

Preprints are preliminary reports that have not undergone peer review. They should not be considered conclusive, used to inform clinical practice, or referenced by the media as validated information.

Distribution of Nutrients and Chlorophyll-a in coastal waters and mesotidal estuary of Ilaje, Ondo state, South Western, Nigeria.

Opeyemi Otolorin Oyatola

Nigerian Institute for Oceanography and Marine Research

Olubunmi Ayoola Nubi

Nigerian Institute for Oceanography and Marine Research

Samuel Olatunde Popoola (popoolaos@niomr.gov.ng)

Nigerian Institute for Oceanography and Marine Research https://orcid.org/0000-0002-4630-7812

Falilu Olaiwola Adekunbi

Nigerian Institute for Oceanography and Marine Research

John Paul Unyimadu

Nigerian Institute for Oceanography and Marine Research

Research Article

Keywords: Nutrients, eutrophication, chloropyll-a, llaje coastal waters, SW Nigeria

Posted Date: March 30th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-255613/v1

License: (a) This work is licensed under a Creative Commons Attribution 4.0 International License. Read Full License

Version of Record: A version of this preprint was published at International Journal of Scientific and Research Publications (IJSRP) on October 12th, 2021. See the published version at https://doi.org/10.29322/IJSRP.11.10.2021.p11840.

Abstract

The nutrients (nitrate, nitrite, phosphate and silicate) of thirty-two stations in Ilaje, coastal waters and estuaries of Ondo state, Nigeria were studied in the month of August (during the wet season). The stations consist of two estuaries; Awoye (A1-A6), Abereke (AB1-AB7), anthropogenic impacted stations (I1-I12) and control stations (C1-C7). The aim of this study is to evaluate the eutrophication status of Ilaje coastal waters and estuaries in response to the stress caused by anthropogenic inputs from land use changes, agriculture, and industrial effluents. Our study reveal highest nitrate (3.20-6.98 mg/l) and phosphate (11.59-17.48mg/L) concentrations at the Abereke Estuaries. The significant correlation of nitrate with chlorophyll-a (p<0.01, r= +0.886) and the low N/P (<0.25) ratio suggest that nitrate is the primary limiting nutrient for phytoplankton production, and accounted for the high chlorophyll-a concentrations in the study area. The strong correlation of nitrite and silicate from the statistical bi-plots at the impacted stations, and the accompanied lowest dissolved oxygen (<5 mg/L) and acidic pH (<6) values suggest nitrite and silicate are sourced from anthropogenic effluents. The mean nitrite concentrations of 0.13mg/L at the impacted stations above the maximum permissible limit of nitrite (0.06 mg/L) for Tilapia production suggest an unfavorable environment for the Tilapia growth at the impacted stations. The chlorophyll-a concentrations scale further showed that the study area is characterized as bad eutrophication status (> 2.21 μ g/L) an indication of the presence of heterogeneous phytoplankton community during the wet season. The study highlights the use of nutrients and chlorophyll-a scaling to determine the eutrophication status of coastal area.

1. Introduction

Tropical estuaries are highly productive due to the essential features of mangroves, which in turn modify the biogeochemistry, nutrients distributions and characteristics of the phytoplankton biomass of the coastal systems (Alongi, 2001; Burford, 2008). Oceans are ecosystems that are guite vulnerable to pollution, they are made up of continental shelf and deep sea. The continental shelf and estuaries are the most productive in terms of food supply and are also more susceptible to pollution loads from sediments transported from tributaries (Eruola et al., 2011). Coastal waters serve as interface between terrestrial environments and the open ocean. They are an important natural resources, esteemed for their ecological richness as well as for the many human activities they support (Ajibare, 2014). The continental shelf and estuaries are continuously under the threat of pollution by biological, physical and chemical contaminants that emanate mainly from weathering, hydrological features, precipitation, erosion, industrial activities, sewage discharge, agricultural land use, and the human exploitation (Liao et al., 2008; Salim and Ashok, 2014). Nutrient concentrations are a common measure in evaluating trophic levels of coastal ecosystems (Balogun and Ajani, 2015). Chronic allochthonous nutrient inputs occur in aquatic ecosystems either from diffuse sources, such as fertilizers or from point sources (e.g., urban and industrial sewage; Popoola et al., 2015). These have led to a chain of events starting from accelerated growth of primary producers (phytoplankton, macroalgae and aquatic plants), to oxygen depletion, and accumulated massive death of aquatic organisms (Cloern, 2001). Nitrogen and phosphorus constituents

play a key role in determining the ecological status of aquatic systems, primary productivity and carbon sequestration in coastal waters. They can speed up eutrophication (a reduction of dissolved oxygen in water).

