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Winkler Titration Assessment of Biochemical Oxygen Demand (BOD₅) in Oka Creek, Toru-Orua, Bayelsa State

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

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ABSTRACT

Aim: The aim of study was to investigate the Biochemical Oxygen Demand (BOD) levels in water samples from the Oka Creek.

Study Design: Qualitative study design.

Place and Duration of Study: Water samples were collected from the Oka Creek, located in Toru-Orua in Sagbama Local Government Area, Bayelsa State, Nigeria. The study lasted for twenty days.

Methods: Water samples were collected from four different locations and depths in the Oka Creek, Toru-Orua, Sagbama Local Government Area of Bayelsa State, Nigeria, at various times. Each sample was transferred into 250 ml bottles labeled L1, L2, L3, and L4. The temperatures of the samples were recorded before transporting them to the chemistry laboratory for treatment. Winkler titration method was employed in analyzing the samples.

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Results: Location L1 recorded the highest BOD value, 28.38 mg/L, measured at sunset (25 °C), from a relatively stagnant region. The high BOD at this location is attributed to minimal photosynthetic activity and significant oxygen consumption by microorganisms. In contrast, L2, collected from the same region at 35 °C during peak sunlight, exhibited a BOD value of 21.76 mg/L. The lower BOD at L2 is due to increased photosynthetic activity. These high values suggest significant sludge deposits, domestic sewage and agricultural runoffs, which could lead to oxygen depletion and negatively impact aquatic life. Sample L3, taken from a deeper, stagnant region at sunset (25 °C), recorded a BOD value of 4.50 mg/L. This moderate BOD level suggests the presence of moderate sludge deposits and agricultural runoff, but higher water flow speed helped mitigate these effects. Location L4, with the lowest BOD value of 3.74 mg/L, was collected during peak sunlight (35 °C). Deeper location and high water flow speed contributed to reduced BOD levels, indicating better water quality and a healthier aquatic environment.

Conclusion: The BOD values at L1 and L2 (28.38 mg/L and 21.76 mg/L) exceed acceptable limits for fish growth. Conversely, BOD values at L3 and L4 (4.50 mg/L and 3.74 mg/L) fall within acceptable limits, suggesting healthier aquatic environment, as evidenced by the yearly bountiful fish harvests in these sections of the Oka Creek.

Keywords: Oxygen; water; BOD; factors; analysis; oka creek.

1. INTRODUCTION

Oxygen is the most abundant element on Earth. It exists primarily in two forms: O_2 (molecular oxygen) and O_3 (ozone). Oxygen is the most abundant element in the Earth's crust. It primarily exists in two forms: O_2 (molecular oxygen) and O_3 (ozone). Additionally, oxygen is a component of numerous compounds, including water (H_2O), and can be found dissolved in water as O_2 molecules. Oxygen is also a component of numerous compounds, such as water (H_2O), and can be found dissolved in water as O_2 molecules [1]. The amount of dissolved oxygen (DO) that water can retain is primarily influenced by temperature, salinity, and atmospheric pressure [2].

The stream system both produces and consumes oxygen. It absorbs oxygen from the atmosphere and from plants through photosynthesis [3]. Oxygen consumption in water can result from various sources, including respiration by aquatic animals, decomposition of organic matter, stormwater runoff from farmland or urban streets, feedlots, failing septic systems, various chemical reactions [4]. biochemical oxygen demand (BOD) refers to the quantity of oxygen that aerobic bacteria require to decompose organic waste [5].

Surface pollutants have a detrimental impact on aquatic life. Contaminants like heavy metals, pesticides, and industrial chemicals can directly poison aquatic organisms, causing illness, deformities, and even death [6,7].

Hydrocarbons from oil spills coat the water's surface, suffocating fish and disrupting the natural behaviors of aquatic organisms Certain pollutants can mimic or disrupt the natural hormones of aquatic organisms, causing reproductive and developmental abnormalities. These contaminants may also affect egg viability. resulting in lower hatching success and a decline in population [9]. Excessive nutrient runoff, mainly nitrogen and phosphorus from agricultural and urban sources, often triggers algal blooms. As these algae die and decompose, they consume oxygen, leading to hypoxic or anoxic conditions that can suffocate aquatic life. Additionally, sediment runoff from erosion can bury aquatic habitats, covering grounds and depriving benthic organisms of oxygen [10].

