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Rainfall water quality assessment in atmospheric deposition of an urban area: A case study of Akure in Nigeria

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Abstract: The physicochemical properties of rainfall and dry deposition of Akure, Nigeria were measured over a period of one year (July 2015 to June 2016) at six different locations. A total of 72 rainwater samples was analyzed for the Total Dissolved Solid (TDS), Temperature, pH, Electrical Conductivity (EC), Free CO_2, and Acidity using standard methods. The mean results depicted - TDS (22.51mg/L), Temperature (28.2ºC), pH (6.92), EC (44.75 µS/cm), Free CO_2 (20.97 mg/L), and Acidity (254.83 mg/L). Only three of the rain water samples were observed in the acidic range (< 4.6) suggesting that the presence of alkaline particles in the samples were not high enough to neutralize acidic species available in the water. Multivariate statistical analyses, such as Factor Analysis as well as Correlation Matrix showed significant anthropogenic pollutant intrusions in the rainwater samples. Cluster Analysis revealed the similarity between TDS and EC and this was confirmed by Pearson Correlation Coefficient (r = 0.99) at a significance level of 0.05. The study suggested that traffic activities were the main sources of deposition in the locations under this study.

Keywords: Rainfall and dry deposition, Physicochemical properties, Factor Analysis, Anthropogenic activities.

1- Introduction

In recent years, there are concerns have increased from total deposition to air concentrations, and surface-air exchange, as they relate to the atmospheric lifetimes of acidifying species, greenhouse gases, and oxidizing species (World Meteorological Organization, 2017). According to World Meteorological Organization (2017), quantification of wet deposition and precipitation chemistry has regularly made over the years in various continents with degrees of success. Acid deposition has been a major environmental concern, areas in which this has resulted in problems, sophisticated, and high-quality measurement systems are developed.

Urbanization in different countries of the world is one of the key factors that led to pollution. Anthropogenic activities in the urban areas have led to air pollution. It is on record that over 2million premature deaths that happen annually are attributed to the urban pollution (WHO, 2011). According to Mohamed et al. (2016), the concern regarding the quality of rainwater is atmospheric pollution from non-anthropogenic and anthropogenic activities. The examples of common chemical pollutants in the environment that emanate from anthropogenic sources are the ionic gases (NO, SO_2 and NOx), these can affect the quality of rainwater.

Pollutants dispersed over long distances by small particles. According to Azimi et al. (2003), when the particles are washed or aggregated by rain are referred to as atmospheric deposition (wet and dry deposition respectively). Dry deposition of particles arises by direct impact with gravitational depositions on water and land surfaces, whereas in wet deposition, gases and aerosols are suspended or deposited in ice crystals or water droplets (Azimi et al., 2003). In dry and wet depositions, atmospheric sources play important roles in the pollution of the environment due to metal. The ratio of atmospheric deposition and that of wet to dry is subject to the distance to the source of emission, the distance of the sources and the sampling site and meteorological factors (Tasic et al., 2009). Bulk (dry and wet) sampling of atmospheric deposition of direct collections provides a good approach to monitoring the environment.

Several types of research have been conducted on rain chemistry to the study based on the chemical composition (Azimi et al., 2003; Tasic et al., 2009; Akoto et al., 2011; Waziri et al., 2012; Subramani and Devaanandan, 2015). Also, many researchers (Selle et al., 2013; Jiang-Qi et al., 2013; Wang et al., 2014; Talukder et al., 2016; Bhuyan and Bakar, 2017) have used multivariate analysis to interpret the data sets, recognize pollution factors, assess water quality parameters with spatiotemporal deviation, and evaluate and categorize water quality.

Monitoring of pollutants in Akure, Ondo State, Nigeria is necessary due to the rapid urbanization, population growth and increase in vehicular movements. It is therefore not out of place if atmospheric fallout of Akure is determined monthly for a year. The main objective of this study was to determine the physicochemical properties of the water from atmospheric deposition within the vicinity of sampling. To achieve this objective, a 2lt plastic container high-density polyethylene (HDPE) was attached to an HDPE funnel to collect rainwater. In a period where there was no rainfall, the aerosol settling on the inner part of the funnel wall was washed into the container with distilled water.

