites. Additional to this, the pH of the water was also needed. Both of these data sets were obtained electronically from Rand Water for the period 1999 to 2005 in the form of Excel data sheets. The basic method used to analyse the samples to determine the metal concentrations was also obtained. The first flush is dependent on rainfall and therefore daily precipitation data at or near the study sites were needed as the second data set. This was electronically obtained from the South African Weather Bureau for Heidelberg and Springs for the period 1999 - 2005 in the form of Excel data sheets. A number of shortcomings to the study were then recognised (section 5.1.2.):

- As there is no official highway rainfall runoff monitoring system in South Africa, data from different sources (Rand Water and the Weather Bureau) had to be used, thus it was found that some rainfall events did not have corresponding water quality data;
- Only one water quality analysis was done per rainfall event, thus resulting in small, random fluctuations in the data; and
- Data from Rand Water only represented the concentration of the dissolved fraction of the metal, therefore there is no way to determine the amount of particulate-bound metals were introduced into the environment.

However, it was found that there was still enough data available to be able to make meaning conclusions about the presence of a seasonal first flush for the selected metals.

Generally, the proof of the seasonal first flush is presented graphically and therefore the methods used for data analysis and presentation of results in this study were based on the study by Lee *et al.* (Lee *et al.*, 2004) (as discussed in section 5.2.). Rainfall and water quality data from rainy seasons (September to April) over the last six years (1999 - 2005) were analysed for each of the study sites to verify the existence of a seasonal first flush.

The results obtained of the data analysis are summarised in table 22.

Table 22: Metals displaying seasonal first flush as well as approximate amount the metal concentrations, at the initial rainfall event, exceeded legal limits at the selected monitoring sites (**a** – No seasonal first flush; **b** – Legal Limit set by TWQR).

	1999/2000	2001/2002	2003/2004	2004/2005
R4	Co – irrigation – 12x [b]LL Mn – irrigation – 48x LL Mn – domestic – 19x LL Mn – aquaculture – 10x LL Mn – aquatic ecosystems – 5x LL Ni – irrigation – 8x LL Ni – livestock – 2x LL Zn – aquaculture – 30x LL Zn – aquatic ecosystems – 460x LL	Co – irrigation – 5x LL Mn – irrigation – 16x LL Mn – domestic – 6x LL Mn – aquaculture – 3x LL Mn – aquatic ecosystems – 2x LL Ni – below legal limits	N/A	Co – irrigation – 4x LL Mn – domestic – 10x LL Mn – irrigation – 25x LL Ni – irrigation – 2x LL Zn – aquaculture – 4x LL Zn – aquatic ecosystems – 55x LL
R5	N/A	[a] Co – irrigation – 5x LL Mn – domestic – 7x LL Mn – irrigation – 18x LL Mn – aquatic ecosystems – 2x LL Mn – aquaculture – 8x LL Ni – below legal limits	Co – irrigation – 3x LL Mn – irrigation – 35x LL Mn – domestic – 14x LL Mn – aquaculture – 7x LL Mn – aquatic ecosystems – 4x LL Ni – below legal limits	[a] Co – irrigation – 3x LL Fe – aquaculture – 13x LL Mn – irrigation – 85x LL Mn – domestic – 34x LL Mn – aquaculture – 17x LL Mn – aquatic ecosystems – 9x LL [a] Ni – below legal limits
B5	Fe – domestic 2x LL Fe – aquaculture – 18x LL Mn – irrigation – 70x LL Mn – domestic – 28x LL Mn – aquaculture – 14x LL Mn – aquatic ecosystems – 8x LL	N/A	[a] Al – domestic – 6x LL [a] Al – aquaculture – 29x LL [a] Al – aquatic ecosystems – 172x LL Fe – domestic – 2x LL Fe – aquaculture – 8x LL Mn – irrigation – 25x LL Mn – domestic – 10x LL Mn – aquaculture – 5x LL Mn – aquatic ecosystems – 3x LL Ni – below legal limits Zn – aquatic ecosystems – 20x LL	N/A

It can be seen that in almost all instances, a seasonal first flush was detected. Also, the concentrations of the metals at the initial rainfall event were usually much higher than the legal limit for the different water use sectors. For example, at the R4 site during the 1999/2000 season the concentration of zinc was approximately 460 times the legal limit set for aquatic ecosystem health. Therefore, it can be concluded that this site is a source of high concentrations zinc that could harm aquatic organisms.

As the results in section 6 show, roads are significant sources of heavy metals that can be introduced into the environment, usually at concentrations much higher than the legal limits set for aquatic ecosystem health and domestic and agricultural use. These high peaks in concentrations are caused by the seasonal first flush, where the heavy metals collect on the road surfaces during long dry periods before being washed away during the first few rainfall events of the rainy season. Therefore, additional study is necessary to further quantify the concentrations of heavy metals and how they are affected by rainfall intensities, preceding dry days and traffic densities. However, as there is no official highway runoff monitoring system in South Africa (Okonkwo & Mothiba, 2005), to accomplish this, it is proposed that dedicated monitoring sites be created that are equipped to take samples of the runoff during a storm event and that the samples are analysed both for dissolved and particulate-bound metals (Sansalone *et al.*, 1996; Hunt *et al.*, 2002; Su & Mitchell, 2003; Lee *at al.*, 2004; Kim *et al.*, 2005; Tuccillo, 2006). Therefore, every rainfall event would have corresponding, and accurate, concentration data, so as to be able to more accurately predict and understand the effect of the total mass load of metals (dissolved and particulate-bound) on the environment. This information would also make it possible to more effectively implement mitigation measures such as BMP’s to protect the environment.