Pollutants can disrupt organisms, causing behavioral changes that impair their ability to locate food, evade predators, or reproduce. Some pollutants also weaken the immune systems of aquatic life, increasing their vulnerability to diseases and infections. This can lead to a decline or even extinction of sensitive species, which reduces biodiversity and weakens ecosystem resilience. Changes in species composition and abundance can upset ecological interactions, resulting in imbalances within the ecosystem. Prolonged exposure to pollutants can population declines and degrade ecosystems. Additionally, certain pollutants may induce genetic mutations in aquatic organisms, potentially impacting future generations and reducing genetic diversity within populations.

Maintaining suitable dissolved oxygen (DO) levels is essential for safeguarding aquatic ecosystems and ensuring the well-being of water bodies. It is vital to regularly monitor and manage these levels to prevent issues like eutrophication and pollution, which can lead to dangerously low DO conditions [11]. Biochemical Oxygen Demand (BOD) is a key indicator in water quality management, offering essential insights into organic pollution levels and the health of aquatic ecosystems. Traditional methods for measuring BOD include the Dilution method. Manometric method. Respirometric method. and Electrode method. the Dilution method, samples are incubated for a set period (5 days at 20 °C for BOD₅ in the standard test) in dark bottles. The initial and final oxygen levels are then measured using either an amperometric sensor or iodometric titration.

Uwidia and Ejeomo [12] investigated the correlation between COD and BOD5 using domestic sewage samples from a sewage treatment plant. Their regression analysis revealed a robust correlation between these two parameters. Yang [13] employed Near-Infrared simultaneously Spectrometry measure to Chemical Oxygen Demand (COD) and Biological Demand (BOD₅)in wastewater. achieving satisfactory results. Rudaru et al. [14] evaluated the biodegradability of various water types in Romania by analyzing the BOD₅/COD ratio (biodegradability index) and found that this ratio varied depending on the type of water studied.

Al-Sulaiman and Khudai [15] investigated the correlation between BOD₅ and COD in the sewage at the Al-Diwaniyah wastewater treatment plant and reported a high degree of correlation.

Alewi et al. [16] investigated the relationship between BOD_5 and COD in 108 water samples from Iraq's southern region, finding a strong correlation with a coefficient of 0.908 and a determination coefficient (R²) of 0.89. In 2019, Andrio and others [17] demonstrated that ozonation pretreatment improved the BOD_5/COD ratio in co-substrates such as tofu wastewater and cow dung. Additionally, tannery wastewater with elevated BOD_5 levels was effectively treated using a $ZnO-Zn/Fe_2O_4$ composite photocatalyst supported on activated carbon, which removed 90 % of BOD_5 within two hours [18].

Ayawei and Bennett [19] measured Biochemical Oxygen Demand (BOD) levels in water samples from Ntanwoba Creek, Port Harcourt, Rivers State, Nigeria. They found elevated BOD values, which were linked to runoff wastewater from nearby agricultural activities and automobile workshops. In contrast, Kwak et al. [20] created software sensors using multiple regression analysis, incorporating dissolved organic carbon (DOC) concentration and UV light absorbance to estimate BOD $_5$ of river water. Their research demonstrated that these software sensors were effective in predicting BOD $_5$ levels in river water.

Dasgupta and Yildiz [21] investigated three types of wastewater in Morris County, USA, finding that industrial wastewaters exhibited the highest BOD₅ values, while pharmaceutical wastewaters had the lowest. Sha and Wei-Xing [22] used spectrophotometric titration measure to Biochemical Oxygen Demand in 20 waste samples within 40 minutes. Mohammed et al. [23] conducted kinetic studies on BOD₅, COD, and chromium removal in tannery effluent using ZnO/ZnFe₂O₄ composite photocatalyst supported on activated carbon, reporting that the photodecomposition followed the pseudo firstorder Langmuir-Hinshelwood model. Faiza et al. [24] documented BOD₅ values ranging from 5.04 to 6.18 mg/L in the Wupa River, Federal Capital Abuja, Nigeria, highlighting Territory, anthropogenic impacts on water quality. Yang simultaneously determined Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD₅) in wastewater using Near-Infrared Spectrometry.

