

## **Analysis of the Spatial and Temporal Variability of Toxic Heavy Metal Concentrations in Ground Water Resources in Upper Sanyati Catchment, Midlands Province, Zimbabwe**

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### **Abstract**

*Upper Sanyati catchment in the Midlands Province of Zimbabwe is important for residential, agricultural, mining and manufacturing activities. These anthropogenic activities are generating large quantities of waste and insitu are toxic heavy metals, whose contamination of the environment is of great concern especially to ground water supplies. The aim of the research was to analyze the spatial and temporal variations of toxic heavy metal loads in ground water resources. A total of two hundred and eighty eight ground water samples were analyzed for toxic heavy metal contents using an atomic Absorption Spectrophotometer Varian SpectraAA-100. The results for the wet season showed mean concentrations of chrome, lead, cadmium and nickel at 0.187, 0.033, 0.049 and 0.04mg/L respectively while the dry season results were 0.36, 0.056, 0.05 and 0.04mg/L respectively. Ground water pH varied between 6.3 and 8.4 at an average temperature of 25<sup>0</sup>C. Water supplies in the study area has higher concentrations of Cr<sup>2+</sup>, Pb<sup>2+</sup> Ni<sup>2+</sup> and Cd<sup>2+</sup> exceeding World Health Organization permissible levels for domestic water users.*

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**Key words:** ground water; toxic heavy metals; contamination; acidity and alkalinity.

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## 1 Introduction

Ground water contains a wide variety of dissolved inorganic species in various concentrations resulting from chemical and biological interactions that take place as it flows in soil subsurface systems (Tawfic et al, 1997). Soils can retain, modify, decompose or adsorb pollutants. Trace element contamination of ground water supplies is a common issue of concern especially from toxic heavy metals that dissolve from soil and waste matter leaching into ground water systems. Toxic heavy metals refer to any metallic chemical element that has a specific gravity of 6, among them cadmium, mercury, lead, chromium and nickel which are highly toxic in minute quantities when released into the environment (Basta, et al, 2005). Ground water arises from rain or other forms of precipitation that soak into the ground and move downwards to fill cracks and other voids in soil or rocks (Todd, 1980). The pathways by which toxic heavy metal elements contaminate ground water vary from direct routes such as advection, mechanical dispersion and molecular diffusion to indirect ways via deposition of atmospheric particulate matter (Atmadja and Bagtzoglon, 2001). Critical factors influencing the dissolution and mobility of these toxic metals is ground water chemistry and most importantly the pH and dissolved oxygen (Appeal, 2002). Ground water pH is fundamental, as it affects the amount of heavy metal adsorption and desorption which are hypothetically much slower under acid conditions resulting in greater concentrations of heavy metals in ground water (Nelson, 2002). In addition aeration of sulphide rich soils leads to a decrease in pH resulting in potential release of heavy metals into ground water resources (Navarro, 2008)..

From a geochemical point of view, ground water is important in the distribution and redistribution of chemical components since it's a major terrestrial compartment in the water cycle (Worral, et al. 2002). Ground water quality mapping is thus important for understanding the distribution and abundance of elements and the changes in local cycles due to spreading contaminants (Bolan, et al 2004). Mining, manufacturing, domestic wastes and agricultural activities are dominating the trace element cycle through environmental enrichment with orders higher than in the natural systems (Eary and Rai, 1987; Cooper, 2002 and Klee and Graedel, 2004).

Mining and mineral processing operations that include, grinding, concentrating ores and disposal of tailings, provide obvious sources for both surface and ground water contamination. Pollution of ground water resources partly arises from mining wastes and effluent exposed to weathering conditions where low quality residues of acidic pH, containing high levels of dissolved metals are produced and released into the environment (Aastrup and Thoholm, 2000). Previous studies by Berger, et al (2004), have shown that oxidation-reduction reactions of mineral and mineral wastes along the Great Dyke of Zimbabwe contribute to higher ground water acidity pH ranging between 3.0 and 5.0. But in some areas of the Great Dyke where calcium and magnesium minerals are present as primary compounds, pH levels increase to greater than 7.0 thereby decreasing trace element concentration levels.

