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Original Research Article

ANALYSIS OF CHEMICAL OXYGEN DEMAND AND TOTAL ORGANIC CARBON IN ACID MINE DRAINAGE POLLUTED WATER BODIES.

Caroline L. Dlamini*, Amos O. Fadiran, Justice M. Thwala

Department of Chemistry, University of Swaziland, Private bag 4,
Kwaluseni, Swaziland.

Abstract
Twenty-five sediment samples and 11 water samples were collected from surface water bodies in the vicinity of the Ngwenya Mine in Swaziland. The sediment samples were analyzed for total organic carbon (TOC) by loss-on-ignition (LOI) in a muffle furnace at 550 °C while the water samples were analyzed for the chemical oxygen demand (COD) using a biological reactor. The sediment samples contained between 1.85% and 18.37% TOC. The sources of the organic carbon (OC) in the water system were both anthropogenic and natural. This result implies that the sediments from all the sites are susceptible to pollution by heavy metals bound as complexes with the OC. Based on the USPH standard of 4 ppm MCL (maximum contaminant level) for COD, 55% of the water samples were polluted with respect to their COD levels. Water containing OC forms carcinogenic and mutagenic trihalomethanes (THMs) on chlorination that is a health risk. Hence the national environmental authority and the water corporation should urgently address this issue with a view of curbing further accumulation of OC in these water bodies. This is much more so as some are the sources of drinking water supply to the capital city.

Keywords: TOC, COD, trihalomethanes, LOI

Introduction

The organic matter in aquatic systems is a complex mixture of molecules consisting of both natural and synthetic organic compounds. Organic compounds are of interest in aquatic systems for several reasons. For instance, their capability to transport soil-derived organic matter through streams and rivers with the corresponding subsequent deposits on sediments provides an important sink for carbon. Reactive substances of organic matter, such as carbohydrates, significantly enhance heterotrophic metabolism in water bodies. Humic and fulvic acids form complexes with metals thereby influencing their behaviour and transport in an aquatic system[1]. Sources of organic matter in fresh waters can either be natural or anthropogenic. Natural sources are

For Correspondence:
caroldlmnATgmail.com
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dominated by contributions from terrestrial materials whose effects are enhanced by shading from the riparian vegetation[2]. Some studies have alluded that about 15% of terrestrial litter is responsible for the total carbon found in lakes[3]. Anthropogenic sources are dominated by agricultural and industrial discharges. The impacts of organic substances on the aquatic environment consequent on man's activities are of growing concern. Chlorinated hydrocarbons including pesticides and herbicides are extensively used in agriculture, industry and homes for pest control[4]. These compounds are often extremely persistent especially in water, soil and biological systems. More often than not these ultimately end up in portable waters either directly or as their derivatives, thus contaminating the water bodies.

Ordinarily organic carbon in drinking water is not a health risk to humans. However, on halogenation the situation becomes reversed as they become hazardous to both man and animals in drinking water[1]. Studies carried out by some other workers indicated that halogenated organic compounds were readily formed as a result of chlorination practice[4]. Trihalomethanes (THMs) produced upon halogenations of OC in water are known for their carcinogenic and mutagenic effects on human health[5,6,7]. The formation of the THMs from the reaction between hypochlorous acid and methyl ketone in humic acids is shown in Equation 1 below[8]:

$$R-CH_3O+3HOCl\xrightarrow{base}CO_2+CHCl_3+2H_2O \qquad (1)$$

Organic carbon is known for exerting a high demand on oxygen in water thereby depleting the available oxygen in an aquatic environment. This is measured by the chemical oxygen demand (COD). The COD is a measure of the oxygen equivalent to that fraction of organic carbon in a sample that can be oxidized by a strong chemical oxidant[9]. Waters with depleted oxygen become anoxic and have bad odours. Such waters are no more suitable for aquatic life and other desired uses. Hence COD is an important parameter for the assessment of water quality and extent of pollution. Thus, COD is a test used to measure the load of organic pollutants in water. In other words, the higher the COD, the higher the degree of pollution of the water body concerned with respect to organic pollutants[10].

