

Research article

THE IMPACT OF REFINERY EFFLUENT IN THE PHYSIOCHEMICAL REGIME OF EKEREKANA CREEK IN OKIRIKA MAINLAND, RIVERS STATE, NIGERIA

*MBANEME, F.C.N., OKOLI, C. G. and EKWEGHI, C.

Department of Environmental Technology, Federal University of Technology, Owerri.

*Correspondence to ebyfranklyn2007@yahoo.com, Phone: +2348037832182.

ABSTRACT

Water aquifers in the Okirika Mainland are susceptible to possible contaminations with carcinogenic aliphatic hydrocarbons originating from the improper treated effluent discharges of the nearby Port Harcourt Refinery Company Limited (PHRCL) production lines. Ekerekana creek in Okirika mainland located within the Niger delta area of Nigeria plays an important ecological role as habitat to aquatic lives. Due to direct effluent discharge from nearby Port Harcourt Refining Company Limited (PHRC) into the Creek, persistent organic pollutants such as petroleum aliphatic hydrocarbons could be among the most serious and important classes of pollutants that enter the aquatic ecosystem. Water samples were collected from 10 sampling locations around the creek and another from the effluent to serve as control, with one liter sterilized amber glass bottles fitted with screw cap and lined with foils. In-situ measurements were done with HORIBA U-I 0 Water Quality Checker to determine pH, temperature, total dissolved solids, turbidity, conductivity, dissolved oxygen and salinity. The samples were analyzed using Gas Chromatography coupled with flame ionization detector (GC-FD). Results showed high concentrations of petroleum aliphatic hydrocarbons that were higher than the WHO maximum permissible limit of 0.002mg/L for Total Petroleum Hydrocarbon. C8 had the concentration of 1.88729 mg/L and C15 had the least concentration of 0.00289mg/L. **Copyright© AJEPR, all rights reserved.**

Key Words: Aliphatic, effluent, hydrocarbons and Port Harcourt Refinery Company Limited.

INTRODUCTION

Water is the most fundamental substance for life and sustainability of terrestrial and aquatic organisms. Although water is essential for human beings, anthropogenic activities have resulted in a significant impairment of its quality. Pollution of the aquatic environment means the introduction by man, directly or indirectly of substances or energy which result in such deleterious effects as harm to living resources, hazards to human health, hindrance to aquatic

activities including fishing, impairment of water quality (with respect to its use in agricultural, industrial and often economic activities) and reduction of amenities (Schwarzbauer, 2006).

Ekerekana Creek in Okrika, Rivers State, serves as the receiving water body of the Port Harcourt Refining Company Limited (PHRC) effluent. Over these years, thick oil scums are seen floating all over the surface of the creek, especially around mangroves and prop roots of aquatic plants. Nevertheless, the creek serves as home to many aquatic foods such as fish, crab, prawn, crayfish, etc. The refinery effluents could increase the potential of the creek to be contaminated with petroleum hydrocarbon pollutants including the aliphatic. In recent times, there have been reports from fishermen in the creek of tainted fish tissues; a development they attributed to possible pollution of the water body with improperly treated refinery effluents. Already, refinery effluents have been classified by several authors, including Garrettson (2001), Mbaneme et al (2012), Ogbuagu et al, (2011 and Okoli et al. (2011) as detrimental to public health, especially where they contain petroleum components such as the aliphatic hydrocarbons. The position of man as a tertiary consumer in the tropic chain makes him most vulnerable to these pollutants as they could build up in aquatic flora and fauna serving his foods.

Water pollution is a serious problem for the entire world. It threatens the health and well being of humans, plants, and animals. As the world became more industrial and smaller due to communications and trade, accidental and purposive hazardous dumping has contributed to the problem of water pollution. All water pollution is dangerous to the health of living organisms, but sea and river pollution can be especially detrimental to the health of humans and animals. Rivers and seas are used as primary sources of potable water by populations all over the world.

