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RESEARCH ARTICLE

SEASONAL VARIATION ON THE EFFECT OF HEAVY METALS (CHROMIUM AND ZINC) ON THE CORROSION POTENTIAL OF *DESULFOVIBRIO DESULFURICANS AND DESULFOVIBRIO VULGARIS* ON THREE METAL COUPONS (STAINLESS STEEL, MILD STEEL AND CARBON STEEL) IN NDONI RIVER.

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ABSTRACT

Seasonal variation on the effects of heavy metals (chromium and zinc) on the corrosion potential of *Desulfovibrio desulfuricans and Desulfovibrio vulgaris* on three metal coupons (stainless steel, mild steel and carbon steel) in Ndoni River was carried out for a period of one year between April 2017 to March 2018.The River is a fresh water ecosystem where sulphur reducing bacteria can be found. *Desulfovibrio desulfuricans* had its highest growth rate in the dry season at 28MPN/100ml and highest growth rate in rainy season at 22MPN/100ml while *Desulfovibrio vulgaris* had its highest growth rate in the same dry season at 26MPN/100ml and highest growth rate in the same rainy season at 19MPN/100ml.The heavy metals (chromium and zinc) were present at a level tolerated by the organisms in the dry season at (1.08mg/l and 1.46mg/l) respectively while the levels of chromium and zinc at the beginning of rainy season were at 0.87mg/l and 1.10mg/l respectively. The corrosion rates of the three metal coupons stainless steel, mild steel and carbon steel were also highest in the dry seasons namely 0.127g, 2.271g, and 4.291g respectively. The TTEST value for chromium(stainless steel, mild steel and carbon steel) are 0.000598, 3.65947E-05 and 4.53205E-06 respectively while that of zinc(stainless steel, mild steel, and carbon steel) are 2.63664E-05, 0.004315319 and 7.74988E-05 respectively. The Correlation value between stainless steel and mild steel was 0.102427567.The Correlation value between mild steel and carbon steel was 0.146927782 while the Correlation value between stainless steel and carbon steel was 0.990278275.

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INTRODUCTION

Pollution of the environment with heavy metals is very common across the globe which is usually caused by increase in geological and anthropogenic activities (Chibuike and Obiora, 2014). The new world trends due to increase in urbanization and industrialization have given rise to serious degradation of the environment (Tume *et al*., 2008, Yang *et al*., 2011). The quality of the spheres namely biosphere, hydrosphere, atmosphere, pedosphere and litosphere are impeded seriously because of pollution from heavy metals and other pollutants (Lourenco *et al*., 2010, Xia *et al*., 2011). The presence of heavy metals in the atmosphere represents a serious threat to the environment and human.

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Heavy metals as natural components of the earth's crust are increasingly found in microbial habitats due to several natural and anthropogenic processes. The work of Moosa *et al*., (2002) showed that current and past mining activities as well as various industrial discharges have contributed large quantities of acid waste waters to the environment and this have affected many microbial habitats as well as their activities. According to Ali and Malik (2011), Alloway (2004) contamination of urban soils with heavy metals has been studied and documented all over the world and in different disciplines due to their implication on human health. Heavy metals can cause surface and ground water pollution and are taken up by plants, released as gases into the atmosphere or bond semi enduringly by soil components such as organic matter and clay particles which can affect human health (Krishna and Gouil, 2007). Also the work of Mgbemena *et al*., (2012) was able to show that the main source of pollution particularly by heavy metals is usually linked with areas of intensive industry and high automobile use. We can also say that the natural sources of heavy metals are weathering of parent rocks. Also there could be several point and non point sources of heavy metals frequently related to the urban land use, economic, industrial and transportation set up (Fong *et al*., 2008). According to Maas *et al*., (2010) they considered soil a sink a well as a major source of pollution and most significant entity for risk evaluation. Vehicular emission, commercial fertilizers, atmospheric deposition of contaminants via dust and aerosols, industrial and domestic waste, thermal power stations based on coal fired and energy industry based on fossil fuel burning could be said to be the source of heavy metals in urban soils (Odewande and Abimbola, 2008; Cheng *et al*., 2009). However microbes have evolved mechanisms to tolerate the presence of heavy metals either by efflux, complexation or reduction of metal ions or to use them as terminal electron acceptors in anaerobic respiration (Gadd, 1992; Nies and Silver, 1995). The first response to toxic metal contamination is a large reduction in microbial activity (Bader *et al*., 2000). This is confirmed by the fact that habitats that have had high levels of metal contamination for years still have microbial population and activities that are smaller than the microbial population in uncontaminated habitats.

