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Seasonal Variation of the Impact of Mining Activities on Ga-Selati River in Limpopo Province, South Africa

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Abstract**—**Water is a very rare natural resource in South Africa. Ga-Selati River is used for both domestic and industrial purposes. This study was carried out in order to assess the quality of Ga-Selati River in a mining area of Limpopo Province-Phalaborwa. The pH, Electrical Conductivity (EC) and Total Dissolved Solids (TDS) were determined using a Crinson multimeter while turbidity was measured using a Labcon Turbidimeter. The concentrations of Al, Ca, Cd, Cr, Fe, K, Mg, Mn, Na and Pb were analysed in triplicate using a Varian 520 flame atomic absorption spectrometer (AAS) supplied by PerkinElmer, after acid digestion with nitric acid in a fume cupboard. The average pH of the river from eight different sampling sites was 8.00 and 9.38 in wet and dry season respectively. Higher EC values were determined in the dry season (138.7 mS/m) than in the wet season (96.93 mS/m). Similarly, TDS values were higher in dry (929.29 mg/L) than in the wet season (640.72 mg/L) season. These values exceeded the recommended guideline of South Africa Department of Water Affairs and Forestry (DWAF) for domestic water use (70 mS/m) and that of the World Health Organization (WHO) (600 mS/m), respectively. Turbidity varied between 1.78-5.20 and 0.95-2.37 NTU in both wet and dry seasons. Total hardness of 312.50 mg/L and 297.75 mg/L as the concentration of $CaCO_3$ was computed for the river in both the wet and the dry seasons and the river water was categorised as very hard. Mean concentration of the metals studied in both the wet and the dry seasons are: Na (94.06 mg/L and 196.3 mg/L), K (11.79 mg/L and 13.62 mg/L), Ca (45.60 mg/L and 41.30 mg/L), Mg (48.41 mg/L and 44.71 mg/L), Al (0.31 mg/L and 0.38 mg/L), Cd (0.01 mg/L and 0.01 mg/L), Cr (0.02 mg/L and 0.09 mg/L), Pb (0.05 mg/L and 0.06 mg/L), Mn (0.31 mg/L and 0.11 mg/L) and Fe (0.76 mg/L and 0.69 mg/L). Results from this study reveal that most of the metals were present in concentrations higher than the recommended guidelines of DWAF and WHO for domestic use and the protection of aquatic life.

Keywords**—**Contamination, mining activities, surface water, trace metals.

I. Introduction

SURFACE water is one of the most influenced ecosystems on earth. Its alterations have led to an extensive ecological degradation such as decline in water quality and availability, intense flooding, loss of species and changes in the distribution and structure of the aquatic biota, thus making them no longer sustainable in providing goods and services [1]. The health of a river system is influenced by various factors which include the geomorphology and geological formations, the chemical, physical and biological quality of the water, the hydrological regimes and the nature of instream and riparian habitats [1], [2]. Each aquatic ecosystem has some natural buffering capacity which allows it to adapt to and compensate for natural changes in the environment such as leaching from the soil or the occasional heavy rain. Water pollution occurs when conditions exceed the water ecosystem's ability to compensate for these changes [3].

Mining activities are responsible for the largest release of metals into the environment. Metals occur naturally in many ores, and are often released in the mineral extraction process. Metals like aluminium, cobalt, copper, cadmium, lead, silver and zinc contained in an excavated rock can come in contact with water and may be leached out under suitable environmental conditions and carried downstream by flowing water through the surface of the rocks [4]. All mining operations have a disruptive effect on the environment [1]. The environmental impact of mining includes erosion, loss of biodiversity, and contamination of soil, groundwater and surface water by chemicals from mining processes [5-6]. Large amounts of water produced from mine drainage, mine cooling, aqueous extraction and other mining processes increase the potential for these chemicals to contaminate ground and surface water. Besides creating environmental damage, the contamination resulting from leakage of chemicals also affects the health of the local population [7].

The large disturbances caused by mining can disrupt environments, adversely affecting aquatic and terrestrial habitats, and wetlands that many organisms rely on for survival. The disruption of site hydrology by large consumption or release of water, manipulation of topography, and the release of particulates and chemicals can all have indirect impacts on various habitats [4-5]. Water draining from coal and copper mines frequently contains sulfuric acid and heavy metals at high concentrations which could contaminate rivers and agricultural lands when used for irrigation purposes [8]. Entry of mine originated contaminants into agricultural soils and rivers may also occur during heavy rainfall events that cause over-bank flooding and /or flooding of tailing dams [8]-[10]. High concentrations of heavy metals in the soils and rivers, accompanied with acidic pH are likely to increase uptake of heavy metals by plants and man, which poses a high risk to the people who consume the agricultural products [8], [11].