Water pollution causes approximately 14,000 deaths per day, mostly due to contamination of drinking water by untreated sewage in developing countries (The Economist, 2008). An estimated 700 million Indians have no access to a proper toilet, and 1,000 Indian children die of diarrhea sickness every day from drinking contaminated waters (The Economist, 2008). Nearly 500 million Chinese lack access to safe drinking water (The NYT, 2007). Public concern over marine oil spills has been clearly augmented since the 1967 Torrey Canyon supertanker accident off the UK coast, when 100,000 tonnes of spilled oil caused heavy pollution of the French and British shores with serious ecological and fisheries consequences. Marshes and sediments in Prince William Sound in Alaska retained oil from the massive oil spill of the Exxon Valdez in 1989 for many years, affecting the development of fish embryos on the bottom. After ten years, pockets of oil remained in these marshes, and mussels, clams, ducks and sea otters showed evidence of harm in some localized areas (Stanislav *et al.*, 2010). It is seldom that a spill occurs right in an area that has been intensively studied prior to the spill. Fiddler crabs were particularly sensitive, and were still affected after seven years. The oil affected their burrow construction — the burrows did not go straight down, but leveled off to a horizontal plane. While this was not a problem during the summer, when winter came the crabs were not below the freezing zone of the marsh as they should have been and froze to death. Benthic communities took about a decade to return to normal. After 30 years, some abnormalities still are noted in fiddler crab burrows in the oiled areas.

In January of 1993, an oil tanker ran aground off the Shetland Islands, Scotland in the United Kingdom. Oil from this tanker spilled into the sea water surrounding the Shetland Islands. This oil threatened seabirds, salmon, sea-trout, gray seals, otters, and other species on and around the islands. Trade around these islands had to be suspended for a time as well (Dopp, 2011).

The various pollutants released into the Okrika creek affect the littoral zone, the shallow waters along the shore where rooted vegetation grow, and the limnetic zone, the open water that sunlight penetrates and where phytoplankton (algae) live. It is uncertain if effects in the creek are caused by eutrophication as a consequence of nitrogen and/or COD and BOD enrichment or pH induced reactions related to acids or other pollutants discharged into the creek. The limited ability of the creek to flush amplifies the pollution damage (Oruibima; 2004, Andah, 2008).

State agencies are mainly responsible for monitoring public water supplies and enforcing the primary and secondary drinking water standards set by the FEPA. Local and National water regulatory agencies must test and treat drinking water and maintain the FEPA standards for quality. These agencies are also responsible for informing the public when any water quality standards have been violated. Given these standards, stream and groundwater supplies should be of high quality. Generally, one compares the values for the various measure of stream and groundwater

quality at a given time and location to the average of those values across the entire watershed. This “average” water quality across a watershed is referred to as the watershed’s “baseline.”

Our primary source of hydrocarbons is petroleum or crude oil which is that thick, black liquid that we find in the earth. Petroleum consists almost entirely of a mixture of alkanes with some alkenes and smaller amounts of aromatic hydrocarbons (Mbaneme *et al.*, 2012). Hydrocarbons are a heterogeneous group of organic substances that are primarily composed of carbon and hydrogen molecules. They are quite abundant in modern society. Some of the most commonly ingested hydrocarbons include gasoline, lubricating oil, motor oil, mineral spirits, lighter fluid/naphtha, lamp oil, and kerosene (Bronstein *et al.*, 2007). Aliphatic chemical compounds belong to the organic class in which the atoms are not linked together to form a ring. One of the major structural groups of organic molecules, the aliphatic compounds include the alkanes, alkenes, and alkynes, and substances derived from them actually or in principle by replacing one or more hydrogen atoms by atoms of other elements or groups of atoms. Aliphatic compounds are acyclic and non-aromatic carbon compounds (IUPAC, 1997). Thus, aliphatic compounds are opposite to aromatic compounds. In aliphatic compounds, carbon atoms can be joined together in straight chains, branched chains, or non aromatic rings (in which case they are called alicyclic). Aliphatic compounds can be saturated, joined by single bonds (alkanes), or unsaturated, with double bonds (alkenes) or triple bonds (alkynes).