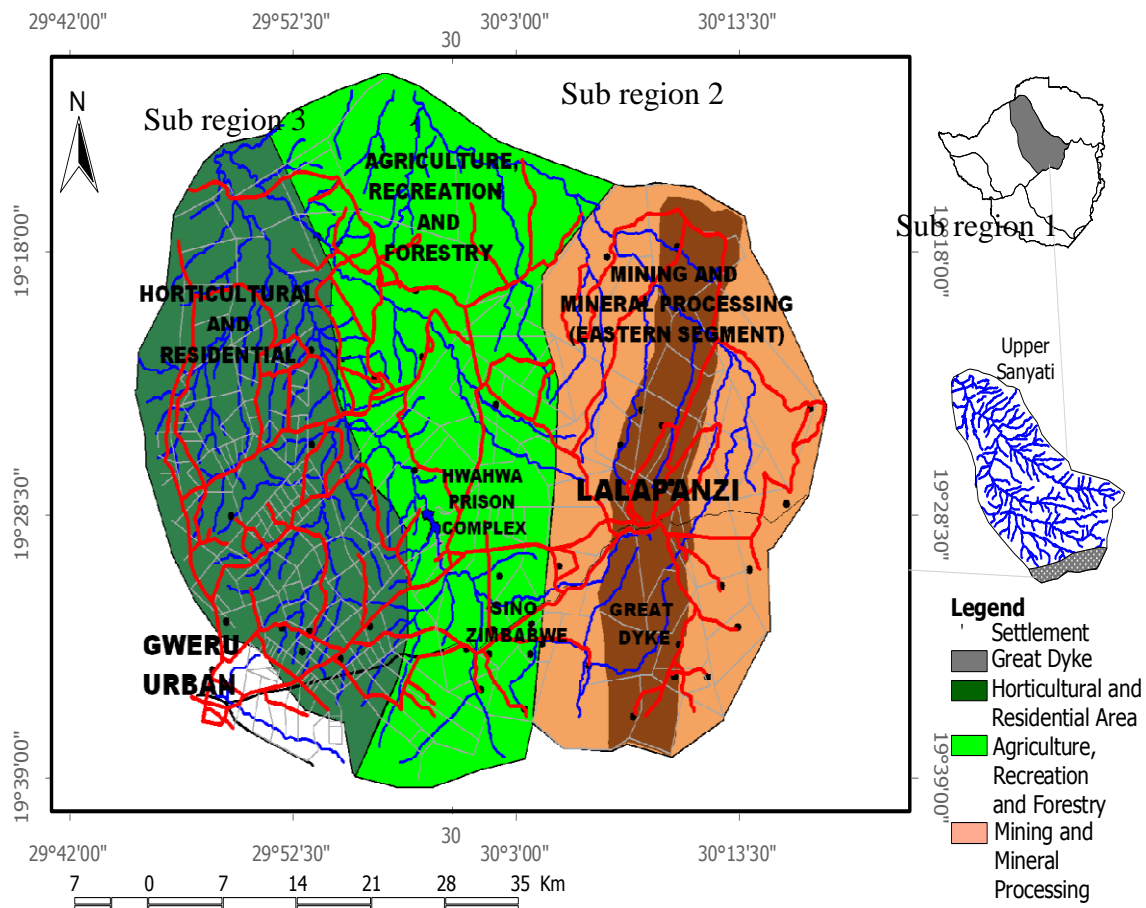
The addition of soil organic matter in water logged cultivated lands results in enhanced carbon dioxide levels that raise the acidity pH. Furthermore fertilizers applied are usually not sufficiently purified during the process of manufacturing and contain impurities among them heavy metals. For instance super phosphates contain highest concentrations of cadmium and zinc as impurities and when applied in areas with sufficient surface water, these heavy metals may leach and infiltrate into ground water (Luo, et al 2000).

Societal demands for food crops, meat, eggs and dairy products has increased over recent decades due to population increase and a rise in living standards. To meet the ever increasing demand for commodities both organic and inorganic fertilizers are applied in agriculture. Both types of fertilizers are major sources of heavy metals. For instance in USA, phosphate fertilizer application together with livestock fodders and manure account for 55% of cadmium deposition at a rate of 0.004mg/kg/year (IAH, 2000). Such increase in cadmium and other trace elements adds to environmental pressure, that threatens ground water quality. Zimbabwe basically an agricultural country, has quadrupled the numbers of its small to medium scale farmers since 2000 (Zimstat, 2010). First and foremost farmers contribute to ground water pollution through use of fertilizers. Existing water quality control measures have made little emphasis on ground water resources that are used mostly by both rural and peri-urban communities (ZINWA, 2009).

Heavy metals in the environment are adsorbed by the soil or absorbed by plants and also form complex compounds with other soil components such as sulphates and nitrates. When toxic heavy metals find their way into ground water resources, their contamination levels vary according to number, intensity, strength, pH and temperature at either point or non point sources. Contamination levels are also dependent upon soil's ability to absorb and degrade chemical elements (IUCN, 1994; Harter, 2005). When ingested by humans or taken up by plants heavy metals do not degrade and in many instances remain persistent as bio-accumulative toxins.

## **2 Study Area**

The study area is sub catchment of upper Sanyati Catchment which covers approximately 168km<sup>2</sup> in area. It extends from 10 km North East of Gweru urban to Lalapanzi 42 km east. (Figure 1) Upper Sanyati catchment is in the Midlands Province on the Highveld of Zimbabwe. It is located at an altitude of 1200m above mean sea level. The topography of upper Sanyati catchment is characterized by peneplains and gently slopes inclined towards the northwest along which Sebakwe River and its tributaries drain.



**Figure 1 Sub section of Upper Sanyati Catchment Physiographic Features and Land use**

The study area is divided into three sub- regions based on land use. Sub- region 1 covers the eastern segment where mining and mineral processing activities are predominant in areas around Lalapanzi. It is part of the Tokwean terrain (composed mainly of gneissic rocks and structurally complex inliers of possibly older greenstone belts of the Zimbabwean craton). Sub-region 1 of study area is the intruded part of the Great Dyke whose geologic setting is made up of a number of distinct tectonostratigraphic terrain assemblages arising from varying geologic events (Wilson and Prendergast, 2001). The greenstone belt is overlain unconformably by an assemblage of mafic and felsic volcanic rocks and conglomerates, sandstones, shale and limestone (Kusky, 1998). Lineaments interpreted from Land sat TM imagery and aerial photographs represent faults, joints and dykes of several ages. These fissured rocks lack primary porosity and aquifers only occur within the weathered regolith and fractured bedrock (Wright, 1997). Ground water level depths range from 3 m in summer to more than 90 m below ground surface during the dry period (ZINWA,2009)..

Sub-region 2 covers the central section of study area that is predominantly under limestone and dolomite bedrock. Quarrying and cement manufacturing as well as small to medium scale agricultural activities are the dominant human activities in this sub-region. Aquifer transmissivity and hydraulic conductivity values range between 0.3 and 0.9 cubic metres per second (ZINWA, 2009). Field evidence shows that average water table fluctuations range between 3 and 5 metres between dry and wet seasons probably due to continuous recharges from Kwekwe River and its tributaries. Sub-region 3 is the western segment of the study area whose rock outcrops are predominantly hornblende–biotitic gneisses. These rock formations

are more often intruded by granites, pegmatite and quartz veins as well as gabbros and dolerite rock types.