Ga-Selati River is found in Pharlaborwa which is located on the eastern region of Limpopo Province of South Africa and has the coordinate of 23°56'0'' South and 31°7'0'' East. It

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falls under Ba-Phalaborwa Municipality in the Mopani District. There is a wide range of land uses in the Phalaborwa area including agriculture, mining activities and settlements (Fig. 1). Large portion of Phalaborwa area is used for mining activities and it serves the central gateway to the Kruger National Park via the Phalaborwa Gate. Tourism and wildlife play a dominant role in the life of Phalaborwa town. It is surrounded by game farms, lodges, game sanctuaries and nature reserves [12].

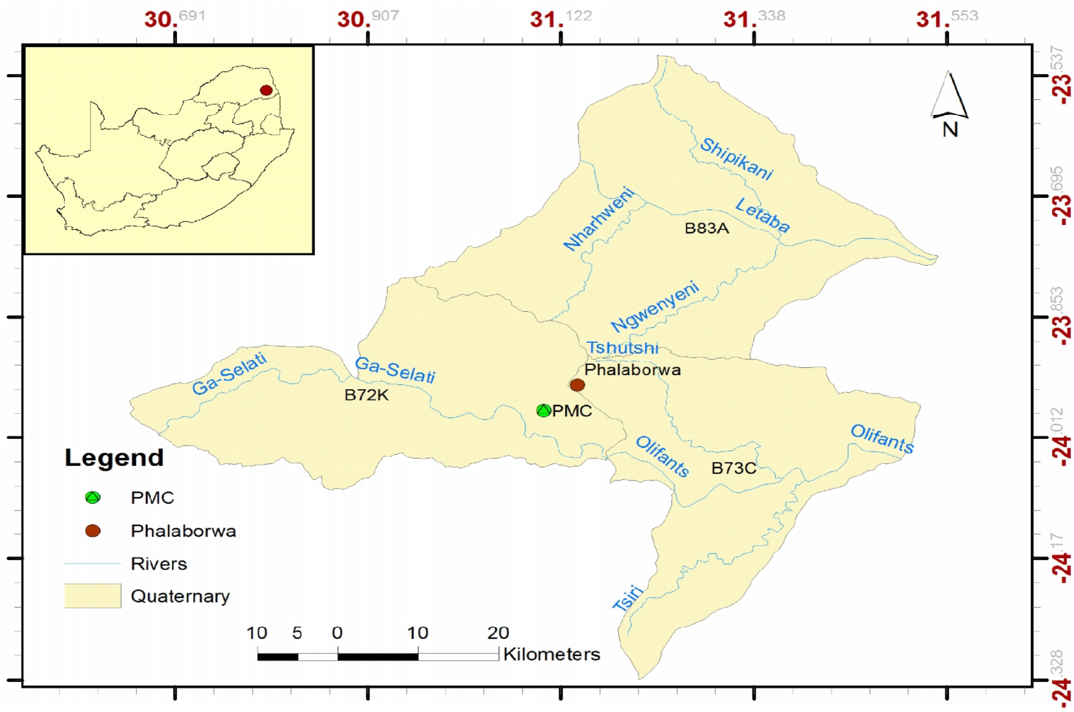

Fig. 1 Map of the study area

II. Experimental

A. Sample Collection, Preparation and Storage

Water samples were collected randomly from eight sampling points (S_1-S_8) between May 2012 and January, 2013 from Ga-Selati River and placed into propylene containers. The containers were rinsed three times with water from the river before collection from both upstream and downstream of the river. One litre sample was collected from eight sampling points. Field measurements of pH, electrical conductivity and total dissolved solids were determined using a portable a 340! multimeter (WTW, Weilheim, Germany), while turbidity measurements were performed with a Tobcon turbidimeter (Orbeco Hellige, Sarasota, FL, USA).

B. Sample Pre-Treatment

3 mL of 55% concentrated nitric acid was added to 100 mL of the sample in 250 mL conical flask. The mixture was subsequently heated on a hot stove (Labcon model MPC 30) in a fume cupboard, until clear fumes were observed from the solution. It was then left to cool for about 10 minutes and later filtered using Whatman No.1 filter paper into a 100 mL conical flask [13].

C. Sample Analyses

Trace metals' analyses in the samples were carried out using Flame Atomic Absorption Spectrophotometer. Na, K, Mg, Fe, Ca, Mn, Cd, Cr, Al, and Pb concentrations were determined using a PerkinElmer 520 atomic absorption spectrophotometer.

