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ASSESSING THE EFFECTIVENESS OF SETTLING PONDS IN TREATING MINE EFFLUENT: A CASE OF MUROWA DIAMONDS MINE

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ABSTRACT

A study was carried out in Zvishavane district of Zimbabwe to assess the effectiveness of settling ponds in treating mine effluent. Total Suspended Solids (TSS), electrical conductivity (EC), pH, Cadmium (Cd), Chromium (Cr), Lead (Pb), Iron (Fe), Zinc (Zn), Manganese (Mn), Mercury (Hg) and Arsenic (As) were measured in the water samples. Water samples were collected monthly at four sampling sites from January to June 2010. The sites were chosen so as to compare its quality in terms of heavy metal concentration before and after treatment using settling ponds. The results showed that the concentration of the following parameters TSS, EC, Pb, Mn, Hg, and As did not show any significant difference during the study period whereas the concentration of pH, Cd, Cr, Fe and Zn in the water samples did differ significantly during the study period. Higher concentrations of TSS, Pb, Mn, and Zn were recorded at the upstream sampling point whereas that of EC was recorded at the entry point to the settling pond. Highest concentrations of Fe were recorded at the discharge point whereas that of pH was recorded in downstream water. As was highest at the entry point and discharge point whereas the concentrations of Cd, Cr, and Hg did not differ significantly with sampling points. Levels of TSS and Cd were above the legally accepted levels and levels of all other parameters studied were significantly lower than the national EMA effluent discharge standards. The research showed that the mine is emitting a 'safer' effluent as compared to water drawn from Runde upstream in terms of heavy metal concentration.

Key words: pollution, effluent, heavy metals, sedimentation, sustainability

INTRODUCTION

Pollution of the aquatic environment is mainly by anthropogenic activities. This results in such deleterious effects and harm to living resources, hazards to human health, hindrance to aquatic activities including fishing, impairment of water quality with respect to its use in agricultural, industrial and often economic activities, and reduction of amenities (GESAMP, 1988). A range of surface water and groundwater pollution problems can be associated with mining activities. Water-pollution problems caused by mining activities include acid mine drainage, metal contamination, and increased sediment levels in surface water sources.

The primary objective of wastewater (industrial effluent) treatment then is to remove or modify those contaminants detrimental to human health or the water, land and air environment. Land disposal, evaporation from ponds, and deep-well injection are occasional options, but usually the only practical outlets for the disposal of treated/untreated wastewater are usually streams, rivers, lakes and oceans. To protect these water resources, the discharge of pollutants into them must be controlled. If left uncontrolled, effluent water can lead to the loss of ecological balance through the change of the water chemistry (Henry and Heinke, 2004)**.** Heavy metals are mainly waste products of anthropogenic activities and their emission often results in the contamination of the surrounding environment (Eeva & Lehikoinen, 2000). Environmental contamination and exposure to heavy metals such as mercury, cadmium and lead is a serious growing problem throughout the world (UNESCO, 1992).

Human exposure to heavy metals has risen dramatically in the last 50 years, says WHO, as a result of an exponential increase in the use of heavy metals in industrial processes and products. Many occupations involve daily heavy metal exposure; over 50 professions entail exposure to mercury alone. In the United States, tons of toxic industrial waste are mixed with liquid agricultural fertilizers and dispersed across America's farmlands (Eeva & Lehikoinen, 2000). According to Mtisi, 2008, the discharge of untreated industrial, municipal, domestic waste and washing of agricultural chemicals into water bodies are the major sources of pollution of Zimbabwean streams and rivers especially in the urban and mining areas.

Disposal of mine effluent to surface water or groundwater can cause serious impacts on water quality for all users (Henry and Heinke, 2004)**.** At Murowa Diamonds mine, all mine effluent and storm flows (surface runoff) go through two settling ponds at the mine where it is allowed to settle before emission into Runde river. Mining and the related operations are thus the most important anthropogenic sources of heavy metals that negatively influence the nearby environment (Conesa *et al*., 2007; Vanderlinden *et al*., 2006; Vanek *et al*., 2005).