Most studies addressing the causes of eutrophication have concentrated on the elements nitrogen and phosphorus, because both nutrients are majorly discharged by human activities. Silicate, however, also plays a crucial role in algal growth and species compositions, for example, the growth rates of diatoms (silica-shelled phytoplankton) are determined by the supply of silicate (Ittekkot et al., 2000). In the estimation of primary productivity, the Chlorophyll *a* indicator is an acceptable and reliable proxy in estimating micro-algal or phytoplankton production levels in aquatic ecosystems (Onyema, 2013). Increase in the phytoplankton biomass can be measured as an increase in the chlorophyll-a concentration. Therefore, chlorophyll-a is a useful expression of phytoplankton biomass and is arguably the single most responsive indicator of nitrogen and phosphorus enrichment in the marine system (Harding, 1994; Balogun and Ajani, 2015).

The Ilaje estuary (Fig.1) is a transgressive mud sector in the southwest Nigeria, and are known for sea foods (e.g., fish, crabs, and periwinkles; Ololade et al., 2008). Pollution there-in are liable to have national, global and ecological health effects, because they are one of the typical estuaries in Nigeria that empty into the Atlantic Ocean. (Adebowale et al., 2008; Ajibare, 2014).

The aim of this research was to: (i) evaluate the nutrient (nitrate, nitrite, phosphate and silicate) status in Ondo coastal waters in response to the stress caused by anthropogenic inputs from land use changes, agriculture, and industries. (ii) determine eutrophication status of the study area using chlorophyll-a scaling proposed by Karydis (1999) and modified by Alexandra *et al.* (2005) as an indicator.

2. Materials And Methods

This study was conducted on the coastal region of Ondo State (Lat. 50.50 'N – 60.09 'N and Lon-. 40.45 'E – 50.05 'E). Total area covered by the study was about 500 km² with emerging communities dispersed within the coast and an increasing population size of 2.2% annually (Adebowale et al., 2008). Tidal regime in the study area are semi-diurnal and meso-tidal, with a range of 1m to 3m from the West of Benin River Estuary to the Calabar with range of spring tide, varying from 1m in the West of the Benin River to the Calabar Estuary (Sexton and Murday, 1994) (Fig.1).

Trading, fishing and farming are the primary occupation of the coastal dwellers, and the area is known for seafood production of diverse species of finfish, crabs, and periwinkles. (Olatunji-Ojo et al., 2019). The fieldwork was conducted in the study area during the rainy period (wet season), in August 2019. Water samples were collected from 32 sampling stations (1-32; Table 1) at depths range between 1.2 and 2.8 m. The sampling stations consist of two estuaries Awoye and Abereke which eventually empties into the Atlantic Ocean. Six stations (A1-A6) were sampled towards the Awoye Estuary, while, seven stations (AB1-AB7) were sampled towards Abereke Estuary Additionally, sampling was conducted at twelve stations (I1-

112) along the communities that settle along the rivers where there are reported cases of human-induced activities arising from marine transportation, oil dispensing, local and international petroleum marketing, pipeline vandalization and seepages, and illegal sand mining activities (Nkwoji et al., 2016). Seven stations (C1-C7), with less population density, and low anthropogenic influence, but characterized by vegetation and mangroves features were selected as control stations (Table 1).

Sampling and Preservation

Water samples were collected with a 2-litres plastic van Dorn sampler into acid-cleaned polyethylene bottles and per-chloric acid was used to fix nutrients immediately. The water samples were then filtered through membrane filters of 0.45 micrometer pore size at the time of sampling and then preserved in accordance with standard method (APHA, 1995). Nitrite and nitrate were analyzed using the standard pink azo-dye methods. Phosphate and silicate were determined using the molybdenum-blue methods. In all cases the dissolved inorganic nutrient analyses followed the methods of Parsons *et al.*, (1984). The Phytoplankton pigments (Chlorophyll-*a*) samples were obtained by filtering the water sampled for each set of samples collected from the creek within 24hrs through Whatman GF/C glass fibre filters (approximately1.2 μ m pore size). Filters and water samples were stored frozen (-20 °C) until analysis. Filters were transferred to tubes containing 90% aqueous acetone solution, ground with a Teflon pestle, and the Chl-*a* extracted in the dark during 24 hours. Extracts were then centrifuged at 300g for 15 minutes and analyzed spectrophotometrically according to the method of Parsons *et al.*, 1984. The pigment concentration was calculated as follows:

Chlorophyll-a(μ g/L) = [26.7*(A664b-A665a)*V extract)/V filtered*L]

Where:

V _{extract} = volume of extract (mL)

V $_{filtered}$ = volume of sample filtered (L)

L = light path length or width of cuvette, cm

664b = corrected absorbance of extract before acidification

665a = corrected absorbance of extract after acidification

The value 26.7 is the absorbance correction factor (A×K)

A = absorbance coefficient for chlorophyll a at 664nm = 11.0

K = ratio expressing correction for acidification = 2.43

Temperature, salinity, dissolved oxygen and pH were determined *in-situ* across the 32 stations with the use of Horiba U-52 multiwater parameters sensor to complement the nutrient and chlorophyll-a

measurements.