Besides hydrogen, other elements can be bound to the carbon chain, the most common being oxygen, nitrogen, sulfur, and chlorine. The simplest aliphatic compound is methane (CH₄). Aliphatic include alkanes (e.g. paraffin hydrocarbons), alkenes (e.g. ethylene) and alkynes (e.g. acetylene). Fatty acids consist of an unbranched aliphatic tail attached to a carboxyl group (IUPAC, 1997). One of the group of organic compounds of carbon (C) and hydrogen (H) in which the carbon atoms have linear branched chain (open), or both types of structures. Aliphatic, as they are informally called, can be divided into paraffinic (saturated) and olefinic (unsaturated) chain types. The simplest aliphatic, paraffinic hydrocarbon is methane, CH₄. The simplest aliphatic, olefinic hydrocarbon is ethylene, C₂H₄ (Schwarzbauer, 2006). The aliphatic hydrocarbons are subdivided into three groups of homologous series according to their state of saturation.

The rest of the group is classed according to the functional groups present. Such compounds can be “straight-chain,” branched-chain or cyclic. The degree of branching affects characteristics, such as the octane number or cetane number in petroleum chemistry. Both saturated (alicyclic) compounds and unsaturated compounds exist as cyclic derivatives. The most stable rings contain five or six carbon atoms, but large rings (macro cycles) and smaller rings are common. The smallest cycloalkane family is the three-membered cyclopropane (C₃H₆).

Saturated cyclic compounds contain single bonds only, whereas aromatic rings have an alternating (or conjugated) double bond. Cycloalkanes do not contain multiple bonds, whereas the cycloalkenes and the cycloalkynes do. Aliphatic compounds have bonding electrons localized within the vicinity of the bonded atoms. Cyclic compounds that do not have delocalized electrons are also aliphatic, as in the alicyclic compound cyclohexane (C₆H₁₂) or the heterocyclic piperidine (C₅H₁₁N) (The RTI, 1992).

The growing concern in recent years with pollution of the aquatic environment by oil has resulted in a number of studies designed to provide information on the distribution of naturally occurring hydrocarbons in aquatic environment and to gain some understanding of possible environmental effects of increasing inputs of petroleum hydrocarbons. In 2007, 7 deaths due to hydrocarbons were reported to US poison control centers (Bronstein *et al.*, 2007).

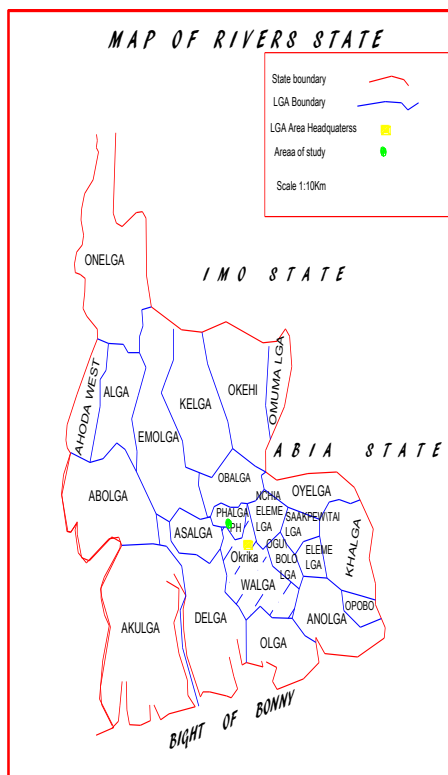
Hydrocarbon exposure can be divided into the following 4 broad categories:

1. Nonintentional nonoccupational exposure: Accidental ingestions are the most frequent type and commonly involve young children tasting a hydrocarbon. Typically, children do not drink large quantities, as hydrocarbons generally taste bad. Adults and older children occasionally consume a hydrocarbon if liquid is placed in an unlabeled can or bottle resulting in accidental ingestion.
2. Recreational exposure: Inhaling of hydrocarbons or other volatile solvents for the purpose of producing a transient state of euphoria is becoming more common. This pattern of use is most common in junior high and high-school aged children.

