

# Natural attenuation of mining pollutants in the transboundary Save River

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## ABSTRACT

The objective of the study was to investigate the role played by the natural environment in protecting the transboundary Save River from the impacts of metals derived from phosphate mining at Dorowa. The study is a follow up study from a previous one that noted that there is natural attenuation at Dorowa. Water and sediment samples were collected in the Save River and the streams that drain the Dorowa dumps. Inductively coupled plasma mass spectrometry (ICP-MS) was used to analyze the cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cd}^{2+}$ ) in the samples. Major anions  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were analyzed by standard chromatography whilst  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  were determined by titration. pH was measured on site. Geochemical modeling of the water composition was conducted with Visual Minteq. The results show that natural attenuation is being achieved through precipitation of solids from the water and subsequent deposition onto the sediments. Six of the metals are almost completely precipitated (Cu 99.99%, Fe 99.39%, Ni 91.24%, Pb 99.87%, Sn 99.99% and Zn 88.66%). However Mn, Co and Cd remain in solution. Thus the natural environment is protecting the Save River which is a transboundary river from the impacts of mining through precipitation of the metals. Users downstream of Dorowa mine are therefore not being affected by mining pollution. This study demonstrates that besides being a legitimate and important user of water, the natural environment can also play a significant role in protecting water quality by attenuating metals naturally. By analyzing costs incurred in several places where alternative methods are employed to remediate metal related pollution the study concludes that natural remediation at Dorowa is saving the nation in environmental costs. Therefore the paper advocates for appreciation of the role that the natural environment plays in protecting ecosystems from the impact of human developments and environmental costs. Subsequently, this calls for recognition of natural environment's role in water resources management for the sustenance of ecosystems and peoples livelihoods.

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## 1. Introduction

The quality of water in and around mining sites is a major environmental issue facing the mining industry in Zimbabwe. The Dorowa ring complex in Zimbabwe comprises one such area because it contains above normal concentrations of heavy metals related to the occurrence of igneous rock phosphate. Weathering and mining of the ore deposits brings about the release of these metals into soils, sediments, groundwater and surface drainages around Dorowa. Thus there is a potential for the discharge of the metals into the nearby Save River which is a transboundary river.

The Save River is in one of the catchments of Zimbabwe with the highest human population (Fig. 1) outside urban areas and spans the administrative provinces of Manicaland, Mashonaland East and Midlands. Consequently changes in water quality around Dorowa have a potential to affect many lives and communities. The catchment is host to unique species and vegetation (Chirinda Forest Reserve and Banti forest) which need protection from human induced pollution. The communities around the Save River use the river water for stock watering, recreation, fishing, irrigation and domestic purposes. Most of these communities have little or no alternative water sources than the river. The Save River drains into Mozambique implying that the changes in the water quality around Dorowa may also affect the other country.

In a preliminary assessment of the water quality in the Save River downstream of the Dorowa phosphate mine in Zimbabwe Meck et al. (2009) noted an increase in conductivity, iron content, manganese content, nitrates and hardness when compared to those taken before the mining area. (Meck et al., 2010a) have

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Fig. 1. Location of Dorowa mine. The Zimbabwe population density map has been used to show that the study area is located in an area of high population density.

shown that the igneous rock phosphates mined at Dorowa mine in Zimbabwe contain metals considered to be toxic to humans and animals. The metals include: copper, lead, zinc, cobalt, nickel iron and manganese. This same study showed that there is natural attenuation of metals around Dorowa therefore no transportation of metals. The attenuation capacity exceeds the mass of contaminant in the area.

