Original Research Article

ASSESSMENT OF THE EXTENT OF PETROLEUM HYDROCARBONS IN BOREHOLE WATER IN EKET L.G.A. AKWA IBOM STATE

ABSTRACT

The study entails determination of Total Hydrocarbon Content (THC) and Total Petroleum Hydrocarbon (TPH) in borehole water of Eket Local Government Area, Akwa Ibom State, Nigeria. This was assessed using standard analytical methods. The samples were collected in triplicate from the study area with a control station. The areas were Ikot Ibiok and Atabong in Eket L.G.A while the control station was at Aka in Uyo L.G.A. The samples were extracted with hexane using liquid-liquid extraction method followed by subsequent clean-up using column chromatography. The determination of TPH was with the aid of gas chromatography fitted with flame ionization detector (GC-FID) while The THC was determined using U-V Spectroscopy. The results showed the variations of total petroleum hydrocarbon (TPH) from 784.395 ± 0.07 to 1120.500 ± 0.05 mg/L. While THC ranges from 938.21 ± 0.08 to 1,583.294± 0.02 mg/L. The average amount of TPH and THC in the water samples collected from all the sampling stations were generally higher than both the DPR limit (50 mg/L) and federal ministry of Environment (FMEnv.) acceptable standard of Petroleum Hydrocarbons in water. This indicates a serious impact of oil industrial activities on the area. Hence, our findings have indicated evidence that the borehole water samples from the study area in Eket L.G.A is under a pollution threat and underscore the need for early remediation if adverse health defects are to be prevented.

KEY WORDS: EXTRACTION, U-V SPECTROSCOPY, GC-FID, BOREHOLE WATER.

UNDER PEER REVIEW

1.0 INTRODUCTION

Water is essential for the survival of human beings, livestock and other living organisms. In Nigeria and some other developing countries, availability of safe drinking water is a sustainability issue. Water sources available to most developing countries are rivers, natural ponds, and rainfall. In few areas, there are underground water supplies through boreholes and water distribution tankers (Alexander *et al.*, 2018). A unique characteristic of the earth, in

comparison with other planets, is the presence of water, covering about 75% of the earth surface (Buckland, 2019). Water is basically classified into surface water and ground water. Surface water refers to rivers, streams, lakes, oceans, ponds and wetland while ground water is present below the earth's surface where it is stored in porous soils and rocks (Zaghden, 2018). Water is very essential for purposes like drinking, power generation, food processing, etc.; thus, it is necessary to ensure that water is adequate both in quality and quantity (Strother *et al.*, 2019). Water pollution is generally caused by the introduction of waste or toxic materials into the environment by nature or by anthropogenic activities. Considering the different segment of the environment (land, air and water), water pollution is significant because it affects the entire ecosystem; thus, the quality of water that is available for utilization is of essence. Globally, water quality is threatened by numerous sources of pollution such as sewage and domestic waste, industrial effluents, agricultural discharge, fertilizers, toxic metals, detergents etc. (Ekanem and Wigger 2020). Underground water can also be contaminated by micro-organisms. The presence of pollutants in water leads to a range of deleterious effects on the ecosystem; for instance, human exposure to high level of heavy metals in water can cause several health problems such as blood disorder, kidney damage and neurological damage (Abdel-Shafy and Mansour 2019). Therefore, researches on measures aimed at protecting or improving water quality will consequently breed ecofriendly situations for man and the entire ecosystem (Suspes *et al*., 2019).Nigeria has been exploring and exploiting crude oil for decades and the consequences on the oil producing and processing areas have become highly problematic in the onshore and offshore installations (Atunbi, 2019). The unpleasant and environmentally undesirable pollution effects of the waste from these explorations calls for best practicable technology in conversion process involved in obtaining petroleum and petrochemical products from crude oil which generate various types of wastes (Weisman, 2018). The wastes can be generally classified into oily

