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Total hydrocarbon content and physicochemical alterations of Kpite oil spill impacted site in Rivers State, Nigeria

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Abstract

Evaluation of four composite oil spill impacted soil samples from Kpite, Rivers state, Nigeria was carried out to determine the extent of pollution. The samples were collected at surface depth (0-15cm) and subsurface depth (15-30cm) after field reconnaissance survey. The value of physicochemical properties as well as the Total hydrocarbon content were quantified using standard analytical methods to ascertain the threat to the natural biodiversity within vicinity of study. Results of pH range from 5.14-5.40; EC: 101.40-186.20; moisture content: 14.40-18.40%; Total organic carbon: 1.31-1.71%; Total organic matter: 2.30-3.00%; Total hydrocarbon content:14326 - 22504 mg/kg. An assessment of the Distribution patterns of normal alkanes and isoprenoids in the samples showed nC_8 to nC_{40}. The computed diagnostic ratios for Pr/Ph, nC_{17}/Pr, nC_{18}/Ph, nC_{25}/nC_{18}, and CPI were: 0.25-0.42; 4.37-6.61; 1.59-3.43; 0.16-1.19 and 0.97-1.06 respectively. The obtained result from the Total hydrocarbon content and physicochemical parameters showed that the soil was heavily impacted and needs some remedial measures to restore the soil to optimum conditions for the support of biodiversity. Total hydrocarbon content exceeded both the intervention and target regulatory standards of Nigeria's Department of Petroleum Resources (DPR) EGASPIN of 5000mg/kg and 50mg/kg respectively. Low Nitrogen, phosphorus and potassium concentration, and fairly high moisture content were implicative of low soil fertility.

Keywords: Hydrocarbons, biodiversity, total organic matter, EGASPIN, de-pollution.

Introduction

The discovery of crude oil in Nigeria has led to continual environmental degradation due to unsustainable exploitation of the Natural resource[1]. Oil spillage is the contamination of the environment with hydrocarbons that are released by anthropogenic causes such as leaking pipelines, well heads, and flow stations, discharge of crude oil from refineries and industries, accidental spills from tanker incidents, spills in connection with illegal tapping of oil wells and from artisanal refining under very primitive conditions[2,]. However, oil spillage especially in the Niger delta region is associated with the intentional sabotage of pipelines[3].

Oil spillage releases several toxic compounds that alters the physicochemical composition of the soil which in turn has a huge effect on Agricultural productivity and fertility. An alteration of the physicochemical characteristics of the environmental media might cause destruction of optimum conditions in which several biodiversity can thrive and exist, thereby leading to loss of important environmental features. Changes in the physicochemical properties of environmental media can also have far reaching effects on the health of organisms, impact ecosystems, soil fertility and food productivity in general. Oil spillage can occur in terrestrial or aquatic ecosystems[4]. Crude Oil spillages that occur in the sea, can be quite difficult to contain because of their ability to spread over a large surface area as a thin film of oil covering large expanse of the water body. Oil spills on land are more readily containable, however, they are no less damaging; without the deployment of fast and effective remedial measures, they also may end up contaminating ground water in which case remediation becomes more complicated and difficult to implement[5].

Total Petroleum Hydrocarbon (TPH) is a very important parameter in the assessment of crude oil. It is a representation of the mass of all hydrocarbons present in oil, inclusive of all the volatile and nonvolatile components that can be acquired or analyzed using a particular procedure. It is also the compound parameter that takes into consideration the environmental pollution that results from all petroleum hydrocarbons present in the sample[6].

Furthermore, in the context of an environmental sample, Total petroleum hydrocarbon refers to the sum of hydrocarbons that can be extracted from the sample (Extractable petroleum hydrocarbons)[6]. Extractable petroleum hydrocarbon (EPH) is also another name for the non-volatile components of crude oil.

This is considered because, according to Ordinioha and Brisibe (2013), a huge fraction of the volatile components of crude oil to 50 percent for the lost at the site of the spill from 24-48 hours after initial occurrence[7]. The United states Environmental Protection Agency (USEPA), declared that the release of total petroleum hydrocarbons into the environment will pose a serious threat to the safety and wellbeing of the general populace by the contamination of water for drinking, reduction of air and water quality, putting agriculture in jeopardy, deteriorating natural habitats and recreational centers, causing fire explosions, reducing food supply, and wasting non-renewable resources[8].