Data Analysis

Data obtained from physical and chemical measurements were statistically analyzed for variance using the Statistical Package for Social Sciences (SPSS), Version 20.0 and was tested at a level (P<0.05) for significance. The mean values were compared with the water quality criteria of the World Health Organization (WHO, 2008).

3. Results And Discussions

Nitrate is the final oxidation product of other nitrogen compounds (nitrification) in toxic seawater having a high redox potential. The nitrate form is generally considered the most stable and predominant dissolved inorganic nitrogen in oxygenated sea water (Al-Akhaly et al., 2020). Nitrate concentrations in both (Awoye and Abereke) estuaries follow similar trends, with a range of 1.85-5.16 mg/l and 3.20-6.98 mg/l respectively (Fig.2a-2b). The nitrate concentration decreases with distance from the Awoye estuary (e.g., from station A2-A6, mean value 3.28 ± 1.45mg/L) in contrast to the Abereke estuary (mean concentration 4.86 ± 1.55mg/L). The mean nitrate concentrations of the impacted and the control stations are 3.54 ± 1.77mg/L and 4.27 ± 1.89mg/L respectively (Fig.2c, Table 2). The control stations showed a decreasing concentration from station C4-C7 (Fig. 2d). The nitrate values in the study area were high compared to the reported values (1.24µg/L and 1.34±0.074mg/L) from the Ondo coastal water (Adebowale et al., 2008 and Bolarinwa et al., 2016). High nitrate levels in the study area could be caused by influx of nitrogen rich flood water arising from the use of nitrogen containing fertilizers, domestic sewage, municipals discharge, animal manure used on cropland, and naturally from atmospheric deposition and the oxidation of ammonia. These influx bring about large amount of contaminated water into the impacted areas and create the formation of algal blooms in typical coastal environments (Sahoo et al., 2016). Accumulation of nutrients from different anthropogenic sources, or enhanced primary productivity could be responsible for highest nitrate concentrations (6.98mg/l) recorded at Abereke Estuary (Table 2). Nitrate concentrations in the study area were within the maximum limit quoted by WHO (2008) (50mg/L), and contributed approximately 21% of the total analyzed nutrient in the study area (Fig.3). Nitrate showed a significant strong positive correlation (p<0.01, r= +0.886) with chlorophyll a (Table 3), with significant difference across the stations. The bi-plot (Fig.4) and the low N/P values (<0.25) from 16 (Redfield ratio; Redfield, 1958; Burfold, 2008) (Table 2) showed that nitrate accounted for the high chlorophyll-a concentrations in the study area and further suggest that nitrate is likely the primary limiting nutrient for phytoplankton production. This study differs slightly from the work of Pérez-Ruzafa et al., (2019) who reported that nitrate, phosphate and silicate showed a significant positive correlation with chlorophyll-a in Mar Menor coastal Lagoon, Spain. Similar studies in the North America coastal systems reported nitrogen as the limiting nutrients for algal populations (Elser et al. 1990 and Downing, 1997).

Nitrite occurs in an intermediate oxidation state between ammonia and nitrate, it can appear as a transient species by the oxidation of ammonia or by the reduction of nitrate (James and Mary, 2015). The

nitrite concentrations of Awoye and Abereke estuaries showed similar trends (Fig. 5a-b), and ranged between 0.01-0.08mg/L and 0.02-0.08mg/L with mean value of 0.04±0.03mg/L and 0.06±0.05mg/L respectively (Table 2). The highest nitrite concentration (0.27mg/L) was recorded at station 112 (Table 2) and suggest high anthropogenic sourced effluents at the impacted stations (Table 1). The statistical biplot further affirms the high concentration of nitrite at the impacted stations (Fig.4). The maximum permissible limit of nitrite for Tilapia production is 0.06 mg/l (Rachman and Adi 2005; El Zokm et al., 2018). The results obtained from our study area suggest that Tilapia will thrive at the Awoye (A1-A6) and Abereke (AB1-AB6) estuaries and the control stations (C1-C6), with mean nitrite values of 0.04 ±0.01mg/L; 0.06±0.05mg/L and 0.05±0.05mgL respectively. However, the mean nitrate concentration of 0.13mg/L at the impacted stations (I1-I12) suggest an unfavorable environments for the Tilapia growth. The non-fishing activities in the impacted stations further support these assumptions. Generally, the values of nitrite recorded in the three (estuaries, control and impacted) study locations were within the maximum limit of 3.0mg/l stipulated by WHO (2008). Nitrite contributed the least percentage (<1%) to the overall nutrient analyzed in this study (Fig.3). In comparison to other studies, the nitrite concentrations in our study is similar to work of Tadesse et al., (2018) who recorded a range of 0.02 to 0.58 mg/L at Rebu river in Oromia region, Ethiopia, East Africa.