### 3 Materials and Methods

An areal scoping of the study area was undertaken in order to obtain borehole locations, elevations, dominant rock types and associated trace elements, temperature and pH. At the end of each month two ground water samples were collected from each of the twelve boreholes under monitoring. A total of two hundred and eighty eight ground water samples were collected from upper Sanyati catchment between January 2010 and December 2011. The ground water samples were collected in plastic containers and immediately transported to the laboratory for analysis. The pH values for each water sample were measured using a standard pH meter. Each ground water sample was subjected to an Atomic Absorption Spectrophotometry analysis for metallurgical assaying. An Atomic Absorption Spectrophotometer Varian SpectrAA-100 was used in the absorption mode to determine concentration level of each toxic heavy metal in ground water samples. Ground water sample was subjected to four aspirations to determine the concentration levels of the following metallic elements, chrome, lead, cadmium and nickel. The results displayed by the spectrophotometer were expressed in parts per million (ppm). The concentration load of each toxic heavy metal per water sample was based upon the absorbance of each metallic element under concern at any given time.

Pollutant load (PL) for each toxic heavy metal per borehole was calculated using equations 1-3

$$\text{POLLUTANT LOAD (PL)} = \sum C_1 \cdot Q_1 \cdot T_1 \dots \dots \dots \text{Eq. 1}$$

$$\text{TWMC} = [\sum C_1 \cdot T_1] / [\sum T_1] \dots \dots \dots \text{Eq. 2}$$

$$\text{FWMC} / \text{TWMC} > 1.0 \text{ NO POINT SOURCE} \dots \dots \dots \text{Eq. 3}$$

Where C<sub>1</sub> = pollutant concentration in the i<sup>th</sup> sample  
 Q<sub>1</sub> = discharge in the sample (mg/ L)  
 T<sub>1</sub> = time interval between successive samples  
 TWMC = Time Weighted Mean Concentration  
 FWMC =Flow Weighted Mean Concentration  
 Sources: (APHA, 1998; Miroslav and Rashkin, 1999).

### 4 Results and Discussion

An area scoping of the study area was undertaken in order to obtain borehole locations, elevations, dominant rock type and associated trace elements, temperature and pH. Field observations and measurements are shown in Table 1.

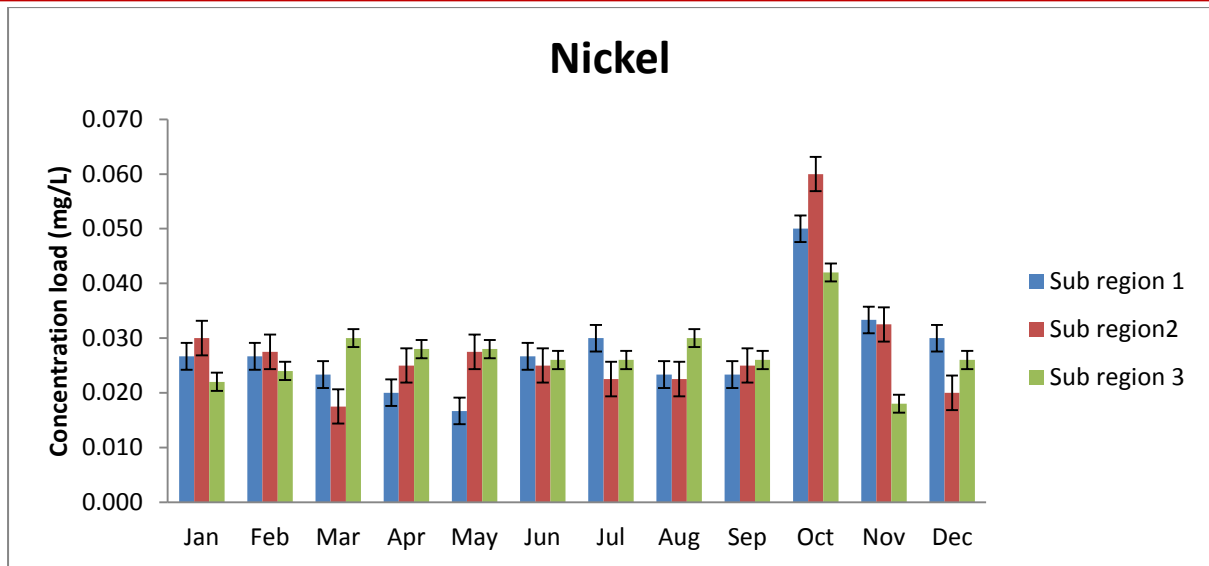
Table 1 Site locations, elevations, main rock outcrops, borehole depths, temperatures, pH values and detected toxic heavy metals and silicate minerals in study area.