2- Materials and Methods

Six sampling sites were selected for the study (Fig 1). The duration of sampling was twelve months (July 2015 to June 2016) and this was done monthly. A total of seventy-two samples were collected. Below is the list of the sampling areas (Table 1):

Table 1: Sampling Areas

S/N	Location	Coordinate	Description
1.	National Museum (Oja Oba) Commercial area	N07°15’ 11.6’’ E005 11’ 40.2’’	High-density traffic,
2.	School of Science and Park, FUTA	N07°18’ 07.6’’ E005 08’ 06.5’’	Low-density traffic residential area
3.	Opposite Fadach Petrol Station Area (Airport Road)	N07°15’29.5’’ E005 13’ 19.5’’	High-density traffic Mechanic workshop
4.	Breeder’s College (Aule Road) Residential and Commercial Area	N07°15’46.6’’ E005 09’ 47.6’’	High-density traffic
5.	National Library (Oda road)	N07°14’00.1’’ E005 12’ 57.0’’	High-density traffic
6.	Jenyo Hotel Area (Ado Road) and	N07°18’19.1’’ E005 14’ 30.5’’	High-density traffic residential area

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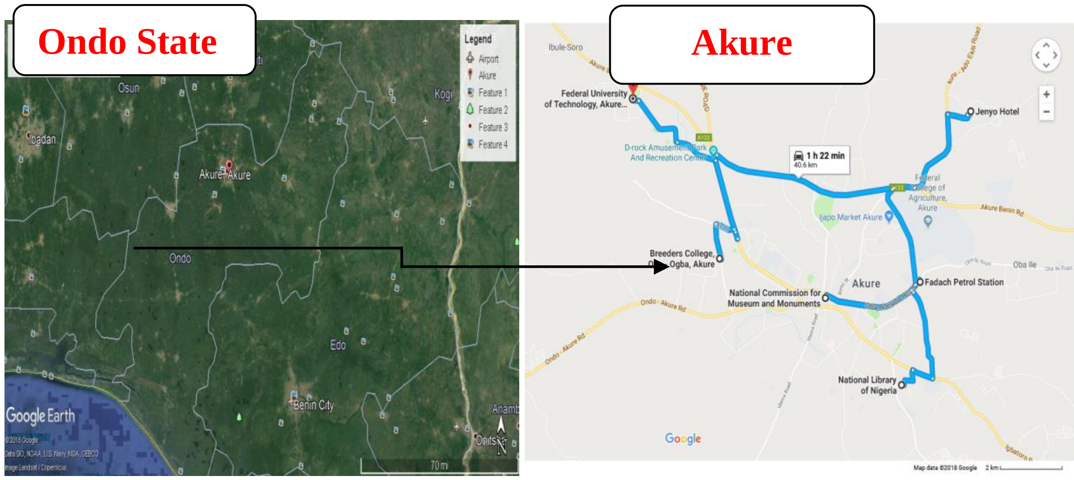

Fig 1: Map of the Akure, Ondo State, Nigeria Showing the Selected Sites (Shown in blue)
Source: Google Earth (2018)

The sample collection has been described elsewhere (Onwudiegwu et al., 2016; Abulude et al., 2018). Rainwater samples were collected once a month, using the sampler, fashioned after the Australian model gauge which was made of a HDPE plastic container (5L), connected to an HDPE funnel. The set-up was placed on the sampling stand 2.0 m above the ground in order to prevent lichen-formation during the sampling period. After a month, the rainwater sample collected was filtered, using Whatman ashless filter paper (11.0cm, Cat. No. 14442 110). The physicochemical parameters (pH, TDS, EC, free CO2, acidity, temperature, of rainwater samples was subjected to appropriate determinations, using standard methods of analyses (Limgis, 2001).

Data obtained (basic descriptions and multivariate analyses) were generated in triplicates and analyzed, using Minitab 16 Statistical Software.

3- Results and Discussion

The results of physicochemical characteristics of the rainwater samples obtained at the different sampling sites in Akure are provided in Table 3.

