PRINT ISSN 1119-8362
Electronic ISSN 2659-1499

Full-text Available Online at
https://www.ajol.info/index.php/jasem
https://www.bioline.org.br/ja

J. Appl. Sci. Environ. Manage.
Vol. 28 (12) 4041-4046, Dec. 2024

Evaluation of Physicochemical Parameters of Ship-Borne Bilge, Ballast and Black Wastewaters Obtained From Ships Docked In Warri Port, Delta State, Nigeria

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ABSTRACT: The impact of oil and grease content of bilge water on Nigeria's coastal environment is significant, hence, the objective of this paper is to evaluate the physicochemical and microbiological parameters of ship-borne Bilge, Ballast and Black wastewaters obtained from ships docked in Warri port, Delta State, Nigeria using appropriate standard techniques. Data obtained show that the levels (mean ± SD) of some of the physicochemical parameters in the wastewaters were pH (6.68 ± 0.28); Cu(1.17 ± 0.2); Fe (2.57 ± 04); Pb (0.5 ± 0.1) and Zn ((1.01 ± 0.40). The results of the analysis shows that the extent of marine pollution based on physicochemical parameters of ship generated wastewater from vessels against the DPR standard are significant and that oil and grease content of bilge water, ship ballast water and garbage waste from Warri port significantly impact on Nigeria's coastal environment. The study therefore recommended appropriate measures of ship disposal and policy implementation and enforcement for strict compliance.

DOI: https://dx.doi.org/10.4314/jasem.v28i12.12

Cite this Article as: TONJOH, A. J; ANYANWU, O. J; OMOROGIEVA, M. O; OKOREFE, O. C. (2024). Evaluation of Physicochemical Parameters of Ship-Borne Bilge, Ballast and Black Wastewaters Obtained From Ships Docked In Warri Port, Delta State, Nigeria. *J. Appl. Sci. Environ. Manage.* 28 (12) 4041-4046

Dates: Received: 22 October 2024; Revised: 20 November 2024; Accepted: 08 December 2024; Published: 18 December 2024

Keywords: Physicochemical; Ballast Water; Bilge Water; Black Water

Ship generated waste is expected to grow significantly in the coming decade within our nations ports and therefore it is imperative to improve on the capabilities of their port reception facilities (Andersson *et al.,* 2016). The round clock problem of environmental pollution and degradation especially of the Nigeria marine environment occasioned by oil spill (Asariotis *et al.,* 2016), exploitation and lifting, gas flaring and introduction of noxious and harmful substances into the marine environment like ballast water has over the years caused the destruction of aquatic life, vegetation and the ecosystem (Bamanga *et al*., 2019). Ironically, the above problem has never been given adequate national attention. Unwholesome practices of ships engaged in coastal trade in Nigeria territorial waters such as sewage disposal at sea, introduction of hazardous substances into sea, Chemicals, ship ballast water, wave erosion, offshore, pipelines, factories and sewage plants directly into the sea or water sources, discharge of sewage, agricultural and toxins from industries, fishing activities and even abandonment of wrecks has equally constituted a serious problem of marine environmental pollution and this has continued to go on unchecked (Bailey, 2015), (IMO,2017). This problem has invariably alienated the indigence of the affected geographical regions from their traditional sources of earning good leaving which is fishing and

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agriculture, thus subjecting them to untold hardship (Gokce, 2014). Furthermore, it has impacted negatively to the development and the international recognition of the Nigeria maritime sector, (Bamanga *et al.,* 2014). Hence, the objective of this paper is to evaluate the physicochemical and microbiological parameters of ship-borne bilge water obtained from ships docked in Warri port, Delta State, Nigeria

MATERIALS AND METHODS

Description of study Area: The Warri Seaport, located in Delta State, Nigeria, lies on the banks of the Warri River. The approximate coordinates of Warri Seaport are: Latitude: 5.5194° N Longitude: 5.7580° E. This seaport is strategically significant for trade and commerce in the Niger Delta region, currently, vessels arriving at Warri Seaport discharge ballast water to maintain stability as cargo is loaded. Conversely, they take on ballast water as cargo is offloaded. The discharge must comply with Nigeria's regulatory framework and international standards, particularly the International Convention for the Control and Management of Ships' Ballast Water and Sediments (BWM Convention) by the IMO.