Location Reading	GPS	Elevation on metres above sea	Dominant Rock Type by sub-region	Borehole Number and depth	Temp °C mean	pH mean	Silicate minerals/ Trace elements

	level					
0204577/785881 4	1480	Great Dyke- Chromite (1)	1/42	28	6.3	Cr, Ni, Pb, Fe, Ca, Mg
0203943/785954 6	1497	Great Dyke- Chromite (1)	2/+40	22	6.9	Cr, Ni, Pb, Fe, Ca, Mg
0203284/786008 6	1499	Great Dyke- Chromite (1)	3/+40	23	6.5	Cr, Ni, Fe, Ca, Mg
0189199/785037 3	1390	Jarosite (Carbonated) (2)	4/40	25	7.2	As, Pb, Cd, Ca, Mg
0189509/785239 9	1375	Carbonated igneous rocks (2)	5/+40	25	6.9	Fe, Cd, Pb, Ni
0185445/785676 0	1358	Carbonated igneous rocks	6/+40	26	7	Fe, Cd, Pb, Ni, Mg
0806363/784950 3	1328	Alluvial deposits/ decomposed granite (3)	7/+40	25	7.2	Pb, Ni, Cr, Fe, Al, Ca
0805566/784919 0	1418	Gibbsite (Aluminium) (3)	8/+40	26	6.5	Pb, Al, Cu, Zn, Ni, Mg
0803014/784837 4	1462	Alluvial deposits/ decomposed granite (3)	9/+40	26	7.2	Ni, Cd, Pb, Ca
0794805/785749 4	1455	Ferruginous sandstones (3)	10/+40	25	6.9	Fe, Cr, Ni, Fe, Ca
0800197/785216 3	1451	Ferruginous sandstones (3)	11/+40	26	7.1	Fe, Cr, Ni, Ca, Mg

Four toxic heavy metals that were detected in ground water samples in the study area during the course of the research at appreciable levels were nickel, chrome, lead and cadmium. Each toxic heavy metal concentration level varied temporarily and spatially depending on month of year and sub region. Figure 2 shows the spatial and temporary distribution of nickel in ground sampled in study area.

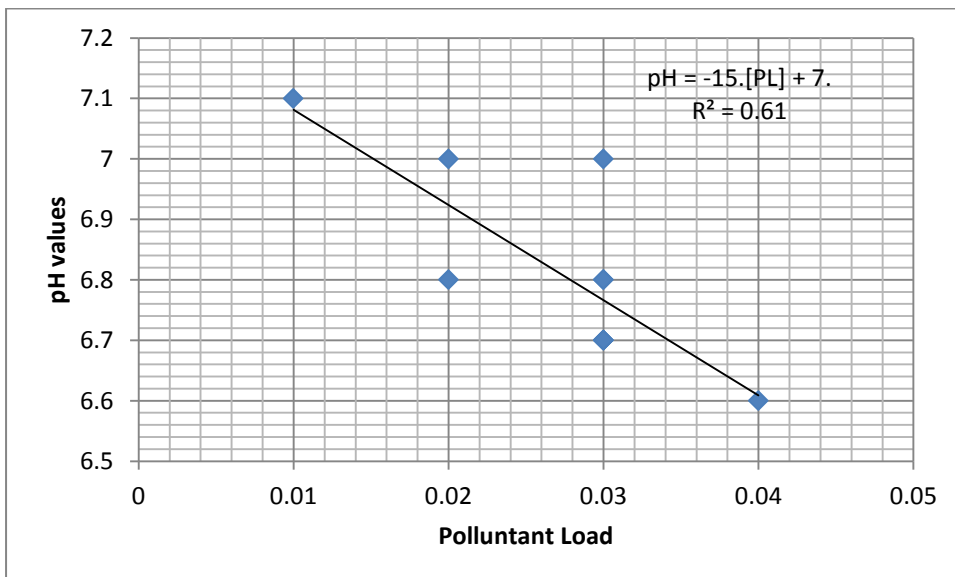




**Figure 2 Time weighted mean ground water nickel concentration (mg/L) in upper Sanyati Catchment by sub-region**

Nickel is heterogeneously distributed in the study area. Time weighted mean ground water nickel concentration was found at 0.031mg/L and 0.025 mg/L for the wet and dry seasons respectively. Elevated nickel concentration in ground water was more profound during the wet season than the dry season, with the highest nickel concentration level of 0.06mg/L recorded in October. There is a significant difference ( $p < 0.05$ ) in nickel content between the wet and dry seasons in all the sub regions. Significant levels of nickel in ground water in study area during the wet season can be associated with the formation of immobile nickel precipitates such as hydroxides, silicates and sulphides (Schekel and Sparks, 2001). While elevated levels of nickel content in ground water during the dry season can be linked to mean acidic pH conditions of 6.5.

**An analysis between nickel in ground water sampled and pH recorded, showed a negative co relationship as shown in Figure 3.**