3. Occupational exposure: This type of exposure is most often industrial, where a worker has either a dermal exposure to the liquid or an inhalational exposure to the vapors.
4. Intentional: This type of exposure usually involves consuming a large amount of the hydrocarbon as an oral ingestion during a suicide attempt.

Toxicity from hydrocarbon exposure can be thought of as different syndromes, depending on which organ system is predominately involved. Organ systems that can be affected by hydrocarbons include the pulmonary, neurologic, cardiac, gastrointestinal, hepatic, renal, dermatologic, and hematologic systems. The pulmonary system is the most commonly involved system (Lifshitz et al, 2003). Pulmonary complications, especially aspiration, are the most frequently reported adverse effect of hydrocarbon exposure. While most aliphatic hydrocarbons have little Gastro-intestinal absorption, aspiration frequently occurs, either initially or in a semi-delayed fashion as the patient coughs or vomits, thereby resulting in pulmonary effects. Once aspirated, the hydrocarbons can create a severe pneumonitis.

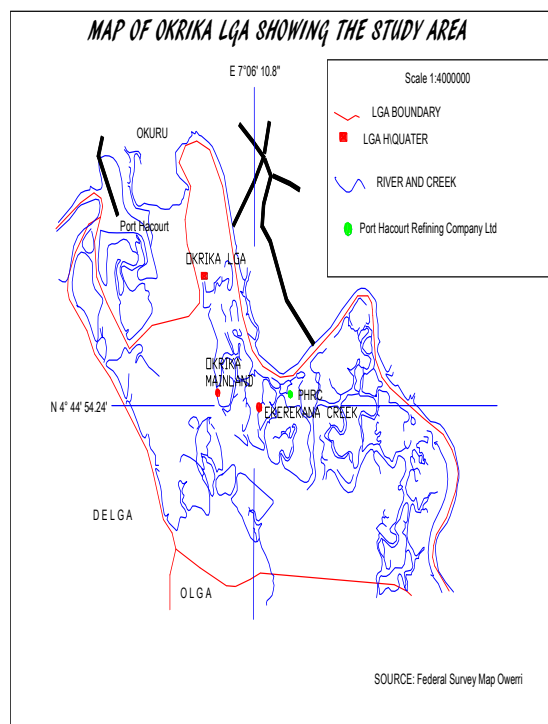
Hydrocarbon pneumonitis results from a direct toxic affect by the hydrocarbon on the lung parenchyma. The type II pneumocytes are most affected, resulting in decreased surfactant production. This decrease in surfactant, results in alveolar collapse, ventilation-perfusion mismatch, and hypoxemia. Hemorrhagic alveolitis can subsequently occur, which peaks 3 days after ingestion (Gross *et al.*, 1963). The end result of hydrocarbon aspiration is interstitial inflammation, intra-alveolar hemorrhage and edema, hyperemia, bronchial necrosis, and vascular necrosis. Rare pulmonary complications include the development a pneumothorax, pneumatocele, or bronchopleural fistula (Rodricks et al., 2003). Prolonged abuse of hydrocarbons can result in white matter degeneration (leukoencephalopathy) and atrophy (Borne *et al*, 2005. Filley *et al* aliphatic, (2004). In addition, prolonged exposure to certain hydrocarbons (eg, n -hexane or methyl-n -butyl ketone ([MnBK]) can result in peripheral neuropathy, blurred vision, sensory impairment, muscle atrophy, and Parkinsonism (Garrettson, 2001). Exposure to hydrocarbons can result in cardiotoxicity (Klein *et al.*, 1986). Most importantly, the myocardium becomes sensitized to the effects of catecholamines, which can predispose the patient to tachydysrhythmias, which can result in syncope or sudden death. Many of the hydrocarbons create a burning sensation because they are irritating to the GI mucosa.