Several microorganisms especially bacteria have been successfully used for the reduction of Cr(vi) to less toxic Cr(iii) (Garbisu *et al*., 1997). Some scholars Konopka *et al*., (1999) came up with the arguement that resistance mechanisms do not offer protection at extremely high levels of free ions and with a lethal toxic effect. Resistance of essential heavy metals such as Cu, Zn, Ni, Co, Cr confront the cell with a special problem because of their requirement to accumulate some of these cations at trace levels and at the same time to reduce cytoplasmic concentrations from potential toxic levels. Resistant bacterial strains solve these problems by a careful regulation that results from the interaction between chromosomally determined cation transport systems and metal resistance system that are mostly determined by plasmids (Brown *et al*., 1999). According to Silver, (1996) many bacterial resistant systems for toxic metals are encoded by plasmids. However bacterial plasmids contain genes that provide extra functions to the cells among which resistance to toxic metal is very important. Also there is the use of different types of microorganisms such as algae, fungi and bacteria that remove metals from solution (Dubey, 2006). This study is looking at the seasonal variation on the effect of heavy metals on the corrodibility of two sulfur reducing bacteria on three metal coupons in a fresh water habitat.

MATERIALS AND METHODS

Study Site: Ndoni River is situated in the coastal area of the Niger Delta of Rivers State, Nigeria. It's a fresh water site and influenced by Niger river influx. The river has a long rainy season from March to October. The dry season is very short, beginning from November and ending in March the following year referred to as harmattan.

Activities along the River: The main industrial activities in this area are dredging and sand wining. The repair of marine boats also occurs here. Lumbering and fish farming activities also takes place here and a market is situated near the river.

Metal Coupons: The steel coupons used for this study namely stainless steel ASTM A316L, mild steel ASTM A283 and carbon steel ASTM A36 was obtained from Nigeria Agip oil company (NAOC).

Heavy Metal Samples: The heavy metals used for this study are compounds of chromium and zinc which were purchased from a standard chemical supply store located at East West road Alakahia, Port Harcourt Rivers state, Nigeria.

Chemical Reagents: All chemical reagents employed in this study were produced by Aldrich Chemical Co, Milwaukee, U.S.A, BDG Chemicals, Poole, England and Sigma Chemical Company, St Louis Missouri, U.S.A.

Ecological Quality Parameters: The following parameters were determined namely pH, Salinity, Conductivity, Total Dissolved Solids, Total Organic Carbon and Heavy Metals (Cr and Zn). The heavy metals were determined using atomic absorption spectrophotometer (Shangai analytica instrument Co. model AA320). To measure conductivity, WTW electronic conductivity meter model, Germany was used. Determination of pH of all the samples was carried out using a pH meter (Jenway model 3015). Parameters such as Total Dissolved Solids, Total Organic Carbon and Salinity were determined employing methods from (APHA, 2000). Total Dissolved Solids were determined by gravimetric method, Salinity by Argentometric method and Total Organic Carbon by Rapid Oxidation method.