This article is aimed at assessing the alterations in the physicochemical characteristics due to the impact of petroleum hydrocarbons on Kpite Soils.

Materials and methods

Sampling method: Four composite quadrants of surface and sub-surface soil were collected from an oil spill impacted site in Kpite community, Tai Local Government of Rivers State. The sampling area of $200m^2$x$200m^2$ was divided into 100 grid plots while samples were collected at two depths, surface (0-15cm) and subsurface (15-30cm) using a soil auger. Surface and subsurface soils were randomly selected from each plot and homogenized to form (4) representative composite samples and taken to the laboratory for analysis. The samples were collected in aluminum foil and taken to the laboratory for analysis.

Laboratory Analysis: Determination of Moisture content: A constant weight of watch glass was obtained and thereafter, 20g of the wet samples were each weighed into the watch glass, and transferred into the oven for 2h at 105°C. The samples were cooled inside a desiccator for 30min before a constant weight of the sample and watch glass after heating and cooling was recorded. Moisture content was estimated as:

$$\%\ \text{Moisture Content} = \frac{[W1-(W3-W2]\times 100}{W1} \quad (1)$$

Where, W1 = weight of sample; W2 = Constant weight of watch glass; and W3 = Weight of sample + watch glass after heating and cooling.

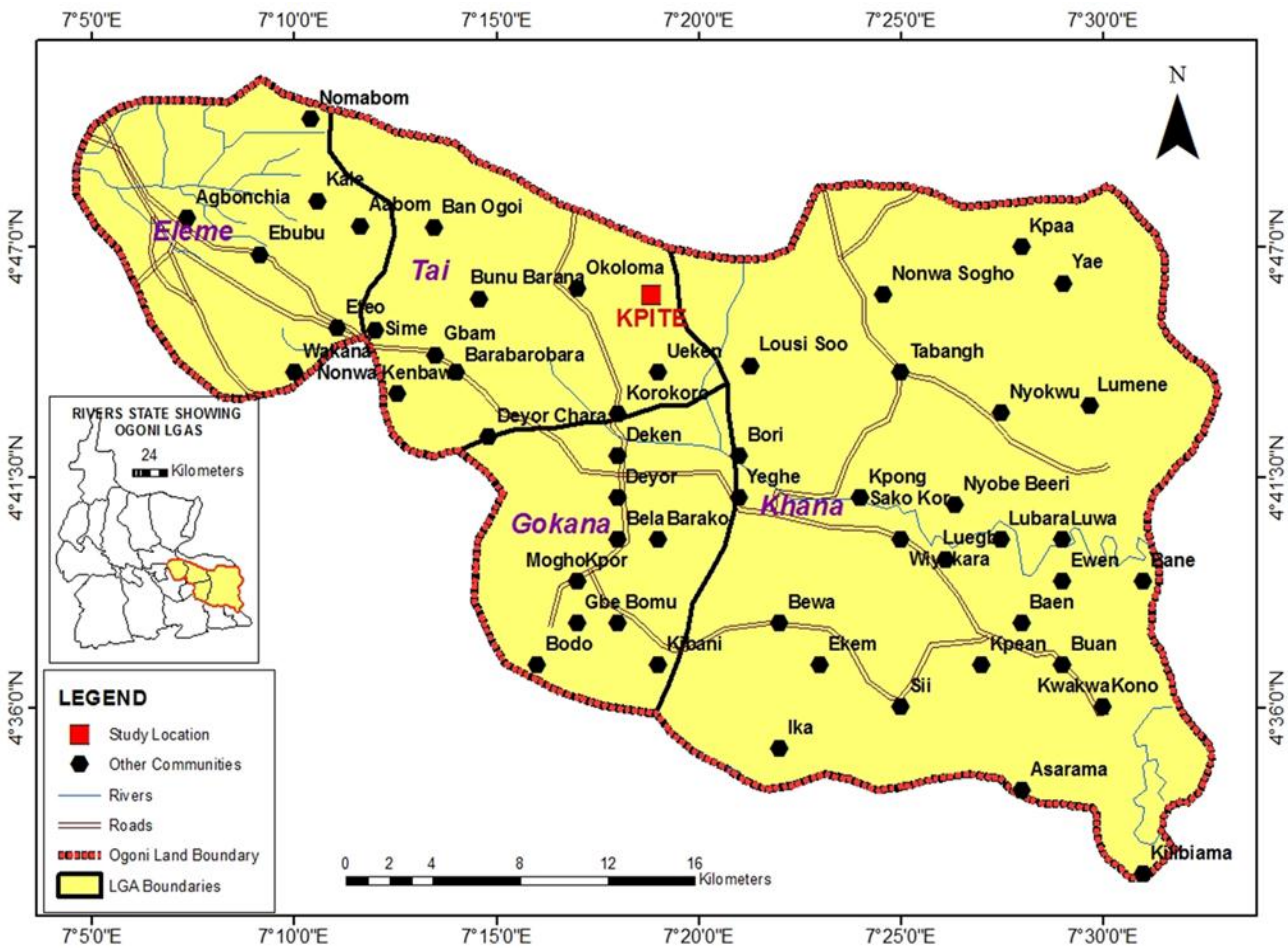

Figure-1: Map of the study area showing Kpite community.

Determination of soil-pH and electrical conductivity (EC): The soil samples were dried to remove moisture, the oven dried soil samples were then crushed and sieved to remove debris. 10g of the dry samples were weighed into labeled vial bottles and 10ml of distilled water was added to 10g of the dry soil samples respectively. The Samples were then agitated for 30 minutes and allowed to stand for 1 hour. The Separated water was then decanted into another vial bottle where the probes of the pH meter and EC meter were respectively immersed into the samples and allowed to stabilize at 25^oC to obtain the individual parameters, and the Results Recorded.