A number of ways to mitigate the large concentrations of dissolved heavy metals introduced into the environment (in the form of BMP’s) can be proposed. These recommendations are discussed in the next section.

8. Recommendations to mitigate environmental impacts:

8.1. Introduction:

The results of this study indicate that the roads under study could provide a significant contribution of dissolved heavy metals to nearby rivers, possibly causing harm to the aquatic environment and all organisms (plants, animals and humans) dependent on the water. **Best Management Practices** (**BMP**'s) are preventative measures utilising biological processes and vegetation which reduce environmental impacts by preventing these soluble pollutants from entering the hydrologic cycle (CGER, 1999).

Possible BMP's that could be implemented at each site will now be discussed, however, refer to section 3.4. for a more detailed exposition of the BMP's mentioned below.

8.2. Recommended BMP's for each study site:

8.2.1. R4 - Rietspruit at N3 (Alberton-Heidelberg) (Green dot in Figure 13):

This site is located where the N3 highway between Alberton and Heidelberg passes over the Rietspruit River. The river flows through open grassland, past expanding formal and informal settlements, areas of spray irrigation and pastures, before flowing into a tributary of the Vaal River.

The **average annual daily traffic** (**AADT**) for 2003 for this highway was 28203 (SA-NRA, 2003), and it was consequently found that this site introduced large concentrations of dissolved metals into the river that could negatively impact the nearby settlements and farms, as summarised in table 22. As such, the most appropriate BMP for this site is an **infiltration basin** as it is the most effective, reliable and versatile BMP available. An infiltration basin is a vegetated, open impoundment where incoming rainfall runoff is stored until it gradually infiltrates into the soil strata, thereby removing both particulate and soluble pollutants (refer to section 3.4.1. for a more detailed description of this BMP). Therefore, as this site is located in open grassland, there would be enough space to construct this cost-effective and low maintenance practice (VDCR, 1999) to remove the large concentrations of cobalt, manganese, nickel and zinc present in the rainfall runoff before it flows into the river towards the settlements and farms.

8.2.2. R5 - Rietspruit at R550 (Hardman's Farm) (Red dot in Figure 13):

This site is located where the R550 road passes over the Rietspruit River, near Hardman's Farm. The river flows past a large mielie farm and formal and informal settlements, before flowing into a tributary of the Vaal River.

The BMP that is recommended for use at this site, since it contributed significant concentrations of dissolved heavy metals into the river which could be detrimental to the nearby agricultural practises, is either an **infiltration basin** or a small **artificial wetland** (also called a wetpond). Wetlands provide physical, chemical, and biological water quality treatment of rainfall runoff. Artificial wetlands also offer natural aesthetic qualities, wildlife habitat, erosion control, and pollutant removal (VDCR, 1999; Beitia *et al.*, 2003) (refer to section 3.4.2.1. for a more detailed description of this BMP). Since this site is located in open country, there would be enough space to construct this low maintenance practice (VDCR, 1999) to remove the high levels of dissolved cobalt, manganese, nickel and iron from the rainfall runoff before it flows into the river headed for the nearby farm and settlements.

8.2.3. B5 - Blesbokspruit at Welgedacht Road (Springs) (Blue dot in Figure 13):

This site is located where Welgedacht Road in Springs passes over the Blesbokspruit River and wetland. The Blesbokspruit wetland forms a component of one of the tributaries of the Vaal River, which provides water for drinking and irrigation to Gauteng, and has been declared as a Ramsar site (AGA, 2004).

As described above, wetlands provide water quality treatment of rainfall runoff, however, as this wetland has been placed on the Montreux Record as being a wetland degraded by excessive pollution (Peck, 2003), additional mitigating measures should be taken. Therefore, the BMP that is recommended for use at this site, as it contributed significant concentrations of dissolved heavy metals into the river which could be detrimental to the wetland, are **biofiltration strips and swales** (refer to section 3.4.3. for a more detailed description of this BMP). They are sections of land next to the highway vegetated with erosion resistant and flood tolerant grasses over which rainfall runoff flows as overland sheet flow. Biofiltration strips and swales are a cost-effective and low maintenance method to provide physical, chemical, and biological water quality treatment of rainfall runoff (VDCR, 1999; Lantin & Alderete, 2002; Scharff *et al.*, 2003) to lessen the amount of dissolved iron, manganese and aluminium entering the protected wetland environment.

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Appendix A: Detailed legislation for: Irrigation, Aquacultural Purposes, Aquatic Ecosystem Health, Livestock Watering, and Domestic Use:

A.1. Aluminium (Al):

Table 23: Effects of aluminium in irrigation water on crop yield and quality (SA-DWAF: Agricultural Use - Irrigation, 1996).

Concentration Range (mg/L)	**Crop Yield and Crop Quality**
Target Water Quality Range < 5.0	Several crops show aluminium toxicity at concentrations as low as 0.1 - 0.5 mg/L in soil solution. Soils have the capacity to adsorb complex aluminium ions, thereby reducing their toxicity to plants
5 - 20	Maximum acceptable concentration for fine textured, neutral to alkaline soils
> 20	Acceptable for irrigation only over the short term on a site specific basis

Table 24: Table of criteria and effects of aluminium on the health of fish (SA-DWAF: Agricultural Use - Aquaculture, 1996).

Concentration (mg Al^{3+}/L)	**Effects**
TWQR < 0.03	No adverse effects on aquatic life at pH > 6.5
0.07	Toxic to stickleback (*Gasterosteus aculaeatus*)
0.1 - 0.105	Toxic to striped bass (*Morone saxatilis*), 21-d LD_{50} for brown trout
1.5	Fatal to brown trout (*Salmo trutta*)

Table 25: The TWQR and criteria for acid-soluble aluminium in aquatic ecosystems (SA-DWAF: Aquatic Ecosystems, 1996).