Phosphorus plays a major role in biological metabolism. It is an essential nutrient element in photosynthesis and other metabolic processes in plants (El Zokm et al., 2018). Higher phosphate concentrations were recorded at Abereke and Awoye estuaries with a mean value of 14.76±2.17mg/L and 8.68±2.60mg/L respectively (Fig.5, Table 2). The phosphate concentrations in our study area were higher than nitrate values. The phosphate concentrations showed similar trends with the chloropyll-a concentrations at the Abereke and Awoye Estuaries with mean values of 18.94±1.83mg/L and 11.29±4.65mg/L respectively (Table 2). These similar trends suggest the occurrence of heterogeneous phytoplankton biomass and productivity at these estuaries. High phosphates concentrations at these estuaries may promote the production of microbes and phytoplankton.

The bi-plot showed correlations among dissolved oxygen (DO), temperature and phosphates (Fig.4). These correlation suggests an enhanced oxygenation conditions which favours the high production of phosphates in the study area. The enriched (>5.0mg/I) DO values across the Abereke and Awoye estuaries (Table 4) further supports these assumptions. Other human induced factors such as inorganic fertilizer , run-off that are composed of dissolved and suspended phosphate, organic waste and effluents from detergents and laundries can trigger the high mean phosphate concentration of the impacted stations and the control stations (Fig 6c-d). Additionally, these observed high phosphate concentration can over-fertilize phytoplankton in the coastal waters and fuel eutrophication in the system. The Phosphate values in this study were above the permissible limit of 5mg/L stipulated by WHO (2008) across the sample stations except at C1, C3, C4, I2, I3 and I7 (Table 2). These results corroborate the work of Ladipo *et al.*, (2012) who reported a mean phosphate concentrations of 9.75±3.24 mg/L in Lagos coastal water, south western Nigeria. The statistical analysis at 95% confidence level also showed significance differences among the sample stations. Phosphate contributed 49% percentage to the overall nutrient analyzed in the study area (Fig.3).

The presence of silicate in aquatic environment is very important for growth of diatoms, due to considerable amounts of silica in the frustuleThe silicate concentration was higher than that of nitrate and nitrite and this could be due to heavy influx of freshwater derived from land drainage carrying silicate leached out from rocks and also from bottom sediments exchanging with overlying water due to the turbulent nature of the coastal water (Rajasegar, 2003; James and Mary, 2015). It can also be sourced from decaying of existing silicate shells from coastal ecosystems. The highest silicate concentration (9.36mg/l) was recorded at the impacted station (I9, Fig.7, Table 2), which support the influence of anthropogenic effluent from discharged run-off at the impacted station, compared to the Abereke and Awoye estuaries. The low pH (<6) and dissolved oxygen (<5mg/L) concentrations at the impacted stations (I2, I4-I9, I11-I12; Table 4) are lower than the specified limit of the WHO (2008), which further indicate anthropogenic sourced pollutants at the impacted stations. The bi-plot (Fig.4) further showed enhanced concentrations of silicate at the impacted stations, which affirm anthropogenic source to the silicate concentrations of our study area. The silicate in the study area was higher when compared to (29.72±8.39 µg/l) recorded in the Gulf of Aden and Arabian Sea Coast, Yemen (Al-Akhaly et al., 2020). However, our reported values were lower when compared to the reported values of Amaranadha et al., (2015) and Bolarinwa et al., (2016) who recorded mean concentrations of 28.29mg/L and 11.80mg/L in the Coastal Water of Pulicat Lagoon (India) and Ondo State, Nigeria respectively (Table 5).

Chlorophyll-a

Phytoplankton has been used as an indicator of change in nutrient loads and also serves as a major group for assessing eutrophication in marine systems. Indeed, its assessment has been required by different legislations (Borja et al., 2012; Garmendia et al., 2013; Alexandra et al., 2015). Chlorophyll-a scaling can be a promising tool if applied at spatial structures and therefore, heterogeneous water masses can be identified regarding their trophic state (Michelakaki and Kitsiou, 2005; Karydis., 2009). Alexandra et al. (2005) modified chlorophyll-a concentrations scale proposed by Karydis (1999) to comply with the five levels of ecological status implied by the Water Framework Directive (WFD). A new eutrophication scale based on chlorophyll-a concentrations was therefore proposed: < $0.1 \mu g/L$ high, 0.1 $-0.4 \mu g/L$ good, $0.4 - 0.6 \mu g/L$, moderate, $0.6 - 2.21 \mu g/L$ poor and $> 2.21 \mu g/L$ bad. Chlorophyll-a varied between 4.28-14.97 µg/L at the Awoye Estuary; 17.11-21.38 µg/L at the Abereke estuaries. The chloropyll-a concentrations at the impacted stations and control stations ranged from 4.28-19.26 µg/L and 5.38-19.96 µg/L respectively (Fig. 8, Table 2). The recorded values across stations showed that the study area can be classified as bad eutrophication status. Broad range of chlorophyll-a content in the study area could be due to the presence of heterogeneous phytoplankton community during the time of sampling (Titus et al., 2017). The recorded low values at A4 and I6 (<5 µg/L) could be attributed to turbidity of the water, which minimized light penetration and eventually led to low concentration of phytoplankton biomass at the two stations. In comparison to other stations, the mean concentrations of chlorophyll-a of our study area (Table 2) is lower to the reported values of Marthe et al., (2015) who recorded 19.2µg/L at Coastal Potou Lagoon, Côte d'Ivoire.