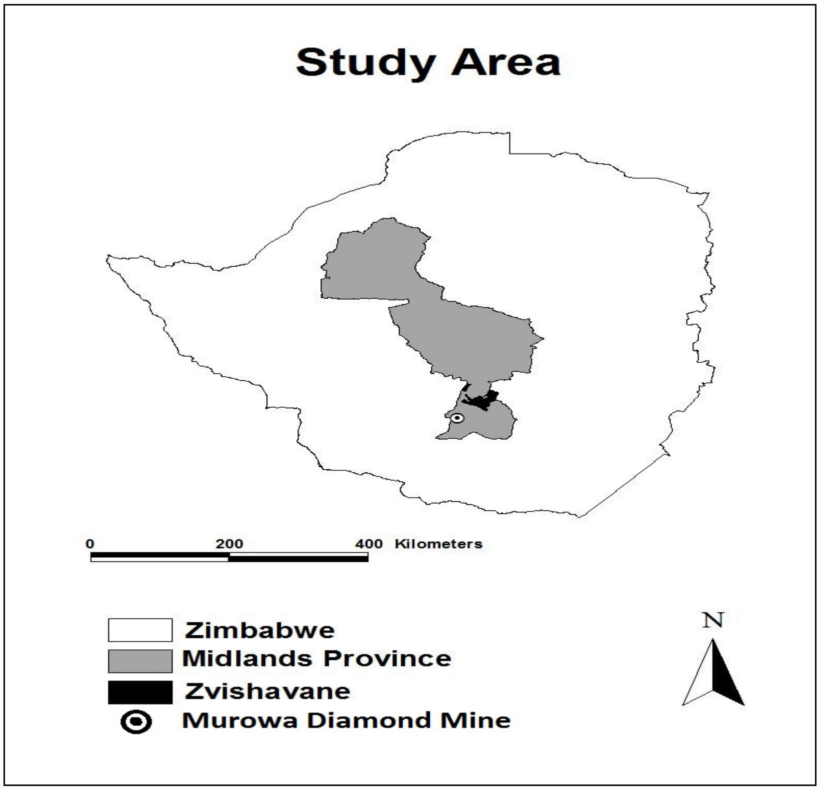
Murowa Diamonds mine received complaints from communities downstream of Runde River claiming that their livestock especially cattle were having miscarriages. The communities were attributing these miscarriages to "water polluted with heavy metals discharged by the mine". In response the mine management argued that diamond mining and processing at Murowa Diamonds used insignificant amounts of chemicals in the processing of diamonds and that effluent water was let through two settling ponds where it was treated before discharge into the river. It was thus of paramount importance to ascertain whether the settling ponds were emitting a 'safe discharge' into Runde River as argued by the mine or not.

The study sought to assess the effectiveness of the settling ponds in treating mine effluent from Murowa Diamonds mine. Specifically, to measure the concentration of heavy metals in upstream water, settling ponds (at entry point and discharge point) and downstream of Runde river approximately 1 km from the discharge point, to determine seasonal changes in the concentration of heavy metals at the sampling sites and assessing if the mine effluent was complying with the local mining/ industrial effluent standards.

MATERIALS AND METHODS

Study Area

The study was carried out in Zimbabwe a country located in Southern Africa. The specific study area is Murowa Diamonds mine in Zvishavane district, Midlands province, south central Zimbabwe. The mine covers approximately 15km^2. The Runde River marks the eastern boundary of the site. The area has a semi arid, hot climate, with hot wet summers and mild dry winters. The average maximum temperature is 28.1^{0}C whilst the average minimum is 14.3^{0}C. Annual rainfall is variable, with distinct wet and dry seasons. The prevailing wind direction is south-south east to easterly with strong westerly direction towards Runde River.



The topography is flat to gently undulating and is interspersed with granite rock outcrops. The granite outcrops are steep and largely uninhabitable, and control the features of the landscape. The land slopes gently in a north-westerly direction towards the Runde River. The geology underlying the mine area is typical of that across the entire region. The kimberlite (diamond bearing) pipes appear to have exploited weaknesses associated with the regional faults and structures of the granite.

The Runde River flows from north to south along the eastern portion of the main area with several of its tributaries intersecting in the mine area. These tributaries drain in a south easterly direction to the confluence of the Runde/Ngezi River (Rio Tinto Zimbabwe, 1999). This catchment is within the summer rainfall area of the Lowveld. The water flow is strongly seasonal in the Runde River. High natural water flows are generally recorded in summer due to the abundant precipitation. In winter the water level in the river decreases, thereby stressing the aquatic ecosystem (Ninham, 2001).

