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Nutrient Fluxes in Polluted Sediments of the Bonny Estuary in Nigeria: An Assessment of the Role of Oxygen

Ogbuagu Dike Henry*, Ogoke Fidelis Chukwuma, Mbuka-Nwosu Iheoma Ezichi

Department of Environmental Technology, Federal University of Technology, Owerri, Nigeria

Abstract

The role played by oxygen in the degradation of nutrients (NO_3^-, PO_4^{3-} and SO_4^{2-}) in sediments of the Bonny Estuary, which is repository to pollutants arising from various industrial and shipment activities in its catchment was investigated. Sediment samples were monitored under aerobic and anaerobic conditions for nutrient fluxes. Harvests and spectrophotometric analyses were made on Days 0, 14, 28 and 42. NO_3^- ion concentrations degraded from 10.21 to 2.72ppm in aerobic and 10.21 to 3.08ppm in anaerobic condition; PO_4^{3-} ions degraded from 122.6 to 92.5ppm in aerobic, and 122.6 to 102.2ppm in anaerobic conditions; while SO_4^{2-} ions degraded from 128.4 to 108.2ppm in aerobic, and 128.4 to 118.2ppm in anaerobic conditions. The degradations of PO_4^{3-} and SO_4^{2-} ions, as well as changes in pH differed significantly over the 42 days experimental period in both aerobic (Sig. F=0.000 each) and anaerobic conditions (Sig. F=0.003, 0.000 and 0.000 respectively) at $p<0.05$. There were also significant differences between degradations in aerobic and anaerobic conditions at the 95% confidence limit. Degradation was steady and the nutrients fluxes were oxygen- and time-dependent.

Keywords

Bonny Estuary, Nutrients Fluxes, Aerobic Condition, Anaerobic Condition, Sediments, Degradation

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1. Introduction

A great deal has been unravelled about the exchanges of oxygen in nutrients across the sediment-water interface and the dynamics of these interactions in estuarine and coastal ecosystems during the last several decades [1]. Boynton *et al*. [2] and Kemp and Boynton [3] observed that sediment oxygen consumption can be an important sink for oxygen and sediment nutrient releases can be a large internal source of both nitrogen and phosphorus to the water column. Both oxygen and nutrients are essential for phytoplankton growth, which can become excessive when nutrient supplies are large. Thus, sediment processes can play an important role in determining water quality conditions by lowering oxygen levels and promoting excessive algal growth.

Sediment investigation in certain seas such as Baltic Sea in South western Finland revealed that nutrients and heavy metals can be buried in marine sediment for different lengths of time, thus reflecting the environmental status of the area [4]. Some pollutants attach to suspended particles in the water and subsequently settle out to the bottom mud/sediment. Through complex chemical, physical and biological interactions, these contaminants may be further transformed and transported to other parts of the aquatic system. At elevated concentrations, contaminated sediments could contribute to many impaired uses in lakes, rivers, and harbours; including fish advisories, habitant impairments, and restriction on dredging.

In addition to providing important habitats for aquatic

* Corresponding author
E-mail address: dike.ogbuagu@futo.edu.ng (O. D. Henry)

organisms, sediments play a significant role in determining the overall environmental quality of an estuarine system. Because sediments are also an important biological habitat, uptake of toxicants into the food web are influenced by toxicant concentrations in the sediments. Contaminated sediments can have serious effects on living organisms [5, 6, 7, 8, 9, 10, 11] and the entire ecosystems [11], including higher mortality, reduced growth rates and impaired reproductive processes in marine organisms. Because many contaminants accumulate in food chains, they can also affect human health through trophic relationships.

Sediments of marine ecosystems are usually depleted of dissolved oxygen; a condition that is generally found in areas that have restricted water exchange. In most cases, oxygen is prevented from reaching the deeper levels by a physical barrier such as mud [12] as well as by a pronounced density stratification in which, for instance, heavier hyper-saline waters rest at the bottom of a basin. Anoxia, among other effects could tremendously slow down the rate of biodegradation of pollutants, especially of the persistent ones such as heavy metals, crude oil and other petroleum pollutants, even in nutrient rich regions.

