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Climate Spectrophotometric Assessment and Health Risks Scrutiny of Nitrate and Cadmium Ions Accumulation in Water Physiques in Southern, Rainforest Belt of Edo State, Nigeria

Emmanuel Ufuah
Department of Civil Engineering, Ambrose Alli University Ekpoma Edo State, Nigeria

Christopher Ehizemhen Igibah (Corresponding Author)
Department of Civil Engineering, University of Benin Edo - State Nigeria
Email: igibahchrist1@mail.com

Lucia Omolayo Agashua
Department of Civil Engineering, Federal University of Technology Akure Ondo State, Nigeria

Ogbiye Adebanji Samuel
Department of Civil and Environmental Engineering, Airforce Institute of Technology Kaduna, Kaduna State, Nigeria

Olumuyiwa. O. Onakunle
Civil Engineering Department, Covenant University Ota, Ogun State, Nigeria

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Abstract

Anthropogenic and industrial activities triggering an alteration on the natural cadmium and nitrogen cycle are deliberated on as one among the most vital environmental concerns. Water quality index (WQI) and skewness, nitrate was 8.37 ± 1.014 in dry season and 3087.87 ± 1.150 for wet season, but cadmium was 0 ± 1.559 in wet season and zero all through the sunny period. Equating results with World Health Organization (WHO) permissible limits, it discovered that nitrate was low throughout both seasons whereas cadmium was 90% above permissible during rainy season, but 100% within limit throughout arid season. The water- physiques in all sites at Ikpoba River in both seasons revealed low disparities (< 20%) with positive linear relationship (R 0.922 ≥ 0.211) for nitrate and (R 0 ≤ 089) for cadmium in dry and wet seasons respectively. What's more, site 1 in the wet season, and all sites in dry season, exhibited no significant dissimilarities (p >0.05) between them, but others indicated significant dissimilarity (p <0.05) for cadmium and nitrate concentrations. In respect to seasonality, all water-physiques scrutinized revealed significant dissimilarities (p <0.05) for both seasons (nitrate and phosphate) concentration. The cadmium-nitrate ratio was very high particularly in the humid season because of the high input of nitrate. The nutrient contagion index displayed slightly to significantly contagion, whereas the water physiques will pose very high non-carcinogenic health risks and threats to users through the oral pathway.

Keywords: Cadmium; Nitrate; Water-bodies; Spectrophotometric; South-south; Nigeria.

1. Introduction

Seasonal variations in ground and surface water flow, precipitation or/ rainfall as well assurface run-off affect the river, stream and lake discharge as well as the levels of river and brook water contagious (Ibe *et al.*, 2020; Igibah *et al.*, 2021). Time and again, majority of people rely on metropolitan water supply and private wells, well-known as boreholes, for their daily water needs (Igibah *et al.*, 2020; Ngozi *et al.*, 2020). The state of water that being utilized by inhabitants around the globe is a crucial factor for ascertaining regularly, especially for its physico-chemical as well as microbial composition, so as to determines if the available water is fit for use. Ingested water with excessive anions, cations and bacterial ions above allowable limits might affectthe inhabitants well being (Enyoh *et al.*, 2018; Verla *et al.*, 2020; Yu *et al.*, 2020). Thus the permissible ions concentrations for numerous ions available in water are presented in the table. A lot of investigations carried out have confirmedabout the health implications ascribedto undesirable water attribute (Igibah and Tanko, 2019; Isiuku and Enyoh, 2020). Chemical contagions, in contrast, will not lead to sudden health concern except when present is in substantial quantities either through accidental exposure / or drinking water from unconfirmed sources (Amu *et al.*, 2021; Chendo *et al.*, 2019). On the other hand, if human being exposed to it for longer periods, they mightlead to health threats. Anion, microbial, heavy metal and cation contamination is well recognized and ubiquitous health threat linked to drinking and domestic water as it creates outbreaks of numerous water-related sicknesses for instance, typhoid, dysentery, cholera, and the rest (De Girolamo *et al.*, 2019; World Health Organization WHO, 2004). Economic status growth which is frequentlylinked with population rising, urbanization and agrarian activities has impelled novel ways of utilizing land, which in turn causes greater demand for hygienic and dirt-free water for domestic and agricultural deeds, as well as industrial processes. For inhabitants to satisfy their insatiable need for water, unrestrained tapping of groundwater or/ boreholesparticularly within thelocalities where the surface water is inaccessible is persistently been witnessed. Surface water portability is affected by nature,such as rainfall occurrence and evaporation processes and man-made deeds through single point or multipoint source (Ali *et al.*, 2018; Ngene *et al.*, 2018). Urbanization and industrialization influences environmental consequences that later cause's negative effect on the groundwater as a source of supply over an extended period. At hand aremany lands open for raw solid unwanted (waste) disposal (Agbazue *et al.*, 2015; Okoye and Orakwe, 2018). The ever-growing populace and accumulation of wastes pose serious environmental, socio-economic problems in the developed and developing nations. Several electronic devices, E-waste products for instances, paint materials, even old batteries, et cetera, derelict with other solid rubbishes put quantities of anions, heavy metals and cations on a pedestal in garbage sites, and lack of apposite separation of toxic wastes may further increase harmful ecological effects.With a swift population growth, urbanization, contagion and contributions from the air via burning of biomass materials stimulate environmental deterioration;predominantly dangers on water supplies attributable to microbial, anions, chemical and cations pollutants will definitely escalate (Cataldo *et al.*, 1985; Ogwueleka and Igibah, 2021). Similarly, waste disposed at dump-sites, burning of unwanted materials, storm water, as well as surface runoff carry contagions to nearest surface and ground water sources. Like, in developing nations, numerous scrutinizes on the impact of haphazard disposal of solid and unwanted wastesin open dumpsites have been scrutinized. In some researches, water attribute information of boreholes in close proximity to refuse dumps wascompared with the dataset from a regulator borehole far-off the dumpsite (Amu *et al.*, 2021; Igibah *et al.*, 2020; Ngozi *et al.*, 2020). Ascertaining the concentration of contagions; vividly, though equating measured variables with international criterions, thus, assessing the level of contagion of water supply are investigated to scrutinize the influence of quality control measures on water attribute and on the risk of exposure of the public to transported groundwater pollutants. Since water quality problems have become a global issue, a proper and proficient monitoring of water quality is a crucial element in health promotion strategy for developing nations.

2. Materials and Techniques

2.1. Description of Scrutiny Region

The water-physiques scrutiny are twelve sites at Ikpoba River, 4^{th} order creek (latitude 5.44 – 7.34^0 N as well as longitude 6.04 – 6.4^0 E) in IkpobaOkha Local Government Area and Benin City. Its headwater originthat traverses River Ethiope in Deita State, mounds from the Ishan Plateau in the norther zone and join rainforest belt of Idogbo suburb of Edo State. The state is in the South-South Zone of Nigeria (Figure 1), while the description of scrutinyregion showing photographs, close land use and actions is displayed in Table 1. Geographically, the whole district has Population of 1,782,000 in 2021, with densely populated area covers roughly 17,802 sq. km^2 and correspond to 2% of the nation's land mass. South-Southern Nigeria is of the wet humid kind climate with mean yearly temperature in the range of between 77 °F (25 °C) and 82 °F (28 °C). The arid season is between November and April with cold harmattan session lasts from December to January. The climate is moist in the southern part and sub-moist in the northern part with each of the seasons lasting roughly six months (Igibah *et al.*, 2020; Ngozi *et al.*, 2020). The rainfall, conversely, of the region and Ikpoba river annually were roughly 2679 and 1411 mm/year respectively, which represent decreasing inland from the Niger Delta coast of country, Nigeria. Thus approximately 70-80% of the dwellers of this precinct are observed to involve in farming, predominantly animal rearing and crop farming. The area of the South-south with the escarpment has an altitude of 550 m in the north and 150m in the south with maximum wind power of 43.8 w/m^2 (Amu *et al.*, 2021) As a final point, the region is characterized by the various Bini or Edoid ethnic culture such as Owans, Binis, Etsako, AkokoEdos and Esans, though speaks Edo language but their dialects vary.

2.2. Sample Collection

Water samplings were gotten from twelve sites of River Ikpoba subsurface at a distance of 10meters apart along the stretch of the river during the wet season (July, 2021) and dry season (November, 2020) respectively. Every sampling was collected with a two hundred and fifty millimeters (250ml) plastic container (bottle) in such a manner that the bottle was filled to the brim roughly thirty centimeters below the water surface, then tightly covered and placed in the cooler box conveying to the laboratory for investigation (Igibah *et al.*, 2020; Ngozi *et al.*, 2020).

2.3. Sample Scrutiny

2.3.1. Nitrate

The Cataldo *et al.* (1985) technique of nitrate investigation was utilized. Two millimeters (2 mL) of each formulated water sample were poured into a two hundred and fifty millimeters (250 mL) conical flask. Eight millimeters (8 mL) of five percent (5%) (w/v) salicylic acid in conc. H_2SO_4 were introduced with thorough mixing.

The mix was permitted to wait for twenty minutes at room temperature for settlement.Then one hundred and ninety millimeters (190 mL) of two meters of NaOH were steadily added to elevate the pH beyond 12. After samples cooling at room temperature, the ratio of salicylic-acid-H_2SO_4 to nitrate sample should not be less than 3: 1 (v/v).

Then spectrophotometrically at λmaximum of 410 nm was utilized to ascertain nitrate absorbance, while the different nitrate concentrations C in the samplings were gotten from calibration curve via the Beer-Lambert equation:

$$C = A / \varepsilon max \quad (1)$$

where, Ɛmax and A are slope and absorbance of the calibration plot respectively.