D. Reagents and Chemicals

All the chemicals were of analytical grade and were used without further purification. Standard solutions of lead nitrate ($PbNO_3$), cupric sulphate ($CuSO_4$), zinc sulphate ($ZnSO_4$), sodium dichromate ($NaCr_2O_7.H_2O$), manganese sulphate ($MnSO_4.H_2O$), 55% nitric acid (HNO_3), chromium(VII), zinc(II), iron(III), manganese(II), nickel(II), potassium dichromate (K_2CrO_4), potassium chloride (KCl), sodium chloride (NaCl) and deionised water were used.

III. Results and Discussion

A. Physicochemical Parameters

The average pH was higher during the dry season (9.38) than the wet season (8.00). Alkaline pH was observed for all the sites. Some of the sites had pH values higher than the recommended guidelines of DWAF [14] and WHO [15]. The difference in the means of pH values in both seasons was statistically significant ($p<0.01$). The values of pH determined varied greatly with those reported for Madanzhe (6.6-6.7), Dzindi (7.4-7.5) and Mvudi Rivers (6.4-6.9) in Limpopo Province of South Africa [16]-[18]. The reason for the alkaline pH could be possibly due to the mining of phosphate rocks and the production of basic fertilizers in the study areas.

TABLE I
SEASONAL VARIATION OF SOME PHYSICOCHEMICAL PARAMETERS

Sampling sites	pH_{wet}	pH_{dry}	EC_{wet} (mS/m)	EC_{dry} (mS/m)	TDS_{wet} (mg/L)	TDS_{dry} (mg/L)	$Turbidity_{wet}$ (NTU)	$Turbidity_{dry}$ (NTU)
S_1	7.95	9.28	69.6	163.2	466.32	1093.4	4.23	2.37
S_2	7.94	9.51	72.0	154.0	469.0	1031.8	5.10	0.95
S_3	7.94	9.81	72.1	156.5	683.1	1048.5	2.19	1.18
S_4	7.44	9.61	164.9	152.3	1104.8	1020.4	5.10	1.17
S_5	8.36	9.51	68.8	87.7	461.0	587.59	5.20	1.18
S_6	7.72	9.28	178.0	124.4	1192.6	833.48	2.29	2.16
S_7	8.35	8.97	69.6	141.4	466.32	947.32	1.78	1.57
S_8	8.31	9.10	70.1	130.1	871.67	871.67	5.20	1.87
Average	8.00	9.38	96.63	138.7	640.72	929.29	3.89	1.57
DWAF	6.5-9.00		70		450		<1	
WHO	6-9		600		500		-	

S_1-S_8: Sampling points along Ga-Selati River

The metals present may not be bioavailable for uptake since the pH of all the sites were alkaline. The high value of pH determined could affect biodiversity of aquatic organisms and likely affect the reproductive cycle of fish. Alkalinity is the capacity of water to neutralize acids, and the alkalinity of natural water is derived principally from the salts of weak acids. Hydroxide, carbonates, and bicarbonates are the dominant sources of natural alkalinity [19]. Reactions of carbon dioxide with calcium or magnesium carbonate in the sediment often result in considerable amounts of bicarbonates. Organic acids such as humic acid also form salts that increase alkalinity [19]. The toxic effect of most metals are influenced with acidic pH. Therefore, most metals may not bio-available for uptake due to alkaline pH determined.

Both EC and TDS values were higher during the dry season than the wet season. The average EC for the wet and the dry seasons were 96.63 mS/m and 138.7 mS/m while the TDS were 640.72 mg/L and 929.29 mg/L, respectively. The values obtained exceeded the recommended values of 70 mS/m (600 mS/m) and 450 mg/L (500 mg/L) for domestic water use [14], [15]. The high levels of EC and TDS determined could be due to surface runoff from waste rocks, dumping sites and tailings in the mines into the river. The high concentration of EC and TDS obtained is consistent with [20].

High EC and TDS values suggest the presence of of bicarbonates, phosphates, chlorides. This usually lead to increase in salinity which changes the ionic composition of the water. This can further cause a shift in biotic communities, limit biodiversity and exclude less tolerant species [21]. Electrical Conductivity is an indicator of the amount of dissolved salts in a stream and it is also used to estimate the amount of total dissolved solids (TDS) rather than measuring each dissolved constituent separately [22]. EC concentration greater than 70 mS/m indicates that the concentration of calcium, sodium, magnesium and total hardness, chloride and sulphate in water may have negative impacts on aquatic organisms.