Total Hydrocarbon Content: The soil samples were extraction using standard methods. 30g of the wet soil sample was homogenized using a spatula in an amber bottle. The homogenized sample was dried using Na_2SO_4 and 30ml of dichloromethane was then added. The sample was agitated for 30 mins, filtered and concentrated to 1ml, The filtrate samples was then analyzed using the GC-FID.

Total organic carbon (TOC) and total organic matter (TOM): Soil sample were air-dried and 0.2g was weighed into a conical flask. 10ml of 1N potassium dichromate solution $K_2Cr_2O_7$ was added and swirled gently to disperse the sample in the solution. 20ml of concentrated tetraoxosulphate (VI) acid was added rapidly into the flask and swirled gently until sample and reagents were mixed and finally swirled vigorously for about a minute. The flask was allowed to stand in a fume cupboard for 30minutes. Five to ten (5 to 10) drops of the indicator were added and the solution titrated with 0.5N $FeSO_4$ until a colour change is observed (maroon colour). A blank determination was carried out to standardize the dichromate[9].

TOC and TOM contents were calculated as follows:

$$\%\ \mathrm{TOC} = \frac{(\mathrm{meqK_2Cr_2O_7 - meqFeSO_4}) \times 0.003 \times 100 \times 1.3}{\mathrm{W1}} \qquad (2)$$

Where: meq $K_2Cr_2O_7$ = 1N×10ml, meq $FeSO_4$=0.5N × Volume of titrant, W1 = Weight of sample, 0.03 = Milliequivalent weight of carbon, 1.30 = Correction factor, TOM (%) = TOC (%) x1.724. 1.724 = Conversion Factor; [%TOM = %TOCx100 /58; since TOC is 58% of TOM]

Determination of Nitrogen: The soil samples were air dried, crushed and sieved to remove impurities. 1g of the soil sample was then digested with 10ml mixture of H_2SO_4, HNO_3 and $HClO_4$ in the ratio 2:2:1 in a heating chamber. The digested samples were filtered and then made up with distilled water in a 100ml standard flask. 25ml of this digested solution was made up to 50ml with distilled water and 5ml of KOH was added to it. The solution was filtered, and 1ml of nester's reagent was added to 25ml of the filtrate and allowed to stand for 15 minutes. The absorbance was then read at 460nm. The analytical instrument was calibrated with a blank prepared by adding 1ml of nesters reagent to 25ml of water.