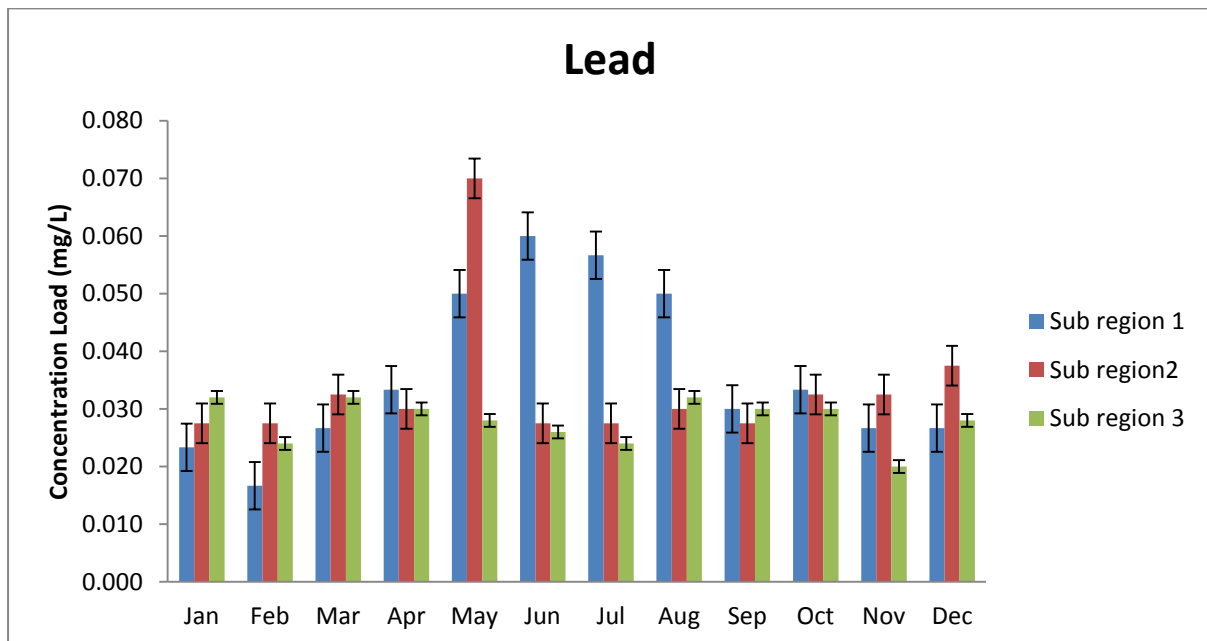


### Figure 3 Ground water nickel content at varying pH values

Nickel content in ground water samples analyzed increased with decreasing pH values. Nickel predominantly exists as a cationic species  $Ni^{2+}$  or in various hydrolysis species such as  $(NiOH^+)$  at near neutral pH levels of 6 - 9 (Baes and Mesmer, 1986). Nickel may also form dissolved complexes in the presence of high concentration of inorganic ions such as carbonate and sulphate (Hummel and Curti, 2003; Chan, et al. 2005).and organic ligands such as dissolved compounds (Bryce and Clark, 1996). The presence of serpentine clay rich soils and organic compounds in the study area may have contributed to the nickel dissolution, adsorption/desorption and mobility through the soil subsystem (Wilkin, 2007).

Thus ground water nickel content's spatial changes may be linked to location where water samples were collected during a particular month/season, proximity of hydrous oxides of chrome and phyllo-silicates from carbonate quarrying and cement manufacturing in the respective sub regions 1 and 2. Nickel has been observed to adsorb onto components encountered in ground water sediments such as clay, iron and manganese oxides and solid organic matter (Nachtegaal and Sparks, 2003). Other complex factors that might have contributed to nickel variation in ground water include hydrological routing, borehole water residence times and volumetric processes all operating at small scales at sub-regional levels.

Spatial and temporary distribution and concentration levels of lead in ground water sampled from the sub regions of the study area are shown in Figure 4.



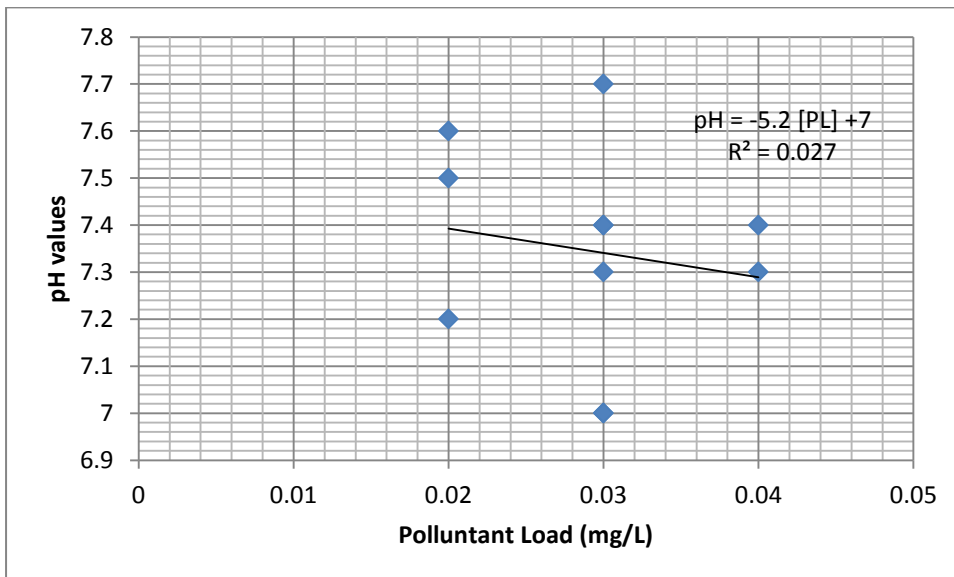
**Figure 4 Time weighted mean ground water lead concentration (mg/L) in upper Sanyati Catchment by sub-region**

Time weighted ground water mean maximum lead concentration of 0.07 mg/L was recorded during the beginning of the dry season in May in sub-region 2 while lowest lead values of 0.015mg/L were recorded in February during the wet season in sub-region 1. On a comparative basis higher lead values in ground water were recorded in May, June, July and



August during the dry season in sub-regions 1 and 2 while sub-region 3 had a near uniform lead content throughout the year. Statistically there is a significant difference ( $p < 0.05$ ) in lead content between the dry and wet seasons in all the 3 sub-regions.

Solution pH plays a dominant role in governing lead solubility in aqueous solutions (Wilkin, et al. 2009). When relationships between ground water lead content and pH values were analyzed, the trend for all seasons showed lead concentration levels increasing with decreasing pH values as shown in Figure 5.