Turbidity which refers to the "cloudiness" of water is caused by particles such as silt, clay, fine organic matter and microscopic organisms that are suspended in the water [2], [23], [24]. The turbidity of Ga-Selati River ranged from 1.78-5.20 NTU during the wet season and 0.95-2.37 in the dry season (Table I). This finding is consistent as runoff from mines and soils could lead to increase in suspended matter in the river during heavy rainfall. Higher turbidity increases water temperatures because suspended particles absorb more heat [25], [26]. This in turn reduces the concentration of dissolve oxygen (DO) because warm water holds less DO than cold water. Higher turbidity also reduces the amount of light penetrating the water, which reduces photosynthesis, thus can harm the aquatic species within river [25], [26]. Increase in suspended solids can clog fish gills, reduce growth rates and decrease resistance to diseases [27]. Thus, with very high levels of turbidity, water might lose its ability to support diversity of aquatic organisms. Values over 35 – 40 NTU might have a negative influence on predatory fish, which hunt on sight [27]. There is no target water quality range for turbidity for aquatic ecosystems. The level of turbidity cannot be linked directly to mining activities as other studies have shown similar turbidity values in non-mining environment [17], [18].

B. Trace Metal Contamination

The concentration of Na varied from 46.26-298 mg/L with an average concentration of 94.06 mg/L during wet season. Some sites showed higher concentration of Na than the threshold value of 100 mg/L. The concentration in dry season was higher (with an average concentration of 196.30 mg/L) than the concentration in the wet season and their levels for both seasons differed significant ($p<0.01$). This could be due to evaporation of water during high temperatures. High sodium concentration contributes to the high level of EC and TDS measured in Ga-Selati River. Although sodium is relatively present in surface water, its increasing concentration has been attributed to anthropogenic activities related to urbanization, mining and increase in population density [28].

High Na concentration have been attributed to erosion of salt deposits and sodium bearing minerals, leaching from landfills, mining sites and runoff of water enriched with sodium [29]. Increase in the concentration of sodium increases the salinity of water and causes undue stress to the aquatic eco-system. Irrigation with Na-rich water can cause damage to crops. Sodium can also be absorbed directly into the plant through their leaves moistened during irrigation. This occurs typically during periods of high temperature and low humidity. The leaf absorption speeds the rate of accumulation of a toxic ion and may be a primary source of the toxicity [30].

The concentration of potassium (K) was not as high as that of Na for both seasons. The average concentration of K for both season was 11.79 mg/L and 13.62 mg/L, respectively (Fig. 2). This concentration was below the recommended guidelines. The mean of K in both the wet and the dry season did not differ significantly ($p>0.05$).

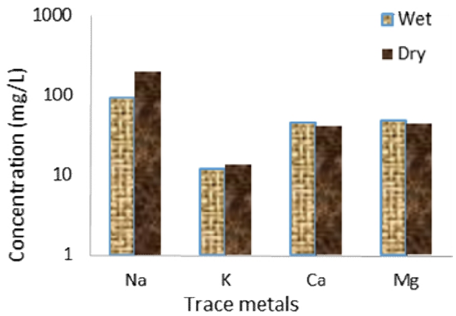

Fig. 2 Seasonal Variation of the concentrations of Na, K, Ca and Mg

TABLE II
MEAN CONCENTRATION OF TRACE METALS IN GA-SELATI RIVER

Metals (mg/L)	$\overline{X}_{wet}$	$\overline{X}_{dry}$	$\sum\left(\frac{\overline{X}wet+\overline{X}dry}{2}\right)$	DWAF	WHO
Na	94.06	196.3	145.18	100	200
K	11.79	13.62	12.71	50	-
Ca	45.60	41.30	43.45	32	-
Mg	48.41	44.71	46.56	30	-
Al	0.31	0.38	0.35	0.15(0.005)	0.2*
Cd	0.01	0.01	0.01	0.005	0.003
Cr	0.02	0.09	0.06	0.05(0.007)	0.05
Pb	0.05	0.06	0.06	0.01(0.00002)	0.01
Mn	0.31	0.11	0.21	0.05(0.18)	0.1*
Fe	0.76	0.69	0.73	0.1	0.3*

* Aesthetic concentration for drinking and food industry requirements

Calcium (Ca) had an average concentration of 45.60 mg/L and 41.33 mg/L during the dry and the wet seasons, respectively and that of Magnessium (Mg) were 48.41 mg/L and 44.71 mg/L, respectively. Ca and Mg ion had comparable concentrations in both seasons. Total hardness (TH) of any river can be calculated and presented in terms of calcium carbonate ($CaCO_3$) by using (1) and (2);

Total Hardness=Calcium Hardness+Magnesium Hardness (1)
(mg/L as $CaCO_3$) (mg/L as $CaCO_3$) (mg/L as $CaCO_3$)

$$\text{Total hardness} = (2.50 \times [Ca^{2+}] + 4.12 \times [Mg^{2+}]) \quad (2)$$