TWQR and Criteria	**Aluminium concentration (µg/L)**	
	pH< 6.5	**pH > 6.5**
TWQR	**<5**	**<10**
Chronic Effect Value CEV)	10	20
Acute Effect Value (AEV)	100	150

Table 26: Effects of aluminium on the health of livestock (SA-DWAF: Agricultural Use - Livestock, 1996).

Concentration Range (mg/L)	**Effects**
	All species
TWQR 0 - 5	No adverse effects
5 - 10	Adverse chronic effects, such as neurotoxicity, may occur but are unlikely if: - feed concentrations are normal - exposure is short term

	- adequate dietary intake of calcium and phosphorus Could even be tolerated in the long term, depending on site-specific factors, for example water requirement
> 10	Adverse chronic and acute effects, such as neurotoxicity, may occur, although: - short-term exposure can be tolerated depending on site-specific factors, such as adequate calcium and phosphate intake and water requirement

Table 27: Effects of aluminium on aesthetics and human health in domestic water use (SA-DWAF: Domestic Use, 1996).

Concentration Range (mg/L)	Effects
TWQR **0 - 0.15**	No acute or chronic health effects occur. Intake from water is <5% of the total dietary intake of aluminium. Generally, no adverse aesthetic effects occur. Very slight discolouration of water may become apparent when iron or manganese is present in association with aluminium at the upper limit of the range
0.15 - 0.5	Intake from water may exceed 5% of the total dietary intake, but no effects on health are expected. Noticeable adverse aesthetic effects (colour) occur when aluminium is present in association with iron or manganese
> 0.5	Intake from water exceeds 5% of the total daily intake, but no acute health effects are expected except at very high concentrations. There may be long-term neurotoxic effects. Severe aesthetic effects (discolouration) occur in the presence of iron or manganese

A.2. Cadmium (Cd):

Table 28: Effects of cadmium in irrigation water on crop yield and quality (SA-DWAF: Agricultural Use - Irrigation, 1996).

Concentration Range (mg/L)	Crop Yield and Crop Quality
TWQR **< 0.01**	Toxic to beans, beets and turnips at concentrations as low as 0.1 mg/L in nutrient solutions. Conservative limits are needed because of cadmium's potential for accumulation in plants and soils to concentrations that may be toxic to humans and animals
0.01 - 0.05	Maximum acceptable as concentration for fine-textured neutral to alkaline soils
> 0.05	Acceptable for irrigation only over the short term on a site-specific basis

Table 29: The target water quality ranges for soluble cadmium for different water hardness values (SA-DWAF: Agricultural Use - Aquaculture, 1996).

Water hardness (mg $CaCO_3$/L)	TWQR for soluble cadmium (μg/L)
0 – 60 (Soft)	**<0.2**
60 – 120 (Medium)	**<0.8**
120-180 (Hard)	**<1.3**
>180 (Very hard)	**<1.8**

Table 30: The TWQR and criteria for total cadmium at different water hardness (mg $CaCO_3$/L) in aquatic ecosystems (SA-DWAF: Aquatic Ecosystems, 1996).

TWQR and Criteria	**Cadmium concentration (µg/L)**			
	<60 (Soft)	60-119 (Medium)	120-180 (Hard)	>180 (Very hard)
TWQR	**<0.15**	**<0.25**	**<0.35**	**<0.40**
Chronic Effect Value (CEV)	0.3	0.5	0.7	0.8
Acute Effect Value (AEV)	3	6	10	13

Table 31: Effects of cadmium on the health of livestock (SA-DWAF: Agricultural Use - Livestock, 1996).

Concentration Range (mg/L)	**Effects**
	All species
TWQR **0 - 0.01**	No adverse effects
0.01 - 0.02	Adverse chronic effects such as anaemia, testicular degeneration, reduced feed intake and milk production and reduced growth may occur, but are unlikely if: - exposure is short term - adequate intake of dietary protein, calcium and phosphorus - feed concentration of cadmium is normal Adverse acute effects such as abortions, still births, hepato- and nephrotoxicity may occur, but suckling and pregnant livestock are principally at risk. Could even be tolerated in the long term, depending on site-specific factors such as water requirement and Ca:P concentrations
> 0.02	Adverse chronic and acute effects (as above) may occur, although short-term exposure could be tolerated depending on: - feed concentrations of cadmium - adequate intake of dietary protein, calcium and phosphorus - water requirement

Table 32: Effects of cadmium on human health from domestic water use (SA-DWAF: Domestic Use, 1996).

Concentration Range (µg/L)	**Effects**
TWQR **0 - 5**	No observable health effects
As a precautionary measure, it is recommended that the TWQR not be exceeded because of the potentially acute and/or irreversible effects of cadmium on human health	
5-10	No observable health effects, unless zinc nutritional status is suboptimal, or in smokers, where there is a slight risk of subclinical effects on long-term exposure
10-20	Threshold for health damage with continuous exposure. Single incidence of exposure will not have observable effects
20-1000	Danger of kidney damage with long-term exposure. Brief exposure, for less than one week should not cause any noticeable damage. Exposure should not exceed one week
>1000	Danger of acute cadmium poisoning, with the possibility of fatalities

A.3. Cobalt (Co):

Table 33: Effects of cobalt in irrigation water on crop yield and quality (SA-DWAF: Agricultural Use - Irrigation, 1996).