With increasing inputs of such pollutants, including nutrients into Estuaries such as the Bonny Estuary in the Niger Delta of Nigeria by the many oil, gas, shipping, and ancillary companies in its vicinity, there is need to investigate the fate of the common and available nutrients in a simulated anoxic and oxygenated conditions as to infer natural removal pattern of the pollutants over time. The evaluation of exchanges between sediments and the water column, as well as mechanisms influencing these processes can provide some of the important information necessary to analyze water quality status of an estuary in particular, and coastal ecosystem in general. The outcome data can so be used as diagnostic and forecasting tools for static nutrient budget computations, calibration and verification of dynamic water quality models [1].

2. Materials and Methods

2.1. Description of Study Area

Bony is located between latitudes 4°22' and 4°32' N and longitudes 7°12' and 7°18' E (Figure 1) in the Niger Delta region of Nigeria. The weather is hot, humid, and subject to heavy rains for about nine months in the year. The ambient temperature is about 33°C during the day, with an average humidity of about 100%. The coolest time is early in the morning, with an average temperature of 22°C. It rains almost all year round in Bonny and the heaviest rains fall from May to October. Average rainfall for Bonny is 3800mm (15").

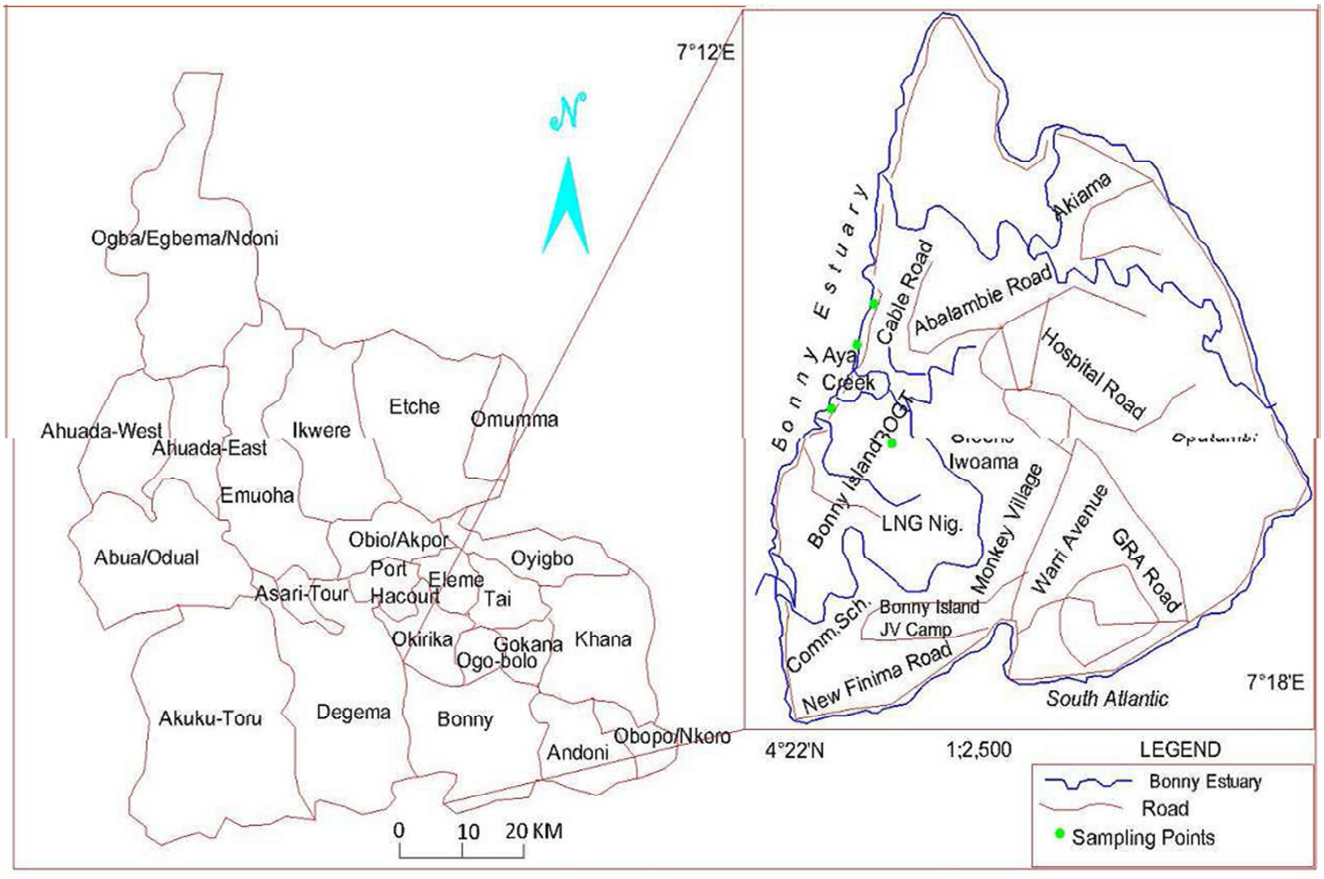

Figure 1. Map of Rivers State showing Bonny Estuary, the study area in the Bonny Local Government Area.

The Bonny Estuary is the main passage for merchant shipping to the inland port of Onne and for tankers and merchant shipping going to Port Harcourt and the Nigerian National Petroleum Corporation (NNPC) refined product terminal at Okirika in the region. The estuary receives effluents and other wastes from a number of industries and ancillary companies on the Island. The Bonny Oil and Gas Terminal (BOGT), the Nigerian Liquefied Natural Gas Complex (NLNG), and other service companies are all located close to the estuary.

2.2. Sample Collection