Solid organic carbon in the river system settles at the bottom forming part of the underlying sediments. This carbon is obtained from the determination of total organic carbon (TOC) in the sediments. Organic carbon in sediments is of environmental concern because it is responsible for the temporary residence and transport of some toxic heavy metals rendering them bioavailable under oxidising conditions[11]. Thus, the higher the TOC the higher the oxidizable fraction of the heavy metals in the sediments and correspondingly, the higher the risk of heavy metal pollution of the water system[11]. It is for these reasons that in this study the analyses of COD and TOC in AMD polluted water bodies of our study area were carried out. The COD was determined using a bio-reactor while the TOC was determined by percentage loss-on-ignition (LOI).

Materials and Methods

Study area

The study area was the Ngwenya Iron Ore Mine, Swaziland, with focus on the existing surface water bodies there. The sampled streams are used by the communities in the study area for domestic purposes; indeed, they are the sole providers of potable water for this area. Some of these streams are feeders for the Hawane Dam which supplies water pretreated by chlorination to Mbabane, the capital city of Swaziland. Figure 1 below shows the areas in the vicinity of the Mine and the streams that source their water from the Ngwenya Mountain where the AMD producing mine is located[11].

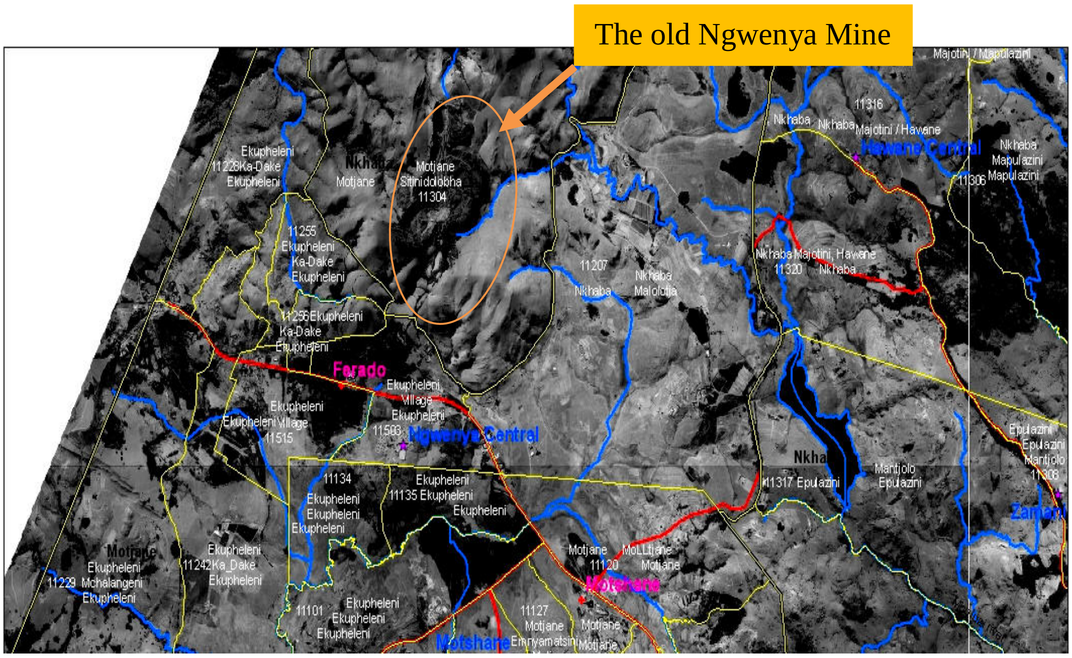


Figure 1 Areas around Ngwenya Mine and streams whose source is the Ngwenya Mountain
Source: Central Statistical Office of Swaziland[12.]

Experimental

Twenty-five sediment samples were collected from selected surface water bodies in the vicinity of the Ngwenya Iron Ore Mine using an auger. About 1 kg of each sample was collected and transferred into a clean plastic bag. These were securely tied, labeled and placed in a cooler box and then transported to the laboratory where they were kept in a chest freezer for the TOC analysis. Eleven water samples were collected into 1 L prewashed polyethylene Bottles[11]. These were also carefully labeled then transported over ice in a cooler box to the laboratory. These samples were filtered using 0.45 µm polymer membrane filters and quickly analysed for COD by a COD reactor. All chemicals used in the experiments were of Analar grade.