Concentration Range (mg/L)	**Crop Yield and Crop Quality**
TWQR < 0.05	A satisfactory concentration for continuous application is 0.05mg/L; 0.1mg/L is near the toxicity threshold of many plants. Generally cobalt does not accumulate in edible parts of plants to levels that are dangerous to consumers
0.05 - 5.0	Maximum acceptable as concentration for fine-textured neutral to alkaline soils
> 5.0	Acceptable for irrigation only over the short term on a site-specific basis

Table 34: Effects of cobalt on the health of livestock (SA-DWAF: Agricultural Use - Livestock, 1996).

Concentration Range (mg/L)	**Effects**
	All species
TWQR 0 - 1	No adverse effects
1 - 2	Adverse chronic effects such as inappetence and weight loss may occur, but are unlikely if: - feed concentrations are normal - exposure is short term Could even be tolerated in the long term, depending on site-specific factors such as nutritional interactions and water requirement
> 2	Adverse chronic effects (as above) may occur, although short-term exposure can be tolerated depending on site-specific factors such as nutritional interactions and water requirement

A.4. Chromium (Cr):

Table 35: Effects of chromium on crop yield and quality (SA-DWAF: Agricultural Use - Irrigation, 1996).

Concentration Range (mg/L)	**Crop Yield and Crop Quality**
TWQR < 0.10	Depending on plant species, nutrient solutions containing 0.1mg/L can induce chromium toxicity
0.10 - 1.0	Maximum acceptable as concentration for fine-textured neutral to alkaline soils
> 1.0	Acceptable for irrigation only over the short term on a site-specific basis

Table 36: The TWQR and criteria for dissolved chromium(III) and chromium(VI) in aquatic ecosystems (SA-DWAF: Aquatic Ecosystems, 1996).

TWQR and Criteria	**Chromium(III) concentration (µg/L)**	**Chromium(VI) concentration (µg/L)**
TWQR	**<12**	**<7**
Chronic Effect Value (CEV)	24	14
Acute Effect Value (AEV)	340	200

Table 37: Effects of chromium on the health of livestock (SA-DWAF: Agricultural Use - Livestock, 1996).

Concentration Range (mg/L)	**Effects**
	All species
TWQR **0 - 1**	No adverse effects
1 - 2	Adverse chronic effects such as diarrhoea may occur, but are unlikely if: - feed concentrations are normal - exposure is short term Can even be tolerated in the long term, depending on site-specific factors such as nutritional interactions and water requirement
> 2	Adverse chronic effects such as diarrhoea and possible carcinogenic effects may occur, although short-term exposure could be tolerated depending on site-specific factors such as nutritional interactions and water requirement

Table 38: Effects of chromium(VI) on human health from domestic water use (SA-DWAF: Domestic Use, 1996).

Concentration Range (mg/L)	**Effects**
TWQR **0 - 0.050**	Risk of cancer induction insignificant No toxic or aesthetic effects
As a precautionary measure it is recommended that the TWQR not be exceeded due to the potentially acute and/or irreversible effects of chromium(VI) on human health	
0.05-1.0	Possible risk of induction of gastrointestinal cancer following long-term exposure
1.0-5.0	Undesirable taste, slight nausea, and increasing risk of cancer induction
>5.0	Risk of acute toxicity

A.5. Copper (Cu):

Table 39: Effects of copper in irrigation water on crop yield and quality (SA-DWAF: Agricultural Use - Irrigation, 1996).

Concentration Range (mg/L)	**Crop Yield and Crop Quality**
TWQR **< 0.2**	Depending on plant species, nutrient solutions containing 0.1 - 1.0mg/L can induce copper toxicity. Yield reduction and crop failure are the main effects of copper-contaminated soils. Generally copper does not accumulate in edible parts of plants to levels that are dangerous to consumers (root crops such as potatoes and radishes have been shown to concentrate copper)
0.2 - 5.0	Maximum acceptable as concentration for fine-textured neutral to alkaline soils
> 5.0	Acceptable for irrigation only over the short term on a site-specific basis

Table 40: The criteria and effects of copper on the health of fish (SA-DWAF: Aquaculture, 1996).

Concentration Range (mg/L)	**Effects**
TWQR **< 0.005**	No known adverse effects
0.006	*Upper limit for continuous exposure in soft water*
0.009	96-hr LD_{50} for striped bass (*Morone saxiatilis*)

0.014	Safe limit for salmonids
0.03	*Upper limit for continuous exposure in hard water*
0.02 - 0.04	Impaired hatching in rainbow trout
0.048	96-hr LD_{50} for Atlantic salmon (*Salmo salar*)
0.07	Avoidance behaviour observed in rainbow trout
1.29 - 1.38	LD_{50} for African Catfish (*Clarias gariepinus*)
0.46	96-hr LD_{50} for goldfish (*Carassius auratus*)
0.6	96-hr LD_{50} for carp (*Cyprinus carpio*)

Table 41: The TWQR and criteria for dissolved copper at different water hardness (mg $CaCO_3$/L) in aquatic ecosystems (SA-DWAF: Aquatic Ecosystems, 1996).

TWQR and Criteria	**Copper concentration (µg/L)**			
	<60 (Soft)	60-119 (Medium)	120-180 (Hard)	>180 (Very hard)
TWQR	**<0.3**	**<0.8**	**<1.2**	**<1.4**
Chronic Effect Value (CEV)	0.53	1.5	2.4	2.8
Acute Effect Value (AEV)	1.6	4.6	7.5	12

Table 42: Effects of copper on the health of livestock (SA-DWAF: Agricultural Use - Livestock, 1996).