The pH ranges between 4.60 and 7.30 with a mean value of 6.92. Out of the total 72 rain events, only three events were observed in the acidic range (< 4.6) which occurred after continuous rains. Alkaline pH in these samples suggested that the influence of anthropogenic sources due to acidic gases was minor and the effect of particulate matters of alkaline nature like dust particles was dominant (Khan and Sarwar, 2014).Similar results have been obtained elsewhere, Croatia (Beyens et al., 2010), India (Meena et al., 2014; Brazil (Cerqueira et al., 2014); Bangladesh (Bhuyan and Bakar, 2017); Nigeria (Abulude et al., 2018); The difference in rain pH can be attributed to variations in the atmospheric composition of aerosols and gas, which can also indicate atmospheric pollution and also variations in the amount of time where the rain droplets were exposed to the environment (Beysens et al., 2006). The pH values in these samples did not exceed the WHO (2011), European Community (2007) and Standard Organization of Nigeria (2007) water limits. The pH values of the samples (90% and above) were within the recommended limits of pH 6 and 9 (bathing water) and 6.5-9.5 (drinking water). It must be noted that these limits did not increase the harmfulness of other substances available in the water (EPA, 2001). pH values govern the activity of many other important parameters of water quality. For example, NH_3 toxicity, chlorine disinfection efficiency, and metal solubility are all influenced by pH. At the extreme, pH value may affect the taste, quality of rainwater. Rainwater pH is an important parameter in predicting the nature of anthropogenic activities.

The average (254.83mg/L $CaCO_3$) and standard deviation (49.50) values showed that the variability of acidity in the samples was considered very high. This variability can be explained by a distance of sources of emission from the sampling location and level of emissions. It must be noted that rainwater is not buffered (completely unbuffered) and so the pH will change all the time depending on the partial pressure of CO_2, the atmospheric concentrations of sulphur and nitrogen oxides, the temperature, and other parameters, examples, are the material of the collecting vessel and the time of collection. The alkalinity of rainwater does not mean that rain has an acidic or alkaline nature; it measures the buffering capacity of the samples due to varying amounts of OH^-, CO_3^{2-}, and HCO_3^- (Khan and Sarwar, 2014).

The electric conductivity (EC) of rainwater samples during the sampling period ranged from 2 μS cm^{-1} to 325 μS cm^{-1}, with a mean of 44.75μS $cm^{-1}$and a standard deviation of 61.55, Skewness (2.33) and Kurtosis (6.22). The average result obtained in this study was far above the 11.3 (±7.65) obtained from rainwater samples from Brazil (Cerqueira et al., 2014), India (33.2 and 20.9 μS cm^{-1} Pune and Delhi respectively (Rao et al., 2016), but lower than the values observed by Abdus-Salam et al. (2014) for Ilorin, Nigeria (108 μS cm^{-1}) and 238-308 μS cm^{-1} for samples harvested in Pakistan (Khan and Sarwar, 2014). The EC looked good as an indicatorof the total concentrations of soluble ions (Zhao et al., 2013). The results obtained by the different authors may reflect seasonal differences in the movement of air masses from the sea coast. The high conductivity values obtained from the water samples were attributed to the strong contribution of dissolved salts of ions (Khan and Sarwar 2014). According to Cerqueira et al. (2014), conductivity was higher in the less rainy season because, in drought seasons, the atmosphere is more polluted, in that the wet scavenging process carries a higher load of compounds which increases the parameter.

Table 2: Quality of Rain Water Samples

Readings		Gradings
TDS 50 to 100	–	Good
TDS 100 to 300	-	Medium good
TDS 300 to 500	-	Okay for drinking.
TDS more than 500 but less than 1000	-	Poor
TDS more than 1000	-	Not recommended for drinking.

Total Dissolved Solids (TDS) of the samples ranged between 1 and 165mg/L with a Coefficient of Variation (CV%) of 138.01. The CV% showed a very high variation. This could be due to the presence of solid particles in the weather of the different location, topography, climate, and pollution levels. The samples from different parts of Pakistan were similar in composition to the results of this study (Khan and Sarwar, 2014), but there were dissimilarities in values elsewhere in Nigeria (Abulude and Akinnusotu, 2016). Rainwater has a TDS value of less than 10 mg/L and regarded as pure water. Drinking water has a TDS reading of 25-250 mg/L, but should not exceed 500 mg/L. Distilled water has a TDS value of 0.5-1.5 mg/L. River water (between 100 and 20,000 mg/L). Seawater (35, 000 mg/L), and Lakes and streams (50-250 mg/L). The chart provided in Table 2 shows the gradings and the quality of water: Drinking water with low TDS may not be harmful because minerals and salts can be obtained from food. High TDS content in rainwater may affect its aesthetic quality, interfere with washing clothes and corroding plumbing fixtures. TDS is a measure of all of the minerals (principally calcium, magnesium, potassium, sodium, bicarbonates, chlorides, and sulfates) present in the water supply.