Sediment samples were collected from seabed at two points from the Bonny River, between the NLNG and the BOGT facilities. The coordinates of the sampling points were 4^0 25'698"North, $7^0$09'325'East and 4^0 26'546"North, 7^0 09'475"East for upstream and downstream sampling points respectively. A pre-grab sampler was deployed from the deck of a Vessel and successive grab samples from about 20 metres depth of the water were emptied into 5 litres container that was internally lined with aluminium foil to prevent external contamination. The collected sediment samples were labelled, transported to the laboratory and preserved in the refrigerator till when needed.

2.3. Laboratory Methods

2.3.1. Treatment of Sediments

The sediments were sieved with the Estuary water through 2.00, 1.00, and 0.50mm mesh size sieves to remove large stones, molluscs, crustaceans and other debris. After allowing them to settle over-night, 1kg of sediments were weighed out and homogenised by mixing thoroughly with the aid of a laboratory mixer for about 10 minutes. The mixer was washed and properly cleaned before mixing a new treatment. The initial concentrations of NO_3^-, PO_4^{3-} and SO_4^{2-} ions, as well as levels of pH in the sediments were determined according to standard methods.

The sediments were then dispensed into separately labelled Petri dishes, ensuring that three concentration treatments (denoted as TR.1, TR.2 and TR.3) were obtained in each experimental batch for a nutrient. The Petri dishes were carefully filled to the top, making sure that there were no air bubble trapped or overflow of sediments. Each concentration was prepared for both anoxic and aerobic conditions; making a total of 12 for anoxic and 12 for aerobic conditions.

2.3.2. Experimental Set-up, Monitoring and Harvest

The laboratory room condition was considered as aerobic environment, while an anoxic environment in the laboratory was created inside anaerobic jar placed in an incubator to simulate the wild sea bed. Samples for anoxic condition monitoring were packed in the anaerobic jar, while those for aerobic condition monitoring were kept under the laboratory condition. The anaerobic jar was further kept in the incubator at 18°C.

Sediments were harvested on days 0, 14, 28, and 42 for all the treatments and the nutrients as well as pH concentrations measured at the intervals.