Concentration Range (mg/L)	**Effects**		
	Horses, pigs and poultry	Cattle	Sheep and pre-weaned calves
0 - 0.5	**a**	**a**	**a**
0.5 - 1	**a**	**a**	**b**
1 - 2	**a**	**c**	**d**
2 - 5	**a**	**d**	**d**
5 - 10	**c**	**d**	**d**
> 10	**d**	**d**	**d**

a - **TWQR**. No adverse effects.

b - Adverse chronic effects such as diarrhoea and liver damage can occur, but may be tolerated if:
- there is adequate Mo and S intake,
- feed concentrations are normal, and
- exposure is short term.

Can even be tolerated in the long term, depending on site-specific factors such as nutritional interactions and water requirement.

c - Adverse chronic effects (as above) may occur, but are unlikely if:
- there is adequate Mo and S intake,
- feed concentrations are normal, and
- exposure is short term.

Can even be tolerated in the long term, depending on site-specific factors such as nutritional interactions and water requirement.

d - Adverse chronic (as above) and acute effects such as liver damage and haemolytic jaundice may occur, although short-term exposure can be tolerated depending on site-specific factors such as nutritional interactions and water requirement.

Table 43: Effects of copper on aesthetics and human health from domestic use (SA-DWAF: Domestic Use, 1996).

Concentration Range (mg/L)	Effects
TWQR **0 - 1**	No health or aesthetic effects
1-3	No health effects. Astringent taste and staining of laundry and plumbing fixtures start appearing
3-30	No health effects. Severe taste and staining problems
30-200	Gastrointestinal irritation, nausea and vomiting. Severe taste and staining problems
>200	Severe poisoning with possible fatalities. Severe taste and staining problems

A.6. Iron (Fe):

Table 44: Effects of iron in irrigation water on crop yield and quality (SA-DWAF: Agricultural Use - Irrigation, 1996).

Concentration Range (mg/L)	Crop Yield and Crop Quality
TWQR **< 5.0**	Not toxic to root uptake by plants in aerated soils. Plant foliage damaged or blemished by iron deposits when wetted during irrigation
5.0 - 20.0	Maximum acceptable as concentration for fine-textured neutral to alkaline soils
> 20.0	Exceeds the maximum acceptable concentration used by most international guidelines

Table 45: The criteria and effects of iron on the health of fish (SA-DWAF: Agricultural Use - Aquaculture, 1996).

Concentration Range (mg/L)	Effects
TWQR **< 0.01**	No known adverse effects on fish
0.2-1.75	General lethal threshold concentration for fish 48hr LD_{50} for brook trout (pH 7.0) is 0.41mg/L 48hr LD_{50} for brook trout (pH 6.0) is 0.48mg/L Reduced growth in coho salmon juveniles at 1.27mg ($Fe(OH)_3$)/L 48hr LD_{50} for brook trout (pH 5.5) is 1.75 mg/L

Table 46: Effects of iron on the health of livestock (SA-DWAF: Agricultural Use - Livestock, 1996).

Concentration Range (mg/L)	Effects
	All species
TWQR **0 - 10**	No adverse effects
10 - 50	Adverse chronic effects such as liver and pancreas damage, may occur, but are unlikely if: - feed concentrations are normal, and - exposure is short term Could even be tolerated in the long term, depending on site-specific factors, such as adequate intake of phosphate and water requirement
> 50	Adverse chronic and acute effects such as diarrhoea, vomiting, acidosis and respiratory failure and liver and pancreas damage respectively, may occur, although short-term

	exposure could be tolerated depending on site specific factors such as adequate intake of phosphate and water requirement

Table 47: Effects of iron on aesthetics, human health and household distribution systems from domestic use (SA-DWAF: Domestic Use, 1996).

Concentration Range (mg/L)	Effects
TWQR **0 - 0.1**	No taste, other aesthetic or health effects associated with consumption and use
0.1-0.3	Very slight effects on taste and marginal other aesthetic effects. Deposits in plumbing with associated problems may begin to occur. No health effects; the water is generally well tolerated
0.3-1.0	Adverse aesthetic effects (taste) gradually increase as do possible problems with plumbing. No health effects
1-10	Pronounced aesthetic effects (taste) along with problems with plumbing. Slight health effects expected in young children, and sensitive individuals
10-30	Severe aesthetic effects (taste) and effects on the plumbing (slimy coatings). Slight iron overload possible in some individuals. Chronic health effects in young children and sensitive individuals in the range 10 - 20 mg/L, and occasional acute effects toward the upper end of this range
30-100	As above. Long-term health effects gradually increase
100-300	As above. Chronic health effects. Acute toxicity may begin to appear
300-3000	As above. Chronic and acute health effects. Accidental iron poisoning from water is rare
3000-30000	As above. Lethal toxicity occurs

A.7. Manganese (Mn):

Table 48: Effects of manganese in irrigation water on crop yield and quality (SA-DWAF: Agricultural Use - Irrigation, 1996).

Concentration Range (mg/L)	Crop Yield and Crop Quality
TWQR < **0.02**	Depending on plant species, nutrient solutions containing a few tenths of a mg/L can induce manganese toxicity
0.02 - 10.0	Maximum acceptable as concentration for fine-textured neutral to alkaline soils
> 10.0	Acceptable for irrigation only over the short term on a site-specific basis

Table 49: The TWQR and criteria for dissolved manganese in aquatic ecosystems (SA-DWAF: Aquatic Ecosystems, 1996).

TWQR and Criteria	Manganese concentration (μg/L)
TWQR	**<180**
Chronic Effect Value (CEV)	370
Acute Effect Value (AEV)	1300

Table 50: Effects of manganese on the health of livestock (SA-DWAF: Agricultural Use - Livestock, 1996).