**Figure 5 Ground water lead content at varying pH values**

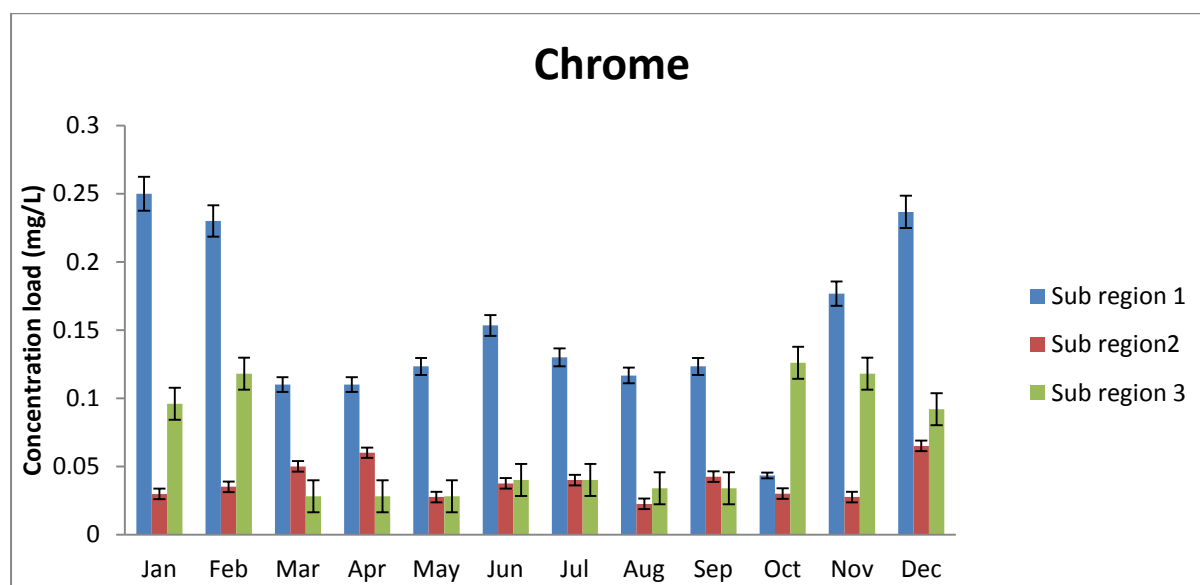
Thus from the results obtained the general aqueous solubility of ground water lead was low at near neutral to alkaline pH levels of 7.4 while moderate and mobile in decreasing pH systems of 7.2. The low pH values of 6.9 during the dry season together with high concentrations of dissolved organic carbon may have contributed to the elevated levels of lead from May to August in sub-regions 1 and 2 while lead content remained relatively low during the wet season .

There were significant differences ( $p < 0.05$ ) in ground water lead content in both the wet and dry seasons in the three sub regions of the study area.

Lead distribution in ground water in study area may be stemming from anthropogenic and natural deposition of particles derived from fossil fuel combustion as well as dolomite dust from limestone quarrying in sub region 2. While base metal chrome waste ores in association with galena ( $PbS$ ), anglesite ( $PbSO_4$ ) and cerrusite ( $PbCO_3$ ) in sub region 1 may have contributed to lead ground water enrichment. Low pH systems averaging 6.3 in sub-region 1 together with concentrations of dissolved organic carbon in sub-region 2 could be responsible for the variations in lead levels in the boreholes. Borehole 6 is in the proximity of WhaWha Prison Complex sewage ponds whose acidic effluent may have influenced ground water lead enrichment. Lower ground water lead values averaging 0.03mg/L and below were recorded in boreholes 4 and 5 in sub-region 2 and boreholes 7 to 12 in sub-region 3. These sub-regions are forested and land use systems include small to large scale livestock rearing activities.

It must be noted that lead is sparingly soluble in ground water over a wide range of pH conditions. Below a pH of 7  $Pb^{2+}$  is more dominant but with increasing pH above 7 the species of  $PbOH^+$ ,  $Pb(OH)_2$  and  $Pb(OH)_3$  become dominant (Wilkin, et al. 2009). Contrary to Lenntech (2011d) findings where it was observed that lead is high (1mg/L) in acidity pH conditions of 6.5 and below in this study it was observed that at pH values of 6.8 to 7.4 that are near neutral to alkaline conditions. Lead content was high at 0.04mg/L.

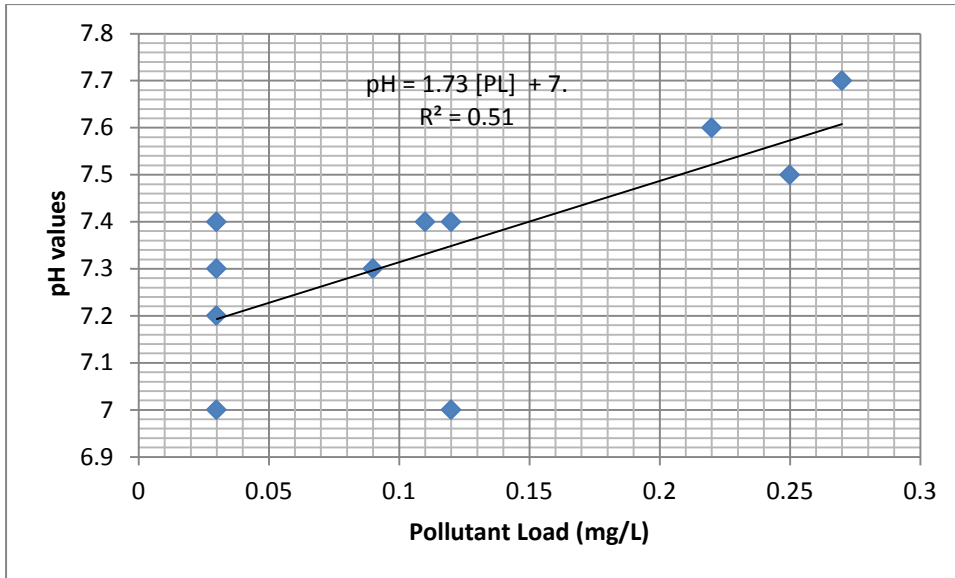
Spatial and temporary distribution and concentration levels of chrome in ground water sampled from the sub regions of the study area are shown in Figure 6.