Microbiological Analysis: After weighing the metal coupons, postgate broth was used to enumerate the sulfur reducing bacteria using the conventional five tubes most probable number method (MPN). Postgate broth samples (10ml, 1ml and 0.1ml) were placed in a series of five tubes. After sterilization they were inoculated with dilutions of scrapings from the metal coupons and enumerated after 7days of incubation in an anaerobic gas jar at room temperature.

Determination of Minimum Inhibitory Concentration (MIC): MIC of the heavy metal resistant bacteria isolates were determined by gradually increasing the concentration of the heavy metals by 0.1mg/l each time on the postgate broth medium until the strain failed to give black precipitate indicating that growth had stopped taking place.

Statistical Analysis: Correlation analysis and students T-test from excel 2010 was employed where value of $P<5\%$ was considered to be significant and $P>5\%$ was considered as not significant for T-test, whereas for correlation analysis +1 (perfect correlation) through 0 (no correlation) to -1 (perfect negative correlation) were taken into consideration.

RESULTS

Results in table 1 are the bacterial count of anaerobic organisms isolated from the fresh water habitat from April 2017 to March 2018. *Desulfovibrio desulfuricans* increased from 8-22 MPN index per 100ml from April to July, decreased from 10-<1 MPN index per 100ml from August to November, and increased again from 2-28 MPN index per 100ml from December to March. Results in table 1b served as control for bacterial count of anaerobic organisms isolated from the fresh water habitat from April 2017 to March 2018. *Desulfovibrio desulfuricans* increased from 13-27MPN index per 100ml from April to July, decreased from August to December from 25-10 MPN index per 100ml, increased again from 20-32 MPN index per 100ml from January to March the next year. *Desulfovibrio vulgaris* increased from 7-19 MPN index per 100ml from April to July, decreased from 11-4 MPN index per 100ml from August to October, and also increased from 9-26 MPN index

Table1. Population of microorganisms isolated from the fresh water habitat.

months	Sulphate reducing bacteria MPN index per 100ml	*Desulfovibrio desulfuricans*	*Desulfovibrio vulgaris*
April	08		07
May	14		10
June	20		17
July	22		19
August	10		11
September	06		06
October	<1		04
November	02		09
December	05		16
January	09		21
February	17		24
March	28		26

Table1b. Control Population of microorganisms isolated from the fresh water habitat upstream.

months	Sulphate reducing bacteria MPN index per 100ml	*Desulfovibrio desulfuricans*	*Desulfovibrio vulgaris*
April	13		10
May	17		12
June	24		18
July	27		20
August	25		20
September	21		17
October	15		14
November	11		12
December	10		13
January	20		18
February	26		24
March	33		27

Table 2. Chemical composition of metal coupons

Element	Carbon steel	Mild steel	Stainless steel
Composition (%)			
Carbon	0.008-0.20	0.15-0.25	0.03 maximum
Manganese	0.45-0.65	0.45-0.65	2.0 maximum
Phosphorus	-	-	0.04 maximum
Sulphur	-	-	0.03 maximum
Chromium	-	-	16-18
Nickel	-	-	10-14
Silicon	0.25-0.60	0.25-0.60	1.0 maximum
Molybdenum	-	-	2.0-3.0
Copper	0.60	0.60	-

Table 3. Minimum inhibition concentration

Sulphur Reducing Bacteria	Zinc	Chromium
Desulfovibrio desulfuricans	1.4mg/l	1.1mg/l
Desulfovibrio vulgaris	1.3mg/l	1.1mg/l

per 100ml from November to March. Results in table 1b which is the control for bacterial count of anaerobic organisms isolated from the fresh water habitat from April 2017 to March 2018. *Desulfovibrio vulgaris* increased from 10-20MPN index per 100ml from April to August, decreased from September to December from 17-13 MPN index per 100ml, increased again from 18-27 MPN index per 100ml from January to March the next year. The chemical composition of the various metal coupons namely stainless steel, mild steel and carbon steel used for this study are shown in table 2. Table 3 is the result of the minimum inhibitory concentration of the heavy metals used for this study namely Zinc and Chromium on the anaerobic organisms which are *Desulfovibrio desulfuricans* and *Desulfovibrio vulgaris*. Figure1 is the goggle earth map of Ndoni River which is the study area and the river is a fresh water habitat located in the south-south geopolitical zone of Nigeria.