UNDER PEER REVIEW

materials, spent catalyst, spent chemicals and other residuals which found their ways into the environment due to incessant release. The increased oil activities have resulted in extensive environmental pollution by oil spills involving blowouts, leakages from tanks or tanker trucks and dumping of waste petroleum products into the environment. The aftermaths of these activities have been documented (Fingas, 2019). Crude oil, when refined contains a wide range of components such as hydrocarbons, heavy metals, dye additives, antioxidants, and corrosion inhibitors (Fusey and Oudot 2019). The refined products show higher toxicity compared to crude oil since metal speciation is altered and new metals added to the matrix during the refining processes (Gallagher, 2018). Total petroleum hydrocarbons (TPH) are a large family of several hundred chemical compounds that originally come from crude oil. They are found in the range of C6 through C35 as mixture containing hundreds to thousands of hydrocarbons including aliphatic (straight carbon chain) and aromatic (carbon ring) compounds. Some hydrocarbon mixtures may also contain priority pollutants including volatile organic compounds (VOCs), semi-volatile compounds (SVOCs) and metals, each of which has its own specific toxicity information (Gouch *et al.,* 2019). The presence of chemical contaminants in the coastal environments from many anthropogenic sources is a major threat to the marine water (Hatje *et al.,* 2020).This study is aimed at studying the extent to which borehole water in Eket local government area is polluted.

UNDER PEER REVIEW

2.0 MATERIALS AND METHODS

2.1 Study Area

The study sites were located in Eket town, Eket local government area of Akwa Ibom State, Nigeria. Six sampling locations were selected within Eket L.G.A and one control from Uyo

L.G.A which occupies the south-central portion of Akwa Ibom State. The study territory spans between Latitudes 04^{o} 33' and 04^{o} 45'N and Longitudes 07^{o} 52' and 05^{o} 02'N. The study sites and their coordinates are presented in the town "Eket" is bounded on the north by Nsit Ubium Local Government Area, on the West by Onna Local Government Area and on the South by Ibeno Local Government Area in the South-South region of Nigeria. The prime occupation of the people is farming and fishing. The presence of oil exploration activities by ExxonMobil and other service companies in the study area, influences activities. (APHA, 2018).