Table 1. Description of scrutiny regiondisplaying photographs, close land use and deeds

Location	Description of activities	Photograph	Close Land use
Outskirt of the city	Riparian settlements		Thinly populated so that disturbance due to human activities is low and localized.
Across the river	Among major dams in Benin Metropolis, Edo State		Then Bendel State Urban Water Board to supply pipe-borne water for domestic purposes.
Benin City	Dam and river		For Commercial activities.
Car washing companies	Edges of the river		Attached to the river in Benin City.
Site Assessment Of the River.			During Dry season.

For every 100 mL prepared colorless, neutral and non-turbid water sampling, one drop of phenolphthalein indicator of 0.05 mL quantities was added. Then two drops of two meters of H_2SO_4 were introduced to expulse pink color created. Besides ten drops (0.5 mL) stannous chloride reagent 1 and 4 mL of molybdate reagent 1 were then poured with thorough mix at room temperature and the blended solution were allowed to cool for eleven minutes. Scrutiny were performed on the samples using obvious Spectrophotometer at λmaximum 690 nm. This adapted techniques is propositioned by WEF (Water Environment Federation), APHA (American Public Health Association), and AWWA (American Water Works Association),

2.4. Data Scrutiny

All data scrutiny was performed via the IBM SPSS Statistics Version 20. Mean, skewness, coefficient of variation and standard deviation were calculated for each twelve water physiques in both seasons. To investigate for significance dissimilarities between season-wise and water-bodies, one-way and two-way analysis of variance (ANOVA) at p <0.05 was carried out. The CV apprises on how cadmium and nitrate quantities vary by season, whereas equation 2 was engaged to calculate % of variation for water quality index.

$$\% \text{ Variation} = \left| \frac{WQI\ \text{(wet season-WQI (dry season)}}{WQI\ \text{(wet season)}} \right| \times 100 \qquad (2)$$

Variation was characterized as little disparity (CV% <20), moderate disparity (CV% = 20-50) and extreme disparity (CV% >50). Linear regression investigation was as well as utilized to ascertain the magnitude of correlation between cadmium and nitrate, and then assessed nitrate to cadmium ratio (N: Cd) to apprise on phytoplankton cum algae bud in the water physiques. Similarly, Nutrient Contagion index (NCI) and human health risks were processed to ascertain the contagion and human health risks of utilizing the water for household activities.

NCI was evaluated via the expression in Eq. (3)

$$NCI = \{C_P \div MAC_P\} + \{C_N \div MAC_N) \quad (3)$$

where CP/N is the average amount /concentration of either cadmium or nitrate in the water-physiques, MACP/N is maximum admissible/acceptable concentration gotten from WHO to be 0.003 mg/L and 50 mg/L for cadmium and nitrate in stream and river water correspondently. The classes for NCI is pigeon-holed as NCI of <1 (no contagion), NCI of 1 ≤ 3 (Slightly contagion), NCI of >3 ≤ 6 (significantly contagion) and NCI of >6 (Extremelycontagion).

Table-2. Cadmium and Nitrate concentration of water physique in both seasons

Parameters	Cadmium (%)		Nitrate (%)	
	Wet season	Dry season	Dry season	Wet season
Mean	0.066 ± 0.0543	0	11.0829 ± 10.215	23.331 ± 4.920
Max±Min	0.16 ± 0.00	0	33.21±0.04	36.02±17.08
CV ±WQI	0.89 ±0	0	0.922±8.37	0.211 ± -3087.87
Variance	0.829	0	104.353	24.127
Skewness	1.559	0	1.014	1.150
Kurtosis	0.922	0	-0.346	1.297
Magnitude of variability	4.330		38.00	
WHO Limits	0.003		50	

Table-3. Stations, Means and Nutrient Contagion Index (NCI) for both seasons

Stations	Rainy Season (Mg/l)		Dry Period (Mg/l)		Rainy Season		Dry Period	
	Nitrate	Cadmium	Nitrate	Cadmium	NCI	Remark	NCI	Remark
1	36.02		4.69		3.18	Significantly contagion	0.53	no contagion
2	27.06		3.28		2.50	Slightly contagion	0.58	no contagion
3	22.36		6.09		2.10	Slightly contagion	0.50	no contagion
4	33.41		20.2		2.27	Slightly contagion	1.21	Slightly contagion
5	21.23		23.4		2.90	Slightly contagion	1.81	Slightly contagion
6	19.92		18.95		3.01	Significantly contagion	1.19	Slightly contagion
7	17.08		27.2		2.08	Slightly contagion	1.55	Slightly contagion
8	27.08		33.21		1.99	Slightly contagion	1.78	Slightly contagion
9	20.05		29.83		1.42	Slightly contagion	2.25	Slightly contagion
10	23.08		5.09		1.60	Slightly contagion	2.94	Slightly contagion
All	23.33		11.08		2.13	Slightly contagion	1.07	Slightly contagion

The grouping for NCI is classified as NCI of <1 (no contagion), NCI of 1 ≤ 3 (Slightly contagion), NCI of >3 ≤ 6 (significantly contagion) and NCI of >6 (Extremely contagion).

Table-4. Stations versus water quality index computation for both seasons

Stations	Wet Season (mg/l)		Dry Season (mg/l)		Wet Season (%)	
	Nitrate	Cadmium	Nitrate	Cadmium	WQI	Status
1	36.02	0.01	4.69		267.21	V.poor
2	27.06	0.03	3.28		347.09	Extremely poor
3	22.36	0.02	6.09		96.71	Good
4	33.41	0.14	20.2		705.45	Extremely poor
5	21.23	0.10	23.4		47.89	Exceptional /Excellent
6	19.92	0.55	18.95		609.40	Extremely poor
7	17.08	0.01	27.2		56.89	Good
8	27.08	0.14	33.21		119.29	Medium
9	20.05	0.16	29.83		37.09	Exceptional /Excellent
10	23.08	0.00	5.09		3.56	Exceptional /Excellent

Furthermore, People might be exposed to cadmium and nitrate in surface water such as river, stream, lake etcetera by two ways via ingestion or oral as well as dermal route when they come in contact with the water. Hence, health threats were assessed from these dual pathways, which are oral plus dermal route threats, then the chronic daily intake (CDI) per unit weight were ascertained via expression in Eqs. (4) and (5).

$$CDI_{oral} = \{C_{P/N} * IR\} \div \{BW_{C/A}\} \quad (4)$$

$$CDI_{Dermal} = \{C_{P/N} * Ki * SA * EV * CF\} \div \{BW_{C/A}\} \quad (5)$$

$C_{Cd/N}$ is mean assessed concentrations of either cadmium or nitrate (Tables 3 & 4), while IR is the rate or proportion of ingesting/ sipping the water which is 0.67 L/day for children (C) and 2 L/day for adults (A), Bw is body weight for youngster (C) with value of 15kg and adult (A) of 70 kg, Ki is the dermal absorptivity coefficient in water which is 0.001 cm/hour for children and adult. Also, SA is the surface area of contactable skin, for children 3416.0 cm^2 as well as 1700.0 cm^2 for adult, EV is Frequency or rate of bathing taken as 1 times/day, and conversion factor (CF) taken as 0.0020 L/cm^3 (Isiuku and Enyoh, 2020; Yu *et al.*, 2020). Analogously, the hazard or imperil quotient (HQ) associated with the usage of the water-physiques for household deeds is also assessed using Eq. (6) and the outcomes is shown in Tables 9 & 10, while the CDI is displayed in Table 7 and 8. Reference dosages (RFD) values were gotten from USEPA; (0.00005 mg/kg.d) and skin(0.0000005 mg/kg.d) for cadmium (Yui et al. 2021), whereas oral (0.000021 mg/kg.d) for phosphate-phosphorus but skin was not available (USEPA 2001).

$$HQ_{oral/Dermal} = CDI_{oral/Dermal} \div RFD_{oral/dermal} \quad (6)$$

The hazard index (HI) were assessed also as the sum-up of HQs and extracted in Eq. (7).

$$HI_{oral/dermal} = HQ_{Cu} + HQ_{N} \quad (7)$$

3. Results and Discussion

3.1. Water Quality Index

The magnitude of variability, kurtosis, variation, mean, skewness and standard deviation for cadmium well as nitrate in arid and wet seasons is displayed in Tables 2. Comparing to World Health Organization (WHO) criterion, the tolerated level of cadmium and nitrate in surface water such as streams, lakes and rivers are 0.003 mg/ l and 50 mg/ lcorrespondingly (World Health Organization WHO, 2004). Cadmium amounts observed for the water-physiques were zero in dry season, but 90% beyond allowed limit in rainy period. Whereas, nitrate amounts observed for the water- physiques were below allowed the limit in rainy and dry period. Relating this investigation with prior published results, such as Sani et al. (2022) that evaluated river water in River Challawa region of Kano in North-Western Nigeria, testified that Cadmium (Cd) concentration in water varied between 0.273 ± 0.0282 and 0.61 ± 0.154 mg/l, with ($p <0.05$) as level of its significant at Site A and B, but not significantly tangible at site C. All the concentration of Cd during arid season are within the standard set by WHO (2003). Likewise Charity (2014) displayed high value of Cadmium quantities during rainy season in Bodo Creek sediment. Osa-Iguehide et al. (2015) also appraise the effect of heavy metals attribute in River Ikpoba in Edo State, discovered low cadmium amount ranging from 0.098±0.004 to 0.138±0.037µg/g, ascribed to low anthropogenic deeds. Whereas, Enuneku and Ineh (2020) also give an account on seasonal dissimilarities in nitrate and cadmium levels of River Ikpoba in Edo state, for dry and humid seasons cadmium was below specified limits in all sites scrutinized but 0.02 mg/kg was observed for only site 7. In spite of this, a research on cadmium concentrations in water- bodies in South-western, exhibited concentrations values between 0.03 and 0.66 mg/kg for cadmium (equaled with current study) in most of the samples gotten from the river (Olatunde et al. 2014). This investigation assessed cadmium quantities that ranged from 0.00 to 0.16 mg/L in wet period, however, in the dry period were 0mg/L in all sites. Also values of phosphate for both wet and dry periods ranged between 3.67 – 13.04 mg/l and 1.88 – 14.20 mg/l respectively. Also a research on nitrate concentrations in water- bodies and lakes in Southeast, exhibited high nitrate amounts (equaled with current study) in most of the samples gotten from the river (Cataldo *et al.*, 1985; Isiuku and Enyoh, 2020). This investigation assessed nitrate quantities that ranged from 17.08 to 36.02 mg/L in wet period, however, in the dry period varied from 3.06 to 33.21 mg/L.