2.3.3. Determination of Nutrients and pH

The mono-calcium-phosphate extraction method was used in the determination of sulphate in sediments. Ten grams of air-dried and sieved soil was put into a 50ml Erlenmeyer flask. Twenty five mililitres of monocalcium phosphate extracting solution was added and the resulting solution shaken at 200 oscillations per minute for 30 minutes. About 0.25 grams of charcoal was added to each sample and shaken for an additional 3 minutes. The solution was then filtered through a sulphate-free Whatman No. 42 filter paper. Ten millilitres of the filtrate was pipetted from the extraction process, selected into a 50ml Erlenmeyer flask, and 1ml of acid "seed" solution added. The solution was swirled and then 0.5g of barium chloride-di-hydrate crystals was added. The mixture was allowed to stand for one minute, then swirled using magnetic swirler in the flask frequently until the crystals were dissolved. Within 3 to 8 minutes, the transmittance was read using a spectrophotometer at a wavelength of 420nm. The absorbance reading was taken by plotting against concentration linear on graph paper. The sulphate concentration from the standard curve for 10 grams sample of soil was then calculated.

Nitrate ion concentrations were determined with the HACH spectrophotometer using the cadmium reduction method. Five grams of a representative sediment sample was shaken with 50ml of 1ml of potassium tetraoxosulphate (VI). Aliquot of the resulting extract was used to determine the nitrate content by the phenoldisulphonic acid method of Pansu and Gautheyrou [13].

For phosphate ions, the extracting solution was first prepared by adding 15ml of ammonium fluoride and 25ml of 0.5N hydrochloric acid to 460ml distilled water. One gram of air-dried sediment that had been sieved through a 2mm mesh size was weighed into a centrifuge tube and 7ml of the extracting solution added. This was shaken for one minute and then centrifuged. Two mililitres of the clear supernatant was transferred into a 20ml test tube, followed by the addition of 5ml distilled water and 2ml ammonium solution. The contents were mixed and 1ml of chloride solution added to it. Within 20 minutes, the percentage transmittance was

measured in a spectrophotometer at 660nm wavelength. The amount of phosphate ion in the sample was determined from the standard curve prepared with phosphate in sediment standard solution [13].

The method of Pansu and Gautheyrou [13] was also adopted in the determination of pH. Air-dried sediment sample was passed through a 2mm sieve and then 20g of it placed in a 50ml beaker. Fourty millilitres of distilled water was added to it and the mixture was stirred with glass rod and allowed to stand for 30minutes. The pH value was read off a Corning (model 7) meter.

2.3.4. Statistical Analysis

The MS Excel 2007 and SPSS V.22.0 softwares were used to analyse data. The One-Way Analysis of Variance (ANOVA) was used to test for homogeneity in mean variance of nutrients concentrations and pH over the experimental period at $p<0.05$. The post-hoc Duncan Multiple Range test was used to separate means, while the student's t-test was used to compare changes in concentrations of the nutrients and pH over the 42 days experimental period at the 95% confidence interval.

3. Results

3.1. Nutrient Fluxes and Time

Variations in mean concentrations of NO_3^-, PO_4^{3-} and SO_4^{2-} ions in sediments over the 42 days experimental period are shown in Figures 2-9. On Days 0, 14, 28, and 42, mean concentrations of NO_3^- ions in aerobic condition were 4.15, 3.88, 2.96 and 2.72 ppm respectively in treatment 1 (TR. 1), 9.84, 8.96, 7.83 and 6.13ppm in TR. 2 and 10.21, 10.02, 8.28 and 6.76ppm in TR. 3 (Figure 2). In anaerobic condition, the concentrations on the respective days were 4.21, 4.05, 3.18 and 3.08ppm in TR. 1, 9.84, 9.06, 8.86 and 8.62ppm in TR. 2 and 10.21, 10.05, 9.64 and 9.42ppm in TR. 3 (Figure 3).

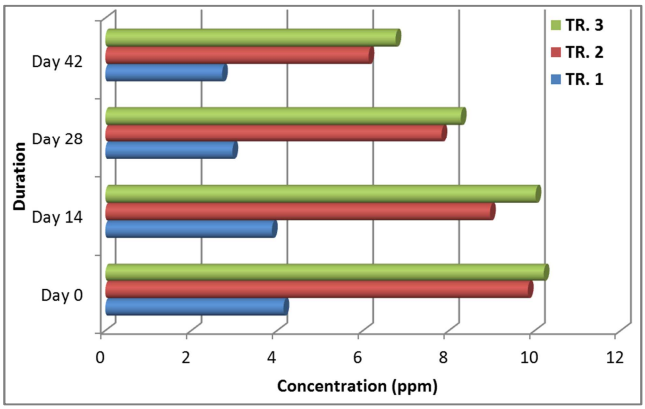

Figure 2. Mean variations in nitrate contents of sediments of the Bonny Estuary under aerobic condition for 42 days.