UNDER PEER REVIEW

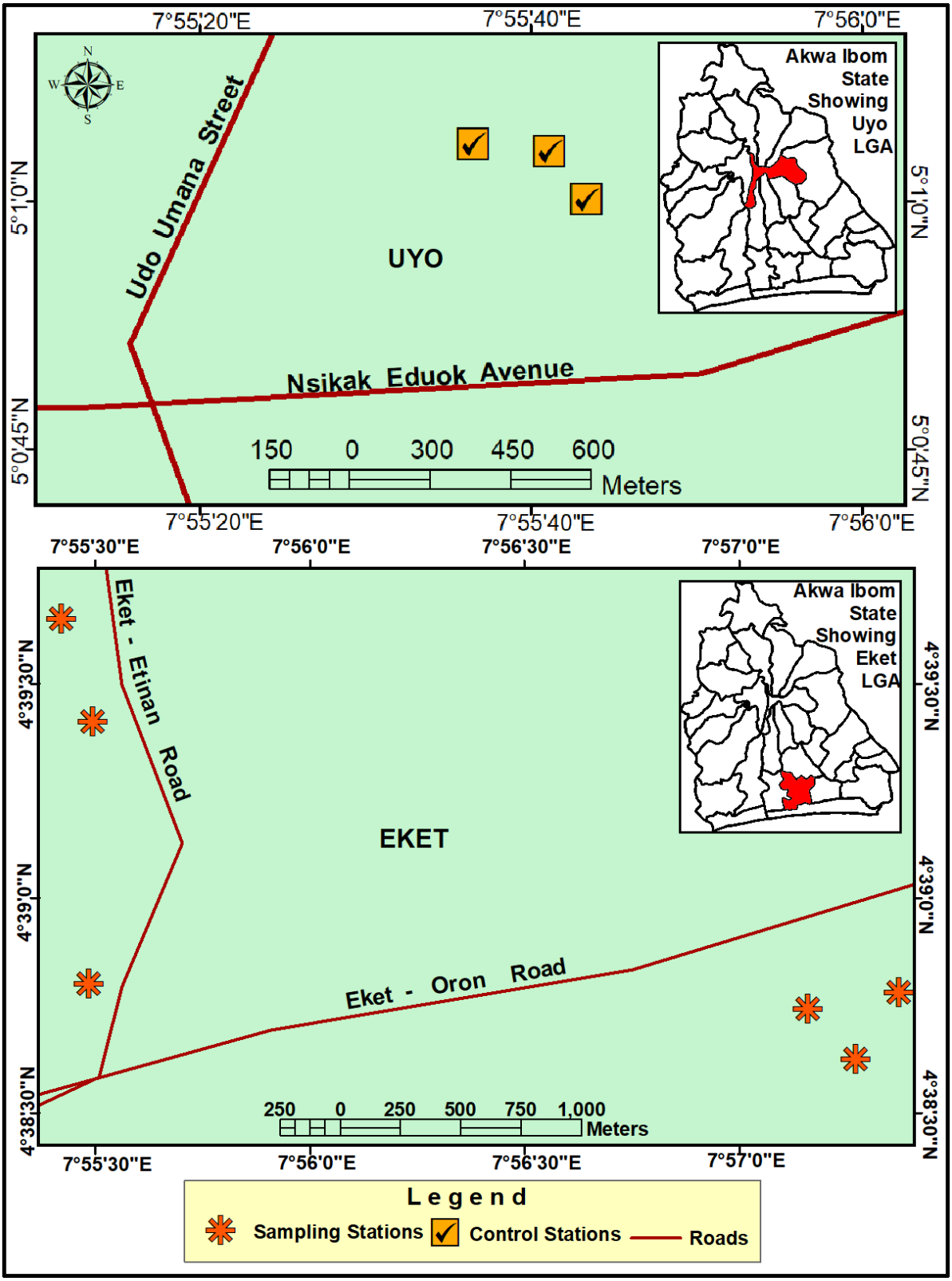

Fig 1: Map of Eket and Uyo L .G.A showing sampling location

Table 1: Coordinates of the sampling locations

SAMPLING SITES	SITE CODE	LATITUDE NORTH	LONGITUDE EAST
A	**A_1**	**04° 38' 872"**	**07° 57'22.296"**
	B	**04° 38' 42.798"**	**07° 57' 12.09"**
	C_1	**04° 38' 44.562"**	**07° 57' 9. 474"**
C	**D**	**05° 0' 59. 478"**	**07° 55' 42. 324"**
	E	**05° 1' 3. 354"**	**07° 55' 38. 088 "**
	F	**05° 1'3. 012"**	**07° 55'41. 118"**

UNDER PEER REVIEW

2.2 Reagents Used for the determination of TPH

The reagent that was used for the determination of total petroleum hydrocarbon in borehole water samples collected from selected sites in Eket L.G.A are; Dichloromethane, n-Hexane, Acetone, Anhydrous sodium sulphate, HPLC silica gel (merged size 60 – 120).

2.3 Apparatus Used for the determination of TPH

Weighing balance**,** Beakers**,** Spatula**,** pH meter**,** 250 ml round bottom flask**,** separating glass funnel**,** GC-FID.