Likewise, from investigation with prior published results, such as Aganigbio et al. (2017) that evaluated river water in Mbanabor region of Anambra in South-eastern Nigeria, testified about low nitrate concentration between 1.01 –13.12 mg/ l. Ezeabasilei et al. (2015) also appraise the effect of water supply attribute in Awka in Anambra State, discovered low nitrate amount of rivers that ranging from 0.01 – 0.21 mg/ l, ascribed to low anthropogenic deeds. Whereas, Verla *et al.* (2020) give an account on seasonal dissimilarities on nitrate levels of River Uramiriukwa in Imo state, for dry and rainy season values varied between 0.90- 0.97 mg/L and 0.55 to 0.98 mg/L correspondently.The extreme value of nitrate ion in the humid period is ascribed to runoff/ overflow from pastures field which are propinquity to the water physiques. Dwellers of this province often involve in agricultural (crop and animal rearing) deeds as one of their main sources of income, beside these goings-on is best achieved via the introduction of both synthetic and natural fertilizers, and consequently, the build-up areas nearer to these farmlands and pastures field are susceptible to this high amount of nitrate mostly where seepage and trickle of waste water happens. Further, except at sites 1 & 6 in the wet period and 1 - 6 in dry period, which exhibited no momentous dissimilarities ($p >0.05$) between them, in contrast remaining indicated momentous dissimilarity ($p <0.05$) for cadmium and nitrate levels (Tables 3&4). As regards to seasonality all water-physiques revealed significant dissimilarities ($p <0.05$) for both seasons (nitrate as well as cadmium) quantities.

The water quality index (WQI) for both cadmium together with nitrate amounts assessed in the water physiques in humid and dry and wet season was scrutinized via algorithm, the WQI of samples collected during the rainy period and humid season were calculated and the outcomesobtained is demonstrated in Table 2&4 and Figure 3&4. Hence, from Tables 4 explanation on water attribute taxonomy based on WQI criterion, which as well as indicates that in dry season 20% Water Quality Index (WQI) of all sampling sites are of exceptionalclass of water, 10% poor, whereas 60 % WQI is within good water and 10% very poor water category in both season. But medium class was 20 and 10% for wet and dry periods respectively. Thus, it can also be pictured that water attribute of the Ikpoba river system declines from arid season to wet period irrespective of the sampling localities (Isiuku and Enyoh, 2020; Verla *et al.*, 2020). Correspondingly, Cd and Ncan be attributed to the microbial or bacterial deeds that get diminished owing to low temperature (T), as a consequence, retaining Dissolve oxygen level at a very disappointing/ or poor range all through the entire period. Equally during arid season, the water attribute deteriorates due to the rise in microbial, anions / or cations goings-on as well as increase in contagions from human deeds. From the WQI dataset gotten during the scrutiny, it look as if there is deteriorating revolutionize in water attributes, especially from upper-stream to lower-stream sites, which in turn, unveils that river Ikpoba water is of badfeatures. Further, the seasonal datasets of WQI enumerate that during wet period, Ikpoba river water is more affected than during aridperiod. This can be attributable to the anions, microbial and cations deeds get reduced because of low temperature, since during arid period, the water feature deteriorated as a result of the increase in anions, microbial /or cations deed as well as increase in contagions concentration. Likewise, the source(s) of these contagions might be from run-off from proximate farmlands, pastures field, close-by towns and atmospheric accretion, and has been verified by other researchers like (Ngozi *et al.*, 2020; Verla *et al.*, 2020). Scholars like Osa-Iguehide et al. 2015 and Enyoh et al. (2018) described cadmium (Cd) ion as a non-degradable as well as non-essential cumulative contagion that have ability of altering marine trophic levels for ages.

Further, cadmium is a non-nutritive metal with a trace component that is harmful to human being and the environment. It among naturally occurrence metals within the globe and oceans, besides it can be introduced to the soil via natural for instances volcanic deed, weathering or crushing of Cd-containing mountain or hill and sea spray and anthropogenic deeds for examples mining or extraction as well as smelting of Zn-bearing ores, waste ignition, fossil fuel combustion, sewage sludge, irrigation waters, compost, and fertilizers gotten from mountainous-phosphate (Agbazue *et al.*, 2015; Verla *et al.*, 2020). Despite the fact that they are not vital to either crop development nor biological systems, farming crops will absorb and accumulate available Cd in the soil together with their genetic features and distinctiveness. Amounts of Cd available within the soil determined its impact negatively on soil ecology soil organisms. Every agro soil produced non-nutritive metals like Cd naturally and in soil enhancement or bio-solids with varying levels of phosphorous (P) fertilizers. The core impact of Cd on human being health is kidney illness, as well as other unpleasant effects like musculo-skeletal, pulmonary, and cardiovascular systems. Besides, uncountable factors such as soil pH, micro and macro-nutrient manures, macrobiotic matter substance, salinity, plants genus plus cultivar, and tillage, stimulate the bio-availability as well as uptake of Cd through plants. Because composts and droppings enhances the danger of Cd moving into the food chain, though some governments from developed nations have imposed limits constrain on the Cd quantities of P fertilizers. Additionally, remark proffers earlier by Andersen (1982), in annual study from 1978 to 1980 at 31 Danish eutrophic lakes.

Fig-2.a. NSFWQI, b) Stations versus WQI computation for both seasons

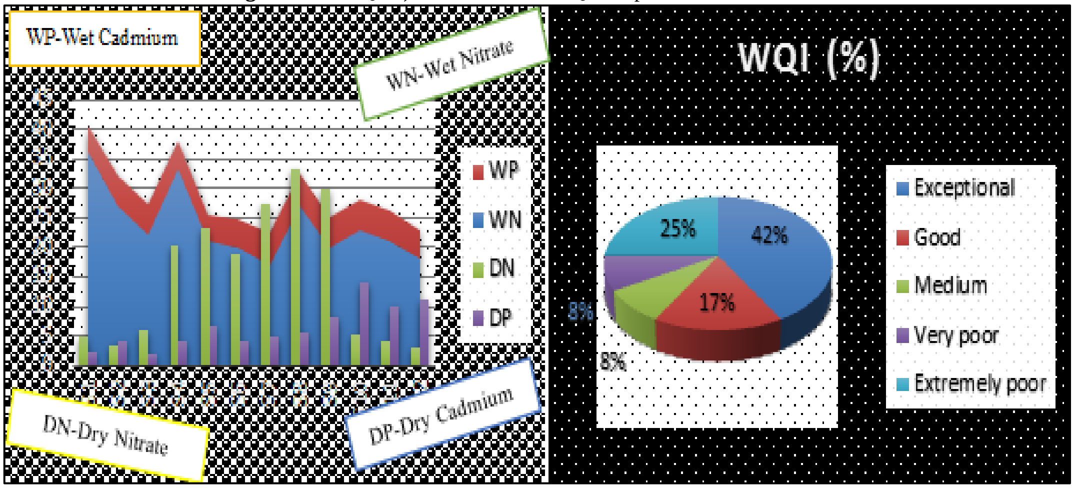


Fig.3. Numerical extraction of anions, microbial and cations parameters during dry period in the study region

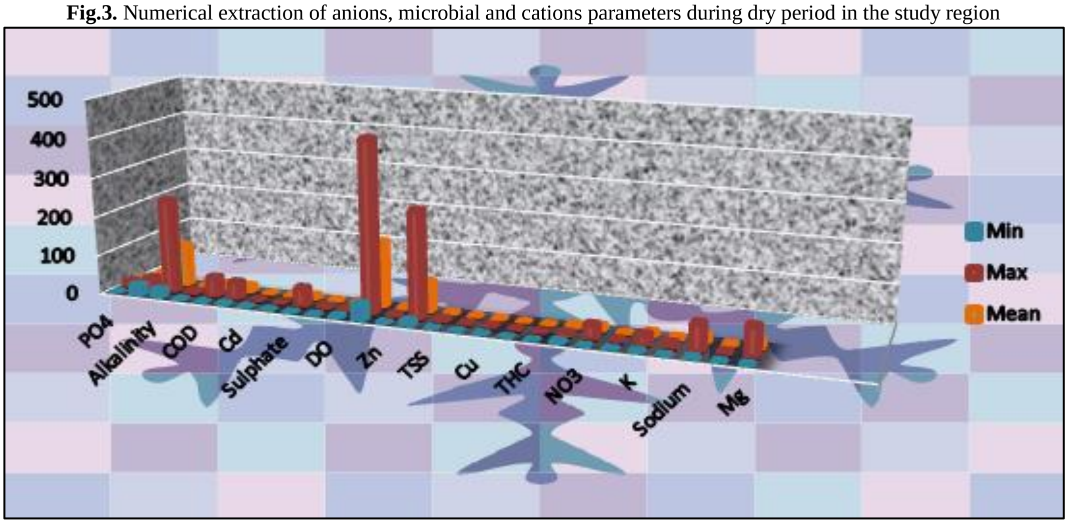


Fig-4. Numerical extraction of anions, microbial and cations parameters during rainy period in the study region