**Figure 6 Time weighted ground water mean chrome content (mg/L) in upper Sanyati Catchment by sub-region**

Time weighted mean ground water chrome concentration in sub-regions 1 and 3 of the study area ranged between 0.25mg/L and 0.15 mg/L during wet and dry seasons respectively. In sub-region 2 ground water systems had chrome concentration levels ranging between 0.02mg/L and 0.052mg/L for all seasons. There were significant differences ( $p < 0.05$ ) in chrome content in ground water systems between the wet and dry seasons. Elevated ground water chrome concentration levels were recorded during the wet season. Generally ground water chrome concentration levels are high in sub-regions 1 and 3 and lowest in sub-region 2.

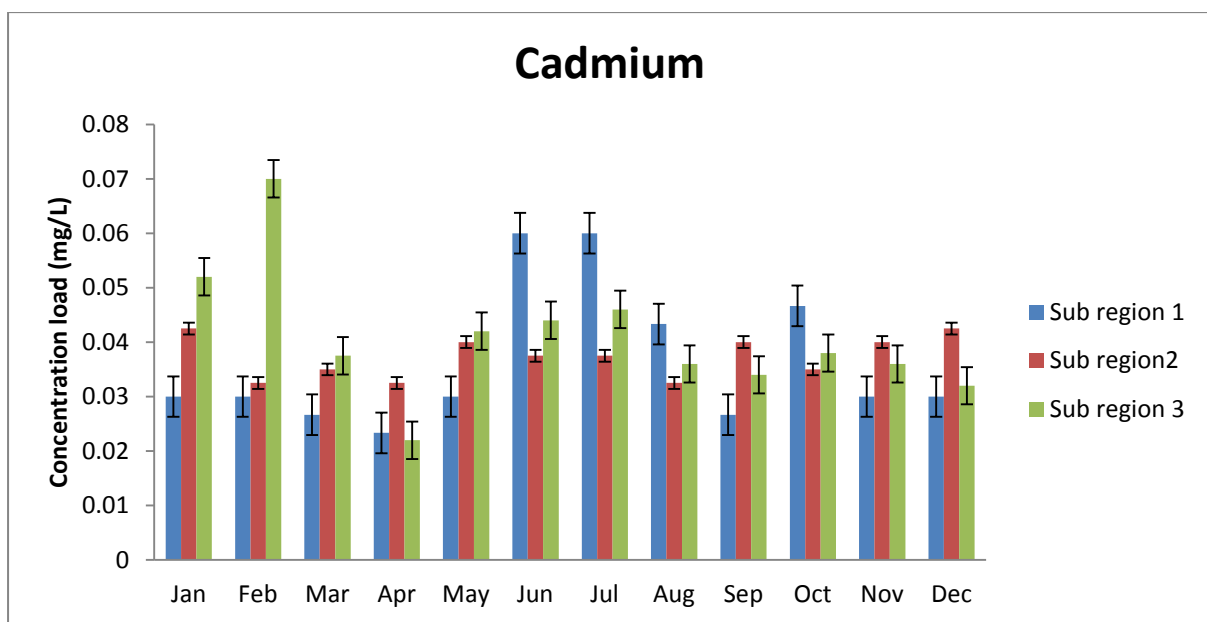
When ground water chrome concentration levels and pH values were analyzed, there was a positive relationship chrome content increased with increasing pH values as shown in Figure 7.



**Figure 7 Ground water chrome content at varying pH values**

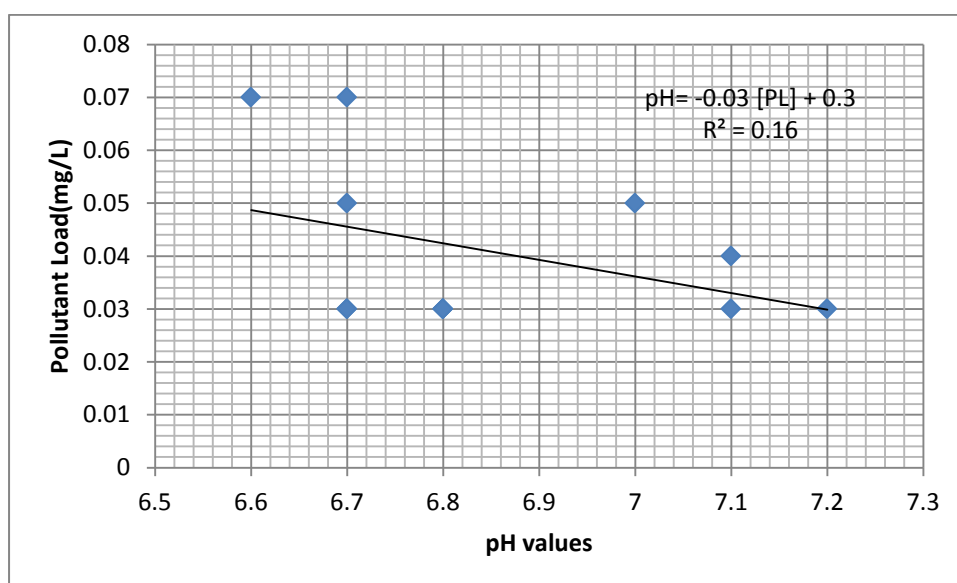
It was observed that in sub region 1 which is a chrome mining and processing area there was an abundance of  $Cr^{3+}$ . The trend in this case was different, there was a high concentration of chrome with decreasing pH of below 6.8. As pH increases to a maximum of 11 the dominant chrome species change through a sequence of hydrolysis products of  $CrOH^{2+}$ ,  $Cr(OH)_2^+$  etc.(Palmer, 1994; Zachary, et al 1989). This may also help to account for the elevated chrome concentration levels at near neutral pH values of 7.1 to 8.4 in sub regions 3 and 2. It must also be noted that chrome ( $Cr^{3+}$ ) under oxidizing conditions, alkaline pH range of 7.1 to 11 and in the presence of  $MnO_2$  part of the chromium may occur as  $Cr^6$  dissolved in ground water. This might help to explain the elevated levels of chrome in ground water in the study area during both the dry and wet seasons during the period of observation.