Vomiting has been reported in up to one third of all hydrocarbon exposures. The chlorinated hydrocarbons, in particular carbon tetrachloride, are hepatotoxic. Usually, the hepatotoxicity results after the hydrocarbon undergoes phase I metabolism, thereby inducing free radical formation. These free radicals subsequently bond with hepatic macromolecules and ultimately cause lipid peroxidation. This metabolite creates a covalent bond with the hepatic macromolecules, thereby initiating lipid peroxidation. The common histopathologic pattern is centrilobular (zone III) necrosis. Liver function test results can be abnormal within 24 hours after ingestion, and clinically apparent jaundice can occur within 48-96 hours. Methylene chloride, a hydrocarbon commonly found in paint remover, is metabolized via the P450 mixed function oxidase system in the liver to carbon monoxide (CO). Unlike other cases of CO exposure, with methylene chloride, CO formation can continue for a prolonged period of time

METHOD OF INVESTIGATION

The methods of data analysis adopted for this study are descriptive analysis, Pearson correlation (r), test of homogeneity, principal component analysis and Pair-wise comparison. Spatial variations were observed using descriptive statistics. Two replicate samples each were randomly collected from 10 sampling points within about 300m of the Ekerekana Creek receiving the Port Harcourt Refining Company effluents and also from the effluent. Water samples for petroleum aliphatic hydrocarbons and other physicochemical parameters were collected from the creek and effluent discharge channel during the wet season (September, 2011) with 1 liter amber glass bottles that



were fitted with screw caps and lined with foils and labeled as follows: CW1, CW2, CW3, CW4, CW5, CW6, CW7, CW8, CW9, CW10 and Effluent. Samples were acidified with concentrated tetraoxosulphate (VI) acid and transported to the laboratory in ice packed cooler to maintain their integrity.

The test of homogeneity in mean variance (single factor analysis variance- ANOVA) was used to determine spatial variations in the aliphatic hydrocarbons. Post-hoc means plots were used for the detection of group means. The principal component analysis (PCA) was used for data reduction resulting in the isolation of the aliphatic components that contributed the greatest variability in the original aliphatic components. The pair-wise comparison of the concentrations of the aliphatic hydrocarbons as well as other physicochemical parameters in effluent and creek samples was made with the student's t-test of significance.

Samples for the determination of the 5-day BOD were also collected in BOD bottles and their initial DO contents determined with the HORIBA U- 10 Water Quality Checker that had been standardized with the phthalate auto calibration fluid. *In-situ* measurements were also made for the determination of pH. Temperature, total dissolved solids (TDS), turbidity, conductivity dissolved oxygen (DO) and salinity

using the HORIBA U- 10 Water Quality Checker that had been standardized with the phthalate auto calibration fluid. Measurement was achieved by switching to the required parameter mode on the instrument and reading off the respective values on the Liquid Crystal Display (LCD).

Water samples for the determination of BOD₅ were left in a dark corner of the laboratory for five days incubation period at a temperature of 20 ± 2 °C (APHA, 1998). On day 5, the dissolved oxygen (DO) of the samples was determined again with the HORIBA U-10 Water Quality Checker.

Results were computed to determine BOD₅ according to the equation:

$$BOD_5 \text{ (mg/L)} = \frac{DO_1 \cdot DO_2}{P}$$

Where DO_1 = Initial Dissolved Oxygen on day 1,

DO_2 = Dissolved Oxygen after incubation on day 5, and P = dilution factor.