DATA COLLECTION

Description of Sampling Sites

Samples were collected from four points, one point was at the river just above a point from where the mine draws its water (at the Weir), the second point was at the entry point into the settling pond, the third point was at the discharge point of the settling pond and the fourth point was at a point beyond the mine's effluent discharge point (Runde 1km downstream).

Table 1. List of sampling sites

Site position	Site name
Site 1: Runde Upstream	Upstream
Site 2: Effluent entry point into settling pond	Entry point
Site 3: Effluent discharge point from settling pond	Discharge point
Site 4: Runde Downstream beyond effluent discharge point	Downstream

Sample Collection

Samples from the four sampling points were collected as grab samples and were collected in sterilized plastic containers and preserved through the addition of 1 ml of sulphuric and nitric acid. Sample bottles were filled completely so as to exclude air in water samples. This was done to avoid reactions such as oxidation and reduction which could alter the sample components. The samples were transported to the laboratory for analysis within 24 hours of collection**.** Laboratory analysis of the water samples were done over a period of six months from January to June of 2010. The analysed parameters were: TSS, EC, pH, Cd, Cr, Fe, Pb, Mn, Zn, Hg and As. The study was done under the repeated measures experimental design.

Laboratory Procedures

The pH was determined using a glass electrode pH meter with calomel reference electrode (Model: Jenco electronics 6071). The pH meter was calibrated using standard buffer solution of pH 4, 7 and 9, following recommendations by Booth, 1982. Electrical conductivity (EC) was measured using a conductivity meter (Metrohm 644 conductometer).

Fe, Zn and Mn concentration were determined using the Atomic Absorption Spectrometer (AAS) that had been calibrated using standards that were prepared from high purity metals, oxides and non-hygroscopic reagent grade salts using deionised water.

Sample analysis for Cr, Cd and Pb using a Unicam Solar M Series Atomic Absorption Spectrometer (AAS) with GF95 Furnace System was done. 100ml of the water sample was filtered through a 51 filter paper into a medicine bottle. The concentration of the metal elements were read on Atomic Absorption Spectrometer (AAS) that had been calibrated using standards that were prepared from high purity metals, oxides and non-hygroscopic reagent grade salts using deionised water.

The filtered samples were then aspirated into the air-acetylene flame and the concentration of the elements was read directly from the instrument.

Determination of Hg and As was done through transferring water samples (100ml) into a BOD bottle. The samples were then digested in diluted potassium permanganate-potassium persulphate solutions and oxidized for two hours at 95°C. Mercury in the digested water sample was reduced with stannous chloride to elemental mercury and measured by the conventional cold vapour atomic absorption technique.

Data Analysis

Statistical analysis was carried out using SPSS 16.0 computer package SPSS 16.0. ANOVA and t-tests were used to compare the means of samples at $P \leq 0.05$. To test the hypothesis, there is no significant difference in the heavy metal concentration between wet and dry seasons; the research used the non-parametric test to the repeated measures ANOVA, Kruskal Wallis test.

To test the hypothesis, there is no significant difference in the concentration of heavy metals at the sampling points; data were analyzed using one-way ANOVA. Means were compared using a post hoc Tukey's Honestly Significant Difference (HSD) tests for differences in the concentration of heavy metals between the sampling points. For the hypothesis, there is no significant difference between the heavy metal concentration in discharged water and the EMA mining industry effluent standards a 2-tailed One-Sample t-test was used. In all analyses, $P < 0.05$ was the criterion for significant differences.

RESULTS AND DISCUSSION

Seasonal Concentration Trends.

The results showed that the concentration of the following parameters TSS, EC, Pb, Mn, Hg, and As in water samples did not show any significant difference whereas the concentration of pH, Cd, Cr, Fe and Zn did differ significantly during the study period as shown in table 2 below.