The total hardness in wet season was higher than in dry season; this is consistent as a result of runoff from the mines, catchment areas and erosion during heavy rain which could have led to the accumulation of Ca^{2+} and Mg^{2+} ions. The river water was categorised to be very hard using the classification system reported by [31]. The high concentrations of Ca^{2+} (41.40-45.60 mg/L) and Mg^{2+} (44.71-48.41 mg/L) can be linked to mining activities in the vicinity of the river. Moodley et al. [32] reported Ca and Mg concentrations in the range of 10.826-14.717 mg/L and 3.148-5.406 mg/L, respectively in Palmet River of South Africa.

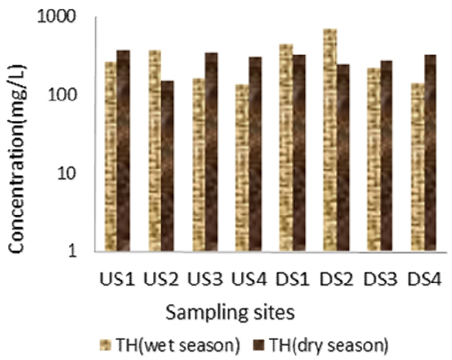

Fig. 3 Seasonal Variation of total hardness (TH) as $CaCO_3$ in Ga-Selati River

The health effects of consuming hard water are strongly associated with the salts dissolved in it [32]. Although a few studies have shown the possible effects of hard water on human health but the World Health Organization (WHO) have reported no adverse effects [33]. Pourkhabbaz et al. [34] reported that Zn and Cu toxicity to fish reduces with increase in the hardness of water the fish lives. The major cause of hardness of water can be attributed to the presence of polyvalent metal ions in the run off from rocks, soils and seepage [33]. Therefore, water sources in a mining environment is more likely to be hard when compared to water sources elsewhere.

Aluminium (Al) is not needed as nutrient for any organism. pH controls its solubility in water. It is soluble, bio-available and toxic when pH value of water is less than four. But when the pH increases and becomes basic, it is soluble but biologically unavailable for uptake by living organisms. The concentration of Al in Ga-Selati River was slightly higher in the dry season (0.38 mg/L) than in wet season (0.31 mg/L), the difference in their means was not significant ($p>0.05$). The mean concentration of Al exceeded the recommended guideline value of 0.15 mg/L for domestic water use [14] and other guidelines for the protection of aquatic life and aesthetic property of water [17], [30].

The concentration of Al determined in this study is higher than 0.049-0.278 mg/L reported for Umgeni River of South Africa but was lower than those reported for Umdloti River (0.037-1.875 mg/L) [35]. High concentration of Al in acidic water are toxic to a wide variety of organisms although the toxicity mechanism is still uncertain [2]. It is believed that its toxic effects are as a result of several determinants which includes the life stage of the organism, pH and the levels of Ca in the water [30]. Al is toxic to various invertebrates and plants and can interfere with calcium ion metabolism [36]. Although the pH is high in dry season, toxicity and fish deaths can occur due to decrease in pH in wet season.

Manganese (Mn) unlike Al is an essential micronutrient for plants and animals but can be toxic when present in high concentrations. Insufficient quantity of Mn in plants can impair photosynthetic productivity causing chlorosis (a yellowing of the leaves) or failure of leaves to develop properly. In vertebrates, deficiency of Mn often manifest in skeletal deformities and reduced reproductive capabilities [30]. Mn had an average concentration of 0.31 mg/L and 0.11 mg/L during the wet and the dry season respectively and the difference of this means was statistically significant ($p<0.02$). Mean concentration of Mn (0.21 mg/L) was higher than the guideline values of DWAF for the protection of aquatic life and for domestic purposes [30].

Iron (Fe) is the fourth most abundant element in the earth's crust and is present in natural waters in varying quantities depending on the geology of the area and other chemical properties of the water body [2], [30]. Fe toxicity depends on the oxidation it exists in aqueous solution. Its toxicity is usually not a cause for alarm because it is not easily absorbed through the gastro-intestinal tract of vertebrates [30]. High concentration of Fe exceeding 0.3 mg/L have poor aesthetic value to the consumers of such water as it imparts colour and unpleasant taste to the water [15]. The concentration of Fe in both the dry and the wet seasons varied from 0.22-1.24 mg/L and 0.16-1.02 mg/L with an average concentration of 0.74 mg/L and 0.69 mg/L, respectively. The concentration of Fe in the river system was above the threshold limit of 0.1 mg/L of DWAF. The mean concentration of Fe for both seasons was not statistically different ($p>0.05$). Fe is an essential micronutrient for all organisms, and is required in the enzymatic pathways of chlorophyll and protein synthesis, and in the respiratory enzymes of all organisms, it also forms a basic component of haeme-containing respiratory pigments [2], [14].