Concentration Range (mg/L)	**Effects**
	All species
TWQR **0 - 10**	No adverse effects
10 - 50	Adverse chronic effects such as weight loss due to inappetence may occur, but are unlikely if: - feed concentrations are normal, and - exposure is short term. Could even be tolerated in the long term, depending on site-specific factors such as adequate intake of calcium, phosphorus and iron and water requirement
> 50	Adverse chronic effects such as weight loss and anaemia (where iron intake is not adequate) may occur, although short-term exposure could be tolerated depending on site-specific factors (as above)

Table 51: Effects of manganese on aesthetics and human health from domestic water use (SA-DWAF: Domestic Use, 1996).

Concentration Range (mg/L)	**Effects**
TWQR **0 - 0.05**	No health or aesthetic effects; marginal aesthetic problems occasionally found in the 0.02-0.05 mg/L range
0.05-0.10	Tolerable range, although slight staining may occur. No health effects
0.10-0.15	Threshold for significant staining and taste problems. No health effects
0.15-1.0	Increasingly severe staining and taste problems. No health effects
1-2	Very severe staining and taste effects. No health effects
2-5	Extreme staining, likely to be aesthetically unacceptable to a large proportion of users. No health effects
5-14	Unacceptable levels of aesthetic effects. Health effects rare
14-20	Very severe, aesthetically unacceptable staining. Domestic use unlikely due to adverse aesthetic effects. Some chance of manganese toxicity under unusual conditions
>20	Domestic use unlikely due to extreme aesthetic effects. Chronic toxicity; at high concentrations, possible acute effects

A.8. Nickel (Ni):

Table 52: Effects of nickel in irrigation water on crop yield and quality (SA-DWAF: Agricultural Use - Irrigation, 1996).

Concentration Range (mg/L)	**Crop Yield and Crop Quality**
TWQR **< 0.20**	Depending on plant species, nutrient solutions containing 0.5 - 1.0mg/L can induce nickel toxicity
0.20 - 2.0	Maximum acceptable as concentration for fine-textured neutral to alkaline soils
> 2.0	Acceptable for irrigation only over the short term on a site-specific basis

Table 53: Effects of nickel on the health of livestock (SA-DWAF: Agricultural Use - Livestock, 1996).

Concentration Range (mg/L)	**Effects**	
	Pigs	All other livestock
0 - 1	**a**	**a**
2 - 5	**a**	**b**
5 - 10	**b**	**c**
> 10	**c**	**c**

a - **TWQR.** No adverse effects.

b - Adverse chronic effects such as reduced growth may occur, but are unlikely if:
- feed concentrations are normal, and
- exposure is short term

Could even be tolerated in the long term, depending on site-specific factors such as nutritional interactions and water requirement.

c - Adverse chronic (as above) and acute effects such as possible adverse reproductive effects may occur, although short-term exposure may be tolerated depending on site-specific factors such as nutritional interactions and water requirement.

A.9. Lead (Pb):

Table 54: Effects of lead in irrigation water on crop yield and quality (SA-DWAF: Agricultural Use - Irrigation, 1996).

Concentration Range (mg/L)	**Crop Yield and Crop Quality**
TWQR **< 0.20**	Application at the rate of 1 000 mm/annum for 100 years would result in lead accumulation to 89 mg/kg in the top 150 mm of soil. Few plants appear to be affected at this level. Yield reduction and crop failure are the main effects of lead contaminated soils. Generally lead does not accumulate in edible parts of plants to levels that are dangerous to consumers (potatoes, lettuce and hay have, however, been shown to concentrate lead)
0.20 - 2.0	Maximum acceptable as concentration for fine-textured neutral to alkaline soils
> 2.0	Acceptable for irrigation only over the short term on a site-specific basis

Table 55: Table of criteria and effects of lead on the health of fish (SA-DWAF: Agricultural Use - Aquaculture, 1996).

Concentration Range (mg Pb/L)	**Effects**
TWQR **< 0.01**	No adverse effects on fish health; TWQR for soft water
0.03	Maximum acceptable upper concentration for brook trout. General upper limit for continuous exposure
0.03 - 0.3	Spinal deformities after prolonged exposure
0.3 - 2.15	96hr LD_{50} for rainbow trout 1.2mg/L; for African catfish (*Clarias spp.*) 1.72mg/L; for Nile tilapia 2.15mg/L

Table 56: The TWQR and criteria for dissolved lead at different water hardness (mg $CaCO_3$/L) in aquatic ecosystems (SA-DWAF: Aquatic Ecosystems, 1996).

TWQR and Criteria	**Lead concentration (µg/L)**			
	< 60 (Soft)	60-119 (Medium)	120-180 (Hard)	> 180 (Very hard)
TWQR	**<0.2**	**<0.5**	**<1.0**	**<1.2**
Chronic Effect Value (CEV)	0.5	1.0	2.0	2.4
Acute Effect Value (AEV)	4	7.0	13	16

Table 57: Effects of lead on the health of livestock (SA-DWAF: Agricultural Use - Livestock, 1996).

Concentration Range (mg/L)	**Effects**	
	Pigs	All other livestock
0 - 0.1	**a**	**a**
0.1 - 0.2	**a**	**b**
0.2 - 0.5	**a**	**c**
0.5 - 1	**b**	**c**
> 1	**c**	**c**

a - **TWQR.** No adverse effects.

b - Adverse chronic effects such as anorexia, emaciation and possible respiratory distress may occur, but are unlikely if
- feed concentrations are normal, and
- exposure is short term.
Can even be tolerated in the long term, depending on site-specific factors such as adequate dietary protein intake and water requirement.

c - Adverse chronic effects (as above) and acute effects such as excessive excitability, frothing from the mouth, muscular tremors, convulsions and hind limb incoordination may occur, although short-term exposure could be tolerated depending on site-specific factors such as adequate dietary protein intake and water requirement.