Liu and Chen [25] predicted biochemical oxygen demand with genetic algorithm-based support vector regression, and reported that support vector regression (SVR) with genetic algorithm (GA) optimizer achieved the best performance with R² of 0.694. Qambar and Khalidy [26] proposed an integrated framework of remote sensing and machine-learning techniques to predict municipal wastewater biochemical oxygen demand (BOD₅)wastewater treatment plants (WWTPs). They compared the performance of wastewater received by two WWTPs in South Kingdom of Bahrain with several supervised machinelearning algorithms and reported that the gradient boost algorithm model obtained the best results. Ngoc et al., [27] used simple BOD biosensor to estimate BOD₅ in food processing wastewater. They concluded that there was a statistical agreement between the results



Picture 1. Fresh fish harvested from Oka Creek during the 2024 fishing festival

obtained from the rapid BOD biosensor and the conventional methods, even with treated wastewater samples. Alotaibi and colleagues [28] used a High Salinity Bioreactor-Based, Wastewater Treatment Plant to correlate the results of Biochemical Oxygen Demand and Chemical Oxygen Demand and reported that R² values obtained made it impossible to predict the result of BOD5 based on COD.

The aim of our research is to measure the Biochemical Oxygen Demand (BOD) levels of Oka Creek in Toru-Orua community of Bayelsa State, Nigeria, using the Winkler method. This river is unique due to its fishing prohibition until the ceremonial four-day fishing festival held annually on February 3rd. During this festival, the community celebrates with plentiful catches, as illustrated in Picture 1, which shows fish caught during the 2024 festival. By analyzing the BOD levels, the research aims to assess the water quality and its capacity to support aquatic life, especially in the context of the community's fishing practices and the annual festival.

2. MATERIALS AND METHODS

2.1 Meterials

All chemicals utilized in the experiments were of analytical reagent grade, sourced from Acros Organics, and were used as received without additional purification.

2.2 Methods

2.2.1 Reagents preparation

0.017 M potassium iodate (KIO₃): 0.89 g of KIO₃ was weighed and dissolved in distilled

water in a volumetric flask, and the solution was made up to a total volume of 250 ml.

Alkaline Sodium lodide (Nal): 5.6 g of sodium hydroxide and 16.6 g of potassium iodide were dissolved in distilled water, and the solution was diluted to a final volume of 100 ml with distilled water.

0.538 M manganese (II) sulphate tetrahydrate (MnSO₄·4H₂O): 120 g of manganese (II) sulphate tetrahydrate was dissolved in distilled water, and the solution was brought up to a final volume of 250 ml.

Fresh starch solution: To prepare a fresh starch solution using established methods, 2.00 g of soluble starch was dissolved in a 100 ml conical flask. This solution was quickly poured into 250 ml of boiling water. The resulting mixture was boiled for an additional 5 minutes. After boiling, 0.02 g of sodium iodide was added, and the mixture was allowed to cool [29].

1.1 H_2SO_4 solution: 30 ml of concentrated sulfuric acid was transferred into a 100 ml flask, followed by the addition of 30 ml of distilled water.

0.1 M solution of sodium thiosulphate: 12.60 g of sodium thiosulfate was weighed and dissolved in distilled water. The solution was then made up to a total volume of 500 ml with distilled water.

Standardization of sodium thiosulfate (Na₂S₂O₃) using potassium lodate (KlO₃):

Standardization of $Na_2S_2O_3$ was calculated using equation (1) and (2).

$$\frac{MS_2O_3^{2-}VS_2O_3^{2-}}{MIO_3^{-}VIO_3^{-}} = \frac{nS_3O_3^{2-}}{nIO_3^{-}}$$
(1)

$$MS_2O_3^{2-} = \frac{MIO_3^{-}VIO_3^{-}nS_3O_3^{2-}}{VS_2O_3^{2-}nIO_3^{-}}$$
(2)

Where

 ${\rm MS_2O_3}^{2-}$ is the molarity of sodium thiosulphate ${\rm MIO_3}^-$ is the molarity of the iodate ${\rm VIO_3}^-$ is the volume of the iodate ${\rm VS_2O_3}^{2-}$ is the volume of thiosulphate ${\rm nIO_3}^-$ is the number of moles of iodate and s the number of moles of thiosulphate ${\rm nS_3O_3}^{2-}$ is the number of moles of thiosulphate