Table 2: Kruskal Wallis test results (*P* ≤ 0.05))

		TSS	EC	pH	Cd	Cr	Fe	Pb	Mn	Zn	Hg	As
January	Mean	199.000	589.750	8.550	0.020	0.030	1.040	0.080	0.270	0.030	0.020	0.020
	S.E	78.180	29.300	0.270	0.003	0.000	0.430	0.030	0.080	0.002	0.005	0.005
February	Mean	131.250	332.750	7.450	0.010	0.010	0.020	0.010	0.050	0.010	0.010	0.010
	S.E	22.580	25.020	0.200	0.000	0.000	0.000	0.000	0.030	0.002	0.000	0.000
March	Mean	160.000	402.250	8.000	0.020	0.020	0.950	0.040	0.070	0.140	0.020	0.010
	S.E	14.330	73.650	0.370	0.005	0.000	0.030	0.010	0.030	0.110	0.010	0.000
April	Mean	168.250	242.000	7.730	0.010	0.010	0.050	0.030	0.020	0.030	0.020	0.010
	S.E	21.280	38.380	0.260	0.002	0.000	0.010	0.010	0.000	0.005	0.001	0.002
May	Mean	110.050	421.750	8.520	0.020	0.010	0.360	0.020	0.080	0.010	0.010	0.020
	S.E	57.420	91.470	0.060	0.003	0.000	0.020	0.000	0.040	0.000	0.002	0.010
June	Mean	238.500	321.000	8.440	0.020	0.020	0.680	0.050	0.140	0.010	0.010	0.020
	S.E	42.670	33.230	0.230	0.003	0.000	0.130	0.030	0.050	0.002	0.002	0.003
H(χ^2=0.05.5)		5.134	8.913	11.275	13.799	13.516	14.166	10.069	9.311	17.978	4.961	3.227
***P* value**		0.379	0.113	0.046	0 .017	0.019	0.015	0.073	0.097	0.003	0.421	0.665
Significance		**NS**	**NS**	*	*	*	*	**NS**	**NS**	*	**NS**	**NS**

a. Kruskal Wallis Test

b. Grouping Variable: month

The levels of pH, Cd, Cr, Fe, and Zn could have been affected by rainfall variations. During the study period, the total monthly rainfall at the mine weather station ranged from 2.0 to 95.3 mm (Figure 1). The highest monthly rainfall occurred in March. The rainfall pattern showed temporal variations (Figure 1).

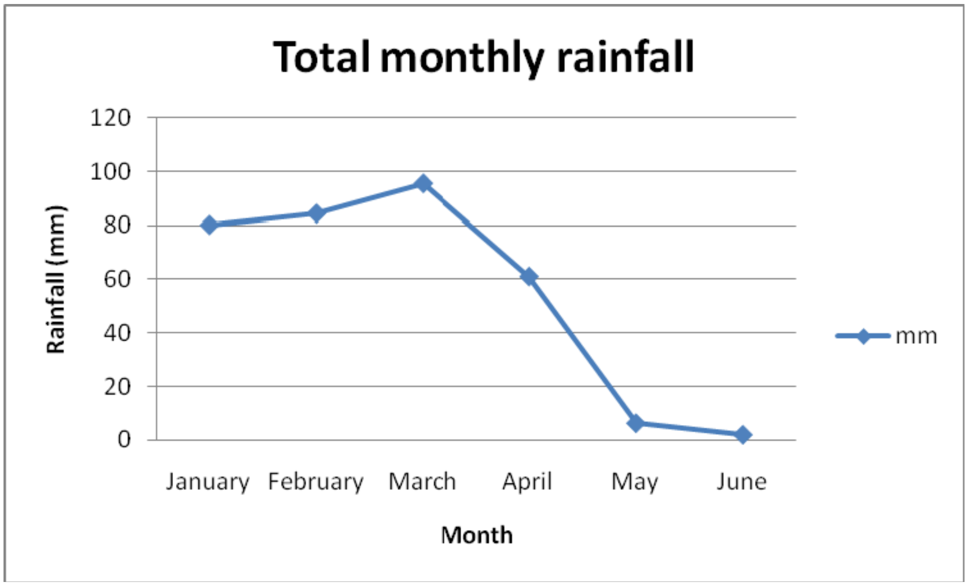


Figure 1 Total monthly rainfall recorded at Murowa mine from January to June 2010.

An abrupt increase in concentration of the following heavy metals (Cd, Cr, Fe, and Zn) was seen in the month of March. A sudden increase in zinc and cadmium concentrations was observed in both upstream and settling pond water in the month of March as well. This may be due to the flushing of pollutants by the March rains. This is consistent with the findings of Aldrich *et al.*, (2002) who observed "marked increases in the total dissolved metal concentrations in the drainage water during rain events ....., depending on the intensity of the rainfall and soil type". Measurements of rainfall and storm events demonstrate the importance of both the former and the latter in trace metal transport (Lawson and Mason, 2001). The highest values of iron were noted in March which coincided with the occurrence of the highest rainfall received in the area during the same month (Figure 1). However the peak in iron concentrations appears to parallel the flush with high rainfall.