There is substantial work on the mineralogy of the Dorowa ring complex, which include that by Barber (1991), Fernandes (1978, 1989), Govere et al. (1995), Johnson (1961), Meck et al. (2010b), Mennel (1946) and Walsh et al. (2001) which give a clear outline of the minerals present but there is relatively limited literature explaining the mechanisms of what happens to the waste and associated metals. Thus this study set out to highlight how the

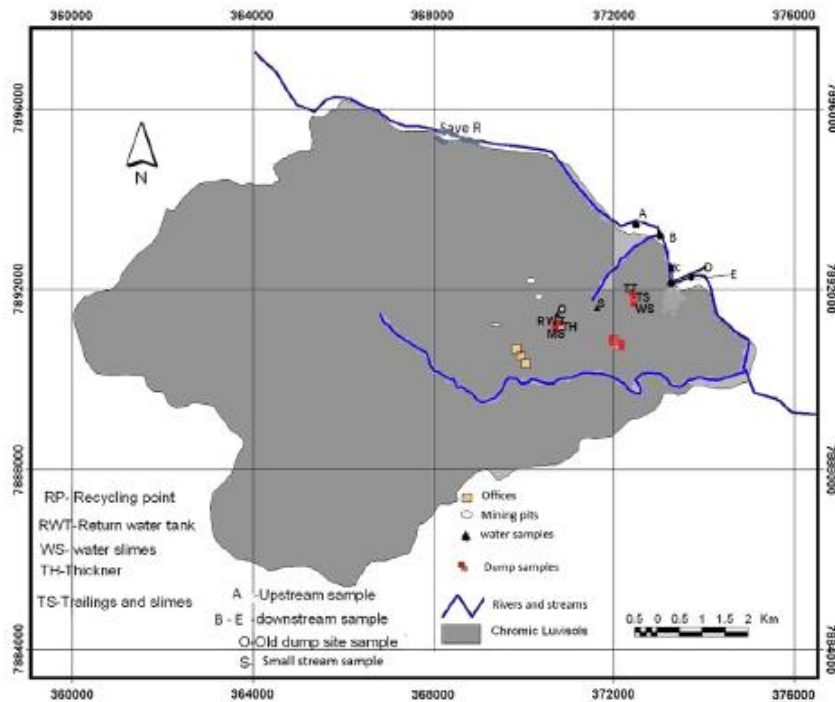


Fig. 2. Sampling locations for the study. Map also shows location of mine, dumps and mining pits in relation to the small stream that was sampled as well as points sampled along the Save River.

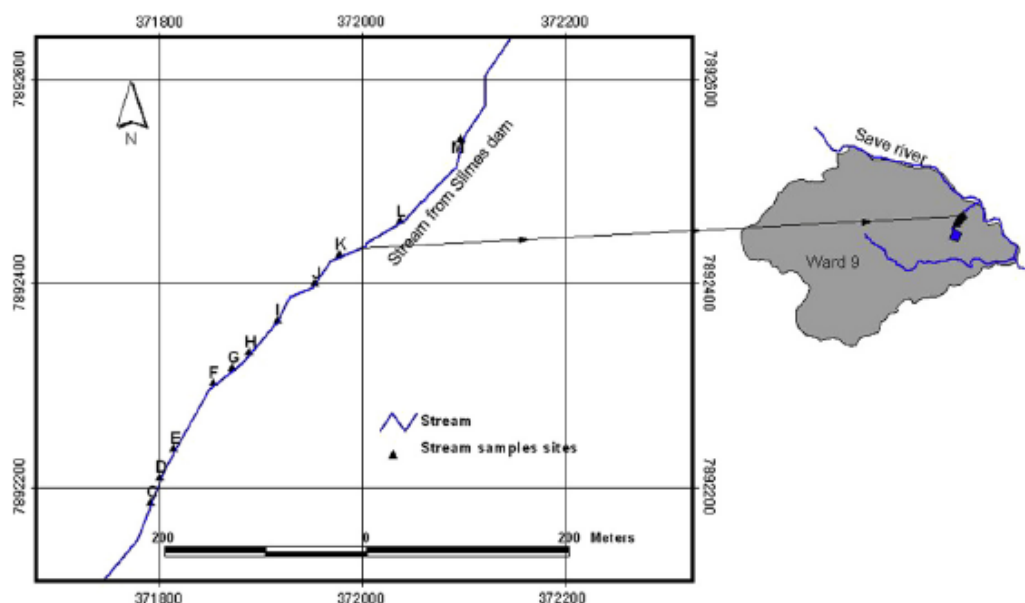


Fig. 3. Expanded Fig. 2 to show the sampled locations along the small stream that drains the dumps.

natural environment is contributing to human welfare by attenuating the metals released during the phosphate mining at Dorowa. Understanding the role played by natural attenuation is crucial and paves a way of giving recognition to this service in the decision making process.