Plate 1: Map showing Warri seaport
Source Google Map

Sample collection and Treatment: This study adopted experimental research design. Waste samples were collected from vessels berthed at different locations. The samples were: black waste, bilge water and ship ballast water. These samples were collected with sterile 75 cm screwed top plastic bottles; they were stored in a temperature of 4◦C. In order to avoid staleness of samples, some of the pollution indicator parameters were determined within six hours of sample collection.

Sample Analysis: The analysis covered physical, chemical and microbiological parameters of the water samples. The parameters tested for were: pH, temperature, conductivity, total dissolved solids, total suspended solids, turbidity, dissolved oxygen, biochemical oxygen demand, chemical oxygen demand, total oil and grease, copper, iron, lead, zinc, aluminum, cadmium, mercury, total coliform count, total heterotrophic bacteria, and total heterotrophic fungi.

Data collection utilized a sampling method whereby water samples from marine cargo vessels at berths were subjected to physicochemical and microbiological analysis according to the American Public Health Association (APHA) method to determine the level of concentration of identified parameters. Standard procedures were applied to prepare our sample for the analysis. Thus, for the sake of brevity, we have in this section omitted the laboratory procedures which followed. These are however attached in Appendix. In the following sections, we discuss the results from the analysis of our samples. Significant values of parameters obtained from the laboratory analysis are compared to the Department of Petroleum Resources (DPR) specified standards for effluent discharges from barges, to guard against: hazards to human health, harm to living organisms (fauna and flora) and aquatic life and impairment of quality of adjacent land, surface and ground waters

Determination of pH: The pH meter was calibrated using standard buffer solutions as per the manufacturer's instructions, and the electrode was rinsed with distilled water between each buffer solution. Bilge water was collected in a clean beaker and the sample was ensured to be free of debris and oils (as much as possible) to avoid interfering with the electrode. The pH electrode was immersed in the bilge water sample and was stirred gently and the reading was allowed to stabilize and the pH value was recorded and displayed on the meter. The electrode was cleansed after each use to avoid contamination and measurements were performed promptly after sampling.

Determination of the temperature: Temperature affects the chemical and physical properties of bilge water, while Materials and Equipment comprise of Digital thermometer and beaker. In preparation, the bilge water was collected in a clean beaker. Measurement the thermometer was inserted into the sample and the sensor was fully immersed is fully submerged but not touching the container and waited for the reading to stabilize and record the temperature in °C. The precautions taken: the pH meter was ensured to be calibrated correctly for temperature compensation and avoiding of contamination of the sensor with grease or debris.

Determination of Conductivity: Conductivity indicates the ability of bilge water to conduct electricity, reflecting ion concentration. Materials and Equipment include the Conductivity meter (calibrated), Distilled water, Conductivity standard solution and a Beaker. Conductivity meter was calibrated using a standard solution according to the manufacturer's instructions and the probe rinsed with distilled water after calibration. The bilge water was collected in a clean beaker. The conductivity probe was immersed in the bilge water sample, stirred gently and allow the reading to stabilize. the conductivity was recorded in µS/cm.
Precautions were taken such as rinsing the probe thoroughly after each measurement and avoiding air bubbles around the probe, as they can affect the accuracy.

Heavy Metals Analysis Using Atomic Absorption Spectroscopy (AAS): To analyze heavy metals in the sample, digestion and quantification steps were taken: Performing the analysis using AAS, and calculating the concentration of metals in the sample. Digestion is necessary to break down organic matter and release the metals into solution. The materials and Sample include: Bilge water, Black water and Ballast water., materials include Nitric acid (HNO_3) and perchloric acid ($HClO_4$) or hydrochloric acid (HCl) for digestion, hot plate or microwave digestion system, Volumetric flask (100 mL) and a Distilled water. Sample Preparation: the bilge, black and ballast water were filtered to remove debris or particulate matter and a measured volume of the sample was taken (100 mL) into a digestion flask. Acid Addition a quantity of 5 mL concentrated nitric acid (HNO_3) was added to the sample. Because of the complex samples, 2 mL hydrochloric acid (HCl)was added to ensure complete digestion. The sample was heated on a hot plate under a fume hood at 120–150°C until the solution becomes clear, thereafter, it was allowed to cool and was diluted with distilled water to a known volume of 100 mL

Atomic Absorption Spectroscopy was used to quantify the metal concentration in the digested sample using PerkinElmer AAnalyst 400. The instrument was calibrated using standard solutions of the metal, Pb, Cd, Cu, Zn. Calibration Curve: standard solutions of 1ppm concentrations were prepared and absorbance for each standard was measured. The digested sample was aspirated into the AAS flame and the absorbance for each metal was measured.