4. Conclusion

The aim of this research is to evaluate the nutrient (nitrate, nitrite, phosphate and silicate) status in response to the stress caused by anthropogenic inputs from land use changes, agriculture, and industries, and eutrophication status of the Ilaje coastal waters, and estuaries, southwest Nigeria, using chlorophylla as an indicator. Thirty-two stations consist of two estuaries Awoye (A1-A6), Abereke (AB1-AB7), anthropogenic impacted stations (I1-I12) and control stations (C1-C7) were sampled.

Our study reveals that the influx of contaminants coming from domestic and industrial effluents, urban storm, and agricultural run-offs has led to the high nitrite, nitrate and silicate concentrations, together with low dissolved oxygen (<5mg/L) and acidic pH (<6) at majority of the impacted stations.

From a biplot of variables it is evident that nitrate and chlorophyll-a values are positively correlated and consequently both are prime factors for primary production in the impacted areas. The level of nitrate in these areas can be traced to diffuse delivery through farmland fertilizer application from adjacent coastal activities. Major factors determining variability in Abereke estuary include phosphate, dissolved oxygen, salinity and temperature. The modified chlorophyll-a concentrations scale further showed that the study area is characterized as bad eutrophication status (> $2.21 \mu g/L$) an indication of the presence of heterogeneous phytoplankton community during the wet season period of the sampling.

Detailed information on seasonal variability of parameters in relation to anthropogenic pressures in the estuaries is not fully resolved in this study. This primarily is the situation as our data is limited to wet months of the year. However, a future study program that considers variability in dry months should robustly complements the present work and project a seasonal dynamic that is representative.

Declarations

ACKNOWLEDGEMENTS

The authors wish to acknowledge other researchers in the Department of Physical and Chemical Oceanography of the Nigerian Institute for Oceanography and Marine Research (NIOMR) for their cooperation during the sampling period.

References

Adebowale K.O, Agunbiade FO, Olu-Owolabi BI. (2008). Impacts of natural and anthropogenic multiple source of pollution on the environmental conditions of Ondo State coastal water Nig J Env Agric Food Chem; 2798-2810.

Adesuyi Adeola Alex, Nnodu Valerie Chinedu, Njoku Kelechi Longinus, et al (2015). Nitrate and phosphate pollution in surface water of Nwaja creek, Port Harcourt, Niger Delta, Nigeria. International Journal of Geology, Agriculture and Environmental Sciences, 3(5): 14-20

Ajibare, A. O., (2014). Assessment of Physico-Chemical Parameters of Waters in Ilaje Local Government Area of Ondo State, Nigeria.International Journal of Fisheries and Aquatic Studies. 1(5): 84-92

Al-Akhaly Ibrahim A., Al-Shwafi Nabil A. and Al-Kabsh Shehab A. (2020). Distribution of Nutrient Salts and Chlorophyll-a in Surface Water along the Gulf of Aden and Arabian Sea Coast, Yemen. SQU Journal for Science, 25(1), 17-25

Alexandra P, Nomiki S, Eleni R, et al (2015). Methods of eutrophication assessment in the context of the water framework directive: Examples from the Eastern Mediterranean coastal areas, Continental Shelf Research, Volume 108, 2015, Pages 156-168, ISSN 0278-4343, https://doi.org/10.1016/j.csr.2015.05.013

Alkan Ali, Serdar Serkan, Fidan Dilek, et al (2013). Physico-Chemical Characteristics and Nutrient Levels of the Eastern Black

Sea Rivers. Turkish Journal of Fisheries and Aquatic Sciences 13: 847-859

Amaranadha N., Sundara raja B.C., Balayerikala N., (2015). Physico-Chemical Parameters for Coastal Water of Pulicat Lagoon, South East Coast of India. Indian Journal Of Research, 4(10): 153-155

APHA, 1995. Standard methods for the examination of water and waste water, Washington, DC, American Public Health Association, 19th ed.

Balogun K. J., and Ajani E. K., (2015).Spatial and temporal variations of Phytoplankton pigments, Nutrients and Primary productivity in water column of Badagry Creek, Nigeria.American Journal of Research Communication. 3(7): 157-172

Bolarinwa J.B., Fasakin E.A., Fagbenro A.O., (2016). Physicochemical Analysis of the Coastal Waters of Ondo State, Nigeria. International Journal of Research in Agriculture and Forestry, 3(11): 13-20

Borja A., Basset A., Bricker S., et al (2012). Classifying ecological quality and integrity of estuaries. In: Wolanski, E., McLusky, D. (Eds.), Treatise on Estuarine and Coastal Science. Academic Press, Waltham, pp. 125–162.