Total Organic Carbon Analysis (TOC)

The sediment samples were taken out of the freezer and defrosted. The sediments were put into pre-washed crucibles by standard operation procedure (SOP) and dried in an oven at 120°C for 24 hours. On the next day the hot sediments were taken out of the oven and cooled in a desiccator to avoid re-absorption of water vapour molecules. The cooled sediment samples were ground with pestle and mortar to ensure that fairly homogenized representative samples were obtained. The pestle and mortar were washed with dilute HNO_3 (0.5 M) and rinsed 3 times with de-ionized water in-between ground samples to avoid cross-contamination. The samples were then passed through 90 µm and 53 µm Modison Test Sieves consecutively in a Retsch AS 200 test sieve shaker for 5 minutes obtaining sub-samples of three different particle sizes. Small size particles are easier to ignite, so they were chosen for the analysis. The sediment samples were analysed for the total organic carbon (TOC) by loss on ignition (LOI). 25 crucibles were washed by SOP and put in an oven at 120°C for 24 hours to free them from organic carbon. After cooling, 1 g of each sediment sample was weighed into each weighed labeled crucible. The sediments were ignited in a muffle furnace at 550°C for 6 hours. After cooling, each crucible containing ignited sample was weighed. The TOC was expressed in percentage of LOI of sediment samples.

Chemical Oxygen Demand (COD)

The fresh water samples were analysed for COD using a bio-reactor obtained from the Swaziland Water Services Cooperation

(SWSC), an accredited laboratory in Swaziland.

Results and Discussion

TOC

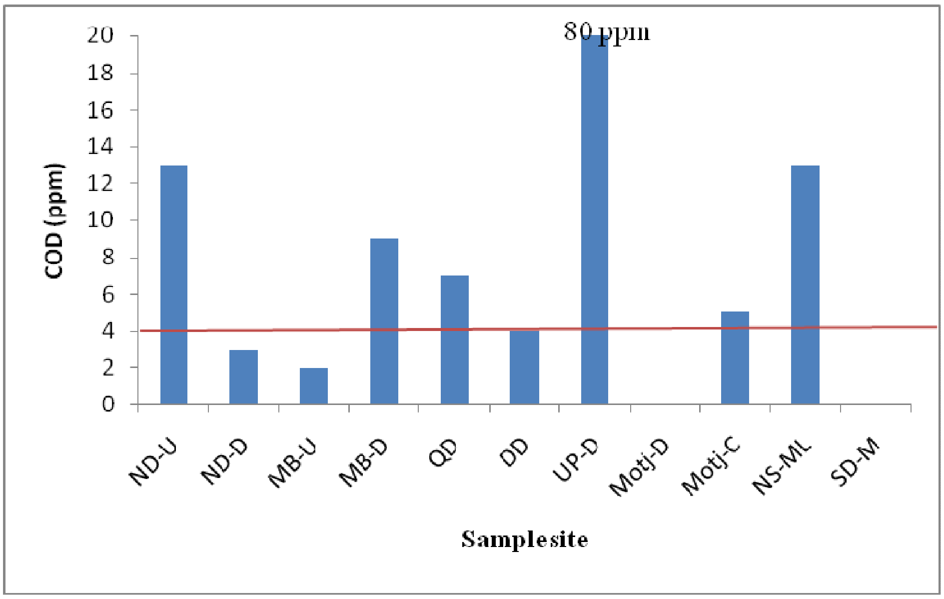
All the investigated sediment samples had some organic carbon. The percentage TOC in each sample is given in Table 1 below. This result implies that in all the sites under investigation there is a possibility of heavy metals trapped as complexes with the organic matter in the sediments. Should the conditions be oxidising enough in the water system these heavy metals would be released from their temporary residence and get into the water column hence transported with the water and polluting the environment along the course of the river. The percentage TOC values ranged from 1.85% to 18.37% as shown in Table 1.