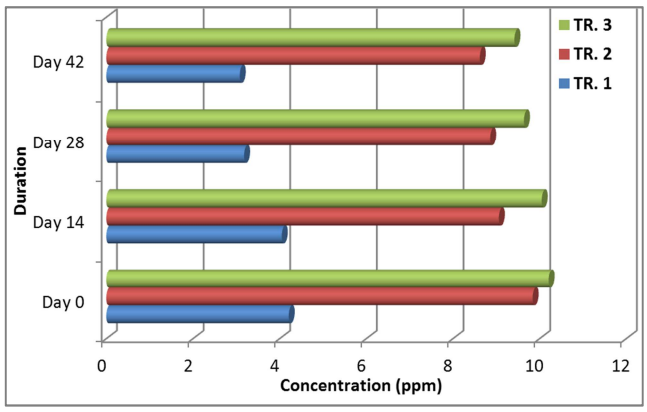

Figure 3. Mean variations in nitrate contents of sediments of the Bonny Estuary under anaerobic condition for 42 days.

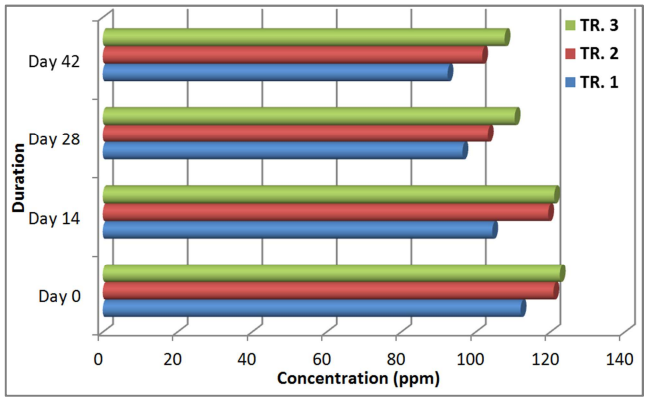

Figure 4. Mean variations in phosphate contents of sediments of the Bonny Estuary under aerobic condition for 42 days.

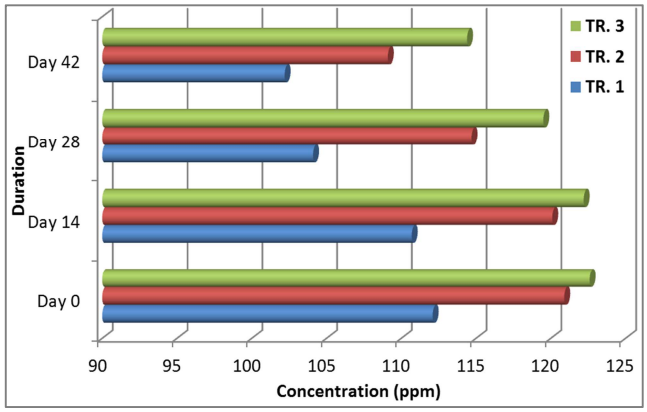

Figure 5. Mean variations in phosphate contents of sediments of the Bonny Estuary under anaerobic condition for 42 days.

On the respective days and in aerobic condition, mean PO_4^{3-} ion concentrations were 112.1, 104.5, 96.5 and 92.5ppm in TR. 1, 104.5, 96.5, 103.3 and 101.8ppm in TR. 2, and 122.6, 121.1, 110.5, and 107.8ppm in TR. 3 (Figure 4). In anaerobic condition, they were 112.1, 110.7, 104.1 and 102.2ppm in TR. 1, 120.9, 120.1, 114.7 and 109.1ppm in TR. 2 and 122.6, 122.2, 119.5 and 114.4ppm in TT. 3 (Figure 5).