## 2. Materials and methods

### 2.1. Study area

Dorowa mine is situated in the Save catchment of Zimbabwe in the south-eastern part of Zimbabwe (Fig. 1). It is part of one of the four alkaline ring complexes in the catchment and is approximately 3.5 km in diameter. The Save River passes through mine and dumps at distances less than 1 km.

### 2.2. Sampling and analyses

Water and sediment samples were collected along the Save River and along one of the streams that drains from the dumps to Save River in March and April of 2010. Five samples were taken from the Save River and 14 from the small stream. Figs. 2 and 3 show the sampling sites in relation to the dumps, river and mine. The sediment samples (0–15 cm in depth) were sampled by hand auger (2.5 cm in diameter) and trowel. Each soil sample comprised a composite of nine sub-samples taken within a 5 × 5 m square. A portable Hanna pH meter model (HI9023C) was used for measuring pH on site.

Water samples were acidified with concentrated HNO<sub>3</sub> and stored in a cooler box with ice until time of analysis. Sediment samples were air dried at the Geology Department. After air-drying for 5 days, the sediment samples were disaggregated by hand and organic material (leaves, twigs and roots) manually removed. The samples were sieved to <2 mm and then ground to a fine powder (<180 μm). The sediment samples were digested in 3:1 concentrated HCl and HNO<sub>3</sub> (aqua regia). Inductively coupled plasma mass spectrometry ICP-MS was used to determine the major cat-

ions (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Fe<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, Sn<sup>2+</sup>, Mn<sup>2+</sup>, Cd<sup>2+</sup>) in the samples. Major anions (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>) were analyzed by standard chromatography, CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> were determined by titration whilst pH values were measured by a portable Hanna pH meter model (HI9023C). Quality control included reagent blanks, duplicate samples, in-house reference materials and certified international reference materials (Ramsey et al., 1995). The precision and bias of the chemical analysis was less than 10%.

A geochemical model Visual Minteq was used to estimate the activities of the metals from the measured total metal concentrations. This geochemical speciation model is capable of computing equilibrium ion activities among dissolved and adsorbed species and their equilibrium solid phase (KTH, 2010). The model uses the interaction of metals with the major anions as a function of temperature, pH and ionic strength. The model takes note of the fact that, among the most important processes for metals are adsorption reactions. Minteq was used to perform adsorption calculations, in addition to performing the straight forward acid–base–complexation–precipitation calculations in the presence and absence of gas with and without redox reactions. The overall objective in terms of environmental fate and transport of contaminants in the environment is generally to arrive at a single distribution coefficient,  $K_d$  (L of solution/kg of solid) that describes the amount of the contaminant on the solid phase versus the amount in the mobile solution phase: The species that are in the aqueous phase are assumed to be mobile thereby available and the species adsorbed to the solid are assumed to be immobile, or not available. The output from Minteq lists the total component in solution and the total component adsorbed. Hence the amount that is available to organisms can be estimated.