Figure 2 is concentration of the heavy metals used in this study namely chromium and zinc against time from April 2017 to May 2018. From April to June, we can see that the concentration of chromium and zinc increased from 0.87 to 0.98 and 1.10 to 1.21 respectively in the months of April to June. From July to August chromium decreased from 0.81 to 0.22. Nothing was recorded for chromium from September to November which later started increasing from December to March the next year from 0.23 to 1.08. For zinc, there was a decrease in July to August, and an increase from September to March the next year. Figure3 represents the corrosion rates of the three metals used in this study namely stainless steel, mild steel and carbon steel against time from April 2017 to May 2018. For stainless steel, corrosion rates increased from May to March the next year. For mild steel, corrosion rates increased from April to August and decreased from September to November and increased again from December to March the

Figure 1. Map of study area Ndoni River

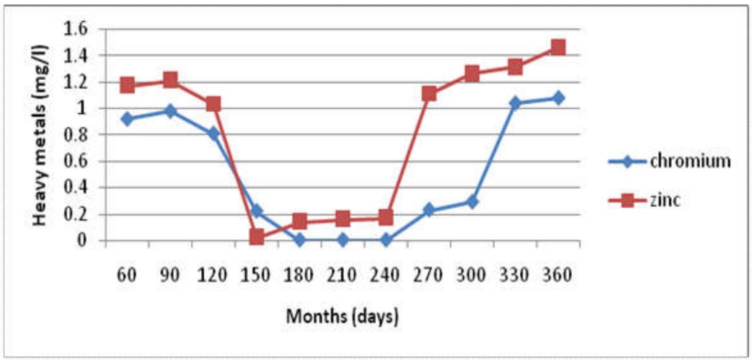

Figure 2. Heavy metals against time

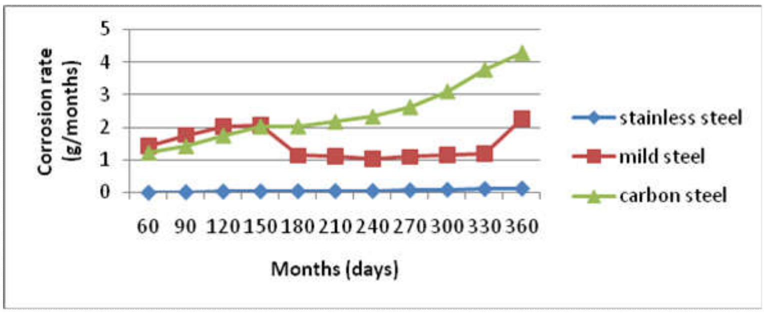

Figure 3. Corrosion rate against time

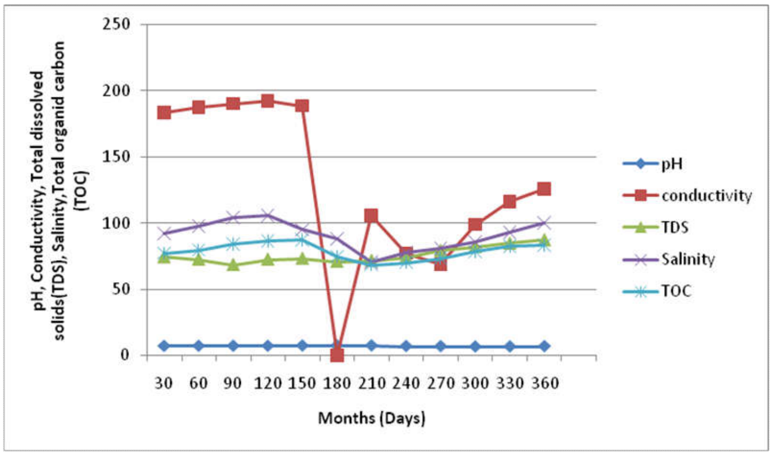

Figure 4. Physico chemical parameters against time

next year. For carbon steel, corrosion rates followed the same trend like stainless steel which increased from May to March the next year. Figure 4 is a graph of various physico chemical parameters monitored which include the pH, Conductivity, Total dissolved solids (TDS), Salinity, Total organic carbon (TOC). The pH increased from 7.2 to 7.6 from April to October 2017 and then decreased from 7.1 in November to 6.7 in January, increase from 6.8 in February to 7.0 in March. Conductivity increased from 183µs/cm to 192.15µs/cm from April to July 2017 then decreased from 188.42µs/cm to 68.93µs/cm from August to December 2017 and increased again from 98.74µs/cm in December to 125.53µs/cm in March the next year. Total Dissolved Solids (TDS) increased from 74.49mg/l to 73.31mg/l from April to August 2017 then decreased to 70.94mg/l then increased from 71.66mg/l in September 2017 to 87.32mg/l in March the next year. Salinity increased from 92.14mg/l to 105.53mg/l from April to July 2017, decreased from 94.82mg/l in August to 70.46mg/l in October 2017 then increased again from 77.81mg/l in November 2017 to 99.71mg/l in March the next year. Total Organic Carbon increased from 77.05mg/l to 87.13mg/l from April to June 2017, and then decreased from 74.52mg/l to 70.09mg/l from September to November 2017, increased again from 73.27mg/l in December 2017 to 83.19mg/l in March the next year.

DISCUSSION

The organisms *Desulfovibrio desulfuricans* and *Desulfovibrio vulgaris* which are both sulphur reducing bacteria was isolated from the Ndoni river a fresh water habitat. From the population of microorganisms isolated from the fresh water environment in table1 we can say comparatively that from beginning of April to June that *Desulfovibrio desulfuricans* had a higher MPN index per 100ml than *Desulfovibrio vulgaris* but the reduction as the months went by in the rainy season from July to October Desulfovibrio vulgaris had a slower reduction in MPN index per 100ml than *Desulfovibrio desulfuricans*. Also from November to January Desulfovibrio vulgaris had a higher rate of MPN index per 100ml than *Desulfovibrio desulfuricans*. This may be attributed to the various adaptability exhibited at different times of the month by these two sulphur reducing bacteria. In the upstream in table1b which serves as