RESULTS AND DISCUSSIONS

In Table 1, physicochemical and microbiological parameters of the sample investigated. pH is an indicator of acidic or alkaline conditions of the water status. The observed value of pH (6.72), indicates that the ship wastewater sample is slightly acidic. The pH increased significantly with different types of ship wastewater and falls below the DPR permissible range. As the acidity of the surface water increases, submerged aquatic plants decrease depriving water fowl of their basic food source. Caustic soda from soaps and detergents from washed materials on board vessels may have been the cause of the increase in pH observed in different samples in this study.

Temperature (27.7) increased significantly over different samples. The range falls within the DPR standards. The temperature difference in any aquatic habitat is affected by weather, and the extent of shade from direct exposure to sunlight. Also, biodegradation of organic matter that enters the water may increase heat Conductivity values recorded in Total Hydrocarbon Content, THC (13.00-17.31mg/l), turbidity (10.70-11.00mg/l), total suspended solids, TSS (779ug/l), and temperature (27^{o}C), all fall within the DPR allowable limits and therefore do not constitute any treat to the recipient marine environment. This was also the case of the chemical oxygen demand, COD (65ug/l), biochemical oxygen demand, BOD (30ug/l), and heavy metals of lead, iron, copper, chromium, and zinc.

Oil and Grease was determined according to API-RP45 method using a Spectrophotometer. The sample was extracted twice with 1:10 ratio of Xylene to sample using a separator funnel. The combined extract after centrifuging was read in the spectrophotometer using Xylene as the reference material t 400nm wavelength. Readings obtained from the spectrophotometer were traced out on the calibration graph and used to calculate the concentration of oil and grease in mg/L in the sample. Conductivity values recorded in this study (336 S/cm) are found to be above the DPR standards. The black wastewater sample recorded the highest value of 500S/cm of conductivity. The increase may be attributed to high levels of dissolved solids in the sample such as: chloride, phosphate and nitrate. It may also be as a result of the storage of the waste product onboard vessels. TDS increased significantly with different samples of ship wastewater with a mean of 606.4 mg/L which is below the DPR permissible limit for discharges in inland or near shore water. The observed high TSS in black wastewater could be attributed to the influx of non-biodegradable solids in the sample.

Table 1: physicochemical and microbiological parameters of the sample investigated

Parameters	Unit	Bilge Water	Ballast water	Black waste	Mean	SD	DPR * Std.	Significant (Mean * > DPR Limit)
Date sampled		9/07/24	24/07/24	24/07/24				
pH	-	6.25	6.73	7.4	6.78	0.28	6.5–8.5	NO
Temperature	OC	29.50	29.75	29.75	29.75	0.36	30	NO
Conductivity	µS/cm	356.0	150.0	490	350	3.40	100	YES
Turbidity	mg/L	256.0	160.0	21.00	145.8	1.58	10	YES
TDS	mg/L	190	129	1499	606.1	5.78	<2000	NO
TSS	mg/L	200	139.2	1999.9	779.4	21.5	50	YES
COD	mg/L	121	68	5.4	65.1	40.60	40	YES
OIL/Grease	mg/L	72.0	20.1	15.90	35.67	12.5	48	NO
DO	mg/L	2.01	2.4	3.40	2.625	0.28	5.0	N0
BOD	mg/L	48	30	13	30.2	7.29	30	YES
Lead	µg/L	0.444	0.12	0.00	0.503	0.101	0.05	YES
Cadmium	µg/L	0.113	0.09	0.25	0.151	0.05	0.003	YES
Iron	µg/L	3.98	1.72	2.02	2.57	40.71	0.3	YES
Copper	µg/L	1.54	0.75	1.291	1.17	0.21	1.5	NO
Chromium	µg/L	0.005	0.006	0.007	0.006	0.001	0.005	NO
Mercury	µg/L	nil	nil	Nil	nil	nil	0.1	NO
Zinc	µg/L	2.00	0.81	0.04	1.01	0.40.7	1.0	NO