## 3. Results

The pH for water ranged from 6.87 to 8.18 with an average of 7.68 whilst that of the sediments ranged from 6.78 to 8.68 with an average of 7.8. The ICP-MS and chromatograph results are given

**Table 1**  
Levels of cations and anions in the samples from the ICP-MS and chromatograph analyses.

Sample description	Ca (%)	Fe (%)	K (%)	Mg (%)	Na (%)	S (%)	Cd (ppm)	Co (ppm)	Cu (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Sn (ppm)	Zn (ppm)	HCO <sub>3</sub> (ppm)	Cl (ppm)	NO <sub>3</sub> (ppm)
Stream pnt 1	5.09	8.25	1.11	4.70	1.62	0.04	0.13	44.60	87.00	1070.00	20.00	13.80	1.60	91.00	312.00	6.00	2.10
Stream pnt 2	4.51	5.93	1.99	2.70	2.36	0.04	0.08	24.30	41.00	864.00	31.00	15.20	1.10	67.00	206.00	6.20	1.80
Stream pnt 3	2.87	1.98	2.49	0.50	1.36	0.04	0.06	9.40	14.00	491.00	12.00	25.70	0.90	22.00	256.00	5.80	1.88
Stream pnt 4	5.34	3.95	1.50	1.60	1.24	0.16	0.10	19.30	37.00	807.00	25.00	22.20	1.20	56.00	278.00	4.20	1.60
Stream pnt 5	5.62	3.13	2.04	1.20	1.49	0.16	0.09	16.00	28.00	687.00	22.00	39.10	1.30	49.00	232.00	5.20	1.20
Stream pnt 6	3.83	1.55	2.51	0.30	1.73	0.04	0.07	6.50	8.30	405.00	10.00	24.40	0.60	23.00	204.00	4.40	1.40
Stream pnt 7	6.60	2.43	1.62	0.60	0.91	0.18	0.20	27.60	15.00	7400.00	16.00	21.80	0.90	27.00	280.00	4.00	1.60
Stream pnt 8	6.44	2.45	1.91	0.70	1.17	0.09	0.07	15.90	15.00	11450.00	17.00	21.60	0.80	32.00	199.00	4.00	1.30
Stream pnt 9	3.08	2.27	1.88	0.60	1.55	0.06	0.06	11.50	13.00	2640.00	17.00	19.90	1.20	27.00	202.00	4.40	0.90
Stream pnt 10	3.61	2.34	0.63	0.90	0.67	0.26	0.06	9.10	21.00	3990.00	14.00	8.30	0.70	73.00	206.00	4.20	1.60
Stream pnt 11	2.73	2.07	1.96	0.60	1.47	0.13	0.07	8.60	14.00	941.00	16.00	19.00	1.10	29.00	189.00	5.20	1.20
Stream pnt 12	2.48	5.67	1.07	1.50	0.88	0.22	0.09	29.30	45.00	3320.00	38.00	26.10	1.90	72.00	224.00	4.20	1.40
Stream pnt 13	33.80	0.68	0.04	0.30	0.27	0.03	0.18	4.50	5.70	376.00	11.00	5.90	0.20	7.00	189.00	4.40	0.90
Stream pnt 14	1.20	0.94	2.29	0.10	0.88	0.01	0.05	3.00	4.50	243.00	4.10	20.30	0.80	22.00	174.00	5.20	0.60
Stream average	6.23	3.12	1.65	1.20	1.26	0.10	0.09	16.40	25.00	2477.00	18.00	20.20	1.02	42.60	225.00	4.80	1.39
River pnt 1	0.30	0.61	2.71	0.10	0.70	<0.01	0.03	2.20	4.60	111.00	4.70	16.60	0.30	6.00	38.00	3.30	0.40
River pnt 2	0.28	0.50	2.89	0.10	0.75	<0.01	0.04	2.20	2.80	185.00	4.10	16.80	0.30	6.00	72.00	3.20	0.20
River pnt 3	0.28	0.52	2.83	0.10	0.75	<0.01	0.05	2.50	3.80	149.00	4.50	16.20	0.40	6.00	26.00	3.00	0.20
River pnt 4	0.30	0.67	2.69	0.10	0.69	<0.01	0.03	2.40	3.50	128.00	6.00	14.90	0.30	8.00	81.00	4.00	0.10
River pnt 5	0.26	0.58	2.80	0.00	0.71	<0.01	0.04	2.50	3.30	233.00	4.70	16.90	0.30	13.00	29.00	3.20	0.20
River pnt 2	0.30	0.85	2.75	0.10	0.75	<0.01	0.06	3.10	4.70	172.00	5.10	19.60	0.40	8.00	44.00	3.30	0.10
River pnt 3	0.65	1.95	2.93	0.20	0.97	0.01	0.10	10.20	15.00	393.00	26.00	28.00	0.80	24.00	36.00	3.00	0.16
River pnt 5	0.56	1.02	3.02	0.20	0.98	<0.01	0.14	5.00	4.90	183.00	11.00	23.00	0.50	17.00	70.00	3.10	0.20
River average	0.37	0.84	2.83	0.10	0.79	0.01	0.06	3.76	5.40	194.30	8.20	19.00	0.41	11.00	50.00	3.30	0.20