To get ${\rm VS_2O_3}^{2-}$, 25 ml of potassium iodate solution was transferred into a 250 ml volumetric flask. 5 ml of 1:1 H₂SO₄ and 15 ml of potassium iodide solution were added to the flask to liberate iodine (I₂). The liberated iodine was then titrated with sodium thiosulphate until a pale yellow solution was obtained. Three drops of freshly prepared starch solution were added, causing

the solution to change to a dark greenish-blue color. The titration with sodium thiosulphate was continued until the solution turned colorless, indicating the endpoint. $ns_2O_3^{2-}$ and nIO_3^{-} were obtained from equation (3).

$$IO_3^- + 6H + 6S_2O_3^{-2-} \longrightarrow 3S_4O_6^{2-} + I^- + 3H_2O$$
 (3)

2.3 Collection of Water Samples

Water samples were collected from four different locations and depths, Fig. 1, in Oka Creek, Toru-Orua, Sagbama Local Government Area, Bayelsa State, Nigeria, at four different times.

Each sample was transferred into 250 ml bottles labeled L1, L2, L3, and L4. The temperatures of the samples were recorded before transporting them to the laboratory for treatment and analysis. To minimize experimental errors, the time between sample collection and treatment was kept between 30 minutes and 2 hours [30].

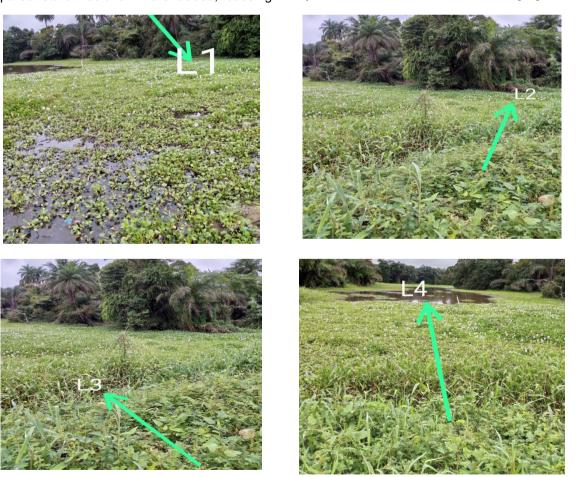


Fig. 1. Locations water samples were collected from in Oka Creek

2.4 Treatment of Water Samples

The Winkler titration method was used to determine the Biochemical Oxygen Demand (BOD) values of the water samples. Each sample was treated with 2 ml of alkaline NaOH solution, and the bottles were tightly sealed to eliminate air bubbles. The samples were manually equilibrated for 20 minutes, and inverted for 5 minutes. Following this, 2 ml of 1:1 $\rm H_2SO_4$ was added, and the bottles were agitated and inverted again for 5 minutes. A clear yellow solution was achieved as the precipitates dissolved. The procedure was repeated three times, and the average BOD value was calculated.

25 mL of the treated water (first fraction) was titrated with a 0.0975 M $Na_2S_2O_3$ solution. The solution initially appeared pale yellow. Following this, 3 drops of freshly prepared starch solution were added, and the titration was continued with the $Na_2S_2O_3$ solution [31,32,33,34]. The method was performed in triplicate, and the average value was determined. Equation (4) was used to calculate the number of moles of $S_2O_3^{2-}$.

$$4I^{-} + O_2 + 4H^{+} \longrightarrow 2I_2 + 2H_2O$$
 (4)

The second fraction of the treated samples were stoppered to avoid air penetration (oxidation) and

incubated in a dark cupboard for five (5) days at 20°C. The samples were incubated to stall further photosynthesis process in the samples. At the end of day 5, the samples were analyzed to determine the final Dissolved Oxygen (DO). The difference between the initial dissolved oxygen and the final dissolved oxygen gave the investigated Biochemical Oxygen Demand (BOD) of the water samples [19].

The value of dissolved oxygen in the four locations was calculated using the formula:

$$BOD_5 = D_1 - D_2$$

Where BOD_5 = biochemical oxygen demand after incubation

 D_1 = initial dissolved oxygen

 D_2 = final dissolved oxygen.