*Source: Results of the experiment based on fieldwork. * Extracts from DPR*

Turbidity is associated with suspended solid concentrations; the turbidity range values recorded in this analysis were low in black wastewater and highest in bilge wastewater with a range of (160, 145.8) NTU which falls above the DPR permissible limit. The high turbidity recorded in bilge water can be attributed to leaks from the machinery equipment of the vessel as stated before in this study

Dissolved oxygen (DO) is a measure of the degree of pollution by organic matter, the destruction of organic substances as well as the self-purification capacity of the water body. The DO of ship wastewater (2.63 mg/L) was lower than the DPR acceptable limit of 5.0 mg/L. DO in liquid provides a source of oxygen needed for oxidation of organic matter when the concentration is high and a lack of it causes the water to become dead or void of aquatic life. The mean value (30.2mg/L) of BOD in ship wastewater was slightly above the DPR acceptable limit of 30 mg/L, which means that discharging wastewater into the marine environment will affect the aquatic life and the ecosystem. The chemical oxygen demand (COD) recorded in this study (26.7 mg/L) was above the DPR standard of 40 mg/L. Observed Iron (Fe) values ranged from 1.72–3.98 (2.57mg/L) and were found to be above the DPR permissible limit of 0.30 mg/L. Iron values increased significantly with different samples of waste and were highest in bilge water.

Copper (1.17mg/L) was below the DPR permissible limit of 1.5 mg/L. Higher bacterial concentrations in sea are strongly linked to total coliform and faecal coliform. A high microbial population in an aquatic system is a reflection of the input of micro-organisms in ship wastewater discharged into the marine environment and the availability of growth supporting organic matter. High counts of bacterial load reflect the level of water pollution as it gives an indication of the amount of organic matter present.

From the result of the experiment, the value of oil and grease content of bilge water (72µg/L > 48µg/L of DPR criteria), hence the research concluded that Oil and grease content of bilge water does significantly impact on Nigeria's coastal environment. However, the mean value of oil and grease contents of the three sample is not significant or below the recommended DPR limit, that is to say that oil and grease content in bilge water was 72ug/l which is more than 50percent of the allowable limit of DPR, even though there was a record of considerable reduction below the allowable limit of DPR for black waste and ballast water. Hypothesis H_0: Ship ballast water does not significantly impact on Nigeria's coastal environment. The findings from the laboratory analysis of ship ballast water sample based on the DPR criteria for water quality shows most of the parameters exceeded the allowable limit of DPR. These include, the conductivity (150 µS/cm > 100 µS/cm), turbidity (160.0 mg/L > 10 mg/L), Total Dissolved Solids, TSS (139.2 mg/L > 50 mg/L), lead, (0.12 µg/L > 0.05 µg/L), Cadmium (0.09 µg/L> 0.003 µg/L), Iron,(1.72µg/L > 0.3µg/L) and Chromium,(0.006 µg/L> 0.005µg/L). However, the above-mentioned parameters that exceeded the allowable DPR limit impact on coastal environment. Hence the researchers conclude that Ship ballast water does significantly impact on Nigeria's coastal environment.

Conclusion: The findings from the study show that there is a significant statistical correlation between Cargo generated from our seaports and the total ship waste also generated. The implication is that the more vessels visit the Nigerian seaport, more Cargo is generated and more Ship waste is also generated. This work has made sufficient contribution to knowledge, these include; the study has been able to identify major biochemical and physical parameters of ballast water and bilge water. Also, the study has being able to find out the relationship between garbage waste from Warri port and the coastal environment of Nigeria. This research found out that, the mean value of oil and grease contents of the three samples is not significant or below the recommended DPR limit, that is to say that the mean oil and grease content in bilge water, ballast water and black waste is within the DPR standard. However, this study contributed that Oil and grease content of bilge water alone significantly impact on Nigeria's coastal environment.

Acknowledgement: The authors extend their appreciation to Tertiary Education Trust Fund for funding this research, with research funding number TETF/DR&D/CE/UNI-NMU/IBR/2024/Vol.1.

Declaration of Conflict of Interest: The authors declare no conflict of interest.

Data Availability Statement: Data are available upon request from the first author or corresponding author or any of the other authors

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