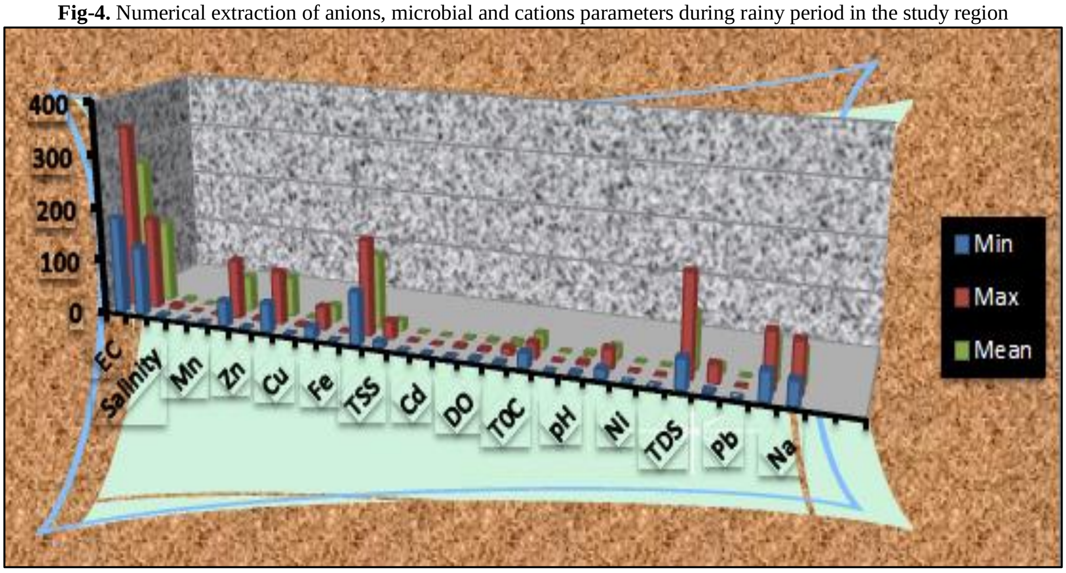


Fig-5. Pie diagram of WQI at each sampling localities

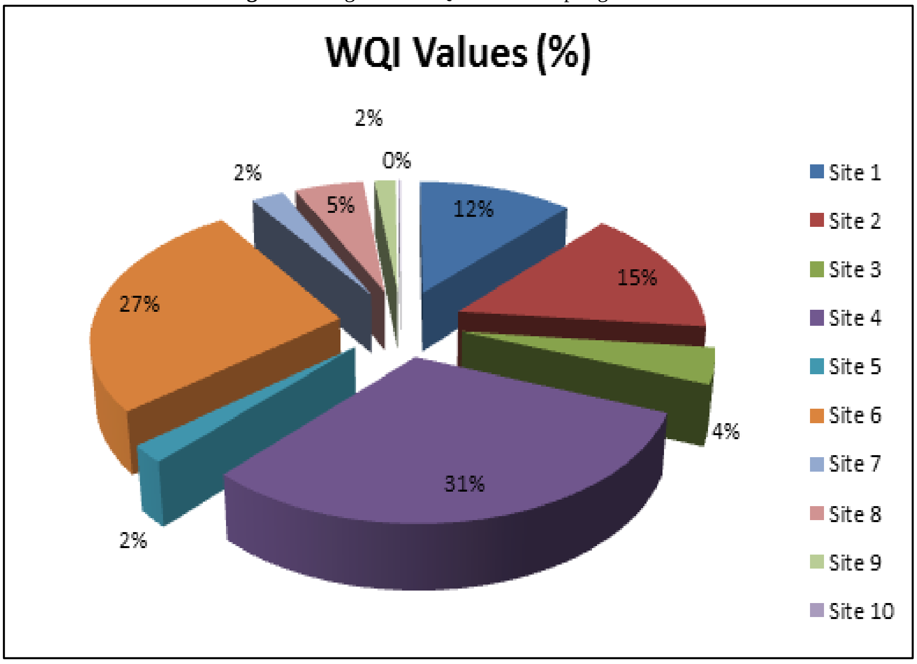


Table-5. Experimental results of dry season microbiological, heavy metals and anions parameters of the research area

Parameters	Minimum	Maximum	Mean	Std. Deviation	Variance	Skewness	Kurtosis
pH	4.3	5.9	4.995	.3956	.156	.216	-.051
Nitrate (NO3)	.04	33.21	11.0829	10.21532	104.353	1.014	-.346
Electrical Conductivity	42	433	165.55	120.152	1.444E4	1.128	-.045
Turbidity	.3	4.8	2.257	1.0679	1.140	.542	.417
Dissolved Oxygen	3.80	5.02	4.5033	.33085	.109	-.573	-.349
Total Dissolved Solids	48.09	150.80	89.7810	31.78885	1.011E3	.704	-.543
Sodium	2.4	64.4	13.923	18.5862	345.448	2.082	3.050
Lead (Pb)	.0000	.0220	.007890	.0083754	.000	.478	-1.392
Sulphate	.154	45.790	8.21627	13.306308	177.058	2.111	3.319
Zinc (Zn)	1.02	3.81	2.3335	.85060	.724	-.394	-.999
Copper (Cu)	.171	2.180	1.35876	.642791	.413	-.263	-.996
Chloride (Cl-)	.00	43.09	24.9505	11.78554	138.899	-.746	-.071
Iron (Fe)	.01	3.00	1.1255	.66025	.436	.961	2.904
Carbonate	12.40	268.40	75.8733	57.51057	3.307E3	2.003	5.450
Total Suspended Solids	.02	5.61	1.9738	1.33835	1.791	1.159	1.748
Nitrite (NO2)	.0000	1.0200	.165233	.2849173	.081	1.955	3.322
Cadmium (Cd)	0	0	.00	.000	.000	4.583	21.000
Nickel (Ni)	0	0	.00	.004	.000	4.284	18.911
Total Hydrocarbon	0	0	.00	.003	.000	2.650	6.239
Phosphate (PO4)	.04	14.20	4.2430	3.83690	14.722	1.258	.950
Temperature	27	30	28.30	.734	.539	.400	-.047
Resistivity	.001	.235	.01737	.050887	.003	4.308	19.100
Alkalinity	20.00	238.00	1.0401E2	62.46451	3.902E3	.773	-.104
Salinity	.05	5.06	2.1486	1.68740	2.847	.054	-1.414
Chromium (Cr)	0	0	.00	.001	.000	3.974	16.360
Manganese (Mn)	0	0	.01	.011	.000	2.395	6.195
Magnesium (Mg)	1.26	72.19	16.9667	19.80226	392.129	1.479	1.483
Potassium (K)	2.09	23.04	9.8711	5.09808	25.990	.616	.616
Total Coliform Count	0	10	3.90	3.548	12.590	.628	-.865
COD	.00	48.25	13.5637	16.39320	268.737	1.210	.152
Calcium	2.04	42.00	15.3785	11.26151	126.822	.914	.360

Table-6. Experimental results of wet season physico-chemical parameters of the research area

Parameters	Minimum	Maximum	Mean	Std. Deviation	Variance	Skewness	Kurtosis
pH	4.1	5.5	4.910	.3534	.125	-.853	.571
Nitrate (NO3)	17.08	36.02	23.3305	4.91194	24.127	1.150	1.297
Electrical Conductivity	182.3	344.1	266.340	52.7906	2.787E3	-.320	-1.244
Turbidity	1.05	4.05	2.2681	.84175	.709	.467	-.512
Dissolved Oxygen	4	4	4.10	.107	.011	.976	1.135
Total Dissolved Solids	55.4	185.6	102.290	28.0338	785.895	1.157	2.812
Sodium	43.27	93.55	62.7405	14.71295	216.471	.536	-.349
Lead (Pb)	.010	.014	.01124	.001300	.000	.718	-.762
Sulphate	47.08	110.40	65.6152	14.94121	223.240	1.516	2.954
Zinc (Zn)	2.09	2.99	2.5552	.25488	.065	-.235	-.760
Copper (Cu)	1.08	3.27	1.6764	.51843	.269	1.917	3.867
Chloride (Cl-)	21.28	43.21	30.6471	4.76488	22.704	.556	1.590
Iron (Fe)	.70	1.24	.9438	.11702	.014	.218	1.262
Carbonate	97.1	177.8	137.231	25.8997	670.796	.315	-1.161
Total Suspended Solids	10.34	33.40	18.7652	7.41456	54.976	.632	-.927
Nitrite (NO2)	.017	.437	.17967	.134638	.018	.098	-1.198
Cadmium (Cd)	.00	.31	.1093	.09055	.008	.451	-.516
Nickel (Ni)	0	0	.00	.000	.000	.529	-1.913
Total Hydrocarbon	.000	.044	.00976	.009864	.000	2.149	6.670
Phosphate (PO4)	3.7	13.0	7.833	2.5022	6.261	.640	.057
Temperature	28.0	28.9	28.357	.2249	.051	.655	.125
Resistivity	.0010	.0390	.013486	.0111397	.000	.390	-.587
Alkalinity	129.3	172.3	151.922	13.6063	185.132	-.470	-.772
Salinity	3.55	7.11	4.7700	.73830	.545	1.352	4.134
Chromium (Cr)	0	0	.02	.054	.003	2.913	8.384
Manganese (Mn)	.012	.033	.02086	.007052	.000	.448	-1.308
Magnesium (Mg)	54.04	99.01	74.1905	12.93148	167.223	-.032	-.905
Potassium (K)	53.02	103.40	72.0657	12.03567	144.857	1.200	1.990
Total Coliform Count	5	34	14.00	9.975	99.500	.910	-.643
COD	4.56	33.04	11.9048	6.60311	43.601	1.926	4.479
Calcium	48.09	98.99	67.1500	13.49413	182.092	.672	-.138