2.4 Reagents Used for the determination of THC

n-Hexane

2.5 Apparatus Used for the determination of THC

250 ml separating funnels, UV-Spectrophotometer, Pipette, 10 ml, Mechanical Shaker

2.6 Sample Collection

Water samples were collected in triplicates for physico-chemical and petroleum hydrocarbons determination from six (6) boreholes in Eket local government area and three (3) from a control station in Aka, of Uyo L.G.A, all in Akwa Ibom state Nigeria. The sampling containers were washed with 3M of nitric acid and rinsed with plenty of distilled water to avoid any contamination from the sampling containers. Standard analytical procedures were followed as the first rushed of the water was not taken. Samples were collected after three minutes of constant running of water (Olubukola *et al.,* .2015) ;(Ikpe *et al*.,2016); (Ikpe *et al*., 2019) ;(Merrl, 2020). The samples containers were rinsed three times with the water to be sampled before collection. The water samples were stored in one litre (1 L) amber glass bottles to avoid photo degradation of any petroleum content in the sample. The sample was later stored in an ice cooler at 4^{o}C, before sample preparation within interval not exceeding fourteen days

2.7 Analysis for the physico-chemical parameter

Standard analytical method was duly followed with the use of a pre calibrated multipurpose electrical conductivity meter (DDSJ 308A) to determine the physicochemical parameters in the water samples, (30 ml) with an intermittent rinsing of the probe with deionised water after every determination to avoid cross contamination. The parameters were; Temperature, Total Dissolved Solids (TDS), Electrical conductivity, Salinity and pH. (APHA, 2009).

2.8 Sample Preparation for TPH Analysis

The Liquid - liquid extraction methods as outlined in U. S. EPA method 3540 (U.S. EPA, 1996) and Ekanem *et al*. (2019) methods were employed for the extraction of the sample. 20 ml of each of the samples from a particular station was measured into a measuring cylinder to

UNDER PEER REVIEW

obtain a true representative sample of the area (stations). A total of 60 ml of the borehole water sample was poured into a separating funnel. Ten ml (10 ml) of the extraction solvent (acetone and dichloromethane ratio 1:1) was poured into the separatory funnel. The mixture was then shaken for 10 minutes and was allowed to settle for 20 minutes. Then the water at the bottom was drained out and the organic layer was collected in a beaker. This was repeated for two times to ensure total extraction, ready for purification.

2.8.1 Purification of the Sample Extract. For GC analysis

Each of the sample extracts was cleaned to remove moisture, polar hydrocarbons, color interferences and any impurities during liquid-liquid extraction method. The samples were cleaned up using column chromatography which was prepared by loading 2g of glass wool in a 10 cm long and 2 cm diameter column. 5 g of silica gel was weighed in to the column and was soaked with 10 ml of n- hexane. Two grams (2 g) of anhydrous sodium sulphate was measured unto the glass wool in the glass funnel on the column chromatography setup; the sample to be purified was poured into the column through the glass funnel and was eluted with 10 ml of n- hexane. The purified sample was collected, and turned into the chromatographic vial sample bottles, ready for GC analysis.

2.9 Sample preparation for THC Analysis

Fifty (50 ml) of water samples were measured into a 150 ml separatory funnel and 10 ml of hexane was added. It was shaken for 2 minutes, and was allowed to settle for 20 minute.

The water layer was drained off and the hexane layer was collected and read using uv-spectrophotometer at wavelength of 460 nm. Merll, (2020).

UNDER PEER REVIEW

2.10 Determination of Total Petroleum Hydrocarbon (TPH)

The determination of TPH contained in the water samples were carried out with Gas Chromatography equipped with Flame Ionization Detector (GC-FID) (Agilent 6890N). A concentrated 1μL of the sample eluted was introduced into the GC vial, with a micro-syringe previously rinsed with DCM (blank) and the sample. The TPH was determined at a specific chromatogram in mg/L (Alinnor and Nwachukwu 2013); (Ikpe *et al*., 2019)

2.11 Determination of Total Hydrocarbon Content (THC)

The determination of THC was carried out by preparing a THC standard stock, of 1000 mg/L. This was done by pipetting 1.18 ml of forcados blend crude oil and making it to 1 litre of n-Hexane, from this the following working standards were prepared; 0, 10,20,40,60,80 and 100 mg/L and read as absorbance at 460 nm using uv- spectrophotometer . A graph of absorbance against concentration was plotted and the slope reciprocal determined which was introduced into a formula, in order to calculate the THC (mg/L). Thus;

$$\text{THC (mg/L)} = \frac{\text{Instrument reading x slope Reciprocal x 10 ml n-Hexane}}{\text{Volume of water sample (50 ml)}} \quad (1)$$