Lead (Pb) is potentially non-essential and hazardous to most forms of life and is considered toxic and relatively accessible to aquatic organisms under suitable environmental conditions [17]. Anthropogenic activities are the major sources of Pb in river systems. Runoff from agricultural lands, wastewater and wastewater effluents, mining activities and petroleum products are major pathways of Pb into the environment. The mean concentration of Pb in Ga-Selati River during dry and wet season were 0.05 mg/L and 0.06 mg/L, respectively and did not show statistical difference at 95% confidence level. All the samples had a concentration higher than the designated guideline values.

Pb toxicity is highly dependent on pH. It is soluble and more toxic to living organisms at acidic pH but it becomes insoluble when the pH is basic. The accumulation of Pb by vertebrate in aquatic eco-system is largely deposited in the bony skeleton, where it does not usually exhibit toxic effects [30], [36]. Low Pb concentrations usually have negative effects on fish. It can cause the formation of a film of coagulated mucous over the gills of fishes and their entire body. This can subsequently lead to fish death due to suffocation. It can also become bio-accumulated by benthic bacteria, freshwater plants and invertebrates which becomes a major pathway to human food chain [23], [36].

The natural occurrence of Chromium (Cr) in water bodies is low. High Cr concentration is usually a pointer to pollution. It is toxic to various kinds of organisms [14], [37]. Cr concentration was lower in the wet season with a mean concentration of 0.02 mg/L due to dilution than in the dry season (0.09 mg/L). The concentration of Cr for both seasons differed significantly ($p<0.05$). All the levels of Cr determined exceeded the recommended guidelines of DWAF and WHO for domestic water (0.05 mg/L) and the protection of aquatic life (0.007 mg/L) [15], [30]. Hexavalent chromium is very toxic to flora and fauna. A temporarily reduced growth phase has been reported for young fish at low chromium concentrations [30]. Green algae are also more sensitive than fish, while bacterial responses to Cr are variable.

Cadmium (Cd) is highly toxic to marine and fresh water aquatic lives. It is less commonly detected in surface waters in high concentration. Cd is hazardous to most forms of life and is considered to be toxic and relatively accessible to aquatic organisms. The main sources of Cd in the environment are due to emissions to air and water from mining, metal smelting, manufacture of alloys, paints, batteries and plastics [2]. Cd had a mean concentration of 0.01 mg/L for both seasons which exceeded the threshold values OF DWAF and WHO. Cadmium is known to inhibit bone repair mechanisms, and is teratogenic, mutagenic and carcinogenic [38], [39]. Bio-available Cd may be accumulated by macrophytes, phytoplankton, zooplankton, invertebrates and fish [30]. Speciation of Cd forms affects its bio-availability; free Cd^{2+} is readily taken up by aquatic plants, whereas organo-cadmium complexes are not absorbed [40]. Its bio-accumulation is also dependent of several factors like water temperature and pH.

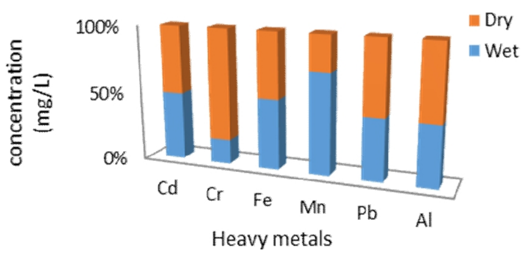

Fig. 4 Seasonal variation of the concentrations of some heavy metals in Ga-Selati River

IV. Conclusion

The concentrations of trace metals in Ga-Selati River exceeded most of the threshold values of DWAF and WHO for domestic water use and the protection of aquatic life. Mining activities have been implicated for the high concentrations of Ca, Mg, electrical conductivity determined as their levels are higher than the background levels in other South Africa Rivers with similar geological formation. Most of the metals found although high is not likely to pose any harm to man due to high pH determined during the course of the study but a drastic change in pH will lead to the bio-availability of these metals with the related consequences. Toxicity to some aquatic organisms is possible with the current water quality status of the river.

REFERENCES

[1] L.N., Poff, D. Allan, M.B. Bain, J.R. Karr, K.L. Prestegaard, B.D. Richter, R.E. Sparks, J.C. Stromberg. "The natural flow regime: A paradigm for river conservation and restoration". *Bioscience*, vol. 47, pp. 769–784. 1997.