The results of the present study showed that the temperature was between 28.0°C and 32.0°C with an average of 28.5°C. The Std. Dev. (3.13) and CV% (11.07) showed that there were not many variations in the temperature of the water samples due to the conditions as at when the samples were measured. Seasonal variations in weather temperature can cause dramatic changes

Table 3: Basic Description of Physicochemical Properties of the samples

Statistical Parameters	TDS (mg/L)	Temp (°C)	pH	EC Free (µS/cm)	CO_2 (mg/L)	Acidity (mg/L $CaCO_3$)
Mean	22.51	28.29	6.92	44.75	20.97	254.83
Std Dev.	31.07	3.13	0.52	61.55	6.97	49.50
CV (%)	138.01	11.07	7.58	137.55	33.23	19.43
Min.	1.00	28.00	4.60	2.00	8.00	140.00
Max.	165.00	32.00	7.30	325.00	48.00	399
Skewness	2.33	-5.78	-1.50	2.33	1.29	0.36
Kurtosis	6.35	43.91	4.81	6.22	3.17	0.65

CV (%) – Coefficient of variation in percent, Std Dev. – Standard variation

in a rainwater temperature. Water temperature influences the biota in a water body by influencing activities such as behavior, respiration, and metabolism. In a similar experience observed by Raghuvanshi et al. (2014), it was noted that the high temperature was recorded during the harmattan period. The high temperature at this period was due to the low water level, high solar radiation, high air temperature and clean atmosphere. The urban heat island effect causes increased rainfall (in amounts and intensity), downwind of cities. Globally, global warming is also causing changes in the precipitation pattern, which includes wetter conditions across eastern America and drier conditions in the tropics.

The minimum value of Free CO_2 was 8mg/L, while the highest was 48mg/L. Other descriptive results were as follows: mean 6.97mg/L, Std Dev: 6.97, CV%: 33.23, Skewness: 1.29, and Kurtosis: 3.17.

The Skewness and Kurtosis were depicted with small sample values. This showed that the samples were not reasonably symmetrical. Variations in the Free CO_2 were not significant among the rainwater samples. The free CO_2, when dissolved in rainwater, contributes to the hardness of water or rainwater.

Free CO_2 reacts with water partly to form calcium bicarbonate and in the absence of bicarbonate gets converted to carbonate releasing carbon-di-oxide. There were not many differences in the values obtained at all the sites (Abulude and Akinnusotu, 2016).

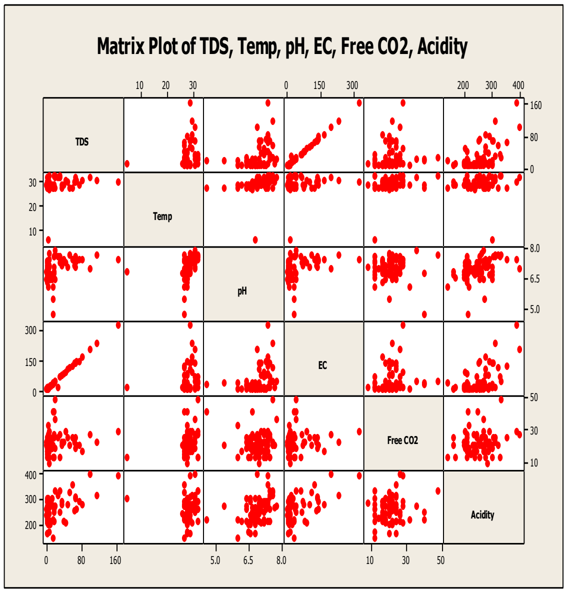

Fig 2: Matrix Plot of TDS, Temp, pH, EC, Free CO_2, and Acidity

Matrix Scatterplot has variables that are written in a diagonal line from top left to bottom right (Fig 2). The variables (physicochemical parameters) were plotted against each other. The first column was an individual scatterplot of TDS and EC, with TDS as the X-axis and EC as the Y-axis. In this graph, scatterplot was replicated in the middle of the top row. Meaning that the boxes on the upper right-hand side of the whole scatterplot were mirror images of the plots on the lower left hand. In the graph, it was shown that there was a correlation between TDS and EC. The matrix scatter plot also depicted weak correlations between EC and Acidity, and pH and EC. The Correlation Coefficient confirmed these.