Determination of Phosphorus: The soil samples were digested with 10ml mixture of H_2SO_4, HNO_3 and $HClO_4$ in the ratio 2:2:1 in a heating chamber. 0.2ml of 0.5% p-nitrophenol indicator was added to 10ml of the digested solution in a conical flask. And made alkaline by the addition of 6N NH_3 solution by drop wise addition and shaking gently. 1N HNO_3 was then used to titrate the solution till it became colorless. 5ml of ammonium molybedate/ammonium vandate reagent was then added to the conical flask and made up to the 50ml mark with distilled water and properly homogenized. The sample was allowed to stand for 30 minutes and the absorption of the solution was measured using a colorimeter at 400nm wavelength setting and the phosphorus content read.

Determination of Potassium: The solution of the digested soil sample was eluted using an Atomic Absorption spectrophotometer and the concentration recorded. The blank was distilled water.

Results and discussion

Total petroleum hydrocarbons content: The analysis of the Total hydrocarbon content of the soil samples revealed that the concentrations far exceeded the intervention and target regulatory limits of 5000mg/kg and 50mg/kg respectively, set by DPR's EGASPIN for total petroleum hydrocarbon content in the soil. This is proof of heavy pollution in the Kpite spill soils. The samples were found to respectively have a total petroleum hydrocarbon concentration of 3731.44, 14387.2, 2598.5 and 6870.07mg/kg. According to Osuji and Nwoye, such high petroleum hydrocarbon alterations pose a huge threat to the sustainability of the environment[10].

They affect plant growth as well as soil productivity and at such can lead to the loss of biodiversity. Osuji *et al.* confirms that high level of hydrocarbon in soil impacts both surface and underground flora and fauna, which are indispensable adjuncts in the biogeochemical cycle that helps nutrients in soil to available for plant use. Remedial procedure is therefore necessary on the site to restore it to optimum environmental standards for the support of environmental sustainability[11].

Physicochemical Alterations: Soil pH and Moisture content: The pH of the various soils ranged from 5.14 – 5.40, implying that the soils are slightly acidic. The optimum pH range for the growth of plants is from 6.5-7.5; an additional 0.5 units on both range ends may also be considered permissible. The pH of Kpite oil spill soils therefore does not fall within the permissible limit and such soil pH levels may have dire consequences on the effective growth of plants and by extension communal source of livelihood. pH in the range of 4.9–5.1 can have serious implications on nutrient availability in the oil-polluted soils[12]. The site therefore may need to be treated with chemicals such as soda lime in order to reduce the acidity of the soil.

Table-1: Result of physicochemical parameters Kpite oil spill impacted site.

Sample	pH	EC (µS/cm)	TOC (%)	TOM (%)	N (mg/kg)	P (mg/kg)	K (mg/kg)	Moisture Content (%)
A	5.14	186.20	1.33	2.30	1140.00	115,500.00	3.727.00	18.40
B	5.26	118.00	1.72	3.00	1490.00	67870.00	3.501.00	18.80
C	5.37	116.40	1.31	2.30	1610.00	38250.00	1.813.00	17.00
D	5.40	101.40	1.58	2.80	1000.00	42570.00	2.857.00	14.40

Table-2: Result of Total hydrocarbon content, n-alkanes and Isoprenoids concentration in mg/kg of Kpite oil spill impacted site.

n-alkanes	A	B	C	D
C8	0.0381	0.156	0.732	0.079
C9	0.03295	0.386	2.0131	0.0595
C10	1.7621	41.9826	23.08	7.3435
C11	16.2786	132.167	59.031	54.6322
C12	21.2243	54.343	34.5992	47.2392
C13	79.6567	156.745	89.6085	145.813
C14	158.11	219.719	26.5758	127.171
C15	100.101	136.952	86.9837	125.908
C16	121.699	545.164	43.078	155.861
C17	148.435	856.225	129.575	581.072
pristane	33.992	-	29.474	87.9504
C18	213.231	849.082	192.35	723.328
phytane	134.096	-	111.63	211.059
C19	140.36	1240.76	50.77	189.103
C20	179.515	1066.46	164.112	235.055
C21	130.302	1090.42	115.816	447.065
C22	159.044	959.792	133.37	405.992
C23	108.192	928.763	98.6746	368.69
C24	100.741	971.169	83.183	376.655
C25	253.088	594.716	30.16	333.513
C26	55.3518	698.407	51.3386	351.145

