CONCENTRATIONS OF HEAVY METALS IN UNTREATED PRODUCED WATER FROM A CRUDE OIL PRODUCTION PLATFORM IN NIGER-DELTA, NIGERIA

ERAKHRUMEN, A. A.

Department of Forestry & Wildlife, Faculty of Agriculture, University of Benin, Benin City, Nigeria
Phone: +234-803-384-0510; **Email Address:** *erakhrumen@yahoo.com*

ABSTRACT

The various stages of petroleum industrial activities are linked with at least a by-product, residue or waste. One of such is an effluent from the mining of crude oil and gas, known as produced water, which contains varying quantities of hydrocarbons and heavy metals, thereby making it to require proper treatment in order to reduce the contaminants load to acceptable levels before being discharged into the environment. However, there are reports that this by-product is sometimes discharged untreated into Nigeria's coastal waters. This study was therefore carried out in order to contribute to efforts at sensitising the various stakeholders concerning this challenge. In carrying out this study, samples of untreated produced water were obtained from a crude oil production platform in Rivers State, Nigeria, using chemically clean amber glass bottles, properly covered with Teflon-lined lids to prevent contamination, transferred to the laboratory in ice boxes, and subjected to atomic absorption spectroscopy for heavy metals detection and quantification in line with standard laboratory procedures. Results showed that the following detected heavy metal ions i.e., Iron, Copper, Manganese, Cadmium, Lead, Nickel and Chromium had mean concentrations, in mglitre^{-1}, of 3.9, 2.5, 2.4, 2.7, 1.4, 2.6 and 1.2 respectively. These values were comparatively higher than the documented required limit for these metals in drinking water and effluent to be discharged into inland water. The prescribed limits for drinking water by World Health Organization (mglitre^{-1}) are as follows: Fe (2.0), Cu (2.0), Mn (0.4), Cd (0.003), Pb (0.01), Ni (0.07) and Cr (0.05).

Key words: Coastal pollution, Produced water, Toxic metals, Crude oil, Petroleum gas

INTRODUCTION

Industrialisation and associated activities, seen as means of development, have various impacts on people's environment and socio-economic characteristics. For instance, the region known as Niger-Delta in Nigeria has the bulk of the country's crude oil and gas deposits, thereby predisposing the region to series of challenges caused by and/or associated with industrial activities related to exploration for and exploitation of the non-renewable natural resources. These activities have series and varying impacts through the release of by-products, residues or waste materials into the environment in concentration levels that are not naturally found in such places. These by-products generated during petroleum production activities can be broadly classified into solid (drilling muds and cuttings) and liquid (produced water and oil) (Ferrari *et al*., 2000).

Technological innovations and advancements in crude oil and gas well drilling have contributed to the prospects for current and future increase in oil and gas production. For example, hydraulic fracturing is a well stimulation process which injects a high volume mixture of water, sand and chemical additives into a geologic formation at high pressures, to open or enlarge fractures in the rock (US EPA, 2010). During hydraulic fracturing, large volumes of a mixture of water and chemicals are pumped under high pressure into the target rock formation, breaking it apart to increase hydrocarbon recovery with the injected fluid mixing with trapped water in the formation. Wastewaters may be returned underground using a permitted underground injection well, discharged into surface waters after treatment to remove contaminants, or applied to land surfaces.

In addition, when crude oil is pumped out of the ground, a mixture of oil, gas and water emerges. After treatment – and in most cases without any treatment – much of this wastewater (also known as “produced water” or “formation water”) is discharged mainly into the Nigerian coastal waters. Discharge of untreated produced water into the country’s coastal waters is a cause for concern in view of the fact that it is the largest waste stream in the exploration and production process and also the largest effluent discharge associated with offshore oil and gas production coupled with the informed projections that the total volume of this type of effluent is to increase with future anticipated development of offshore oil and gas reserves worldwide (Ray and Engelhardt, 1992; Gordon *et al*., 2000). This and other by-products from the earlier-mentioned oil industrial activities have been identified to contain varying quantities of noxious compounds.

These noxious compounds, in the form of hydrocarbons and heavy metals, are observed to have caused major environmental/ecological damage in this region leading to various socio-economic and health challenges. Pollution by heavy metals is of particular importance owing to their non-biodegradability, accumulative capabilities and toxicity to life-forms (Henry, 2000; Ghosh and Singh, 2005; Neff *et al*., 2006; Erakhrumen, 2012). There is therefore the need to be constantly acquainted with the concentration levels of toxic substances, such as heavy metals, in untreated produced water generated from oil production platforms in the country. In line with this concern, this study was carried out to evaluate the concentrations of major heavy metals in untreated produced water from a designated oil production platform in Amenem, Rivers State, Nigeria.