Table 4: Correlation Coefficient of the Physicochemical Properties of the samples

	TDS	Temp	pH	EC	Free CO_2	Acidity
TDS	1					
Temp	0.188	1				
pH	0.355	0.259	1			
EC	0.996	0.177	0.344	1		
Free CO_2	0.175	0.251	-0.053	0.169	1	
Acidity	0.572	0.040	0.419	0.419	0.151	1

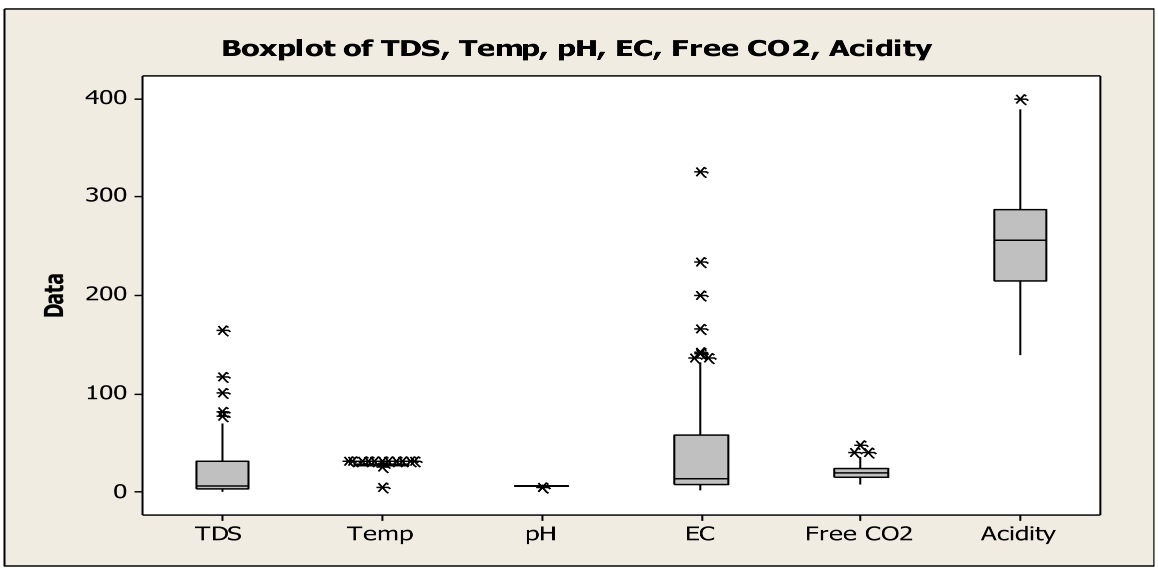

Fig 3: Boxplot of the Physciochemical Properties determined

All the physicochemical properties of the rainwater samples except acidity and Free CO_2 skewed to the right, which means they are nonsymmetrical (Fig 3). Free CO_2 has its interquartile range in the sample, while acidity has its range in the upper quartile. The reason for the skewing to the right was that there were large variations in the values of physicochemical properties recorded in the study. The boxplot is a visual display presents five different statistical tools in a study - the minimum, the lower quartile, the median, the upper quartile and the maximum. It is an indicator of centrality, symmetry, spread and tail length of the population and sample.

Pearson's product moment correlation matrix was done to identify the relationships among parameters to strengthen the results from multivariate analysis (Table 2). The Pearson correlation coefficient (r) was calculated from the physicochemical concentration in order to predict the possibility of a common source (Table 4). Significant positive correlations were found between pH and EC (r = 0.34), pH and TDS (r

= 0.35), pH and acidity (r = 0.419s), EC and TDS (r = 0.99), EC and acidity (r = 0.41), acidity and TDS (r = 0.57) depicting the influence of crustal aerosols. In Nigeria significant effect of crustal aerosols in neutralizing rainwater, acidity is already observed.