C27	80.3207	659.314	73.5072	246.738
C28	217.241	557.747	61.8938	229.108
C29	229.25	524.713	164.398	235.951
C30	239.063	585.178	187.66	244.723
C31	194.89	545.525	167.075	195.783
C32	147.458	248.58	121.539	144.324
C33	87.97	-	81.2226	64.1391
C34	12.28	284.855	10.5954	27.7323
C35	102.85	94.4818	74.0319	160.601
C36	85.025	104.55	57.9152	110.064
C37	106.42	130.344	40.5783	119.017
C38	77.43	83.5563	1.233	85.9322
C39	-	24.6825	0.3997	30.8649
C40	-	0.2457	0.2936	0.3573
Total	3731.44	14387.2	2598.5	6870.07

Table-3: Diagnostic ratios n-alkane and Isoprenoids.

Sample	Pr/Ph	nC_{17}/Pr	nC_{18}/Ph	nC_{25}/nC_{18}	CPI
A	0.25	4.37	1.59	1.19	0.99
B	-	-	-	0.67	0.97
C	0.26	4.40	1.72	0.16	1.06
D	0.42	6.61	3.43	0.46	1.01

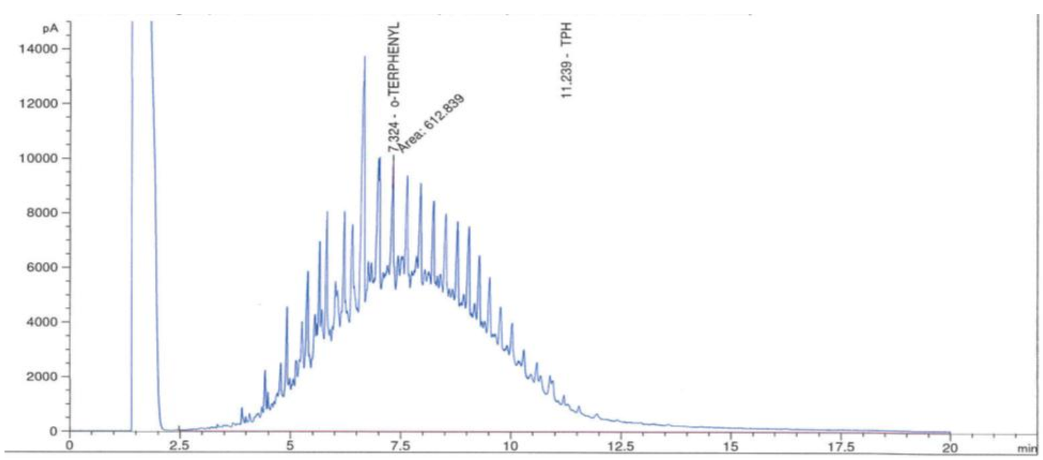

Figure-2: Representative chromatogram of Total petroleum hydrocarbons for oil spill samples.

The moisture content of the samples ranged from 14.4-18.4%. These moisture content values are fairly high, with sample A and B, having the highest moisture content.

Electrical Conductivity: The Electrical Conductivity (EC) of the samples ranged from 101.4 to 186.2µS/cm, the electrical conductivity was observed to decrease from sample A to sample D. Akubugwo *et al*. and Arias *et al*. in a similar research stated that the ideal soil electrical conductivity for optimum plant growth is 0.2-1.2mS/cm. The low electrical conductivities of the samples might be an indication of reduced metabolic activities; this would also explain the low percentage of organic matter and organic carbon present in the samples. The low electrical conductivities of the sample may therefore correlate to reduced fertility of the soil[13,14].

Nitrogen, Phosphorus and Potassium: The values of Nitrogen and Potassium in the soils are observed to be a lot lower than the recommended values of 15,000 and 10,000mg/kg, while phosphorus values was observed to far exceed the recommended standard of 2000mg/kg. The extremely high phosphorus values may not be as a result of crude oil spillage on the soils, but could have been influenced by the addition of inorganic fertilizers to the soil. The low concentrations of Nitrogen and Potassium can infer low levels of agricultural productivity[15]. There are also research indications that over nutrient supplementation in the soil could also induce low levels of agricultural productivity[16-18].