Table 58: Effects of lead on human health from domestic water use (SA-DWAF: Domestic Use, 1996).

Concentration Range (µg/l)	**Effects**
TWQR **0 - 10**	No danger of any adverse effects by exposure from water
It is recommended that the TWQR not be exceeded due to the potentially acute and/or irreversible effects of lead on human health	
10-50	No danger of any adverse health effects except for a slight risk of behavioural changes and possibility of neurological impairment, where the exposure to lead from other sources, such as food, is not minimised
50-100	Possible neurological damage where the nerve and brain tissues are developing, that is, in foetuses and young children. Young children and pregnant women should avoid exposure
100-300	Definite danger of neurological impairment in children. Alternative water supply should be used by sensitive groups (children and pregnant women)
>300	Symptoms of chronic lead poisoning are possible with continuous exposure

A.10. Zinc (Zn):

Table 59: Effects of zinc in irrigation water on crop yield and quality (SA-DWAF: Agricultural Use - Irrigation, 1996).

Concentration Range (mg/L)	Crop Yield and Crop Quality
TWQR **< 1.0**	Toxic to many plants at concentration of 1mg/L and less in nutrient solutions. The TWQR should protect most plants from absorbing toxic concentrations of zinc, even when grown on acid sandy soils
1.0 - 5.0	Maximum acceptable as concentration for fine-textured neutral to alkaline soils
> 5.0	Acceptable for irrigation only over the short term on a site-specific basis

Table 60: The target water quality ranges of dissolved zinc for salmonids and cyprinids (SA-DWAF: Agricultural Use - Aquaculture, 1996).

Water hardness (mg/L $CaCO_3$)	TWQR soluble zinc (mg/L)	
	Salmonids	**Cyprinids**
10	0.03	0.3
50	0.2	0.7
100	0.3	1.0
500	0.5	2.0

Table 61: The target water quality ranges and criteria for dissolved zinc in aquatic ecosystems (SA-DWAF: Aquatic Ecosystems, 1996).

TWQR and Criteria	Zinc concentration (μg/L)
TWQR	**<2**
Chronic Effect Value (CEV)	3.6
Acute Effect Value (AEV)	36

Table 62: Effects of zinc on the health of livestock (SA-DWAF: Agricultural Use - Livestock, 1996).

Concentration Range (mg/L)	Effects
	All species
TWQR **0 - 20**	No adverse effects
20 - 40	Adverse chronic effects such as inappetence, anaemia icterus and diarrhoea may occur, but are unlikely if - feed concentrations are normal; - calcium intake is adequate; and - exposure is short term Could even be tolerated in the long term, depending on site-specific factors such as nutritional interactions and water requirement
> 40	Adverse chronic effects (as above) and acute effects such as haemolysis and icterus may occur, although short-term exposure could be tolerated depending on site-specific factors (as above)

Table 63: Effects of zinc on aesthetics and human health from domestic water use (SA-DWAF: Domestic Use, 1996).

Concentration Range (mg/L)	**Effects**
TWQR **0 - 3**	No aesthetic or human health effects
3-5	Slight opalescence or bitter taste. No health effects
5-10	Clearly discernable bitter taste and opalescence. No health effects
10-50	Bitter taste; strong opalescence. Some instances of chronic toxicity expected
50-700	Bitter taste; milky appearance. Acute toxicity with gastrointestinal irritation, nausea and vomiting
>700	Bitter taste; milky appearance. Severe, acute toxicity with electrolyte disturbances and possible renal damage

Appendix B: Detailed water quality data for a number of heavy metals at study sites R4, R5 and B5 (Figure 13):

B.1. R4 - Rietspruit at N3 (Alberton-Heidelberg):

Table 64: Detailed water quality data for rainy season 1999/2000 at site R4.

Rainfall event	Event total rainfall (mm)	Normalised cumulative rainfall	Preceding dry days (PDD)	Co (mg/L)	Mn (mg/L)	Ni (mg/L)	Zn (mg/L)
2000-01-31 to 2000-02-02	20.5	0.25	5	0.61	0.96	1.6	0.92
2000-02-06 to 2000-02-15	156	0.44	3	0.36	1.5	0.57	0.22
2000-02-29 to 2000-03-06	232.5	0.73	4	0.48	0.2	0.74	0.2
2000-03-14 to 2000-03-21	77.5	0.83	7	0.3	0.1	0.6	0.1
2000-04-04	10	0.88	4	0.23	0.1	0.1	0.1
2000-04-30 to 2000-05-03	29.5	0.96	8	0.46	0.1	0.1	0.1

Table 65: Detailed water quality data for rainy season 2001/2002 at site R4.

Rainfall event	Event total rainfall (mm)	Normalised cumulative rainfall	Preceding dry days (PDD)	Co (mg/L)	Mn (mg/L)	Ni (mg/L)
2001-10-13 to 2001-10-27	95	0.27	23	0.24	0.32	0.18
2001-11-08 to 2001-12-02	103.4	0.49	7	0.16	0.13	0.09
2001-12-08 to 2001-12-13	34.5	0.54	5	0.08	0.09	0.07
2002-01-12 to 2002-01-19	32.5	0.64	3	0.18	0.05	0.05
2002-01-23 to 2002-02-01	83.5	0.77	3	0.17	0.08	0.05
2002-02-12 to 2002-02-14	29	0.84	4	0.11	0.1	0.06
2002-02-25 to 2002-03-07	22	0.88	6	0.08	0.1	0.05
2002-03-11 to 2002-03-12	13	0.91	3	0.19	0.1	0.05

Table 66: Detailed water quality data for rainy season 2004/2005 at site R4.