Cloren JE (2001.) Our evolving conceptual model of thecoastal eutrophication problem; Marine EcologyProgress Series 211:223-253.

Downing, J.A. 1997. Marine nitrogen: phosphorus stoichiometry and the global N:P cycle. Biogeochemistry, **37**: 237–252.

Elser, J.J., Marzolf, E.R., and Goldman, C.R. 1990. Phosphorus and nitrogen limitation of phytoplankton growth in the freshwaters of North America: a review and critique of experimental enrichments. Can. J. Fish. Aquat. Sci. **47**: 1448–1477

El Zokm Gehan M., Tadros Hermine R.Z., Okbah Mohamed A., et al (2018). Eutrophication assessment using TRIX and Carlson's indices in Lake Mariout Water, Egypt. Egyptian Journal of Aquatic Biology & Fisheries, 22(5): 321-339

Eruola, A. O., Ufoegbune, G. C.,Ojekunle, et al (2011). Analytical Investigation of Pollutants in Lagos Coastal Waters, Nigeria.Advances in Analytical Chemistry. 1(1): 8-11

Garmendia M., Borja A., Franco J., et al (2013). Phytoplankton composition indicators for the assessment of eutrophication in marine waters: Present state and challenges within the European directives. Mar. Pollut. Bull. 66 7–6.

Harding, L.W., (1994). Long-term trends in the distribution of phytoplankton in Chesapeake Bay: roles of light, nutrients and stream flow. Marine Ecology-Progress Series 104: 267-267

Ittekkot V., Humborg C., Schäfer P., (2000). Hydrological Alterations and Marine Biogeochemistry: A Silicate Issue?. BioScience 50(9): 776-782

James Balgan Anand D. and Mary Jelastin Kala S (2015). Study on Hydrographic properties in the coastal waters along South East Coast of India. American Journal of Engineering Research, 4(6): 203-214

Karydis M (1999) Evaluation report on the eutrophication level in coastal Greek areas. University of the Aegean, Mytilini, February 1999 (in Greek)

Karydis M (2009). **E**utrophication assessment of coastal waters based on indicators: a literature review. Global NEST Journal, 11(4):373-390.

Ladipo M.K., Ajibola V.O. and Oniye S.J (2012), Application of Multivariate Statistical Methods to Assessment of Water Quality in Selected Locations of Lagos Lagoon, Nigeria, Environmental Research Journal, **6**(3), 141 -150.

Liao, S., Gau, H., Lai, W., Chen, J., and Lee, C (2008). Identifiation of pollution of Tapeng Lagoon from neighbouring rivers using multivariate statistical method.Journal of Environmental Management, 88(2): 286–292

Marthe Y.K., Lanciné G.D., Bamory K., Aristide D.G., Ardjouma D (2015). Seasonal and Spatial Variations in Water Physicochemical Quality of Coastal Potou Lagoon (Côte d'Ivoire, Western Africa). Journal of Water Resource and Protection, (7):741-748

Michelakaki M., and Kitsiou D (2005) Estimation of anisotropies in chlorophyll α spatial distributions based on satellite data and variography, *Global Nest Journal*, **7**, 204-211.

Onyema I.C (2013). Primary production and nutrients in an Open Tropical Lagoon. Nature and Science.11(3): 102-106

Parsons, T. R., Y. Maita, and C. M. Lalli (1984). A manual of chemical and biological methods for seawater analysis. Pergamon. Press 173.

Pérez-Ruzafa A., Campillo S., Fernández-Palacios J.M., et al (2019). Long term dynamics in nutrients, chlorophyll a, and water quality parameters in a coastal lagoon during a process of euthrophication for decades, a sudden break and a relatively rapid recovery. Frontiers in Marine Science, 6(26): 1-23

Popoola S.O, Nubi, O.A., Adekunbi, F.O, et al (2015). Vertical profiling and contamination risk assessment of some trace metals in Part of the Lagos Lagoon axis. International Journal of Science, Technology and Society 3(4): pp 186-193.

Rachman B., Adi S., (2005). Practices for Carp and Tilapia Grow Out in Cages, Sukabumi Research Water Aquaculture Development Center, Department of Fisheries and Marine Affairs, West Java, Indonesia.

Rajasegar M (2003). Physico-chemical characteristics of the Vellar estuary in relation to shrimp farming. *J. Environ. Biol. 24:* 95-101.

Redfield, A.C (1958). The biological control of chemical factors in the environment. American Science 46, 205–222.