The highest concentrations of pH, EC, Cr, Fe, Pb, Mn, Hg and As were observed in the month of January, whereas TSS and Cadmium were at their highest concentration in June. Constituent concentrations in runoff decrease with increasing rainfall intensity due to dilution (Edwards and Daniel, 1993). The concentration of Zn was at the highest level in the month of March. The lowest concentrations of pH, Cd, Cr, Fe, Pb, Zn, Hg and As were recorded in the month of February whereas that of EC and Mn in the month of April. TSS was at its lowest in the month of May with a value of 110.05mg/L.

The other parameters such as TSS, EC, Pb, Mn, Hg and As did not differ significantly with seasons. TSS levels were high throughout the study period maybe due to the mining activities and suspended solids that could have been from gold panning activities and from farmlands through surface runoff. The results also showed no significant difference in the lead concentrations in the water from the four sampling points. Lead concentrations were seen to decrease with an increase in rainfall; this can be attributed to dilution due to high rainfalls received during the study period.

The results showed no significant difference in the concentrations of manganese in the water from the four sampling points during the study period as shown in Table 2. Levels of manganese, however, in the water column were lower than the average during the months when high rainfall was received and is shown to be higher than the average when rainfall was low which could have been a result of the dilution effect as well.

Comparison Of Sampling Points

In order to identify sources of the various heavy metals that is either from sources found in Runde Upstream or the mine, and whether the settling ponds are effectively treating the wastewater the results of heavy metal concentration at the four sampling points are presented in Table 3.

Table 3: ANOVA Results

		TSS	EC	pH	Cd	Cr	Fe	Pb	Mn	Zn	Hg	As
Upstream	Mean	218.200	388.670	8.310	0.020	0.020	0.640	0.070	0.160	0.100	0.020	0.010
	S.E	65.950	46.530	0.200	0.004	0.003	0.360	0.030	0.080	0.070	0.003	0.002
Entry Point	Mean	162.170	395.170	7.920	0.020	0.020	0.370	0.030	0.090	0.020	0.020	0.020
	S.E	23.440	61.710	0.280	0.003	0.003	0.120	0.010	0.030	0.010	0.003	0.003
Discharge	Mean	159.170	311.000	7.800	0.020	0.010	0.720	0.020	0.100	0.020	0.020	0.020
	S.E	10.330	56.300	0.280	0.003	0.002	0.290	0.010	0.030	0.010	0.003	0.000
Downstream	Mean	131.830	378.500	8.410	0.020	0.020	0.330	0.030	0.070	0.020	0.010	0.010
	S.E	24.890	46.600	0.200	0.004	0.003	0.140	0.020	0.040	0.000	0.000	0.001
F (3,20)		0.940	0.530	1.500	0.330	1.220	0.610	1.860	0.700	1.030	2.360	1.200
***P* Value**		0.440	0.670	0.250	0.800	0.330	0.620	0.170	0.590	0.400	0.100	0.340
Significance		NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS

N.B: NS No significant difference

The results show that the concentrations of all the studied parameters did not differ significantly with sampling points as shown in table 2 above. High mean concentrations of TSS, Pb, Mn and Zn were observed at the upstream sampling point. The high levels of TSS in river water can be attributed to agricultural runoff and gold panning activities along the river's banks. High amounts of suspended solids and sediments are carried in by runoff from farmlands and mining activities upstream such as from Sabi gold mine which is found upstream of the river. High levels of Pb and Zn can be attributed to sewage emissions by Zvishavane city council located 40km upstream of Runde river.

The results show a general reduction in the concentrations of TSS, Pb, Mn and Zn at the entry point to the settling pond from high levels recorded at upstream sampling point. A reduction in the concentrations of TSS, Pb, Mn and Zn at entry point to the settling ponds can be attributed to effective raw water treatment processes employed by Murowa Diamonds to produce portable water for diamond processing. This can also be coupled with the fact that the mine might not be adding any significant loads of Pb, Mn and Zn to the water during its mining activities.