Table-7. WQI relative weight during wet season for each parameter

S/No	Parameters	WHO Limits (Sn)	Test Results (Vn)	Weightage (Wn)	Quality Rating (qn)	[(Wn*qn)]
1	pH	6.5	5	0.15385	320	49.23077
2	Nitrate	50	22.36	0.02000	27	0.54000
3	EC	1000	266.8	0.00100	2	0.00200
4	Turbidity	5	1.34	0.20000	3.8	0.76000
5	DO	5	4.4	0.20000	104.1666667	20.83333
6	TDS	500	132.1	0.00200	2.64	0.00528
7	Sodium	200	93.55	0.00500	13.8	0.06900
8	Lead	0.01	0.01	100.00000	30	3000.0000
9	Sulphate	250	69.01	0.00400	9.744	0.03898
10	Zinc	3	2.58	0.33333	81.66666667	27.22222
11	Copper	2	1.47	0.50000	102.55	51.27500
12	Chloride	250	43.21	0.00400	13.36	0.05344
13	Iron	1	0.91	1.00000	108	108.00000
14	Carbonate	250	97.08	0.00400	75.16	0.30064
15	TSS	5	11.23	0.20000	2.4	0.48000
16	Nitrite	0.5	0.322	2.00000	0	0.00000
17	Cadmium	0.003	0.02	333.33333	0	0.00000
18	Nickel	0.02	0	50.00000	15	750.00000
19	THC	0.001	0.012	1000.00000	200	200000.0000
20	Phosphate	5	5	0.20000	80.28	16.05600
21	Alkalinity	600	129.3	0.00167	23.15	0.03858
22	Calcium	200	79.04	0.00500	41.8	0.20900
				∑ = 1488.16718		∑ =204025.
Z = [∑(Wn*qn)]/[(∑Wn)] = 367.208						
WQI = -267.208%						

Table-8. WQI relative weight during dry season for each parameter

S/No	Parameters	WHO Limits (Sn)	Test Results (Vn)	Weightage (Wn)	Quality Rating (qn)	[(Wn*qn)]
1	pH	6.5	5.3	0.15385	360	55.38462
2	Nitrate	50	20.2	0.02000	32.4	0.64800
3	EC	1000	67.3	0.00100	5	0.00500
4	Turbidity	5	1.6	0.20000	22.4	4.48000
5	DO	5	4.3	0.20000	103.125	20.62500
6	TDS	500	84.8	0.00200	6.6	0.01320
7	Sodium	200	4.3	0.00500	14.2	0.07100
8	Lead	0.01	0.012	100.00000	60	6000.00000
9	Sulphate	250	45.79	0.00400	8.712	0.03485
10	Zinc	3	2.33	0.33333	93	31.00000
11	Copper	2	1.186	0.50000	52.25	26.12500
12	Chloride	250	20	0.00400	10.28	0.04112
13	Iron	1	1.01	1.00000	198	198.00000
14	Carbonate	250	46.2	0.00400	44.84	0.17936
15	TSS	5	3.02	0.20000	46.6	9.32000
16	Nitrite	0.5	0.001	2.00000	0	0.00000
17	Cadmium	0.003	0	333.33333	0	0.00000
18	Nickel	0.02	0	50.00000	15	750.00000
19	THC	0.001	0.01	1000.00000	0	0.00000
20	Phosphate	5	4.024	0.20000	105.8	21.16000
21	Alkalinity	600	23.4	0.00167	22.55	0.03758
22	Calcium	200	42	0.00500	46.95	0.23475
				∑ = 1488.16718		∑ = 7117.35
Z = [∑(Wn*qn)]/[(∑Wn)] = 103.56 WQI = 3.560%						

3.2. Results of Climate Change Impact on Hydrological Response using SWAT

Figures 2a&b displayed watershed description where the soil water simulation (SWAT) analysis was done. From the result of Figures 2a&b, eleven (11) sub-basins were identified from the delineation of the watershed and prominent among the sub-basins are; Ekosodin, Idunmwowina, University of Benin, Echuwa, Temboga and Ikpoba sub-basin.

The total area of the entire sub-basins put together including the landuse area, the soil groups and the topography of the watershed.Furthermore, the total soil area of each of the eleven (11) sub-basins including their landuse area, the soil groups and the topography of the sub-basin is presented in Tables 1-4.Result of Tables 1-4shows that the sub-basins have a total soil area of 581.7862ha and 12.4487ha while the landuse definition is categorized into agriculture (total area of 298.0437ha and 7.6838ha) and residential (total area of 283.7424ha and 4.7659ha representing Temboga and Ikpoba sub-basins respectively.Since land use land cover change is one of the key indicators of climate change, the response of the watershed to change in land use land cover over a period of time was employed to study climate change within the watershed taking into account the soil group that is dominant within the watershed and the watershed elevation pattern. The soil map which defines the dominant soil group within the watershed is presented in Figure 3.

Fig-2. A. Definition of watershed used for simulation and, b) Delineated watershed showing all the sub-basins

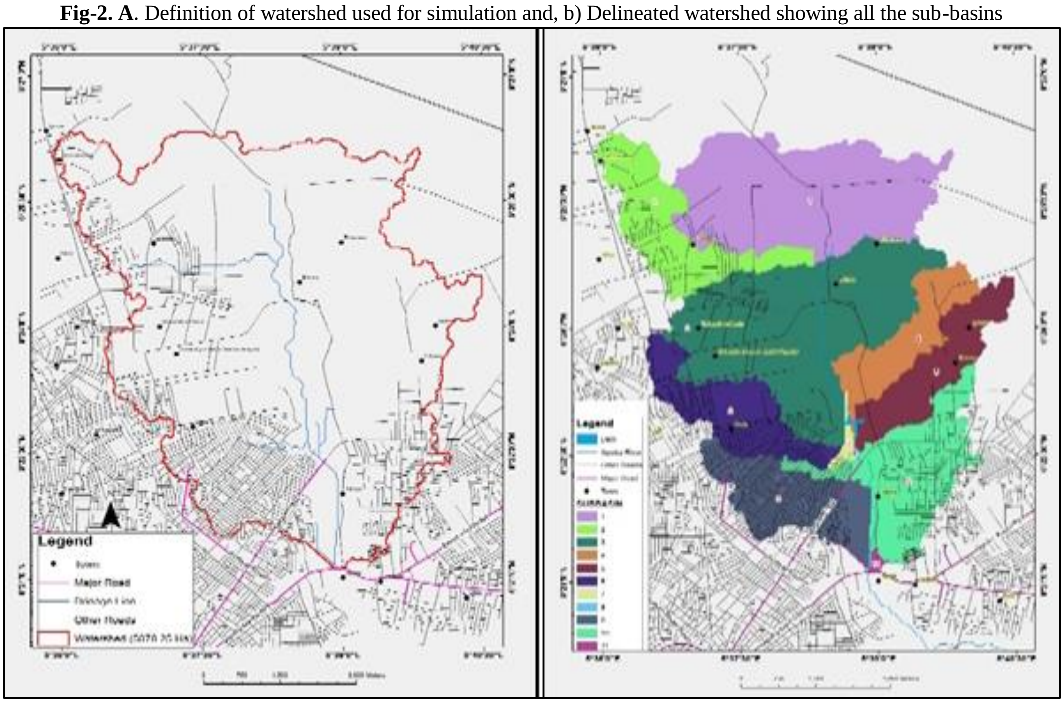
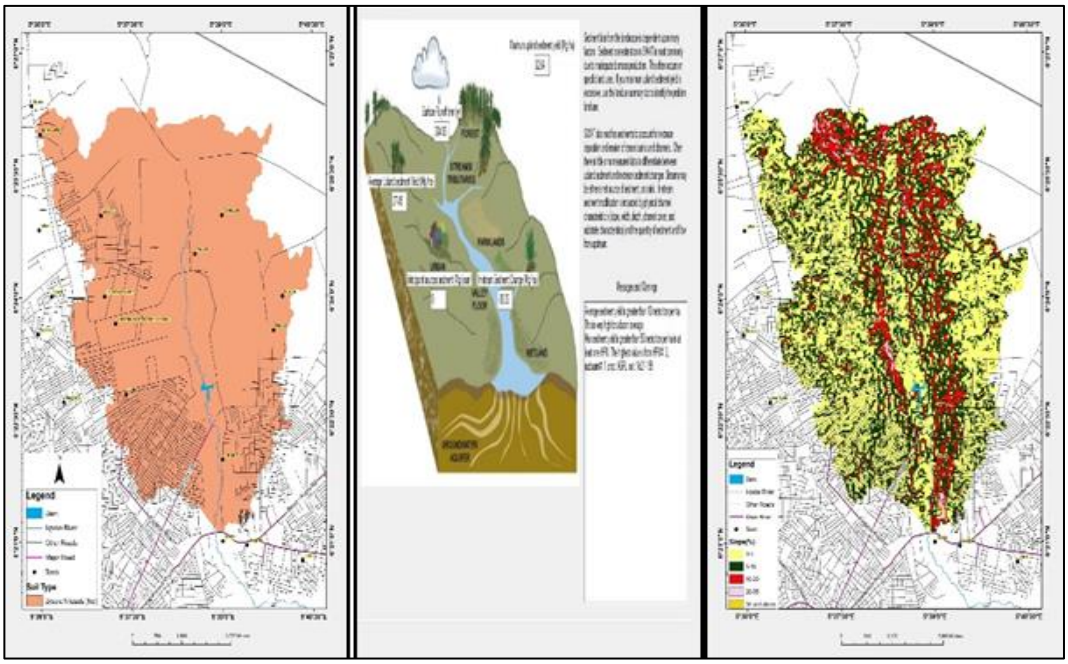