Cluster Analysis (CA) is an effective tool to find out the similarity and dissimilarity of the influencing factors on different data sets (Wang et al., 2014). Moreover, CA is an important tool for characterization and simplification of datasets, based on their behavior. The dendrogram is the arrangement plots, according to their similarity or dissimilarity. The closeness of clades that are of the same height showed how similar they are to each other and vice versa. The higher the difference in height, the greater the dissimilarity. In Fig 4, out of all the variables studied, TDS and EC showed the greatest similarity, showing their positive correlation because they are caused by the same source. This predicted a possibility of a common source. CA (Dendogram) was performed to show the similarity among the variables and identify their sources of origin. The dendrogram depicted five numbers of clusters, the numbers of similarity observation were 2, 3, 4, 5, 6 each having 99.8%, 78.5%, 70.9%, 62.9%, and 62.6% respectively.

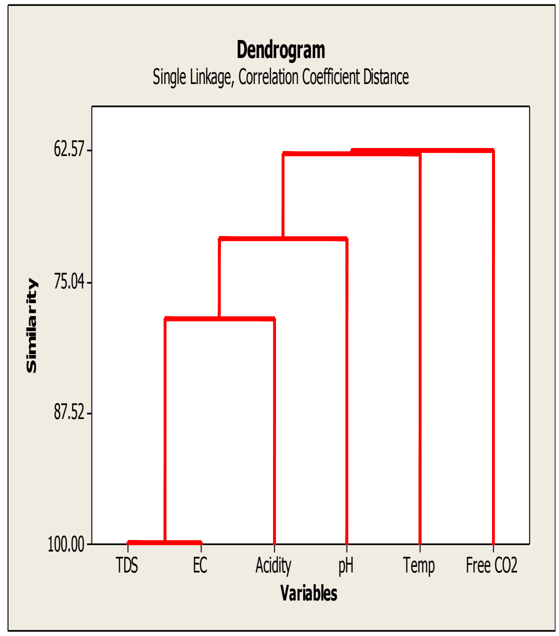

Fig 4: Dendogram Plot of the Physciochemical Parameters

Table 5: Factor

	Factor 1	Factor 2	Factor 3	Factor 4	Communality
TDS	**0.958**				**1**
Temp			**-0.985**	**0.980**	**1**
pH		**0.955**			**1**
EC	**0.964**				**1**
Free CO_2					1
Acidity	**0.352**				**1**
Variance	2.020	1.009	1.005	1.005	6
% Var	33.7	16.8	16.8	16.7	1

Analysis of the Physicochemical Properties of the samples

Factor analysis (FA) was applied to the physicochemical composition of samples. Table 5 depicted the values of the parameters on which the FA was applied. Significant principal components were picked on the basis of an eigenvalue > 1. FA showed the most vital factors that affected the water quality of the study area. Factor 1 had an initial Eigenvalue of 7.948 and a total variance of 33.7%, with the strong positive loading of TDS, EC, and acidity that resembled the loading of pollution, mainly caused by the anthropogenic effect. Factor 2 had a loading pH, while Factor 4 had a loading of temperature. From this FA study, it may be concluded that the source of FA 1 may originate from a mixed source of anthropogenic inputs, particularly from traffic in the study area.

Conclusion

The present study aimed to characterize the physicochemical parameters of rainwater samples. The sampling was conducted between July 2015, and June 2016. Only three rainwater samples were observed in the acidic range (< 4.6) suggesting that the presence of alkaline particles in the samples were not high enough to neutralize acidic species available in the water. The multivariate analyses performed showed that there were correlations and similarities between TDS and EC. It may be concluded that anthropogenic activities - traffic could have an influence on the parameters analyzed. Abbasi et al.(2017) showed that The most important factor in vehicle pollutant emission is the traffic flow that includes traffic volume, speeds and density as main factors, as well as other factors, such as drivers' behavior in starting to move, the vehicle types, traffic management method, and traffic signs locations in the streets.

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Conflict of Interest

There is no conflict of interest.

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