Sahoo M, Mahananda M R, Seth P (2016). Physico-Chemical Analysis of Surface and Groundwater around Talcher Coal Field, District Angul, Odisha, India. Journal of Geoscience and Environment Protection, 4: 26-37

Salim A. B., Ashok K. P (2014).Surface Water Quality Assessment of Wular Lake, A Ramsar Sitein Kashmir Himalaya , Using Discriminant Analysis and WQI. Journal of Ecosystems. 1-18

Titus L.P., Deepananda Ashoka K.H.M, Cumaranatunga P.R.T (2017). Physicochemical environment of Malala Lagoon in Southern Sri Lanka. Sri Lanka J. Aquat. Sci., 22(2): 129-139

WHO (2008). Guidelines for Drinking Water Quality: Recommendations. 3rd edition. Geneva: World Health Organization; 2008; 1:515.

Tables

Table 1. Sampling stations, codes and their coordinates.

Station number	Station Code	Latitude (N)	Longitude (E)	Station Name
1	A1	5.913333	4.965106	Awoye Estuary and nearest station
2	A2	5.912	4.965	Awoye Estuary and nearest station
3	A3	5.91247	4.966616	Awoye Estuary and nearest station
4	A4	5.916983	4.970616	Awoye Estuary and nearest station
5	A5	5.92363	4.966	Awoye Estuary and nearest station
6	A6	5.931966	4.95865	Awoye Estuary and nearest station
7	C1	5.940866	4.95053	Control area
8	C2	5.944566	4.943966	Control area
9	C3	5.952	4.936	Control area
10	C4	5.95855	4.9275	Control area
11	C5	5.97795	4.91066	Control area
12	C6	6.001567	4.888817	Control area
13	C7	6.015433	4.8772	Control area
14	11	6.0637	4.82555	Impacted area
15	12	6.07355	4.814783	Impacted area
16	13	6.101066	4.789833	Impacted area
17	14	6.109533	4.78285	Impacted area
18	15	6.119717	4.76975	Impacted area
19	16	6.128933	4.7579	Impacted area
20	17	6.1333	4.749266	Impacted area
21	18	6.148717	4.73115	Impacted area
22	19	6.9789	4.715083	Impacted area
23	110	6.176517	4.7024	Impacted area
24	111	6.184825	4.693966	Impacted area
25	112	6.192717	4.682166	Impacted area
26	AB1	6.20485	4.670933	Abereke Estuary and nearest station
27	AB2	6.23	4.649683	Abereke Estuary and nearest station

1				
28	AB3	6.2424	4.636633	Abereke Estuary and nearest station
29	AB4	6.242517	4.622566	Abereke Estuary and nearest station
30	AB5	6.237433	4.617133	Abereke Estuary and nearest station
31	AB6	6.237033	4.61195	Abereke Estuary and nearest station
32	AB7	6.234217	4.618217	Abereke Estuary and nearest station

Table 2. Concentrations (mg/L) of nitrates, nitrite, phosphate, silicate and chlorophyll-a and nitrate/phosphate ratio of the study area

Sample No.	Nitrate (mg/L)	Nitrite (mg/L)	Phosphate (mg/L)	Silicate (mg/L)	Chloropyll-a (mg/L)	N/P
A1	3.22	0.08	12.45	3.12	12.83	0.006
A2	4.94	0.02	6.28	3.33	14.97	0.003
A3	5.16	0.06	8.43	4.26	17.11	0.007
A4	1.85	0.02	10.24	5.86	4.28	0.002
A5	2.36	0.01	9.3	6.74	9.98	0.001
A6	2.12	0.03	5.39	4.69	8.55	0.006
Mean	3.28	0.04	8.68	4.67	11.29	0.005
SD	1.49	0.03	2.6	1.42	4.65	0.012
C1	5.88	0.02	4.22	8.93	18.18	0.005
C2	5.94	0.16	5.74	5.44	19.96	0.028
C3	4.03	0.09	2.46	5.07	14.97	0.037
C4	6.46	0.02	4.71	4.34	19.96	0.004
C5	3.58	0.03	8.37	7.21	13.9	0.004
C6	1.61	0.04	7.29	7.82	5.35	0.005
C7	2.37	0.01	8.98	6.86	8.55	0.001
Mean	4.27	0.05	5.97	6.52	14.41	0.008
SD	1.89	0.05	2.37	1.64	5.67	0.021
11	1.78	0.11	5.26	5.49	9.98	0.021
12	4.8	0.09	4.12	4.47	15.68	0.022
13	5.52	0.03	3.85	7.86	17.11	0.008
4	2.87	0.04	10.64	6.53	11.76	0.004
15	1.93	0.02	5.04	4.95	5.7	0.004
16	0.67	0.07	6.38	5.57	4.28	0.011
17	2.48	0.58	2.76	3.29	14.97	0.21
18	3.88	0.12	11.72	6.95	16.04	0.01
19	5.92	0.05	12.88	9.36	19.94	0.004
110	6.18	0.02	12.58	4.24	19.25	0.002
111	2.47	0.13	11.29	7.28	12.83	0.012