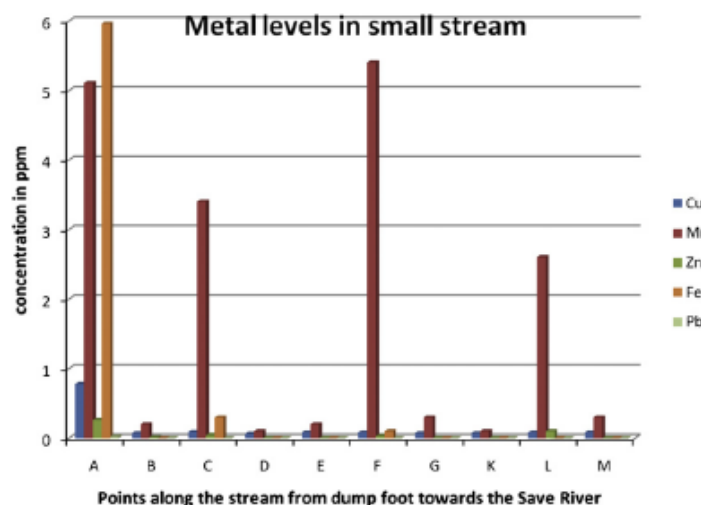


Fig. 4. Metal levels in the small stream draining the dumps showing declining metal concentrations with distance from the mine an exception is manganese.

in Table 1. The table gives levels of cations and anions in the samples. The levels are given as either a percentage of major elements parts per million for minor elements. Thus for stream point 3 Mg makes 0.5% (0.5 parts per every 100) of the total elements in the sample whilst Cd makes 0.06 ppm of the elements present. Fig. 4 graphically show the declining metal concentrations with distance from the mine. Distribution of components between dissolved, sorbed and precipitated extracted from Visual Minteq is given in Table 2.

The data shows that the metal levels in the Save River are lower than those in the streams draining from the dumps. The levels of metals in the small stream decline with distance from the dump to the Save River. An exception is manganese which peaks up throughout the small stream. Fig. 4 graphically shows the declining metal concentrations with distance from the mine. Analysis shows that there is natural attenuation of metals in the streams that drain

the dumps such that the levels of metals reaching the Save River are insignificant. Speciation model shows that cobalt, cadmium and manganese are the only metals that are soluble. The other six metals are almost completely precipitated (99.99% for copper, 99.39% for iron, 91.24% for nickel, 99.87% for lead, 99.99% for tin and 88.66% for zinc). The metals will precipitate as tenorite, iron hydroxide, nickel hydroxide, as lead hydroxide, tin oxide and zincite respectively.

#### 4. Discussion

When these metals are precipitated from the water they get deposited onto sediments and are therefore not transported with the water. The precipitation of these metals from the water and subsequent deposition onto the sediment is responsible for the



**Table 2**  
Distribution of elements' components between dissolved, sorbed and precipitated as extracted from Visual Minteq modeling.