MATERIALS AND METHODS

Brief description of Niger-Delta Region

The Niger-Delta region has the largest Delta in Africa and third largest in the world. This region has most of the country's crude oil deposit (HRW, 1999) and encompassed an area of approximately 70,000 km^2 accounting for about 7.5% of the country's total land mass, covering a coastline of 560 kilometers, about two-third of the country's entire coastline. The region accounts for about 23% of Nigeria's total population and is among those with the highest population density in the world with 265 people per square kilometers and this population is expanding at a rapid rate of 3% per annum, according to the records of Niger Delta Development Commission.

The Niger Delta coast extends from the mouth of the Benin River, in the west, for about 500 km to the mouth of the Imo river in the east. The Delta is arcuate in plan-form and is rimmed by a chain of sandy barrier islands approximately 2000 km^2 in area (Ajao *et al*., 1996). This Delta experiences a tropical climate consisting of a rainy season (April to October) and a dry season (November to March). Diurnal temperature is high reaching 34°C to 35°C. Relative humidity is high throughout the year and is rarely below 60%. High rainfall of between 3000 mm and 4000 mm is experienced during the months of May to September with a short dry break in August.

Sourcing of Produced Water samples

Samples of untreated produced water was collected in August, 2011, from Total oil production platform in Amenem, about 35 kilometers from Port Harcourt in Rivers State, Nigeria, using ten 1 litre chemically clean amber glass bottles and properly covered with Teflon-lined lids in such a way as to completely protect all the water samples from any external contamination. All the bottles containing the untreated produced water samples were properly labelled for identification and transferred to the laboratory, in ice boxes, for laboratory analyses targeted at detecting and quantifying the concentrations of heavy metals in the samples.

Laboratory analyses of Produced Water samples

A solution of Ammonium pyrrolidine dithiocarbamate (APDC), 1% (w/v) in distilled, deionised water was prepared and purified by shaking the APDC solution with an equal volume of Methyl isobutyl ketone (MIBK), with the phases allowed to separate and retaining the aqueous (lower) phase. The produced water samples were filtered through 0.45 micron Millipore® filter and acidified with Hydrochloric acid, (HCl) to a pH of 4. A 750 ml aliquot of the filtered acidified produced water sample was placed into a 1 litre polypropylene flask with 35 ml of MIBK followed by 7 ml of 1% APDC solution added to it and equilibrated for 30 minutes on a mechanical shaker. This was analysed immediately for presence and concentration levels of heavy metals, in five replicates, using Perkin-Elmer 30303B Atomic Absorption Spectrophotometer in conformity with the appropriate standard method described by Perkin-Elmer Corporation, (1996).

RESULTS AND DISCUSSION

The results obtained from the laboratory analyses to determine the concentrations of some heavy metals in the untreated produced water samples are tabulated in Table 1. In addition, Table 1 also contain the heavy metal limits for drinking water (WHO, 2008) and effluent limitations concerning some heavy metals for Inland/Near shore oil and gas installations for oily waste water (EGASPIN, 2002). The analysed produced water contained the following heavy metal ions in the following mean concentration levels: Iron (Fe) 3.9 mglitre^{-1}, Copper (Cu) 2.5 mglitre^{-1}, Manganese (Mn) 2.4 mglitre^{-1}, Cadmium (Cd) 2.7 mglitre^{-1}, Lead (Pb) 1.4 mglitre^{-1}, Nickel (Ni) 2.6 mglitre^{-1} and Chromium (Cr) 1.2

mglitre^{-1}. These values are comparatively higher than the tabulated heavy metal limits for drinking water and effluent limitations for Inland/Near shore oil and gas installations for oily waste water (Table 1). Nevertheless, it is important to note here that there is the need to avoid ambiguity when analysing constituents of produced water from different sources.

Avoiding ambiguity in this regard is important owing to the fact that samples of produced water from different sources may have their physical and chemical properties varying considerably depending on the geographical location of the field, the geological formation with which the produced water has been in contact for a relatively short or long period e.g., few days to thousands of years, and the type of hydrocarbon product being produced from the well, the lifetime of a reservoir (Johnsen *et al*., 2000; ANL, 2009), among others. For example, in the earlier part of the life of an oil well, oil production is high and water production is low. However, as the production age of the well increases, the oil production decreases while the water production increases (ANL, 2009). As noted earlier, produced water contains different substances such as hydrocarbons, heavy metals, inorganic salts, production chemicals and oil field chemical residues in various proportions.