Mean SO_4^{2-} ion concentrations in aerobic condition on the respective days were 128.4, 126.5, 119.3 and 108.2ppm in

TR. 1, 125.9, 123.6, 116.6 and 112.07ppm in TR. 2, and 126.40, 124.2, 118.4 and 113.5ppm in TR.3 (Figure 6). In anaerobic condition, it was 128.4, 125.0, 121.5 and 118.2ppm in TR.1, 125.9, 124.2, 120.7 and 119.4ppm in TR. 2 and 126.4, 125.3, 121.8 and 119.6ppm in TR. 3 (Figure 7).

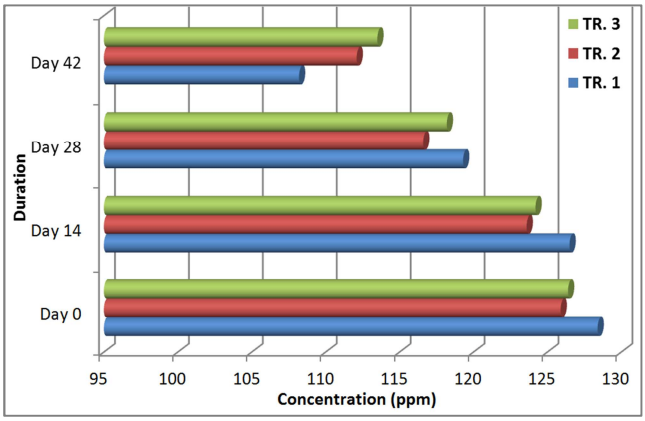

Figure 6. Mean variations in sulphate contents of sediments of the Bonny Estuary under aerobic condition for 42 days.

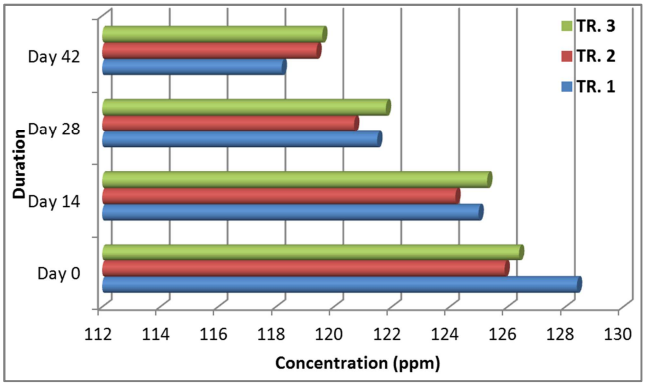

Figure 7. Mean variations in sulphate contents of sediments of the Bonny Estuary under anaerobic condition for 42 days.

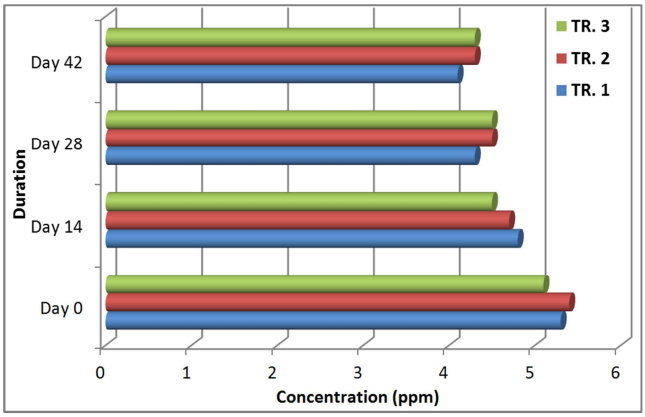

Figure 8. Mean variations in pH levels of sediments of the Bonny Estuary under aerobic condition for 42 days.

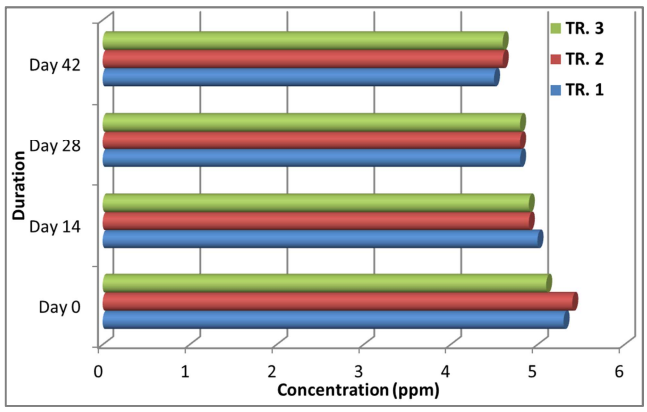

Figure 9. Mean variations in pH levels of sediments of the Bonny Estuary under anaerobic condition for 42 days.