Fig-3.a. Soil map of the watershed showing the dominant soil group, b) Maximum upland sediment yield within the watershed and c) Slope definition within the watershed

a **b**



a b c

Table-9. Physiognomies of sub-basin 1 (Ekosodin) used for SWAT model

		Area [ha]	Area[acres]	%Wat.Area	%Sub.Area	
SUBBASIN #	1	1115.6887	2756.9225	21.97		
LANDUSE:						
	Forest-Mixed --> FRST	844.8935	2087.7741	16.64	75.73	
	Agricultural Land-Generic --> AGRL	270.7952	669.1484	5.33	24.27	
SOILS:						
	Nd21-1559	1115.6887	2756.9225	21.97	100.00	
SLOPE:						
	0-5	388.0691	958.9382	7.64	34.78	
	10-20	258.5072	638.7842	5.09	23.17	
	5-10	469.1124	1159.2001	9.24	42.05	
HRUs						
1	Forest-Mixed --> FRST/Nd21-1559/0-5	267.7275	661.5679	5.27	24.00	1
2	Forest-Mixed --> FRST/Nd21-1559/10-20	223.4296	552.1056	4.40	20.03	2
3	Forest-Mixed --> FRST/Nd21-1559/5-10	353.7365	874.1006	6.97	31.71	3
4	Agricultural Land-Generic --> AGRL/Nd21-1559/10-20	35.0776	86.6786	0.69	3.14	4
5	Agricultural Land-Generic --> AGRL/Nd21-1559/0-5	120.3417	297.3703	2.37	10.79	5
6	Agricultural Land-Generic --> AGRL/Nd21-1559/5-10	115.3759	285.0995	2.27	10.34	6

Table-10. Physiognomies of sub-basin 2 (UNIBEN) used for SWAT model

		Area [ha]	Area[acres]	%Wat.Area	%Sub.Area	
SUBBASIN #	2	487.1681	1203.8167	9.59		
LANDUSE:						
	Residential --> URBN	225.8936	558.1943	4.45	46.37	
	Agricultural Land-Generic --> AGRL	261.2745	645.6224	5.14	53.63	
SOILS:						
	Nd21-1559	487.1681	1203.8167	9.59	100.00	
SLOPE:						
	5-10	171.1148	422.8331	3.37	35.12	
	0-5	302.9582	748.6248	5.97	62.19	
	10-20	13.0952	32.3588	0.26	2.69	
HRUs						
7	Residential --> URBN/Nd21-1559/5-10	77.6678	191.9209	1.53	15.94	1
8	Residential --> URBN/Nd21-1559/0-5	148.2258	366.2734	2.92	30.43	2
9	Agricultural Land-Generic --> AGRL/Nd21-1559/5-10	93.4470	230.9123	1.84	19.18	3
10	Agricultural Land-Generic --> AGRL/Nd21-1559/0-5	154.7323	382.3513	3.05	31.76	4
11	Agricultural Land-Generic --> AGRL/Nd21-1559/10-20	13.0952	32.3588	0.26	2.69	5

Table-11. Characteristics of sub-basin 10 (Temboga) used for SWAT model

		Area [ha]	Area[acres]	%Wat.Area	%Sub.Area	
SUBBASIN #	10	581.7862	1437.6227	11.46		
LANDUSE:						
	Residential --> URBN	283.7424	701.1417	5.59	48.77	
	Agricultural Land-Generic --> AGRL	298.0437	736.4810	5.87	51.23	
SOILS:						
	Nd21-1559	581.7862	1437.6227	11.46	100.00	
SLOPE:						
	0-5	290.3603	717.4947	5.72	49.91	
	5-10	213.6653	527.9776	4.21	36.73	
	10-20	77.7606	192.1503	1.53	13.37	
HRUs						
51	Residential --> URBN/Nd21-1559/0-5	143.2919	354.0816	2.82	24.63	1
52	Residential --> URBN/Nd21-1559/5-10	107.6719	266.0627	2.12	18.51	2
53	Residential --> URBN/Nd21-1559/10-20	32.7785	80.9974	0.65	5.63	3
54	Agricultural Land-Generic --> AGRL/Nd21-1559/0-5	147.0683	363.4131	2.90	25.28	4
55	Agricultural Land-Generic --> AGRL/Nd21-1559/10-20	44.9821	111.1529	0.89	7.73	5
56	Agricultural Land-Generic --> AGRL/Nd21-1559/5-10	105.9934	261.9149	2.09	18.22	6

Table-12. Characteristics of sub-basin 11 (Ikpoba) used for SWAT model

		Area [ha]	Area[acres]	%Wat.Area	%Sub.Area	
SUBBASIN #	11	12.4497	30.7639	0.25		
LANDUSE:						
	Residential --> URBN	4.7659	11.7768	0.09	38.28	
	Agricultural Land-Generic --> AGRL	7.6838	18.9871	0.15	61.72	
SOILS:						
	Nd21-1559	12.4497	30.7639	0.25	100.00	
SLOPE:						
	10-20	4.0851	10.0944	0.08	32.81	
	20-35	0.2918	0.7210	0.01	2.34	
	0-5	3.6960	9.1330	0.07	29.69	
	5-10	4.3769	10.8154	0.09	35.16	
HRUs						
57	Residential --> URBN/Nd21-1559/10-20	2.3343	5.7682	0.05	18.75	1
58	Residential --> URBN/Nd21-1559/20-35	0.2918	0.7210	0.01	2.34	2
59	Residential --> URBN/Nd21-1559/0-5	0.6808	1.6824	0.01	5.47	3
60	Residential --> URBN/Nd21-1559/5-10	1.4590	3.6051	0.03	11.72	4
61	Agricultural Land-Generic --> AGRL/Nd21-1559/0-5	3.0152	7.4506	0.06	24.22	5
62	Agricultural Land-Generic --> AGRL/Nd21-1559/10-20	1.7507	4.3262	0.03	14.06	6
63	Agricultural Land-Generic --> AGRL/Nd21-1559/5-10	2.9179	7.2103	0.06	23.44	7

From the soil map of Figure 3a, it was observed that the dominant soil ground within the watershed is Dystric Nitosols which belongs to the silty clay group that is easily susceptible to detachment by the forces of running water (river bank erosion). Further analysis produced Figure 3b, the maximum upland sediment yield within the watershed and Figure 3c, the watershed slope definition. Result of Figure 3b revealed that the surface runoff is 304.93mm/yr while the maximum upland sediment yield within the watershed is 82.64Mg/ha. Result of Figure 3c revealed that the watershed is relatively flat with pockets of undulation. This is agreement with researchers such as Arnold et al. 1998 that used The Soil as well as Water Assessment Tool (SWAT) with the Penmann–Monteith equation to analyze and ascertain likely evapotranspiration the Halilrood Basin. Investigator like Melsen et al. (2018) disclosed that_apart from rainfall (RF) for the runoff activities, there is need forother parameters such as relative humidity (RH), solar radiation (SR),maximum and minimum air temperature (MMAT), and wind speed (WS). Conversely, only RF and MMAT are steadily stipulated by all climate or/ models. The technique was successfully verified between 1995 – 2003 with value of 0.86 for the calibration time. this technique is exceptional to the SWAT climate originator, which was slightly successful having value of 0.71 during application to the baseline period. The enhanced performance of their approach shows that the parameters are more consistently represented, because WS, SR and MMAT are taken directly daily with same climate circumstances (regarding precipitation happening) with equivalent month versus long-time period. Besides, they symbolize valid values for a raining or dry time which otherwise known as rainfall happening criteria. During scrutinizing of the hydrologic response of the basin to weather variation, rainfall together with temperature forecasts gotten from the scenarios are utilized, with concentration on influences on seasonality and changeability. Regarding to rainfall, the vicissitudes and variations are not as distinct among the bias corrected techniques as for temperature. Largely, rainfall declines as well become more changeable, capricious and variable. Wider pronounced reductions are seen between the first to the second half of the era especially after moving mean of 10-year, a fall up to –30.12% in 2030. The maximum rainfall is greater within the scenario (at least 142 mm) and summaries the improved probability of life-threatening rainfall events. Further, range have greater values, whereas the medians also displayrelated and analogous event. Since indicators such as seasonality, timing and effectiveness are identified to indicates a more robust reaction to weather variation compared to magnitude and enormity (Ali *et al.*, 2018; Igibah *et al.*, 2021), hence the seasonality of climatology data as an imperative feature were considered, specifically the anticipated weather variables seasonality in similarity with observed data. All predicting greater temperatures with the equivalent seasonal style. Throughout summer change of temperature is faintly above other periods. Right through the year, not just that the forecast medians constantly beyond the average monthly scrutinized, nevertheless the anticipated minimum temperature is as well as bigger, that is more conservative prognostications of temperature which in turn resulted to warmer meteorological conditions in the scrutiny zone. What's more, the practical bias modification techniques initiate various results. The medians display higher temperature for experimental and simulation results. Meanwhile, historical data and projections or simulation revealed February and March as the hottest month respectively.