Produced water undergoes changes in its physical chemistry including precipitation of heavy metals after being discharged and mixed with ambient seawater (Azetsu-Scott *et al*., 2007). It has been noted by some workers that with effective dilution, acute toxic effects of this and other types of effluent water are not expected to be found beyond 0.05 km from the discharge point (Johnsen *et al*., 2000), however, since heavy metals cannot be biodegraded coupled with their capability to accumulate, even far away from the discharge point, most especially in shallow waters, it has been observed that elevated concentrations may be detected in these places particularly where industrial activities were not known to have taken place in the past or to be ongoing. This was the observation of Erakhrumen, (2014) in soil and water obtained from a mangrove forest where there were no ongoing or past on-site explorations for and exploitation of crude oil and other industrial activities.

This observation might be because mangrove forests grow in high- and low-tide areas and experience the alternation of ebb and flow. The sheltered slack-water conditions allow the deposition of fine particles enriched with metals, organic matter and minerals (Ramanathan *et al.*, 1999). Deposition of toxic substances may negatively impact on regenerative capability of these fragile forests whose tree seedlings require newly deposited mud to get them established. In addition, this may also negatively impact on some of mangrove's functions such as source of medicines, alcohol and other products (Kathiresan and Bingham, 2001) including some important environmental and economic functions such as breeding ground for fish and other marine organisms, among others (Janssen and Padilla, 1996). Polycyclic aromatic hydrocarbons and heavy metals are considered the most harmful contaminants in produced water (Middledich, 1984).

This is one of the reasons why it is always necessary to be acquainted with the prevalent chemical properties of both treated and untreated produced water in order to be able to develop effective treatment methods for reducing the toxicity to prescribed acceptable limits before disposal. The results for analysed produced water samples in Table 1 are those for untreated effluent requiring treatment before discharge into the environment as specified by Nigeria's regulations. These values for the untreated effluent in Table 1 might be similar to or vary from those obtained from other sources in this study area but it showed that untreated produced water from this oil production platform contain high concentration level of some heavy metal ions when compared to the other values tabulated in Table 1 as the permissible limit for drinking water (WHO, 2008) and that for disposal into inland waters as stipulated in EGASPIN, (2002) by the Department of Petroleum Resources, one of Nigeria's regulatory agencies in charge of the petroleum sector.

While the setting up of permissible limit for substances, such as heavy metals, in effluents to be disposed, is a laudable effort towards environmental protection, it is also important to note that enforcements for compliance with these limits are necessary. This is partly because discharge of untreated effluents into the water bodies is mostly done during drilling operations. In addition, it has also been noted that produced water treatment systems currently in use by most oil producing companies is primarily designed to remove particulate or dissolved oil and therefore has little effect on the concentrations of dissolved petroleum hydrocarbons and other noxious substances. These values in Table 1 are for untreated produced water that were meant for treatment before eventual discharge into the ocean water; however, there are reports in literature where higher values for these substances were also recorded for supposedly already treated produced water meant for disposal.

Evaluation of heavy metal contents and their concentration in untreated produced water was done for samples from a production platform in this study in order to give an idea of its chemical property before they are treated for compliance with disposal regulatory limit. Nevertheless, similar studies, such as Oboh *et al*., (2009), Isehunwa and Onovae, (2011) and Onojake and Abanum, (2012), which evaluated heavy metals content and their concentration in produced water samples from multiple sources in other locations within the region, also recorded similar observations as those in this study. It is however noteworthy that this submission does not necessarily imply that outcomes of such similar analyses will be similar for all untreated produced water sourced from oil and gas production platforms in this region but rather it reinforces the need for constant proper monitoring of the physical and chemical properties of this type of effluent including its adequate and reliable treatment before being discharged into the country’s coastal waters.