Component	Total dissolved (mg/L)	Dissolved (%)	Total sorbed (mg/L)	Sorbed (%)	Total precipitated (mg/L)	Precipitated (%)
Ca <sup>2+</sup>	1.5540E+00	100.000	0	0.000	0	0.000
Cd <sup>2+</sup>	8.0072E-08	100.000	0	0.000	0	0.000
Cl <sup>-</sup>	1.3539E-04	100.000	0	0.000	0	0.000
Co <sup>2+</sup>	2.7828E-04	100.000	0	0.000	0	0.000
Cu <sup>2+</sup>	4.4587E-08	0.011	0	0.000	3.9180E-04	99.989
Fe <sup>2+</sup>	3.4189E-03	0.613	0	0.000	5.5473E-01	99.387
H <sup>+</sup>	-9.7905E-04	100.000	0	0.000	0	0.000
K <sup>+</sup>	4.2087E-01	100.000	0	0.000	0	0.000
Mg <sup>2+</sup>	4.7302E-01	100.000	0	0.000	0	0.000
Mn <sup>2+</sup>	4.5087E-02	100.000	0	0.000	0	0.000
Na <sup>+</sup>	5.4990E-01	100.000	0	0.000	0	0.000
Ni <sup>2+</sup>	2.6847E-05	8.757	0	0.000	2.7974E-04	91.243
NO <sub>3</sub> <sup>-</sup>	9.9236E-05	100.000	0	0.000	0	0.000
Pb <sup>2+</sup>	1.2937E-07	0.133	0	0.000	9.7366E-05	99.867
S(O)	3.2498E-02	100.000	0	0.000	0	0.000
Sn(OH) <sub>2</sub>	4.7824E-06	0.006	0	0.000	8.6051E-02	99.994
Zn <sup>2+</sup>	7.3906E-05	11.341	0	0.000	5.7777E-04	88.659

protection of the natural environment as the deposited solids are not carried downstream with the water. Meck et al. (2010a) have elaborated some of the geochemical processes that are leading to natural attenuation of metals at Dorowa as precipitation due to the alkaline pH of the area, adsorption of metal onto hydroxides, presence of minerals that increases adsorption, presence of phosphate rock and natural dilution. The current almost 100% precipitation of metals from the water draining the dumps is dictated by the water chemistry and existing redox conditions.

The natural environment has for 40 years played a significant role of protecting the environment through precipitation of metals. Nevertheless the risk of pollution through release of these metals still exists if the redox conditions change. Some of the ways in which metal remobilization can occur is through water acidification and transportation of the sediments to the Save River. Therefore there is need for monitoring the natural attenuation taking place at Dorowa and maintaining the redox conditions currently existing.

Several authors among them EIPPCB (2001), Ford and Walker (2002) and Miller (2000) give an indication of the costs of remediating metal related problems arising from mining activities which in most cases runs into billions of dollars. According to Ford and Walker (2002), the mean unit cost per yard ranges from US\$7.23 to US\$26.15. A study on the costs of mining waste by the European Integrated Pollution Prevention and Control Bureau (EIPPCB) in 2001 found out that remediation costs vary considerably from mineral to mineral and from mine to mine. The EIPPCB study notes that for zinc and copper mines, waste management typically accounts for about 1.5–2.0% of total financial costs. The ITRC Mining Waste Team (ITRC, 2010) collected case studies from mine sites throughout the United States and one from New Brunswick, Canada using an online survey tool and observed that costs of capping, covers, and grading carried out as part of remediation range from \$1.73/m<sup>2</sup> to \$23.46/m<sup>2</sup> with an average cost of \$4.94/m<sup>2</sup>. A summary of reclamation alternatives and cost estimates done by for the Piegan–Gloster Millsite in Montana shows costs ranging from zero for no reclamation to 2.7 million for waste in-place containment (USEPA, 2005). Miller (2000) notes that most approaches used to achieve a decrease in health and environmental risk associated with mining cost a lot of money and are time-consuming. He further observes that alternative methods of treating impacted soil and groundwater have accelerated the rate of expenditure without a corresponding acceleration in the rate of environmental cleanup. The general conclusion that can be made is that mines use significant resources in remediating mine sites. It should also be noted that most mines have incurred relatively modest costs of higher waste management standards without becoming uncom-

petitive on the world market. However, the recent steep fall in commodity prices will make mining less profitably if the waste requires remediation. After analyzing the experiences of the innovative and traditional remediation systems and the costs involved it can be concluded that the natural remediation taking place around Dorowa is saving the nation billions of dollars that would otherwise have been used on metal clean up. The other advantages of the natural attenuation taking place include:

- No generation of waste during attenuation.
- No potential for cross-media transfer as the metals are settling on sediments.
- No disturbance to ecological receptors.
- *In situ* destruction of the toxic species.

If evaluated in economic sense these advantages will also show that the environment is lowering the costs which could have been incurred if active remediation had been employed. Several authors who include Costanza et al. (1987), Herman et al. (2001), Hester (2010) and Loomis et al. (2000) note that the value of ecosystem services cannot be easily traceable through well functioning markets. Nevertheless the ecological services provided by the environment have huge economic value. As noted by Costanza et al. (1987) ecosystem services in the form of waste assimilation represent a major benefit derived by humans directly or indirectly, from ecosystem functions. According to the 17 major categories that Costanza et al. (1987) grouped ecosystem services into, the alkaline environment at Dorowa belongs to category 9 (waste treatment) because it is removing excess metals from water thereby controlling pollution and detoxifying the water.

The alkaline environment at Dorowa is improving water quality by saving on potential treatment costs. These treatment cost savings do not show up in any market neither is it mentioned anywhere thus this paper is highlighting the contributions to human welfare. The service is of a purely public goods nature and accrues directly to humans without passing through the money economy at all. Costanza et al. (1987) estimated that globally, ecosystems provide at least US\$33 trillion dollars worth of services annually. Though we may never have a very precise estimate of the value that the natural environment is providing at Dorowa it is worth noting and giving recognition to this service in the decision making process. As observed by Jewitt (2002), society derives a wide array of important benefits from biodiversity and the ecosystems in which it exists that are essential to human existence. Nonetheless limited stakeholder participation still exist in most African states despite the presence of adequate supportive

structures and organizations as noted by Nare et al. (2006). Kujinga (2002) concludes that effective stakeholder participation is being hampered by lack of proper representation. This lack of proper representations stems from the fact that some players such as the environment itself are left out as planners in most cases do not realize the role of environment. Swatuk (2005) notes that most national master plans are being written or revised within the Southern African Development Community (SADC) thus in these revisions it is advisable to planners to take ecosystem services into considerations. Emerging payments for ecosystem services (PES) systems such as the government-funded Working for Water (WW) programme successfully implemented in South Africa (Turpie et al., 2008) should be emulated in appreciation of the role played by environment. Legal requirements can aid the uptake of the PES systems.

## 5. Conclusions

The current analytical data shows that the natural environment is actually protecting the transboundary Save River from the metals released from Dorowa mine through metal precipitation. Natural attenuation, has not only been demonstrated to be effective against the metals released as it ties them before they reach the receptors, but it is also doing so on a relatively short distance. During the four decades of phosphate mining at Dorowa, metals were discharged into the drainage system (small streams draining the dumps) but there is no evidence of this in the Save River. Thus there are no transboundary impacts arising from the metals released during the phosphate mining taking place at Dorowa. The implications of the findings of this paper are that the downstream communities are at the present safe as a result of the natural attenuation. However, the alkaline conditions need to be maintained if the downstream users are going to remain protected.

This study has appended data to the many observations made by several other authors that ecosystem services provide an important portion of the total contribution to human welfare on this planet. In doing so it is vital to take note of the fact that many ecosystem services are literally irreplaceable thus there is need for additional research to maintain and upkeep these environments. It is also worth noting that downstream users cannot be excluded from the benefits of improved water quality. While these benefits are often quite small per person, the non-rival nature of this service results in enjoyment by millions of people who use this transboundary river passing through Dorowa. Therefore, the total social benefits can be considered to be large.

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