Spatial and temporary distribution and concentration levels of cadmium in ground water sampled from the sub regions of the study area are shown in Figure 8.



**Figure 8 Monthly mean cadmium concentration (mg/L) in upper Sanyati Catchment by sub-region**

Analysis of cadmium concentration in ground water shows that mean cadmium levels in the study area is highest at 0.07mg/L during the wet season in sub-region 3 when ground water pH values are more acidic. During the dry season cadmium concentration in ground water is at 06mg/L when pH values are moderately acidic to alkaline state at pH values of 6.9. Cadmium concentration in ground water in the study is variably high in both the dry and wet seasons during specific months of February, June and July. When ground water cadmium concentration levels and pH values were analyzed, there was a negative co-relationship, thus cadmium content increased with decreasing pH values as shown in Figure 9.



**Figure 9 Ground water cadmium content at varying pH values**

The fractional abundance of Cd-OH species in water is a function of pH, Lindsey (1979) posits that where adsorption and desorption behaviour of cadmium is more significant at pH levels of between 9 and 12. Varying cadmium concentration levels in ground water sampled may be associated with seasons, thus during the wet season cadmium complexes of Cd<sup>2+</sup>, Cd(OH<sup>+</sup> and Cd(OH)<sub>2</sub> may be the most significant species at pH values of 7.4. Whilst at moderately acidic pH values to near neutral alkaline levels cadmium carbonate and cadmium sulphate become more significant, as it becomes soluble under the following: CdCO<sub>3</sub> + H<sup>+</sup> = Cd<sup>2+</sup> + HCO<sub>3</sub> and CdS + H<sup>+</sup> = Cd<sup>2+</sup> + HS.

Elevated cadmium concentrations in the study area were generally linked to sulphide ores of iron, zinc and lead. Soil weathering may also be contributing to the release of Cd<sup>2+</sup> ion that is generally soluble and mobile in water especially in sub region 2's agricultural areas where cadmium might have formed aqueous complexes with both inorganic and organic ligands. Inorganic cadmium complexes including cadmium hydroxide, cadmium carbonate, cadmium chloride and cadmium sulphate commonly found in ground water are associated with fertilizer application.

**5 Conclusion**

Highest mean levels of chrome, lead, cadmium and nickel recorded in ground water in the study area during the two year period were 0.18mg/L, 0.056mg/L, 0.06mg/L and 0.04mg/L

respectively. Chrome had the highest mean concentration of 0.18mg/L whilst nickel had the least mean concentration of 0.015mg/L. The order observed for the toxic heavy metals in this study were as follows; Cr >Pb> Cd >Ni.

When mean heavy metal flow weighted concentration was divided by mean time weighted concentration the pollutant loads of the four toxic heavy metals in ground water sampled were found below 1.0, reflecting non point sources of origin. It can therefore be concluded that the temporary abundance of toxic heavy metals in ground water in the study area is a function of pH variations, geology, land use system and organic matter. Fundamentally solution pH plays an important role in the solubility and adsorption of toxic heavy metals in ground water systems. Thus the general trend is that at low acidic pH values cationic heavy metals in ground water become soluble and mobile and with increasing pH values at near neutral to alkaline conditions heavy metals tend to form complexes with silicates, hydroxides and sulphides in the subsurface environments (Biala, 2000). Observations made in this study are that the abundance of toxic heavy metals namely chrome, lead, cadmium and nickel in ground water increase with acidity pH below 6.5 but also increase at near neutral to alkaline conditions occurring in the form of heavy metal complexes.

It was further observed that organic matter in soil is fundamental; it adsorbs toxic heavy metals particularly at low pH values. Thus the acidic pH in ground water in boreholes in sub region 3 of the study area linked to intensive livestock breeding areas with large amounts of waste may have contributed to elevated levels of toxic heavy metals. Dissolved carbon from organic wastes mobilizes the heavy metals in the sub-surface environment resulting in elevated levels of these metals in ground water resources (Srikanth et al. 1993). Furthermore in areas where agriculture is predominant high levels of cadmium have been recorded.

Toxic heavy metal water quality parameters for domestic uses were compared against WHO Drinking Water Specifications (2004) for the study area see Table 2.

Table 2 Seasonal toxic heavy metal contaminant levels in study area compared with WHO (2004) drinking water specifications.

Toxic heavy metals analyzed	Water Quality parameters in study area upper Sanyati catchment in Wet Season (mg/L)	Water Quality parameters in study area upper Sanyati catchment in Dry Season (mg/L)	WHO Maximum Permissible levels (mg/L)
Chrome	0.187	0.36	0.05
Lead	0.033	0.056	0.01
Cadmium	0.049	0.05	0.03
Nickel	0.04	0.04	0.02

All the four toxic heavy metals detected were found above the maximum permissible limits required. Exposure risks by humans from toxic heavy metals are dependent upon the solubility and bioavailability of these contaminants in soil and ground water.

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