Rainfall event	Event total rainfall (mm)	Normalised cumulative rainfall	Preceding dry days (PDD)	Co (mg/L)	Mn (mg/L)	Ni (mg/L)	Zn (mg/L)
2004-12-13 to 2004-12-23	44.5	0.37	4	0.2	0.5	0.49	0.11

2005-01-07 to 2005-01-23	147.3	0.65	3	0.11	0.09	0.18	0.04
2005-03-14 to 2005-03-15	22.5	0.78	3	0.1	0.17	0.17	0.03
2005-04-19	6	0.96	3	0.1	0.13	0.11	0.03

B.2. R5 - Rietspruit at R550 (Hardman's Farm):

Table 67: Detailed water quality data for rainy season 2001/2002 at site R5.

Rainfall event	Event total rainfall (mm)	Normalised cumulative rainfall	Preceding dry days (PDD)	Co (mg/L)	Mn (mg/L)	Ni (mg/L)
2001-09-14 to 2001-09-19	73.1	0.12	134	0.15	0.37	0.19
2001-10-13 to 2001-10-27	95	0.27	23	0.11	0.22	0.07
2001-10-13 to 2001-10-27				0.08	0.09	0.07
2001-11-08 to 2001-12-02	103.4	0.49	7	0.06	0.07	0.06
2001-11-08 to 2001-12-02				0.09	0.07	0.07
2001-11-08 to 2001-12-02				0.07	0.1	0.05
2001-12-08 to 2001-12-13	34.5	0.54	5	0.06	0.09	0.05
2002-01-12 to 2002-01-19	32.5	0.64	3	0.15	0.05	0.05
2002-01-23 to 2002-02-01	83.5	0.77	3	0.11	0.05	0.05
2002-02-18	5	0.85	3	0.23	0.16	0.06
2002-02-25 to 2002-03-07	22	0.88	6	0.06	0.12	0.05
2002-04-15	3	0.92	6	0.07	0.12	0.05

Table 68: Detailed water quality data for rainy season 2003/2004 at site R5.

Rainfall event	Event total rainfall (mm)	Normalised cumulative rainfall	Preceding dry days (PDD)	Co (mg/L)	Mn (mg/L)	Ni (mg/L)
2003-11-10 to 2003-11-12	32.5	0.11	21	0.17	0.71	0.23
2003-11-20 to 2003-11-26	58.2	0.22	3	0.03	0.28	0.18
2003-12-08	22	0.26	11	0.07	0.5	0.19
2004-02-13 to 2004-02-17	76	0.69	7	0.02	0.13	0.07
2004-04-19	24	1.00	18	0.08	0.13	0.18

Table 69: Detailed water quality data for rainy season 2004/2005 at site R5.

Rainfall event	**Event total rainfall (mm)**	**Normalised cumulative rainfall**	**Preceding dry days (PDD)**	**Co (mg/L)**	**Fe (mg/L)**	**Mn (mg/L)**	**Ni (mg/L)**
2004-11-14 to 2004-11-21	18.3	0.14	17	0.015	0.13	1.7	0.05
2004-11-27 to 2004-11-30	53	0.23	5	0.015	0.06	1.2	0.05
2004-12-13 to 2004-12-23	44.5	0.37	4	0.14	0.03	0.58	0.2
2005-01-02 to 2005-01-03	7.2	0.39	9	0.09	0.04	0.68	0.14
2005-01-07 to 2005-01-23	147.3	0.65	3	0.15	0.04	0.12	0.16
2005-03-14 to 2005-03-15	22.5	0.78	3	0.015	0.03	0.41	0.08

B.3. B5 - Blesbokspruit at Welgedacht Road (Springs):

Table 70: Detailed water quality data for rainy season 1999/2000 at site B5.

Rainfall event	**Event total rainfall (mm)**	**Normalised cumulative rainfall**	**Preceding dry days (PDD)**	**Fe (mg/L)**	**Mn (mg/L)**
1999-11-06 to 1999-11-09	26.2	0.05	8	0.18	1.4
1999-12-02 to 1999-12-12	124.3	0.19	3	0.19	0.74
2000-02-03 to 2000-02-15	318.3	0.73	7	0.15	0.62
2000-03-17 to 2000-03-21	121.5	0.89	10	0.11	0.59

Table 71: Detailed water quality data for rainy season 2003/2004 at site B5.

Rainfall event	**Event total rainfall (mm)**	**Normalised cumulative rainfall**	**Preceding dry days (PDD)**	**Al (mg/L)**	**Fe (mg/L)**	**Mn (mg/L)**	**Ni (mg/L)**	**Zn (mg/L)**
2003-10-17 to 2003-10-21	56.5	0.08	3	0.08	0.24	0.49	0.15	0.04
2003-11-02 to 2003-11-03	16.5	0.11	11	0.09	0.11	0.35	0.1	0.009
2003-11-16 to 2003-11-18	19	0.16	3	0.33	0.19	0.23	0.12	0.01
2004-01-15 to 2004-01-22	105.5	0.44	5	0.86	0.18	0.18	0.09	0.009
2004-02-22 to 2004-02-26	70.8	0.66	3	0.07	0.1	0.19	0.1	0.01