Total Organic Carbon and Total Organic Matter: The Total organic carbon and total organic matter contents ranged from 1.33%- 1.58% and 2.3% to 2.8% respectively for the four samples. Sample B had the highest TOC and TOM content, while sample C had the lowest TOC and TOM content. Sample A and sample C were observed to be quite identical in their TOC and TOM content. These percentage are generally low. It is expected that the degradation of oil by microorganisms in the soil would increase the organic content of the soil by adding more carbon to it. Low values of TOM and TOC could be as a result of the spilled oil limiting metabolic activities that could facilitate the increase of organic content from petroleum hydrocarbons by reducing the ability of the microbial community to break down the carbon chains. Note that the TOM and TOC presence in the soil are synonymous with their humus content. Low values are at such characteristic of low fertility in the soil and may be correlated to low agricultural productivity[12].

The implication of the obtained results are that the soils from the impacted study site of kpite community in the Niger delta, are heavily polluted and in need of remedial intervention. The pollution of the soils may also have contributed to changes in the physicochemical properties of the environment such as its fairly high acidity that sits above the optimum prescribed standard for the effective growth of plants in the region. As a result of this, it is advised that redial measures must be undertaken in the study area to restore the impacted site to proper and optimum condition for the support of biodiversity in the environment.

n-alkanes, Isoprenoids and Petroleum hydrocarbon content: Results of the n-alkane and isoprenoid analysis showed hydrocarbon distribution range of n-C_8 to n-C_{40}. Aliphatic hydrocarbons compounds lower than C_8 were not detected by the analytical instrument. This might be as a result of the loss of these compounds on site via evaporation, or evaporation during sample processing, as the n-alkane compounds less than C_8 are very volatile. More also the loss of the light end n-alkanes (carbon numbers lower than C_8) compared with the suspected source oil, may show that the spilled oil was only slightly weathered subsequent to the spill incidence and the chemical composition of aliphatic components had not undergone significant alteration. Computation of the Carbon preference index (CPI) of the n-alkanes gave a range of 0.99-1.06 for the crude oil impacted samples. According to researchers a CPI value about 1.0 indicates matured crude oil samples, while a CPI of greater than 1.5 may depict immature crude oil source with presence of modern plants in it. The values obtained for the CPI index of the soils therefore showed that the source of the hydrocarbons in the soils were petrogenic in nature[19,20].

The nC_{17}/Pr and nC_{18}/Ph ratios are used as biodegradation indicators for oil spilled impacted soils. The source oil can be also used to monitor the effect of microbial degradation on the loss of hydrocarbons at the spill site. The computed nC_{17}/Pr ratios for soil samples A, C and D were 4.37, 4.40 and 6.61 while nC_{18}/Ph were 1.59, 1.72 and 3.43 respectively. Sample B showed heavy degradation with the pristane and phytane heavily attacked (Table-2). Biodegradation may lead to significant alteration in the chemical and physical properties of spilled oils. Lightly degraded oils shows substantial loss of the low-molecular-weight n-alkanes, however the ratios of n-C_{17}/pristane and n-C_{18}/phytane (Table-3) have been found to be practically unaltered from the evaluated source oil in soil samples, heavily degraded samples shows n-alkanes, and even the isoprenoids in some cases been completely lost[19]. The presence of the humps in the chromatograms samples A, C and D of the soils can also infer to minimal or slight biodegradation.

Conclusion

This research showed high level of hydrocarbon contamination from Kpite oil spill impacted soil, which is an indication of severe pollution of the soil under investigation. Results of the physicochemical analysis and main fertility indices such as nitrogen, phosphorus, potassium, Total organic carbon and Total organic matter contents showed alteration in the soil properties. The n-alkanes and isoprenoid diagnostic ratios suggests mild degradation had occur in the crude oil impacted soil and the source of spill was petrogenic. These conditions will eventually lead to low soil fertility, which in turn implies low agricultural productivity and reduced source of livelihood in the affected area. It is highly recommended that adequate clean-up and depollution measures should be implemented immediately to restore the soil fertility and boast agricultural yield in the area. Liming is also encouraged to improve the pH of the soil to make it suitable for the growth of various crops. The productivity of the region is greatly under threat and proper measures must be instituted to remedy the environmental situation if the loss of agricultural viability in the area is to be mitigated and prevented.

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