Mean pH values in the sediments on the days under aerobic condition were 5.3, 4.8, 4.3 and 4.1 respectively in TR.1, 5.4, 4.7, 4.5, and 4.3 in TR. 2 and 5.1, 4.5, 4.5 and 4.3 in TR. 3 (Figure 8). In anaerobic condition, they were 5.3, 5.0, 4.8 and 4.5 in TR. 1, 5.4, 4.9, 4.8 and 4.6 in TR. 2 and 5.1, 4.9, 4.8, and 4.6 in TR. 3 on the respective days (Figure 9).

The ANOVA test revealed that over the experimental period, the concentrations of PO_4^{3-} and SO_4^{2-} ions, and pH differed significantly in aerobic (Sig. F=0.000 each) and anaerobic (Sig. F=0.003, 0.000 and 0.000 respectively) conditions at $p<0.05$.

A post-hoc mean separation using the Duncan Multiple Range test confirmed that in aerobic condition, NO_3^- ion concentrations were significantly different, and in anaerobic condition, there were no significant differences on all the days. PO_4^{3-} ion concentrations differed significantly between Days 0 and 42, 14 and 42 and 28 and 42, while SO_4^{2-} ion concentrations differed significantly between Days 0 and 14, 0 and 28, 0 and 42, 14 and 42, and 28 and 42 (Table 1).

3.2. Nutrient Fluxes and pH by Treatment

Mean separation using Duncan Multiple Range Test at $p<0.05$ revealed that under aerobic condition, NO_3^- ion concentrations differed significantly between TR. 1 and TR. 2, and between TR. 1 and TR. 3; PO_4^{3-} ion concentration differed between TR.1 and TR. 2 and TR. 1 and TR. 3; while SO_4^{2-} ion concentration and pH showed no significant difference between all the treatments. In anaerobic condition, NO_3^- ion concentrations differed significantly between TR. 1 and TR. 2, TR. 2 and TR. 3 and TR. 2 and TR. 3; PO_4^{3-} ion concentrations differed between TR. 1 and TR. 2 and TR. 1 and TR. 3; while SO_4^{2-} ions concentration and pH showed no significant differences in all the treatments (Table 2). A pair-wise comparison in concentrations of the nutrients and pH using Student's t-test revealed that there were significant differences between aerobic and anaerobic conditions (Table 3) at the 95% confidence interval.

Table 1. Mean separation in concentrations of nutrients and pH in sediments over 42 days using Duncan Multiple Range Test ($p<0.05$).

Parameters	Days			
	0	14	28	42
NO_3^- aerobic	8.0678^a	7.6211^{ab}	6.3556^{ab}	5.2067^b
NO_3^- anaerobic	8.0889^a	7.7222^a	7.2278^a	7.0711^a
PO_4^{3-} aerobic	118.5444^a	115.0111^a	103.4333^b	100.7000^b
PO_4^{3-} anaerobic	118.5333^a	117.6667^a	112.788^{ab}	108.5556^b
SO_4^{2-} aerobic	126.8889^a	124.7667^b	118.1444^C	111.2444^d
SO_4^{2-} anaerobic	126.8889^a	124.8333^b	121.3111^C	119.0556^d
pH aerobic	5.2556^a	4.6446^b	4.4444^C	4.2333^d
pH anaerobic	5.2556^a	4.9222^b	4.8222^b	4.5667^C

Concentrations with same superscripts along same rows are not significantly different at $p<0.05$

Table 2. Mean separation in concentrations of nutrients and pH in sediments by Treatments using Duncan Multiple Range Test ($p<0.05$).