[2] Canadian Council of Ministers of the Environment. Canadian water quality guidelines. Environment Canada, Ecosystem Conservation Directorate, Evaluation and Interpretation Branch, Guidelines Division, Ottawa, Ontario. Pp 17-30, 2008.

[3] H.F. Dallas, J.A. Day, D.E. Musibono, E.G. Day. "Water Quality for Aquatic Ecosystems: Tools for Evaluating Regional Guidelines". WRC Report No 626/1/98. pp 240. 1998.

[4] Safe Drinking water foundation. Mining and water pollution www.safe**water**.org/PDFS/.../Mining+and+**Water**+Pollution.pdf. Accessed 4th May, 2015.

[5] J.H.J. van Vuren, H.H. du Preez, V. Wepener, A. Adendorff, I.E.J. Barnhoorn, L. Coetzee, P. Kotzé, G. Nussey. "Lethal and Sub-lethal Effects of Metals on the physiology of fish: An Experimental Approach with Monitoring Support". WRC Report No. 608/1/99. pp 283. 1999.

[6] W.H. Langer, B.F. Arbogast, "Environmental impacts of mining natural aggregate deposit and geoenvironmental models for resource exploitation and environmental security" NATO Science Partnership Sub-Series 2, 80:151-169. 2003.

[7] V. Wepener, J.H.J. van Vuren, H.H. du Preez. "Application of the equilibrium partitioning method to derive copper and zinc quality criteria for water and sediment: A South African perspective". *Water SA* vol. 26:97-104. 2000.

[8] G.M. Ochieng, E.S. Seanego, O.I. Nkwonta. "Impacts of mining on water resources in South Africa: A review. *Sci. Res. Essays*, vol. 5, no. 22, pp. 3351-3357, 2010.

[9] US EPA (2004). Drinking Water Advisory: Consumer Acceptability Advice and Health Effects Analysis on Sodium. EPA 822-R-03-006. www.epa.gov/safewater/ccl/pdf/sodium.pdf. Accessed on the 1st November, 2013.

[10] V. Munnik, G. Hochmann, M. Hlabane and S. Law. "*The Social and Environmental Consequences of Coal Mining in South Africa A case study,* Environmental Monitoring Group, Cape Town, South Africa pp 2-22. 2010.

[11] A. Boularbah, C. Schwartz, J.L. Morel. "Heavy metal contamination from mining sites in south morocco, assessment of metal accumulation and toxicity in plants". *Chemosphere,* vol. 63, pp. 811-817. 2006.

[12] E. Dobb. 1996. Acid mine drainage; mining and water pollution. Environmental mining council of BC. Harper's Magazine; March, 2000. http://www.miningwatch.ca/updir/amd.pdf. Assessed on 3 April, 2013.

[13] Ogola, J. S.; Chimuka, L.; Maina, D. Occurrence and fate of trace metals in and around treatment and disposal facilities in Limpopo Province, South Africa: A case of two areas. In Proceeding of the IASTED International Conference on Environmental Management and Engineering, Banff, Alberta, Canada, 6 – 8 July 2009, pp. 92–97.

[14] DWAF. Quality of Domestic Water Supplies Volume 1: Assessment Guide, 2nd ed.; 1998. Pretoria, South Africa

[15] World Health Organization. Guidelines for Drinking-water Quality 4th edn. World Health Organization, Geneva, Switzerland. 2011.

[16] J.O. Okonkwo, M. Mothiba. Physico-chemical characteristics and pollution levels of heavy metals in the rivers in Thohoyandou, South Africa. *Journal of Hydrology* vol. 308, pp. 122–127. 2005.

[17] J.N. Edokpayi, J.O. Odiyo, S.O. Olasoji. "Assessment of heavy metal contamination of Dzindi River, in Limpopo Province, South Africa*". Int. J. Nat. Sci. Res*, vol. 2, no. 10, pp. 185-194. 2014.

[18] J.N. Edokpayi, J.O. Odiyo, T.A.M. Msagati and N. Potgieter. "Temporal Variations in Physico-Chemical and Microbiological Characteristics of Mvudi River, South Africa". *Int. J. Environ. Res. Public Health vol. 12*, pp. 4128-4140. 2015.

[19] P. Vaishali, P. Punita. "Assessment of seasonal variation in water quality of River Mini, at Sindhrot, Vadodara". *Int. J. Enviro. Sci.* vol. 3, no. 5, pp. 1-13, 2013.

[20] P. Gupta, S. Roy. "Evaluation of spatial and seasonal variation in groundwater quality at Kolar Goldfield, India". *Am. J. Environ. Eng.* vol. 2, no. 2, pp. 19-30. 2012.