RESULTS AND DISCUSSION

Concentrations of aliphatic hydrocarbons in water samples wide variations were observed in the concentrations of the component aliphatic hydrocarbons detected in water samples of the creek (Table 1.). C₈ concentrations ranged between 0.01909 and 1.88729 (0.28856 + 0.17980) mg/L while C₉ concentrations ranged between 0.00803 and 0.76546 (0.30590 ± 0.61605) mg/L. However, C₁₀ concentrations ranged between 0.03624 and 1.37871 (0.22732 ± 0.12869) mg/l, C₁₁ concentrations ranged between 0.02095 and 0.32712 (0.10090 ± 0.03156) mg/L and C₁₂ concentrations ranged between 0.00933 and 0.32806 (0.10 158 ± 0.03398)mg/L. C₁₃ aliphatic hydrocarbon ranged between 0.00351 and 0.13117 (0.03916 ± 0.01205) mg/L, C₁₄ ranged between 0.00468 and 0.14030 (0.04638 ± 0.01329) mg/l, C₁₅ ranged between 0.00284 and 0.31623 (0.06649 ± 0.02980) mg/l, while C₁₆ ranged between 0.00345 and 0.22162 (0.07113 ± 0.02484) mg/L. Minimum and maximum concentrations (mean ± standard error) of C₁₇, C₁₈ and C₁₉ aliphatic chains were 0.00799 and 0.09331 (0.04416 ± 0.00880), 0.00961 and 0.20289 (0.07078 ± 0.02179), and 0.00670 and 0.37752 (0.07527 0.0355 1735) mg/L, respectively.

Spatial variations in Aliphatic Hydrocarbon contents

Longitudinal spatial variations were observed in concentrations of the aliphatic hydrocarbons measured in this study. Minimum concentrations of 0.01909, 0.00803 and 0.3624 mg/L were recorded for C₈, C₉ and C₁₀ at CW4, CW7 and CW7, respectively (Fig.1). However, maximum concentrations of 1.88729, 0.76546 and 1.37871mg/L were all recorded in CW9 for the respective aliphatic hydrocarbons.

Minimum concentration of 0.02095, 0.00933 and 0.0035mg/L were recorded for C₁₁, C₁₂ and C₁₃ at CW7, CW1 and CW3 respectively. Hence, maximum concentration of 0.32712, 0.32806 and 0.13117mg/L were recorded each in CW9, CW4 and CW9 for the respective aliphatic hydrocarbons.

Minimum concentration of 0.00468, 0.00284, and 0.00345mg/L were recorded for C₁₄, C₁₅, and C₁₆ at CW9, CW2 and CW3 respectively. Therefore, maximum concentration of 0.14030, 0.31623 and 0.22162mg/L were indicated each in CW8, CW9 and CW9 for the respective aliphatic hydrocarbons.

Minimum concentration of 0.00799, 0.00961, and 0.00473mg/L were recorded for C₁₇, C₁₈, C₁₉ and C₂₀ at sampling points CW3, CW6 CW3 and CW7 respectively.

However, maximum concentration of 0.09331, 0.20289, 0.37752 and 0.16832mg/L were recorded at CW9 for the first three hydrocarbons and CW2 for C₂₀ respectively.

The test of homogeneity in mean variance of concentrations of the aliphatic hydrocarbons across the sampling points revealed significant inequality [$F_{(21.59)} > F_{crit(3.86)}$] at $P < 0.05$ (Appendix 2). A further structure of group means that utilized effluents as predictor variable revealed that turbidity (220.12), TDS (4520), and conductivity (8200) was responsible for the observed inequality at all the sampling points (Figs.7-15).

Principal Components Analysis (PCA)

The communalities table (Appendix 3) reveals high initial and extraction communalities; indicating that the extracted components represent the variables well. The Total Variance Explained output (Table 2) shows Extraction Sums of Squared Loadings that consists 4 PCs explaining as high as 90.134% of the variability in the original 15 variables. The rotation (Table 3.) maintains the cumulative percentage of variation explained by the extracted components, but that variation is now spread more evenly over the components.

The Scree plot (Fig.15) represents the eigenvalue of each component in the initial solution in graphical form. The extracted components are on the steep slope, while the component on the shallow slope contributed little (9.866%) to the solution. The last big drop occurred between the 4th and 5th component.

The rotated component matrix (Table 4.) shows that the 1st component was most highly correlated with C₁₅ (0.960), the second with C₂₀ (0.891), the third with C₁₈ (0.5 54) and the fourth with C₁₂ (0.93 8). The Scatter plot matrix of component scores (Fig.15) shows that other than between

Factors I and 3 which showed normal distributions, the other Factors (FAC_2 and FAC_4) have slightly skewed distributions.