Parameters	Treatments		
	TR. 1	TR. 2	TR. 3
NO_3^- aerobic	3.4283^b	8.1925^a	8.8175^a
NO_3^- anaerobic	3.6317^C	9.0958^b	9.8325^a
PO_4^{3-} aerobic	101.3917^b	111.3833^a	115.49147^a
PO_4^{3-} anaerobic	107.2667^b	116.2333^a	119.6583^a
SO_4^{2-} aerobic	119.5333^a	120.6000^a	120.6083^a
SO_4^{2-} anaerobic	122.5417^a	123.2583^a	123.2667^a
P^H aerobic	4.6000^a	4.6167^a	4.7250^a
P^H anaerobic	4.8417^a	4.8833^a	4.9500^a

Treatments with same superscripts along same rows are not significantly different at $p<0.05$

Table 3. Pair-wise comparison in mean concentrations of nutrients and pH in sediments under aerobic and anaerobic conditions using Student's t-test ($p<0.05$).

Parameters	Mean	SE	r	Sig. r	t	Sig. t
NO_3^- aerobic	6.813	0.454	0.943	0.000	-4.492	0.000
NO_3^- anaerobic	7.520	0.4473				
PO_4^{3-} aerobic	109.422	1.640	0.914	0.000	-6.642	0.000
PO_4^{3-} anaerobic	114.386	1.160				
SO_4^{2-} aerobic	120.247	1.068	0.964	0.000	-4.825	0.000
SO_4^{2-} anaerobic	123.022	0.530				
pH aerobic	4.647	0.688	0.920	0.000	-7.584	0.000
pH anaerobic	4.892	0.45				

4. Discussion

This study clearly revealed that nutrients in marine sediments are degradable, especially in aerobic condition. This biodegradability detracts from persistence or recalcitrance of the Persistent Organic Pollutants (POPs) group in sediments of Estuaries as noted by Unlu *et al.* [14] in the Ambarli Port area of the Sea of Marmara in Turkey, Chen and Chen [15] in sediments of Kaohsiung Harbor in Taiwan and Mostafa *et al.* [16] in sediments of the western harbour of Alexandria in Egypt. The study also demonstrates that the sediments act as a long-term source of nutrients in the estuaries and other water bodies, and that they undergo greater internal recycling following external loading events. In the absence of continued external loading and burial, conversion of labile forms of the nutrients to less reactive forms and other reactions slowly reduce the rate of internal recycling. This observation had been made by Anderson [17] in sediments of the Canyon Lake in California, wherein he observed that the capacity for sediments to serve as a long-term source of nutrients, effectively functioning as a long-term buffer system that can supply nutrients and fuel algal growth for many years, has led to a number of control strategies to inhibit internal recycling. Consequently, particular emphasis has been placed on control of phosphorus, since it is the most common limiting nutrient especially in freshwater systems.

Degradation rates of the nutrients progressed steadily from Day 14, through Day 28 to Day 42. This indicates a time-dependent degradation process. Maximum degradations were recorded at the end of the experiments, and this implies that duration or time is a determinant factor in biodegradation of pollutants in the sediment samples. The degradation of PO_4^{3-} and SO_4^{2-} ions differed markedly between aerobic and anaerobic conditions; with higher degradations recorded in aerobic than anaerobic conditions. This confirms the all important role of oxygen in biodegradation and flux patterns of nutrients in sediments, an observation that has also been made by Ogbuagu *et al.* [18].

Degradation pattern of nutrients was also significantly different between treatments or concentrations. This indicates a dose-related degradation rate of the nutrients, in addition.

Oxygenation (aerobiosis) clearly aided degradation, as confirmed by the ANOVA test. This again underpins the role of oxygen in the enhancement of biodegradation process by aerobic microorganisms. It further underscores the role of oxygen in sediment pollutants detoxification and recycling/purification of aquatic media.

However, pH did not vary significantly during degradation. This implies that degradation was not pH-dependent; a detraction from the work of Ogbuagu *et al.* [18] on degradation of petroleum pollutants in sediments of the same Estuary in Nigeria.

5. Conclusion

It could be concluded that degradation rates of the nutrients (PO_4^{2-}, SO_4^{2-}) in marine sediment samples were time and dose-dependent. Degradation rates also differed markedly as the experiment progressed and was enhanced by oxygen, but not pH-dependent.

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