[21] W.S. Phyllis, L.J. Laur. "Effects of total dissolved solids on aquatic organisms. Technical Report no. 01-06". http://www.adfg.alaska.gov/static/home/library/pdfs/habitat/01_06.pdf. Accessed on the 17th of June, 2012.

[22] K. Farrell-Poe. "Water quality and monitoring". http://cals.arizona.edu/watershedsteward/resources/docs/guide/(10)Water%20Quality.pdf. 2000. Accessed on the 17th June, 2013.

[23] DWAF. Quality of domestic water supplies. Sampling Guide 2. Department of Water Affairs and Forestry, Department of Health and Water Research Commission. 1999

[24] J. P. Michaud. "A citizen's guide to understanding and monitoring lakes and streams". Washington State Department of Ecology, Puget Sound Water Quality Authority, Olympia, WA. pp 66. 1995.

[25] F.X. Browne "Lake and Watershed Monitoring Handbook: Lake Wallenpaupack" Watershed Management District. Hawley, PA © F. X. Browne, Inc. 2003. Pp2-58

[26] K.A. Morgenstern, D. Donahue, N. Toth. McKenzie River Watershed Baseline Monitoring Report 2000 to 2009. Eugene Water & Electric Board, January 2011 pp1-144. http://www.eweb.org/sourceprotection/baseline. 2011. Accessed 21st April, 2015.

[27] B. Davies, J.A. Day. "Vanishing Waters. University of Cape Town Press, Cape Town, South Africa". pp 487. 1998.

[28] M. K. Steele, J.A. Aitkenhead-Peterson. Long-term sodium and chloride surface water exports from the Dallas/Fort Worth region. *Sci. Total Environ.* vol. 409, pp. 3021–3032. 2011.

[29] Water Stewardship Information Series (2007). Sodium in Groundwater. http://www.env.gov.bc.ca/wsd/plan_protect_sustain/groundwater/library/ground_fact_sheets/pdfs/na(020715)_fin2.pdf. Accessed 25th April, 2015

[30] DWAF. South African Water Quality Guidelines. Volume 7: Aquatic Ecosystems. Edited by S Holmes, CSIR Environmental Services, CSIR Environmental Services, Pretoria, South Africa, 1996.

[31] P. Sengupta. "Potential Health Impacts of Hard Water". *Int. J. Prev. Med.* 4:866-75. 2013.

[32] K. Moodley, S. Pillay, K. Pather, H. Ballabh. Heavy Metal Contamination of the Palmiet River: KwaZulu Natal South Africa. *Int. J. Sci. Res. Environ. Sci.*, vol. 2, no. 11, pp. 397-409, 2014.

[33] WHO. Hardness in Drinking-water Background document for development of WHO *Guidelines for Drinking-water Quality* WHO/SDE/WSH/03.04/06 can be obtained from Marketing and Dissemination, World Health Organization, 20 Avenue Appia, 1211 Geneva 27, Switzerland. 2003.

[34] A. Pourkhabbaz, M.E. Kasmani, V. Kiyani and M.H. Hosynzadeh Effects of water hardness and Cu and Zn on LC50 in Gambusia holbrooki. *Chem. Spec. Bioavailab.*, vol. 23, no. 4, pp. 224-228, 2011.

[35] A.O. Olaniran, K. Naicker and B. Pillay. Assessment of physico-chemical qualities and heavy metal concentrations of Umgeni and Umdloti Rivers in Durban, South Africa. *Environ Monit Assess.* 186:2629–2639. 2014.

[36] H.F. Dallas, J.A. Day. "The effect of water quality variables on riverine ecosystems: a review". Water Research Commission Report No TT 224/04, Pretoria. pp 222. 2004.

[37] B.V. Lenntech. "Water treatment solutions". http://www.lenntech.com/ro/water-hardness.htm. Accessed on the 1st November, 2013.

[38] A. Rani, A. Kumar, A. Lal, and M. Pant. Cellular mechanisms of cadmium-induced toxicity: a review. *Int. J. Environ. Health Res*, vol. 24, no. 4, pp. 378–399. 2014,

[39] A. Sarkar, G. Ravindran V. Krishnamurthy. A brief review on the effect of cadmium toxicity: from cellular to organ level. *Int. J. Bio-Technol. Res.* vol. 3, no. 1, pp. 17-36, 2013.

[40] J.O. Duruibe, M.O.C. Ogwuegbu, J.N. Egwurugwu. Heavy metal pollution and human biotoxic effects. *Int. J. Phys. Sci.* vol. 2, no. 5, pp. 112-118, May, 2007.