112	4.01	0.27	10.02	5.67	19.25	0.027
Mean	3.54	0.13	8.05	5.97	13.9	0.016
SD	1.79	0.16	3.8	1.71	5.17	0.042
AB1	3.37	0.15	14.84	2.77	17.11	0.01
AB2	6.86	0.08	15.61	4.28	21.38	0.005
AB3	4.29	0.03	14.82	5.46	17.82	0.002
AB4	4.15	0.02	11.59	3.11	19.25	0.002
AB5	3.2	0.09	12.26	4.82	17.11	0.007
AB6	6.98	0.04	16.73	4.83	21.38	0.002
AB7	5.14	0.02	17.48	5.8	18.53	0.001
Mean	4.86	0.06	14.76	4.44	18.94	0.004
SD	1.55	0.05	2.17	1.14	1.83	0.023

Table 3. Pearson correlation matrix between analyzed and chlorophyll-a (chl-a).

	Nitrate	Nitrite	Phosphate	Silicate	Chl-a
Nitrate	1				
Nitrite	-0.146	1			
Phosphate	0.247	-0.21	1		
Silicate	-0.039	-0.264	-0.079	1	
Chl-a	.886**	0.131	0.348	-0.154	1

** Correlation is significant at the 0.01 level (2-tailed).

Table 4. Concentrations of pH, dissolved oxygen (mg/L), Salinity (‰) and temperature (°C) of the study area.

Station number	Station Code	рН	DO (mg/L)	Salinity (‰)	Temperature (°C)
1	A1	6.07	9.62	2.70	24.33
2	A2	5.96	9.04	2.50	24.17
3	A3	5.99	8.86	2.40	24.12
4	A4	5.83	8.02	2.40	24.10
5	A5	5.87	8.06	2.30	24.05
6	A6	6.11	8.44	2.10	24.04
	Mean	5.97	8.67	2.40	24.14
	SD	0.11	0.62	0.20	0.11
7	C1	5.96	7.66	1.90	24.08
8	C2	6.07	7.59	1.80	24.05
9	C3	6.07	7.29	1.70	24.02
10	C4	5.63	6.76	1.20	24.06
11	C5	5.67	7.31	0.90	24.02
12	C6	5.17	5.78	0.90	23.87
13	C7	5	5.96	0.40	23.91
	Mean	5.65	6.91	1.26	24.00
	SD	0.43	0.77	0.56	0.08
14	1	5.2	6.03	0.00	23.88
15	12	4.72	3.99	0.00	23.91
16	13	5.49	5.08	0.30	23.99
17	14	5.31	4.21	0.00	24.12
18	15	5.19	4.48	0.40	24.21
19	16	5.18	4.34	0.40	24.31
20	17	5.28	3.51	0.50	24.48
21	18	5.76	4.16	1.10	24.53
22	19	5.98	3.87	0.80	24.52
23	110	6.55	6.63	1.01	24.71
24	111	6.19	4.79	1.90	24.23
25	112	6.66	4.98	3.50	23.96

	Mean	5.63	4.67	0.83	24.24
	SD	0.60	0.91	1.08	0.25
26	AB1	7.49	8.21	5.79	24.81
27	AB2	7.66	8.43	5.78	25.11
28	AB3	7.96	8.06	6.00	25.01
31	AB6	8.02	9.48	6.43	25.01
32	AB7	8.03	11.73	6.37	25.07
	Mean	7.83	9.18	6.07	25.00
	SD	0.24	1.53	0.31	0.12

Table 5. Comparison of Nutrients concentrations of the study area with other published values

Location/ (authors)	Nitrate (mg/L)	Nitrite (mg/L)	Phosphate (mg/L)	Silicate (mg/L)	Chl-a (mg/L)
Coastal Waters of Ondo State, Nigeria	1.34	0.27	3.58	11.8	-
(Bolarinwa et al., 2016)					
Coastal Water of Pulicat Lagoon, India	-	-	-	28.29	-
(Amaranadha et al., 2015)					
Lagos Lagoon Nigeria	4.86		9.75	-	-
(Ladipo et al., 2012)					
Coastal Potou Lagoon, Côte d'Ivoire	0.003	0.004	0.063	-	0.02
(Marthe et al., 2015)					
llaje coastal water, Ondo state Nigeria	3.94	0.08	9.18	5.51	14.62
(This study)					

Figures



Map of the study area showing the sampling locations.



Nitrate concentrations in surface water.



Percentage distributions of Nutrients in the study area



bi-plot statistical distribution showing that the nutrient distribution at Awoye-Abereke estuary is influenced different variables



Nitrite concentrations in surface water.



Silicate concentrations in surface water.



Phosphate concentrations in surface water.



Chlorophyll-a concentrations in surface water.