High mean concentrations of EC were recorded at the entry point to the settling pond as shown in figure 2. Electrical conductivity is a useful indicator of the salinity or total salt content and thus it is a good indicator of heavy metal pollution in a water sample.

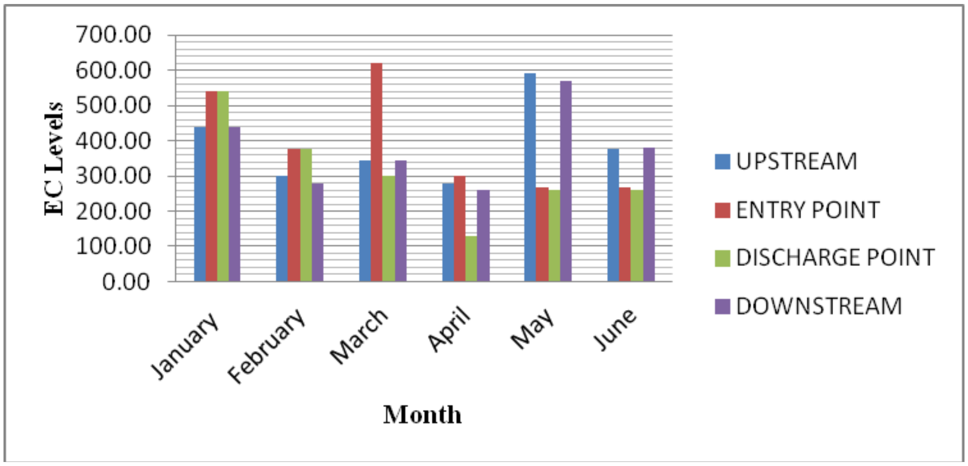


Figure 2

High levels of EC at entry point can thus be attributed to a high concentration of metal ions at entry point to the settling pond. Lower mean levels of EC were recorded at discharge point from the settling pond. The reduction in EC levels at discharge point can be attributed to the reduction in heavy metal concentration in discharge water as compared to settling pond influent.

High mean levels of Fe were recorded at the discharge point from the settling pond (figure 3). This high discharge of Fe from the settling pond can be attributed to a sustained high level of Fe in the settling pond. This can be attributed to anaerobic conditions created when the settling pond is full and thus reducing the amount of oxygen available to react with free oxygen to convert it into ferrous oxygen which then settles down to the sediments. This results in a lot of Fe in solution.

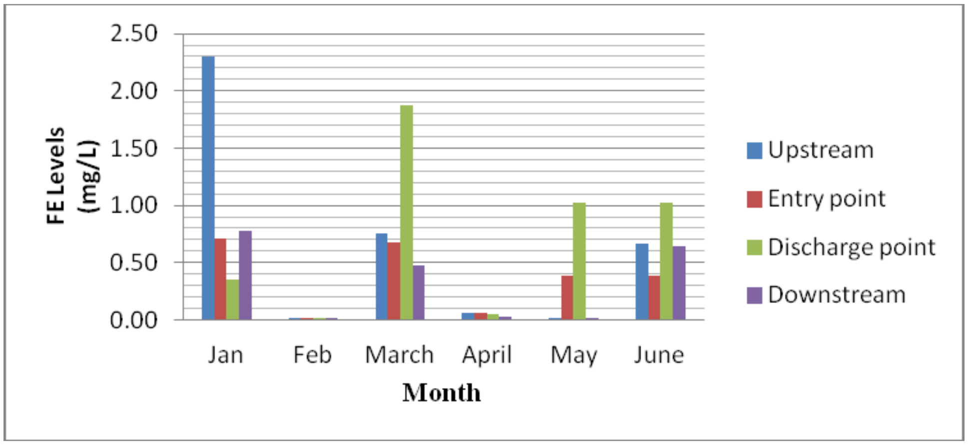


Figure 3

Lower mean Fe concentrations were, however recorded in downstream water. The explanation can be that as the water flows into the river from a higher ground by gravity it gets mixed with a lot of oxygen which then reacts with the iron forming iron oxide which then settles in the river's sediments. The other explanation is that the Fe could have been diluted in the abundant water supply in the river. Downstream water had the highest pH levels. At high pH levels the availability of heavy metals in water is reduced and thus this can be the reason for the reduced Fe levels at this sampling point.

Levels of Cd did not differ significantly throughout the study period as shown in figure 4 below.