UNDER PEER REVIEW

3.0 RESULTS AND DISCUSSION

Table 2: Result of Physicochemical analysis of Water in Eket L.G.A

SAMPLE PARAMETERS	Unit	SITE A	SITE C	WHO STANDARDS
Temperature	^{o}C	28.5	28.4	25°C
TDS	mg/L	21.9	99.3	500
Electrical Conductivity	µs/L	48.3	196.2	50
Salinity	%	0.00	0.01	---
pH		6.5	6.0	6.5-8.50

UNDER PEER REVIEW

3.1 Temperature

The degree of temperature of the sampling site A(28.5°C) was slightly higher than that of the control site C (28.4°C) as indicated in Table 2, but was lower than the WHO standard for portable water which makes the water suitable for consumption purposes. Temperature negatively impact water quality by enhancing the growth of micro – organisms which may incease taste, odour, color and corrosion problem (UNICEF, 2008). Therefore it is important that borehole water temperature is not too high in order not to have microbial multiplication. Temperature affects biological, chemical, and physical activities in the water (Yilmaz and Koc, 2014) besides, increase in temperature of water decreases solubility of gases such as O_2, CO_2, N_2, and CH_4.

3.2 Total Dissolved Solids (TDS)

This is the measure of the amount of solutes dissolved in water (Ikpe *et al.*, 2019). The concentration of TDS recorded for site A (21.9 mg/L) is lower than that of the control (99.3 mg/L) site. The result of TDS of the water from the control site (Atabong, Eket) is far lower than the WHO maximum allowable level of TDS (500 mg/L). High concentrations of TDS in water samples could be linked to seapage into the groundwater from domestic and industrial waste dump close to the study sites. It could also be as a result of direct discharge of chemicals, domestic waste waters, run-off from roads etc. which finally washed into the

UNDER PEER REVIEW

natural water. The ions that constitute the amount of TDS include carbonate, bicarbonates, chlorides, sulphate, phosphates and nitrate of calcium, magnesium, sodium, potassium, organic ions and other ions.The possible cause of low concentration of TDS could be attributed to minimal presence of these chemicals in the groundwater. High content of dissolved solids increases the density of water and influence osmoregulation of fresh water organisms. This reduces solubility of gases (like oxygen) and utility of water for drinking, irrigation, and industrial purposes. High TDS is responsible for the wide spread of gastric human system, produce undesirable taste, gastro intestinal irrigation and corrosion. Consequently low TDS values may indicates the low mineral content of the water (Olubukola *et al*., 2015)

3.3 **Electrical Conductivity (EC)**

This is a measure of dissolved ionic component and hence electrical characteristic. The electrical cconductivity gives an indication of the amount of total dissolved components in water (Yilmaz and Koc, 2014) ;(Ogbeeifun *et al*., 2019)

The electrical conductivity of the borehole water obtained from site A (48.3µs/cm) is lower than the control (196.2 µs/cm) and the WHO (2009) standards (50 µs/cm). The high conductivity recorded at the control stations could be attributed to salts water intrusion from run-off during wet season. The low values observed in the study sites indicate freshness of the water. These results also revealed that the values of this parameter are within the permissible limit of WHO. The increase conductivity of the water may promote corrosion because of the ionic presence.

3.4 Salinity and pH

UNDER PEER REVIEW

The water salinity (0.00) is negligible and suitable for consumption and agriculture. The range of pH in the water sample from site A is 6.50 which indicate mild acidity and that of the control site (6.0). These results have met the WHO limit for pH (6.5- 8.50), also in line with the study carried out by Ikpe *et al*., 2019 within the region. The acidic nature of the water samples in Eket L.G.A was an indication of water pollution and maybe attributed to metals seepage into the ground water, (such zinc, lead, mercury, cadmium etc.) through improper disposal of used cans of aerosol, tyres and other disinfectants deposited in the landfill as waste.