3. RESULTS

Biochemical Oxygen Demand (BOD) levels were measured in water samples from Oka Creek, in Toru-Orua, Bayelsa State, Nigeria, using the Winkler titration method. All titrations were performed in triplicate and the results are as presented in Table 1, and graphically represented in Fig. 2,

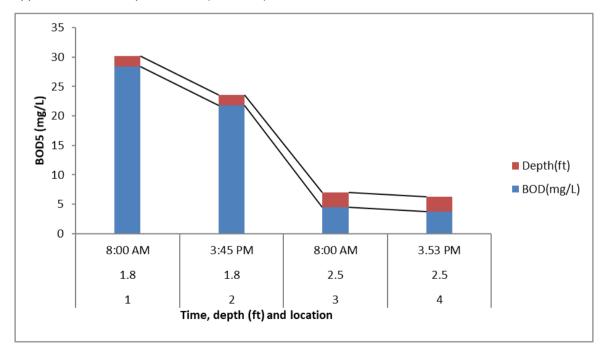


Fig. 2. Graphical representation of the data showing the depth and BOD₅ values at different locations, along with the time of sample collection from Oka Creek

Table 1. BOD₅ values in Oka Creek

S/N	Location	Depth(ft)	Time of sample collection (Central African Time)	D ₁ (mg/L) Mean ± S.D	D ₂ (mg/L) Mean ± S.D	BOD₅ (mg/L) Mean ± S.D
1.	L1	1.8	8:00 am	64.10 ± 0.03	35.72 ± 0.02	28.38 ± 0.01
2.	L2	1.8	3:45 PM	59.20 ± 0.02	37.44 ± 0.01	21.76 ± 0.01
3.	L3	2.5	8:00 am	$25:30 \pm 0.03$	21:50 ± 0.01	$4:50 \pm 0.01$
4.	L4	2.5	3:53 PM	19.34 ± 0.03	15.60 ± 0.02	3.74 ± 0.01

4. DISCUSSION

This study was conducted during the summer season in January 2024, just before the festive period in February, and the selection of 1.8 and 2.5 feet as sampling depths for BOD analysis in the Oka Creek was a deliberate choice aimed at capturing the variations in oxygen demand across distinct environmental conditions. By selecting these depths, the study leveraged the anticipated differences in light penetration. photosynthetic activity, and human impact at the 1.8-foot level, as well as the expected reduction in these factors at the 2.5-foot level. The 1.8-foot depth, closer to the surface, was expected to reflect higher BOD levels due to the more pronounced influence of these environmental variables. Meanwhile, the 2.5-foot representing a slightly deeper zone, anticipated to reveal lower BOD values as a result of the better mixing and reduced accumulation of organic matter. This strategic depth selection allowed for a comprehensive analysis of how BOD varies with depth, providing critical insights into the Creek's oxygen dynamics under varying environmental conditions.

The results as presented in Table 1 and Fig. 1, demonstrate how location, depth, water flow rate, time of sampling, and temperature significantly affect BOD values and, consequently, the health of the aquatic ecosystem.

Location L1 recorded the highest BOD value of 28.38 mg/L, indicating severe organic pollution. This sample was collected from a relatively stagnant area at sunrise with a temperature of 25 °C. The absence of sunlight at sunset reduced photosynthetic activity, which typically contributes to oxygenation of the water. Consequently, there was an increased consumption of dissolved oxygen microorganisms decomposing organic material, leading to the high BOD value. The elevated BOD levels reflect substantial pollution from sources such as sludge deposits, domestic sewage, and agricultural runoff. Such high levels

of organic matter can severely deplete the dissolved oxygen in the water, creating an environment that is detrimental to fish and other aquatic organisms that rely on oxygen for survival. The results suggest that the ecological health of this area is significantly compromised due to high pollution levels.

Location L2 had a BOD value of 21.76 mg/L, measured at midday with a temperature of 35 °C. The increase in temperature and sunlight during midday enhances photosynthesis, which can lead to an increase in dissolved oxygen and a slight reduction in BOD compared to L1. Despite this improvement, the BOD value at L2 remains elevated, indicating continued significant organic pollution. The slightly reduced BOD levels compared to L1 highlight that while increased sunlight can help mitigate some of the pollution effects, it is not sufficient to bring the BOD within acceptable limits. The persistence of high BOD values at L2 underscores the need for addressing pollution sources to improve water quality.