Table 1: Results of analyses for sampled untreated produced water and some permissible limits for heavy metals in drinking water and effluents

	Heavy metals and their mean concentration levels in produced water samples (mglitre^{-1})						
	Fe	Cu	Mn	Cd	Pb	Ni	Cr
Results from this study (Each value is the mean of five experimental replicates)	3.9±0.02	2.5±0.01	2.4±0.01	2.7±0.01	1.4±0.01	2.6±0.02	1.2±0.01
	Permissible limits for heavy metals in drinking water and effluents (mglitre^{-1})						
	Fe	Cu	Mn	Cd	Pb	Ni	Cr
Guideline values for drinking water quality (WHO, 2008)	2.0 (Approx.)	2.0	0.4	0.003	0.01	0.07	0.05
Inland effluent limitations (Fresh waters) (EGASPIN, 2002)	1.0	1.5	NA	NA	0.05	NA	0.03
Near shore effluent limitations (Brackish/Saline waters) (EGASPIN, 2002)	No limit	No limit	NA	NA	No limit	NA	0.05

NA: Not Available

CONCLUSION

The outcome of this study is in line with reports that untreated produced water contains varying quantities of chemicals and elements, such as heavy metals, that are toxic to human and other life-forms. The essence of the study is to make contribution to efforts at sensitising the various stakeholders concerning this challenge and the prescribed solutions. Currently, there are set limits for concentrations of heavy metal in produced water and other effluents before they are discharged into the environment. These limits, set by various regulatory agencies and others interested in environmental protection, are expected to be adhered to by the industrial outfits concerned. Nonetheless, there are documented reports that some of these outfits sometimes do not ensure strict compliance to these limits. This claim is however subject to scientific monitoring and verifications.

Ensuring compliance to these limits can only be achieved if the mandatory sampling, analysis and monitoring of effluents, such as produced water, is carried out regularly to determine the prevalent physical and chemical parameters before and after treatment. The regulatory agencies in Nigeria are not only to ensure this but are also to work towards sustainable short, medium and long term operational guidelines and strategies aimed at ensuring continuous reduction in the concentration of toxic substances in produced water and other effluents before being discharged into the environment. It is expected that these measures will contribute to efforts at reducing in number the sources of toxic pollutants from these industrial activities into the environment.

ACKNOWLEDGEMENT

The author acknowledges the funding support for, and permission to publish scientific articles from an International Foundation for Science (IFS) funded study entitled "Evaluation of Dendroremediation Capability of Nigerian Red Mangrove (*Rhizophora racemosa* G.F.W. Meyer) in the Niger-Delta Region" through the IFS Grant W/4505-1, from Stockholm, Sweden.

REFERENCES

Ajao, E.A., Oyewo, E.O. and Unyimadu, J.P. (1996): A Review of the Pollution of Coastal Waters in Nigeria. Nigerian Institute for Oceanography and Marine Research (NIOMR) Technical Paper No. 107 of March, 1996. 20 pages.

ANL, Argonne National Laboratory, (2009): Produced Water Volumes and Management Practices in the United States. Document Prepared by C.E. Clark and J.A. Veil for the US Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory, Environmental Science Division, Argonne National Laboratory Document: ANL/EVS/R-09/1. 64 pages.

Azetsu-Scott, K., Yeats, P., Wohlgeschaffen, G., Dalziel, J., Niven, S. and Lee, K. (2007): Precipitation of Heavy Metals in Produced Water: Influence on Contaminant Transport and Toxicity. *Marine Environmental Research*, 63(2): 146-167.

EGASPIN, Environmental Guidelines and Standards for the Petroleum Industry in Nigeria, (2002): A Document Issued by the Department of Petroleum Resources, Lagos in 1991 with Revised Edition for 2002, 415 pages.

Erakhrumen, A.A. (2007): Phytoremediation: An Environmentally Sound Technology for Pollution Prevention, Control and Remediation in Developing Countries. *Educational Research and Review*, 2(7): 151-156.

Erakhrumen, A.A. (2012): Studies on Phytoextraction Processes and Some Plants' Reactions to Uptake and Hyperaccumulation of Substances. In: Anjum, N.A., Pereira, M.E., Ahmad, I., Duarte, A.C., Umar, S. and Khan, N.A. (Eds.) Phytotechnologies: Remediation of Environmental Contaminants. Taylor & Francis. pp. 521-540.

Erakhrumen, A.A. (2014): Potentials of *Rhizophora racemosa* for Bio-Indication and Dendroremediation of Heavy Metal Contamination in a Mangrove Forest, Ondo State, Nigeria. *Nigerian Journal of Agriculture, Food and Environment*, 10(4): 1-5.

Ferrari, G., Cecconi, F. and Xiao, L. (2000): Drilling Wastes Treatment and

Management Practices for Reducing Impact on HSE: ENI/AGIP Experiences. A Paper with Document ID: SPE-64635-MS Presented at the Society of Petroleum Engineers (SPE) International Oil and Gas Conference and Exhibition held in Beijing, China, between 7 and 10 November, 2000. 11 pages.