Table 1 Total organic carbon as % TOC in the sediment samples

sample ID	sample (g)	LOI (g)	%TOC
D	1.08	0.09	8.33
ND-U	1.01	0.06	5.94
ND-WL	0.94	0.11	11.70
ND-D	1.06	0.13	12.26
UP-D	1.1	0.1	9.09
DD	1	0.07	7.00
ML-(C)	1.07	0.12	11.21
ML-(1)	1.02	0.09	8.82
ML-(2)	1.09	0.09	8.26
ML-(3)	1.08	0.02	1.85
ML-(4)	1.09	0.06	5.50
HD	1.14	0.17	14.91
MB-U	0.98	0.18	18.37
MB-D	1.05	0.12	11.43
NG-(M)	1.09	0.12	11.01
Motj-(1)	1.01	0.09	8.91
Motj-(2)	1.15	0.18	15.65
Motj-(3)	1.11	0.11	9.91
Motj-D	1.02	0.1	9.80
Motj-C	1	0.09	9.00
MS-ML	1.09	0.06	5.50
ML-MS-YBW	1.09	0.12	11.01
NS-ML	1.04	0.13	12.50
SD-M	1.04	0.07	6.73

COD

COD is the measure of the amount of organic carbon (OC) in water. The higher the OC the greater the chemical oxygen demands. The COD determined in this study was only for dissolved organic carbon (DOC) because the water samples were each filtered through 0.45 µm polymer membrane filter to remove all the coarse organic matter from it. The COD values obtained for the water samples are given in **Figure 2** below. The maximum allowed limit for COD in water is set at 4.0 mg/L by the USPH Standard[7].



Fugure 2 COD levels in water samples from selected sites and the maximum allowed limit for this water pollution parameter

In the present investigation, 55% of the analysed water bodies have COD levels higher than the recommended limit of 4 ppm. The UP-D sampling point, a dam, recorded the highest COD value of 80 ppm. This could be as a result of agricultural wastes transported into the water from the cultivated fields around the dam[13]. This result may also be attributed to the decaying vegetation that was in the dam according to some other similar studies[14].There is also a wattle trees forest next to it from which fallen leaves were transported into the dam by runoff during rainstorms which are frequent in this area. Insecticides, herbicide and pesticides from domestic activities around the dam are also suspected to leach into the dam and thereby enhance the carbon content in its water. The NS-ML and ND-U sites both recorded the second highest COD of 13 ppm. Both sites are found in the vicinities of human settlements whose domestic activities are suspected to be responsible for the observed high degree of COD pollution. The riparian vegetation along the streams may also contribute to the high organic matter by the leaves falling into the water and by the shade they provide which enhances microbial activities. MB-D may be polluted due to the same reasons given for the former two sites i.e. NS-ML and ND-U. The QD and Motj-C may be polluted by the contribution of the riparian vegetation only because there are no human settlements around these two sites. The other sites were free from COD pollution because their COD values were below the set standard. In the site MB-U, there was no COD probably because the sampling point is in the proximity of the source of the river hence the water was still free from anthropogenic organic pollutants and the vegetation along the stream were short grasses that may hardly fall off to contaminate the water. The COD for the site DD recorded just the MCL (4 ppm). Therefore, to avoid an increase beyond this level, all the factors capable of enhancing its value should, as much as possible, be suppressed.

Conclusion and Recommendations

All the analysed sediments contain organic carbon which is capable of trapping heavy metals as complexes. These heavy metals can be released into the overlying water column, be transported with the water and ultimately pollute the environment they come in contact with. The OC in the sediments can also be broken into fine particles that would be suspended in the water. These suspended solids enhance the COD of the water hence increasing its pollution risks. Some of the water from the streams in the Ngwenya area needs attention with respect to organic carbon pollution. These important streams had high COD values which is an indication of pollution due to oxidizable organic matter[15, 16]. Action must be taken to manage especially the water being treated by chlorination for supply to the capital city of Swaziland. The population in the city bear the risk of the carcinogenic and mutagenic trihalomethanes (THMs) that result from the chlorination of water with high TOC levels[8]. It is recommended that the Swaziland Environment Authority and Swaziland Water Services Corporation explore safe, environmentally friendly and cost effective water treatment strategies to replace this hazardous chlorination currently practised.

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