Relationship between the physicochemical parameters and Petroleum Aliphatic Hydrocarbons

The correlation table shows that pH correlated significantly with C₁₈ (r=0.771) at p<0.01 (Table 4), BOD correlated with C₁₄ (r=0.644) at P<0.05 and TSS correlated with C₉ (r=-0.798) and C₁₉ (r=-0.802) at p<0.01. It also influenced significantly the aliphatic hydrocarbons C₁₁ (r=-0.714), C₁₀ (r=-0.722) and C₈ (r=-0.647) at p<0.05. Salinity had significant influence on C₁₃ (r=0.699) at p<0.05.

Comparison of concentrations of aliphatic hydrocarbons and physicochemical parameters in Effluent and Creek

The plot of mean concentrations of the aliphatic hydrocarbons reveals that except C₉ and C₁₀, the levels of the other aliphatic hydrocarbons (C₈, C₁₁, C₁₂, C₁₃ and C₁₄) in the creek followed the same increasing and decreasing trends as in effluent samples (Fig.16). Figure17 shows that other than C₁₆ and C₁₉, the concentrations of C₁₅, C₁₇, C₁₈ and C₂₀ followed the same trend in both the creek and effluent samples.

However, pHs, temperature, DO and BOD values followed the same trend in both the effluent and creek samples (Fig.18). The creek and effluent samples revealed the same trends in conductivity, TDS, turbidity, TSS and salinity (Fig.19).

Though the student's t-test of significance (Appendix 4) reveals that the levels of the parameters measured correlated significantly (Sig. r=0.000), they did not differ markedly between the effluent and creek samples (sig. t = 0.193) at p<0.05.

Table 1: Concentration of the petroleum aliphatic hydrocarbons (mg/l), and physicochemical parameters in Ekerekana Creek

	Range	Minimum	Maximum	Mean	Std. Error
C8	1.86820	0.01909	1.88729	0.2885550	0.17980229
C9	0.75743	0.00803	0.76546	0.3058950	0.06160452
C10	1.34247	0.03624	1.37871	0.2273150	0.12868577
C11	1.30617	0.02095	0.32712	.01009000	0.03155760
C12	0.31873	0.00933	0.32806	0.1015750	0.03397888
C13	0.12766	0.00351	0.13117	0.0391570	0.01204530
C14	0.13562	0.00468	0.14030	0.0463760	0.01329440
C15	0.31339	0.00284	0.31623	0.0664940	0.02979822
C16	0.21817	0.00345	0.22162	0.0711280	0.02483693
C17	0.08532	0.00799	0.09331	0.0441550	0.00879565
C18	0.19328	0.00961	0.20289	0.0707810	0.02179469
C19	0.37082	0.00670	0.37752	0.0752700	0.03551735
C20	0.16359	0.00473	0.16832	0.0514540	0.01641690
pH	1.45	6.20	765	6.4650	.13505
TDS	2200.00	1800.00	4000.00	2926.0000	199.38349
Temp	0.30	25.00	25.30	25.1500	.03416
Conductivity	600.00	4500.00	5100.00	4800.0000	56.27314
DO	0.40	3.60	4.00	3.8000	.03429
BOD	0.40	1.40	1.80	1.6000	.04082
TSS	6.20	45.00	51.20	48.4200	.54238
Turbidity	18.00	244.00	262.00	255.4300	1.93700

Salinity	1.10	36.20	37.30	36.7340	.16776
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TSD=total dissolved solids, **DO**=Dissolved Oxygen, **BOD**=Biological Oxygen Demand,
Tss=Total Suspended Solids

Table 2: Total Variance Explained for the Extraction sums of square loading of components

Component	Total	% of Variance	Cumulative %
1	7.554	58.110	58.110
2	1.940	14.919	73.030
3	1.208	9.292	82.322
4	1.016	7.812	90.134