control, the two sulphur reducing bacteria had higher MPN index per 100ml throughout the season though *Desulfovibrio desulfuricans* had higher MPN index per 100ml than *Desulfovibrio vulgaris*. This could be attributed to the fact that there was no major activity upstream and the availability of suitable conditions for the proliferation of the sulphur reducing bacteria were not always washed away easily by the river tide. This is in accordance with the work of Ugboma and Wali, (2018). Also the introduction of little or no heavy metals upstream due to lack of activities in this place unlike the downstream helped the sulphur reducing bacteria to proliferate more there. This is in accordance to the work of Badder *et al*., (2000). These organisms play a role in corrosion by inducing oxygen gradient which accelerates corrosion by acting as a depolarizer to form ferrous ions and oxidizing ferrous ions (Fe^{2+}) to ferric ions (Fe^{3+}). This latter reaction normally take place in pH values higher than 4 as observed in the pH values found in this study where the highest pH was at a value of 7.7 and the lowest pH was at a value of 6.7. Microorganisms especially *Desulfovibrio desulfricans* isolated from this study depolarize surface by directly removing corrosion products such as hydrogen formed at the cathode and this depolarization encourages biocorrosion and this maintains corrosion current (Battersby *et al.,*1985). Microorganisms are also known to destroy protective coatings of various types and this is attribute to *Desulfovibrio desulfuricans* which produce hydrogen sulphide which cause hydrogen blistering and embrittlement in metals and structural fittings (Raloff, 1985). Table 2 showing the chemical composition of metal coupons showed that the alloying elements of stainless steel namely chromium and nickel offered great protection to the metal coupon thereby leading to minimal corrosion recorded in both rainy and dry season unlike the other metal coupons used in this study. This could be said to be attributed to the fact that the alloying elements occur in the lower part of the electrochemical series and are less reactive in nature. The less corrosion protection witnessed by mild steel coupons and carbon steel coupons used in this study could be due to the fact that they are made of manganese, phosphorous, copper, carbon and silicon which are more reactive in nature hence giving these metal coupons less protection from corrosion. According to Jaganathan *et al*., (2011) chromium and nickel are more toxic to microorganisms to higher levels of speciation. They showed that 13% chromium is required for stable passivity of Fe-Cr alloy in acidic and neutral solution not containing inhibitors. From this study we can see that corrosion rates, heavy metal concentrations and microbial population could be said to have reduced in the rainy season than in the dry season where some significant increase was observed. This could be attributed to runoffs and dilution of the water bodies by heavy rains that increased the water bodies. This study showed higher proliferation of microorganisms in areas with little or no concentration of heavy metals which was used as the control as shown in table 1b. This is in accordance to the works of Badder *et al*., (2000) which states that the first response to toxic metal contamination is a large reduction in microbial activity. This is confirmed by the fact that habitats which have had high levels of metal contamination for years still have microbial population and activities that are smaller than the microbial population in uncontaminated habitats.