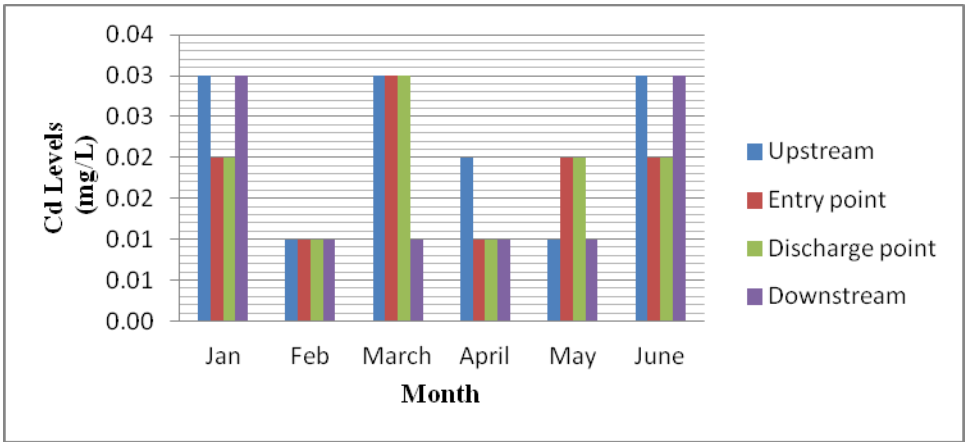


Figure 4

Concentrations recorded in upstream water were almost similar to those recorded at the other three points. The reasons for high Cd levels in upstream water range from natural weathering processes, mining activities upstream, fertilisers and pesticides used on farmlands. Ineffectiveness of the settling ponds in removing Cd from solution might be the cause for high levels of Cd in discharge water whose values are equal to those of the entry point. The explanation behind the ineffectiveness of the settling ponds in removing Cd from solution could be due to the fact that the water already in the settling pond could be having the same concentration of Cd as the influent hence the lack of a concentration gradient for Cd to fall out of solution by sedimentation.

Higher mean concentrations of Hg and Cr were recorded in upstream, at entry point and in downstream water as shown in figure 5a and 5b respectively.