Ghosh, M. and Singh, S.P. (2005): A Review on Phytoremediation of Heavy Metals and Utilization of its By-Products. *Applied Ecology And Environmental Research*, 3(1): 1-18.

Gordon, D.C., Griffiths, L.D., Hurley, G.V., Muecke, A.L., Muschenheim, D.K. and Wells, P.G. (Eds.). **(**2000): Understanding the Environmental Effects of Offshore Hydrocarbon Development. Canadian Technical Report of Fisheries and Aquatic Sciences 2311, p. 82.

Henry, J.R. (2000): An Overview of Phytoremediation of Lead and Mercury. NNEMS Report. Washington, D.C, pp. 3-9.

HRW, Human Right Watch, (1999): The Price of Oil: Corporate Responsibility and Human Rights Violations in Nigeria's Oil Producing Communities. Published by Human Right Watch, 193 pages. HRW Index No. 1-56432-225-4. ISBN: 156432-225-4. Retrieved on 06/10/2014 at 13:40 hours from: *http://www.hrw.org/reports/1999/nigeria/index.htm*

Isehunwa, S.O. and Onovae, S. (2011): Evaluation of Produced Water Discharge in the Niger-Delta. *ARPN Journal of Engineering and Applied Sciences*, 6(8): 66-72.

Janssen, R and Padilla, J. E. (1999): Preservation or Conversion? Valuation and Evaluation of a Mangrove Forest in the Philippines. *Environmental and Resource Economics*, 14: 297-331. Published by Kluwer Academic Publishers.

Johnsen, S., Frost, T.K., Hjelsvold, M. and Utvik, T.R. (2000): The Environmental Impact Factor - A Proposed Tool for Produced Water Impact Reduction, Management and Regulation. A Paper with Document ID: SPE-61178-MS Presented at the Society of Petroleum Engineers (SPE) International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production, held in Stavanger, Norway, between 26 and 28 June, 2000. 13 pages.

Kathiresan, K. and Bingham, B.L. (2001): Biology of Mangroves and Mangrove Ecosystems. *Advances in Marine Biology*, 40: 81-251.

Middledich, B.S. (1984): Ecological Effects of Produced Water Discharges from Offshore Oil and Gas Production Platforms: Final Report on American Petroleum Institute (API) Project. API: Washington D.C. No. 248.

Neff, J.M., Johnsen, S., Frost, T.K., Utvik, T.I.R. and Durell, G.S. (2006): Oil Well Produced Water Discharges to the North Sea. Part II: Comparison of Deployed

Mussels (*Mytilus edulis*) and the DREAM Model to Predict Ecological Risk. *Marine Environmental Research*, 62**:** 224-246.

Oboh, I., Aluyor, E. and Audu, T. (2009): Post-Treatment of Produced Water before Discharge Using *Lorffa cylindrical*. *Learndo Electronic Journal of Practices and Technologies*, 14: 57-64.

Onojake, M.C. and Abanum, U.I. (2012): Evaluation and Management of Produced Water from Selected Oil Fields in Niger Delta, Nigeria. *Archives of Applied Science Research*, 4(1): 39-47.

Perkin-Elmer Corporation, (1996): Analytical Methods for Atomic Absorption Spectroscopy. A Manual Published by Perkin-Elmer Corporation, US. 310 pages.

Ramanathan, A.L., Subramanian, V., Ramesh, R., Chidambaram, S. and James, A. (1999): Environmental Geochemistry of the Pichavaram Mangrove Ecosystem (tropical), Southeast Coast of India. *Environmental Geology*, 37: 223-233.

Ray, J.P. and Engelhardt, F.R. (1992): Produced Water - Technological/Environmental Issues and

Solutions. Proceedings of the 1992 International Produced Water Symposium, San Diego, California,

February 1992, edited by J.P. Ray and F.R. Engelhardt. *Environmental Science Research*, volume 46. Plenum Press, New York & London.

US EPA, U.S. Environmental Protection

Agency, (2010): Hydraulic Fracturing Research Study. Office of Research and Development. Document EPA/600/F-10/002. Retrieved on 24/09/2014 at 20:25 hours from: *http://www.epa.gov/safewater/uic/pdfs/hfresearchstudyfs.pdf*

WHO, World Health Organization, (2008): Guidelines for Drinking-Water Quality: Incorporating the First and Second Addenda, Volume 1, Recommendations. Third Edition: 668 pages. ISBN 978 92 4 154761 1. Retrieved on 02/11/2014 at 05:45 hours from: *http://www.who.int/water_sanitation_health/dwq/fulltext.pdf?ua=1*