Location L3 exhibited a lower BOD value of 4.50 mg/L, with the sample taken from a deeper, stagnant area at sunrise and a temperature of 25 °C. Although the sample was collected at a time similar to L1, the lower BOD at L3 suggests that the impact of organic pollutants was less severe. This can be attributed to the higher water flow rate at L3, which likely facilitated the dispersion of pollutants and reduced bacterial loads. Additionally, the depth of the water at L3 may have contributed to better mixing, preventing the accumulation of high concentrations of organic matter. The lower BOD indicates that the water quality at L3 is relatively better, and the conditions are more favorable for aquatic life compared to L1 and L2.

Location L4 had the lowest BOD value of 3.74 mg/L, sampled at midday with a temperature of 35 °C. The combination of increased sunlight and a higher water flow rate promoted photosynthesis and further reduced the BOD.

The deeper water at L4 likely contributed to better mixing and reduced accumulation of organic matter, resulting in significantly improved water quality. The low BOD value at L4 reflects pollution. minimal impact from organic suggesting that this location offers a healthier environment for aquatic organisms. conditions at L4 are more favorable compared to the other locations, supporting the notion that sunlight and water flow play crucial roles in improving water quality.

Overall, the high BOD values at Locations L1 (28.38 mg/L) and L2 (21.76 mg/L) exceed the acceptable limits [19] for aquatic life, indicating severe organic pollution that could adversely affect fish and other aquatic species. In contrast, the lower BOD values at Locations L3 (4.50 mg/L) and L4 (3.74 mg/L) are within acceptable limits, reflecting better water quality and a more suitable environment for aquatic organisms. The yearly bountiful fish harvest in these locations could be attributed to these favorable conditions.

These findings emphasize the critical need for targeted pollution management strategies to address the sources of high BOD and to improve overall water quality in the Oka Creek. Effective pollution control measures and continuous monitoring are essential to maintaining the health and sustainability of the Creek's ecosystem. Addressing the identified pollution sources, enhancing water flow, and increasing sunlight exposure in polluted areas could help mitigate the adverse effects and ensure the long-term viability of aquatic life in the creek [35].

5. CONCLUSION

This study assessed the Biochemical Oxygen Demand (BOD) levels in the Oka Creek at Toru-Bayelsa State, Nigeria, Orua. revealing significant spatial and temporal variations influenced by environmental factors such as location, depth, water flow rate, time of sampling, and temperature. Location L1 recorded the highest BOD value of 28.38 mg/L, indicating severe organic pollution, likely due to sludge deposits, domestic sewage, and agricultural runoff. The high BOD levels at L1, coupled with stagnant water and minimal sunlight, pose a substantial threat to aquatic life, far exceeding acceptable limits for fish growth.

In contrast, Location L4 exhibited the lowest BOD value of 3.74 mg/L, reflecting significantly improved water quality. This low BOD is

attributed to conditions favoring photosynthesis, such as increased sunlight and higher water flow, which help to reduce organic pollution. The moderate BOD values at Locations L2 and L3, 21.76 mg/L and 4.50 mg/L respectively, further highlight the influence of environmental factors on water quality, with L2 still showing notable pollution and L3 indicating more favorable conditions.

These findings emphasize the critical need for targeted environmental management strategies, particularly in areas with high BOD values, to mitigate pollution and safeguard aquatic ecosystems. Continuous monitoring of BOD levels is essential to ensure sustainable water quality and preserve the ecological health of the Oka Creek.

6. RECOMMENDATION

To improve water quality in the Oka Creek, reduce pollution bγ improving waste management enforcina discharge and regulations, enhance flow by increasing water circulation in stagnant areas, promote vegetation by establishing buffer zones to absorb runoff, monitor regularly by tracking BOD and water quality, and engage the community through education and involvement.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Author(s) hereby declare that NO generative Al technologies such as Large Language Models (ChatGPT, COPILOT, etc) and text-to-image generators have been used during writing or editing of manuscripts.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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