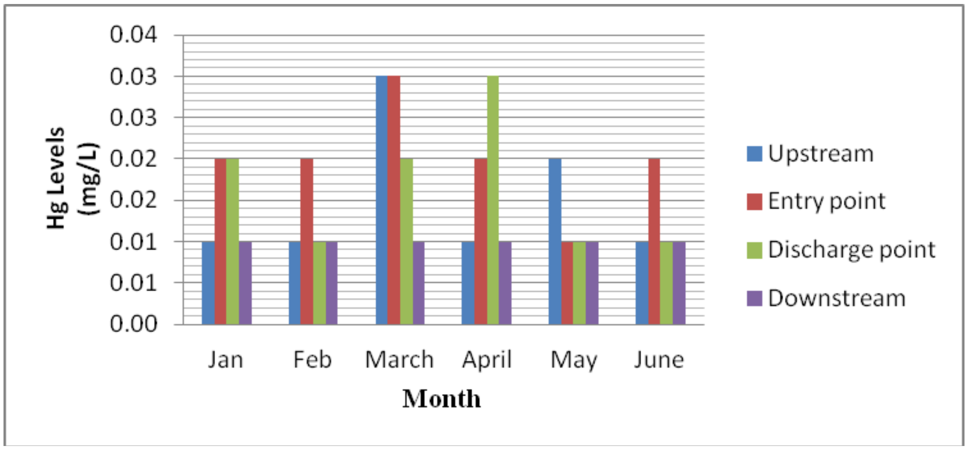


Figure 5a

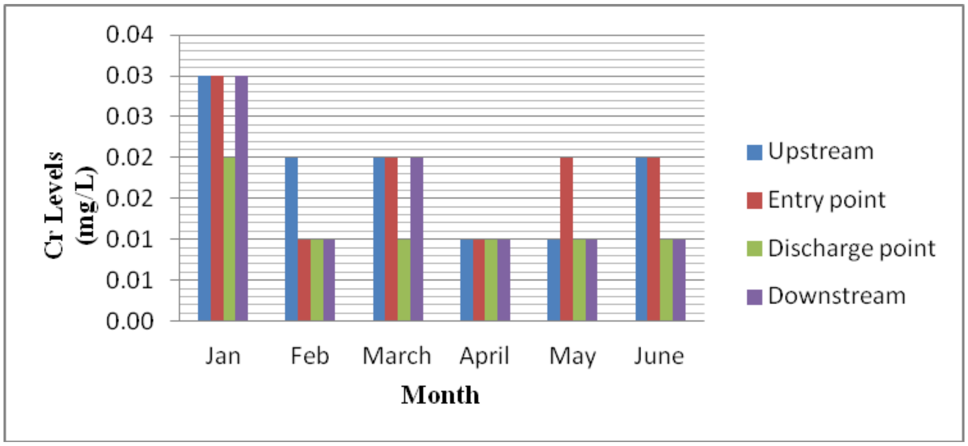


Figure 5b

Lower mean Cd concentration was observed at discharge point. The reason can be that a concentration gradient existed between influent and water already in settling pond. Cr could have adsorbed to suspended solids and thus fall out of solution as the solids settle out.

Heavy Metal Concentration (Mg/L) in Discharge Water Compared to EMA Mining/ Industrial Effluent Standards.

The study results show that except for TSS and Cd all other parameters were within or significantly lower than the EMA industrial effluent standards.

Table 4 One Sample t-test Results

	TSS	EC	pH	Cd	Cr	Fe	Pb	Mn	Zn	Hg	As
Mean	159.170	311.000	7.600	0.020	0.010	0.720	0.020	0.100	0.020	0.020	0.020
S.E	10.330	56.300	0.280	0.003	0.002	0.300	0.006	0.030	0.010	0.003	0.003
T_5 Value	12.990	-9.500	2.880	2.710	-23.000	-9.400	-4.720	0.120	-73.130	2.000	-10.000
***P* Value**	0.000	0.000	0.030	0.040	0.000	0.390	0.005	0.910	0.000	0.100	0.000
EMA	25.000	1000.000	6.00-9.00	0.010	0.050	1.000	0.050	0.100	0.500	0.010	0.050
Sig	$*^a$	$*^b$	$*^b$	$*^a$	$*^b$	NS	$*^b$	NS	$*^b$	NS	$*^b$

NB. All parameters with the * do differ significantly with the EMA standards either above or below the limit such that $^{(*a)}$ shows parameters which are significantly higher than the set standard (constituting a breach of the standard) and $^{(*b)}$ shows parameters which are significantly lower than the set standard.

This can be attributed to removal of pollutants from upstream water at the raw water treatment plant and the fact that the mine might not be contributing significant amounts of such pollutants in its effluent. The other reason for the low concentrations of the parameters below the set standards in discharge water can be attributed to an effective treatment offered by the settling pond.

TSS and Cd levels were significantly higher than the set industrial effluent standards. TSS concentrations were higher than the set standard of 25mg/L, with a mean discharge of 159.17mg/L being recorded. The high levels of TSS in discharge can be attributed to short circuiting of the settling pond due to high volumes of influent that are received by the pond daily and thereby inhibiting particle settling. This being a mining environment, large quantities of TSS are realised daily from ore crushing and processing.

The average cadmium concentration in the discharge water was in the range 0.02 mg/L – 0.03mg/L which is in the range of polluted regions. Levels of Cd higher than the set standard recorded in discharge water throughout the study period can be attributed to high Cd levels in river water and the probable failure of the raw water treatment plant and the settling pond to remove the metal from solution.

CONCLUSIONS

Based on the findings of the research the following conclusions were made:

1. Results show that seasons have an influence on the concentrations of the Cd, Cr, Fe and Zn in water with the concentration of these metals in water increasing with an increase in rainfall received caused by the flushing of pollutants from surrounding land uses.
2. There were no significant differences in the concentrations of the heavy metals at the four sampling points. There was also an overall decrease in the study parameters between upstream and settling pond water throughout the study period. This therefore, might mean that the raw water treatment plant at the mine is very effective. There was also an overall decrease in the levels of the parameters between entry point and discharge point suggesting that the settling ponds are effective in treating mine effluent.
3. The results also showed that the mine is emitting a 'safer' effluent as compared to raw water drawn from Runde upstream in terms of heavy metal concentration. The discharge from the mine lies in the blue category of the EMA permitting system.
4. The presence of high concentrations of heavy metals in upstream water points to the fact that there are other possible polluters upstream of Runde beyond Murowa Diamonds effluent discharge point.

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