The minimum inhibition concentration of zinc and chromium for *Desulfovibrio desulfuricans* is 2.2mg/l and 1.2mg/l respectively while that of *Desulfovibrio vulgaris* is 2.0mg/l and 1.0mg/l respectively. From the study we can say that these two sulphur reducing bacteria corroded the metal coupons more when the minimum concentration of the heavy metals were not toxic for them. This is in accordance to the argument of Konopka *et al*., (1999) which states that resistance mechanisms in microorganisms do not offer protection at extremely high levels of free metal ions and with a lethal toxic effect. Resistance of essential heavy metals such as Cu, Zn, Ni, Co, Cr confront the cell with a special problem because of their requirement to accumulate some of these cations at trace levels and at same time to reduce cytoplasmic concentrations from potential toxic levels. The physico-chemical parameters such as Total Organic Carbon, Total Dissolved Solids, Salinity and Conductivity from this study was also high during the dry season than in the rainy season following same trend as corrosion rates of the metal coupons, minimum inhibitory concentration of heavy metals and proliferation of microorganisms apart from the pH which was between 6.7 and 7.7. This could also be attributed to runoffs and heavy rains especially around June, July and August which may have affected the physico-chemical parameters. There was a significant difference between stainless steel corrosion and chromium concentration. Same to mild steel corrosion and chromium concentration and carbon steel corrosion and chromium concentration. The significant difference was higher in carbon versus chromium than in mild steel versus chromium and stainless steel versus chromium. There was also significant difference in stainless steel corrosion and zinc concentration, same to mild steel corrosion and zinc concentration and carbon steel corrosion and zinc concentration. The significant difference was higher in carbon steel corrosion versus zinc concentration followed by mild steel corrosion versus zinc concentration and stainless steel corrosion versus zinc concentration respectively.

Conclusion

From this study it has been proven that higher concentration of heavy metals especially zinc and chromium beyond the minimum inhibitory concentration acceptable by the two sulphur reducing bacteria used in this work reduce the corrodibility potentials of these microorganisms thereby creating a big risk of heavy metal pollution in our water ways. Point sources of these heavy metal pollutions should be checked regularly to guide against constant deposition of these heavy metals in these aquatic environments.

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