3.3. Nutrient Contagion Index

Generally nutrient contagion index (NCI) for the surface water such as rivers, streams and lakes account for possible summation impact of phosphate and nitrate on ecofriendly environs and environmental health. This aid to swiftly ascertain the overall quality of river waters. The computed NCI is presented in Tables 3& 4. From Table 3&4, only at sites, 1 (0.44), 2 (0.81), 3(0.38), 4(0.80) and 6 (0.81) in dry season (0.69) that there was no contagion, all other water-bodies were slightly contagion in dry season. For dry period, site 3 < site 1 < site 4 < site 2 < site 6 < site 7 < site 8 < site 5 < site 9 < site 10. In wet season, apart from sites 7 (5.07) and 1 (5.79) that are significantly contagion, site 10 was slightly contagion, while remaining waterbodies investigated were slightly contagion in the following order; site 3 > site 1 > site 4 > site 2 > site 6 > site 7 > site 8 > site 5 > site 9 > site 10. Similarly, this investigation also displays NCI values between 1.13 – 54.35 in wet period while in the dry period varied from 0.38 – 2.84. For total proportion of NCI (%) slightly, significantly and extremely contagion were 10, 20 and 70% respectively during wet season, whereas slightly and no contagion was 50% during dry period (Table 5), whereas the annual mean NCI for wet season (23.81) and dry season (1.12) displayed that the water-bodies were extremely and no contagion respectively (Table 4). This signifies that throughout the year the water physiques are too enhanced, thus is at high risks of eutrophication.

3.4. Health Risks Assessments

3.4.1. Chronic Daily Intake

Human beings might be exposed to phosphate and cadmium in surface water (river, stream and lake) by two ways via ingestion or oral and dermal route when they come in contact with the water. Therefore, health risks were computed from these two pathways. The CDI of both nitrate and cadmium for children and elderly/adult in the water physiques via ingestion/oral and dermal/skin pathways is displayed in Tables 6& 7. CDI values larger than 1 always specify chronic intake or ingestion and thus risks and threat to humans. CDI through drinking exhibited lower amounts for phosphate in both seasons for children and elderly. Cadmium for elderly and children during rainy period was below 1, but zero throughout dry season for elderly and youngsters. Meanwhile, nitrate for elderly during raining period, was at extreme in station 1 (1.029), while sites 1, 2, 4, 8 and 10 (all proximate to Benin city), was also very high for children in wet season. In dry season, the water-bodies indicated high risks for nitrate especially station 5 (1.045), station 7 (1.215), station 8 (1.484) and station 9 (1.332), s. Chronic consumption of nitrate and cadmium into the human body system is detrimental because it causes serious health challenges. Correspondingly, all dermal pathway assessed displayed low chronic intake that all values below 1 for all ages (Tables 6&7). This scrutiny showed that children and youngsters normally had greater total intake comparing with adults. Numerous studies have testified similar results for other contagions in water and ascribed it to little body shape and immature organs of children or youngsters.

3.4.2. Hazard Quotient (HQ) and Hazard Index (HI)

The assessed non-carcinogenic hazard quotient and index via the scrutiny pathways on youngster and elderly are displayed in Tables 8&9. For hazard index and quotient i.e HI and HQ >1, it specifies likely adversative health impact of a chemical to elderly and/or youngster from intake via diverse pathways, besides HI of greater quantities designate potential non-carcinogenic threat matter for all chemical consumed by elderly or children (Enuneku and Ineh 2020; Osa-Iguehide et al. 2015).Nitrate for elderly during raining period, was at extreme in station 1 (1.029), while sites 1, 2, 4, 8 and 10 (all proximate to Benin city), was also very high for children in wet season. In dry season, the water-bodies indicated high risks for nitrate especially station 5 (1.045), station 7 (1.215), station 8 (1.484) and station 9 (1.332), whereas elderly throughout wet season HQsoral cadmium was higher in six sites, site 9 (9.20), site 8 (8.00), site 4 (8.00), site 6 (2.80), site 2 (1.72) and site 3 (1.14) i.e greater than 1 means risk, whereas during dry period all sites were zero means no risk.Hence, HQsoral cadmium for children displayed greater values beyond 1 (i.e values from 1.78 to 14.4) in nearly all the sites except site 1 (0.9), site 7 (0.9) and site 10 (0.00).

Correspondingly, all dermal pathway assessed for nitrate displayed low chronic intake that all values below 1 for all ages (Tables 7&8). On the contrary, both HQs_{dermal} as well as HI_{dermal}(cadmium) are nearly below 1for elderly group except site 4(13.6), site 8 (13.60) and site 9(1.55) Further, children group investigation displayed eight sites out of ten scrutinized to be above 1 with lowest value of 1.822 and higher value of 14.58, while the remaining two sites; to be precise, site 1 (0.911), site 10 (0.00) shows no danger throughout wet season. Besides, cadmium during dry season were zero and valueless for children and elderly, while cadmium all HIoral (children and elderly) for both seasons displayed extremely high values. This scrutiny showed that children and youngsters normally had greater total intake comparing with adults. Numerous scrutinizes have testified similar outcomes for other contagions in water (Iba et al., 2021) as well as ascribed it to little body shape and immature organs of youngsters.Also nearly all HI_{dermal} (youngsters) except site 1(0.091), site 7(0.911) and site 10 (0.00) throughout wet period are also beyond 1, demonstrating dangers of non-carcinogenic health risks. But only two sites with value of 13.6 and 13.6 for site 4 and 8 respectively during wet period demonstrated high values. The outcomes from the scrutiny revealed that children (29104.40 & 31700) mostly had high HI compared to adults (18652.80 & 20300.00) during wet and dry season respectively.

Greater intake of nitrate causes methemoglonaemia in youngster which might also create mental retardation if the child survives. Moreover, nitrate in the bod may reduce to nitrite which is NO_2^- which oxidizes with amines to create carcinogenic nitrosamines (Okoye and Orakwe, 2018). Greater intake of cadmium causes flu-like or chronic sicknesses such as muscle pain, chills, lung, and fever in youngster and elderly. Moreover, cadmium high exposure due to human deeds associated with industrialization also generated bone or itai-itai sickness that characterized by osteomalaecia that is related with renal tubular dysfunction, which was first discovered in Japan in 1960s (Okoye and Orakwe, 2018).

4. Conclusion

The investigation concluded that the water physiques scrutinized in South-southern, Nigeria are not yet contaminated by nitrate in both arid and wet periods as the assessed values were less than the World Health Organization acceptable limit. Cadmium was 100% and 10% not yet contaminated throughout wet and dry season respectivelyas the assessed values were compared with the World Health Organization permissible limit. Besides the nitrate to cadmium ratio was significantly high in the raining season, which proposes great supply of largely nitrate nutrients via runoff from neighboring farmlands and pastures field during rainfall. Also, cadmium a non-nutritive metal with a trace component that is harmful to human being and the environment, is among naturally occurrence metals within the globe and oceans, besides it can be introduced to the soil via natural for instances volcanic deed, weathering or crushing of Cd-containing mountain or hill and sea spray and anthropogenic deeds for examples mining or extraction as well as smelting of Zn-bearing ores, waste ignition, fossil fuel combustion, sewage sludge, irrigation waters, compost, and fertilizers gotten from mountainous-phosphate. Hazard index greater than one which is extreme level was discovered during rainy and sunny period by cadmium and nitrate at higher threats for children to elderly. Whereas CR_{dermal} (elderly and children) was insignificance and less than one throughout dry as well as wet seasons respectively. By and large, the water physiques are at eutrophication dangers and preventive measures should be put in place to lessen anthropogenic and industrial actions around the region especially throwing of rubbishes and debris directly into the water bodies and hence increase the unwanted nutrients in this water physiques. Irrefutably, without hesitation there is need for more investigations with larger sampling size to produce more data and enlighten more precisely the status of zinc, COD, chronium, alkalinity as well as phosphate in water physiques of South-southern Nigeria.

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Table-13. Stations, Means and Nutrient Contagion Index (NCI) for both seasons

Stations	Wet Season (Mg/l)		Dry Season (Mg/l)		Wet Season		Dry Season	
	Cadmium	Phosphate	Cadmium	Phosphate	NCI	Remark	NCI	Remark
1	0.01	12.3	0	2.19	5.79	Significantly contagion	0.44	no contagion
2	0.03	9.8	0	4.03	11.96	Extremely contagion	0.81	no contagion
3	0.02	8.23	0	1.88	8.32	Extremely contagion	0.38	no contagion
4	0.14	8.01	0	4.02	48.27	Extremely contagion	0.80	no contagion
5	0.10	12.34	0	6.72	35.80	Extremely contagion	1.34	Slightly contagion
6	0.05	13.04	0	4.07	19.28	Extremely contagion	0.81	no contagion
7	0.01	8.71	0	5.01	5.07	significantly contagion	1.00	Slightly contagion
8	0.14	7.23	-	5.60	48.12	Extremely contagion	1.12	Slightly contagion
9	0.16	5.09	0	8.24	54.35	Extremely contagion	1.65	Slightly contagion
10	0.00	5.67	0	14.20	1.13	Slightly contagion	2.84	Slightly contagion
Mean					23.81	Extremely contagion	1.12	no contagion

The grouping for NCI is classified as NCI of <1 (no contagion), NCI of 1 ≤ 3 (Slightly contagion), NCI of >3 ≤ 6 (significantly contagion) and NCI of >6 (Extremely contagion).