Table 3: Total Petroleum Hydrocarbon Analysis

SITE A	SITE C (Control)	DPR(2019)	FMEnv.(2009)
1120.500±0.05 mg/L	**784.395±0.07 mg/L**	**50.00 mg/L**	**300 mg/L**

3.5 Total Petroleum Hydrocarbon (TPH)

Total petroleum hydrocarbon in the borehole water was evaluated in all the sampling points. The result is summarized in Table 3. The TPH concentration in the study area varied widely across the sampling stations from 1120.500 ± 0.05 to 784.395 ± 0.07 mg/L. the highest concentration was observed at Site A, maybe attributed to commercial activities such as engine oils from trucks, engine oil spills from mechanic workshop around the area. Creeks that receive sewage from oil industries operating in the area and improper clean up after oil spillage could account for the higher concentration of TPH in the site. However the TPH

UNDER PEER REVIEW

concentration at Site C (control) exhibited low concentration due to less anthropogenic activities and less commercial activities in the area. The Spatial distribution of petroleum hydrocarbons in water matrix is depicted in Table 3. The high levels of total petroleum hydrocarbon contamination observed in this study are comparably higher than the levels obtained by Olver, (2012) where the overall level of TPH recorded in their study in the petroleum contaminated site ranges from 54±7 to 345±4 mg/L. Also, study conducted by Akomah and Osayande, (2017) is in line with this study, with TPH ranges from 34.32 - 1746.6 mg/L and 29.49 -1141.0 mg/L.

Table 4: Total Hydrocarbon Content Analysis

SITE CODES	THC (mg/L)	CONTROL	DPR(2002)
A_1	**1,583.294±0.02**	**799.251±0.02**	**0.6 mg/L**
B	**1,641.132±0.08**		
C_1	**1,475.331±0.10**		
D	**996.063±0.21**		
E	**938.214±0.12**		
F	**954.111±0.08**		

UNDER PEER REVIEW

3.6 Total Hydrocarbon Content (THC)

Total hydrocarbon content of borehole water was evaluated in all the six sampling stations and results are summarized in Table 4 above. The THC concentration in the study area varied

across the 6 sampling stations from 938.214 ± 0.12 to 1,641.132 ± 0.08.mg/L .The highest was observed at site B, followed by A_1, C, D, F and E respectively. The high concentration of THC observed in some borehole water samples may have been caused by spillage and leakage from filling station operating in the area. The highest concentration recorded at site B could be attributed to urban discharges and vehicular emission from vicinity of the filling stations. Okoh and Trejo-Hernandez (2019) in their report attributed the higher concentrations of THC in the port of Ngqura marine to urban discharge and vehicular emissions from that region. The result obtained for borehole water samples in some communities in Rivers state, Nigeria by Hatje *et al.,* (2020), indicated that the mean concentration was higher (3,307.766 ± 0.07 mg/L) than that reported in this study.

But the low concentration of THC in site E may be due to less anthropogenic activities in the area.

4.0 Conclusion

The study determined the presence of total petroleum hydrocarbons (TPHs) and total hydrocarbon content (THC) in borehole water within Eket. It was found that there was pollution of the underground and borehole water. This may be attributed to seepage of petroleum contaminants from the oil exploitation and exploration within the area into underground water through human activities such as dumping and burning of waste in the area. The study also revealed the presence of TPHs and THC at the control site (Uyo). The concentration of these pollutants recorded was above the permissible values of the Department of Petroleum Resources (DPR) and Federal Ministry of Environmenta. Hence, the findings reveal the need for a holistic and sustainable monitoring and remediation of the environment.

UNDER PEER REVIEW

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UNDER PEER REVIEW

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UNDER PEER REVIEW

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UNDER PEER REVIEW

UNDER PEER REVIEW