Table-14. Water quality index versus Variation computation for both seasons

Sites	WQI Wet Season (%)			Dry Season (%)			Coefficient of variation CV	
	Cd	P	Status	Cd	P	Status	%	Rating
1	0	80.29	Good	0	63.0	Very poor	22.0	Normal variation
2	0	196.00	Poor	0	105.8	Medium	46.0	Normal variation
3	0	246.00	Very Poor	0	27.23	Good	89.0	High-level variation
4	0	120.38	Medium	0	85.60	Good	29.0	Normal variation
5	0	80.28	Good	0	80.86	Good	-0.72	Little variation
6	0	60.24	Good	0	80.84	Good	34.23	Normal variation
7	0	60.54	Good	0	40.64	Exceptional/Excellent	32.87	Normal variation
8	0	60.65	Good	0	40.24	Exceptional/Excellent	33.65	Normal variation
9	0	63.00	Good	0	60.69	Good	3.37	Little variation
10	0	105.8	Medium	0	63.10	Good	40.47	Normal variation

The ranking for variation is classified as CV of <20% (Slight variation), CV of 20 ≤ 50 (Normal variation), and CV of >50% (High-level variation).

Table-15. Chronic Daily Intake (CDI) Phosphate and Cadmium (Adult)

Sites	CDI_{oral}				CDI_{dermal}			
	Wet season		Dry season		Wet season		Dry season	
	Cadmium	Phosphate	Cadmium	Phosphate	Cadmium	Phosphate	Cadmium	Phosphate
1	$2.91*E^{-4}$	0.351	0.00	0.063	$4.86*E^{-7}$	0.0006	0.00	0.00011
2	$8.61*E^{-4}$	0.280	0.00	0.115	$1.46*E^{-6}$	0.0005	0.00	0.00020
3	$5.72*E^{-4}$	0.235	0.00	0.054	$9.71*E^{-7}$	0.0004	0.00	$9.131 \times E^{-5}$
4	$4.12*E^{-3}$	0.229	0.00	0.115	$6.80*E^{-5}$	0.0004	0.00	0.00020
5	$2.91*E^{-4}$	0.353	0.00	0.192	$4.85*E^{-6}$	0.0006	0.00	0.00033
6	$1.40*E^{-3}$	0.373	0.00	0.116	$2.43*E^{-6}$	0.0006	0.00	0.00020
7	$2.91*E^{-4}$	0.249	0.00	0.143	$4.85*E^{-7}$	0.0004	0.00	0.00024
8	$4.11*E^{-3}$	0.207	0.00	0.160	$6.80*E^{-5}$	0.0004	0.00	0.00027
9	$4.60*E^{-3}$	0.145	0.00	0.235	$7.77*E^{-6}$	0.0003	0.00	0.00040
10	0.00	0.162	0.00	0.406	0.00	0.00028	0.00	0.00069

Table-16. Chronic Daily Intake (CDI) Phosphate and Cadmium (Children)

Sites	CDI_{oral}				CDI_{dermal}			
	Wet season		Dry season		Wet season		Dry season	
	Cadmium	Phosphate	Cadmium	Phosphate	Cadmium	Phosphate	Cadmium	Phosphate
1	$4.51*E^{-4}$	0.549	0.00	0.098	$4.56*E^{-6}$	0.0056	0.00	0.00099
2	$1.32*E^{-3}$	0.438	0.00	0.180	$1.37*E^{-5}$	0.0044	0.00	0.0018
3	$8.91*E^{-4}$	0.368	0.00	0.084	$9.11*E^{-6}$	0.0037	0.00	0.00085
4	$6.32*E^{-4}$	0.358	0.00	0.180	$6.38*E^{-5}$	0.0036	0.00	0.0018
5	$4.52*E^{-3}$	0.551	0.00	0.300	$4.56*E^{-5}$	0.0056	0.00	0.0031
6	$2.22*E^{-3}$	0.582	0.00	0.182	$2.27*E^{-5}$	0.0059	0.00	0.0019
7	$4.53*E^{-4}$	0.389	0.00	0.224	$4.56*E^{-6s}$	0.0040	0.00	0.0023
8	$6.32*E^{-3}$	0.322	0.00	0.250	$6.38*E^{-5}$	0.0033	0.00	0.0025
9	$7.21*E^{-3}$	0.227	0.00	0.368	$7.29*E^{-5}$	0.0023	0.00	0.0037
10	0.00	0.253	0.00	0.634	0.00	0.0026	0.00	0.0064

Table-17. Hazard quotient (HQ) of Phosphate and Cadmium in wet and dry seasons (Adult)

Sites	HQ_{oral}				HQ_{dermal}			
	Wet season		Dry season		Wet season		Dry season	
	Cadmium	Phosphate	Cadmium	Phosphate	Cadmium	Phosphate	Cadmium	Phosphate
1	0.58	17550	0.00	3150	0.097	-	0.00	-
2	1.72	14000	0.00	5750	0.291	-	0.00	-
3	1.14	11750	0.00	2685	0.194	-	0.00	-
4	8.00	11450	0.00	5750	13.6	-	0.00	-
5	0.80	17650	0.00	9600	0.97	-	0.00	-
6	2.80	18650	0.00	5800	0.486	-	0.00	-
7	0.58	12450	0.00	7150	0.0971	-	0.00	-
8	8.00	7250	0.00	8000	13.60	-	0.00	-
9	9.20	7250	0.00	11750	1.554	-	0.00	-
10	0.00	8100	0.00	20300	0.00	-	0.00	-

Table -18. Hazard quotient (HQ) of Phosphate and Cadmium in wet and dry seasons (Children)

Sites	HQ_{oral}				HQ_{dermal}			
	Wet season		Dry season		Wet season		Dry season	
	Cadmium	Phosphate	Cadmium	Phosphate	Cadmium	Phosphate	Cadmium	Phosphate
1	0.9	27450	0.00	4650	0.911	-	0.00	-
2	2.60	21900	0.00	9000	2.732	-	0.00	-
3	1.78	18400	0.00	4200	1.822	-	0.00	-
4	12.6	17900	0.00	9000	12.75	-	0.00	-
5	9.0	27550	0.00	15000	9.11	-	0.00	-
6	4.4	29100	0.00	9100	4.55	-	0.00	-
7	0.9	19450	0.00	11200	0.911	-	0.00	-
8	12.6	16100	0.00	12500	12.75	-	0.00	-
9	14.4	11350	0.00	18150	14.58	-	0.00	-
10	0	12650	0.00	31700	0.00	-	0.00	-

Table-19. Hazard Index (HI) of Phosphate and Cadmium in wet and dry seasons (Adult and Children)

Site	HI_{oral}				HI_{dermal}			
	Adult		Children		Adult		Children	
	Wet	Dry	Wet	Dry	Wet	Dry season	Wet	Dry season
1	17550.58	3150	27450.90	4650	0.097	0.00	0.091	0.00
2	14001.72	5780	21902.60	9000	0.291	0.00	2.73	0.00
3	11751.14	2685	18401.78	4200	0.194	0.00	1.82	0.00
4	11458.00	5750	17912.60	9000	13.6	0.00	12.75	0.00
5	17650.80	9600	27559.00	15000	0.97	0.00	9.11	0.00
6	18652.80	5800	29104.40	9100	0.486	0.00	4.55	0.00
7	12450.58	7150	19450.90	11200	0.097	0.00	0.911	0.00
8	7258.00	8000	16112.60	12500	13.60	0.00	12.75	0.00
9	7259.20	11750	11364.40	18150	1.55	0.00	14.58	0.00
10	8100.00	20300	12650.00	31700	0.00	0.00	0.00	0.00

Table-20. Carcinogenic risk (CR) of Phosphate and Cadmium in wet and dry seasons (Adult and Children)

Site	CR_{oral}		CR_{oral}		CR_{dermal}		CR_{dermal}	
	Adult		Children		Adult		Children	
	Wet	Dry	Wet	Dry	Wet	Dry season	Wet	Dry season
1	17550.58	210	1830.06	310	0.0065	0.00	0.006	0.00
2	933.45	385.33	1460.17	600	0.019	0.00	0.18	0.00
3	783.41	179	1226.79	280	0.194	0.00	0.12	0.00
4	763.87	383.33	1194.17	600	0.91	0.00	0.85	0.00
5	1176.72	640	1837.27	1000	0.064	0.00	0.61	0.00
6	1243.52	386.67	1940.29	606.67	0.032	0.00	0.30	0.00
7	830.04	476.67	1296.73	746.67	0.0065	0.00	0.061	0.00
8	483.87	533.33	1074.17	833.33	0.91	0.00	0.85	0.00
9	483.95	783.33	757.63	1210	0.10	0.00	0.97	0.00
10	540.00	1353.33	843.33	2113.33	0.00	0.00	0.00	0.00