Table 3: Total Variance Explained for Rotation Sums of Squared loading

Component	Total	% of Variance	Cumulative %
1	5.484	42.182	42.183
2	3.197	24.592	66.774
3	1.804	13.874	80.648
4	1.233	9.485	90.134

Table 4: Rotated Component Matrix of the aliphatic hydrocarbons

Aliphatic Chain	Components			
	1	2	3	4
C15	0.960			
C20		0.891		
C18			0.554	
C12				0.735

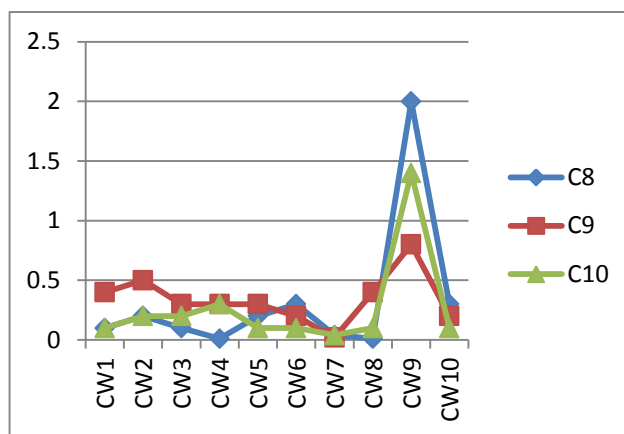


Fig. 1: Spatial variations in concentrations of aliphatic hydrocarbons (C8-C10) in Ekerekana Creek

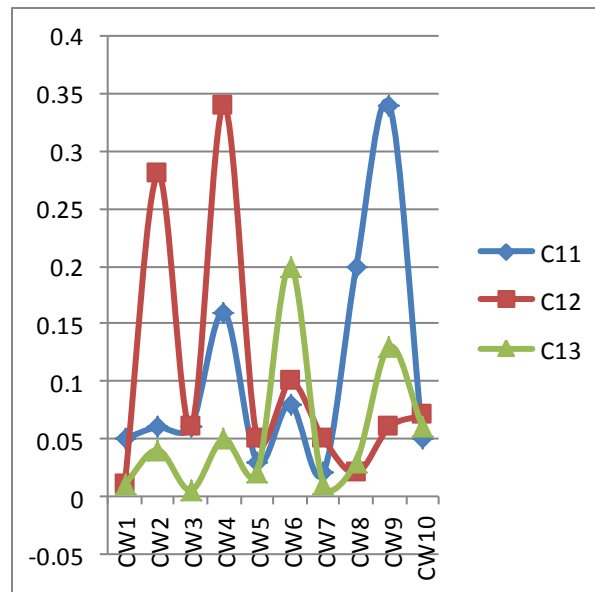


Fig. 2: Spatial variations in concentrations of aliphatic hydrocarbons (C11-C13) in Ekerekana Creek

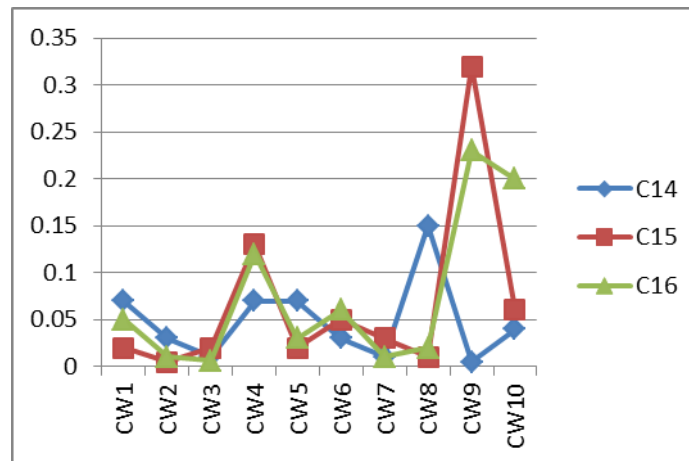


Fig. 3: Spatial variations in concentrations of aliphatic hydrocarbons (C14-C16) in Ekerekana Creek

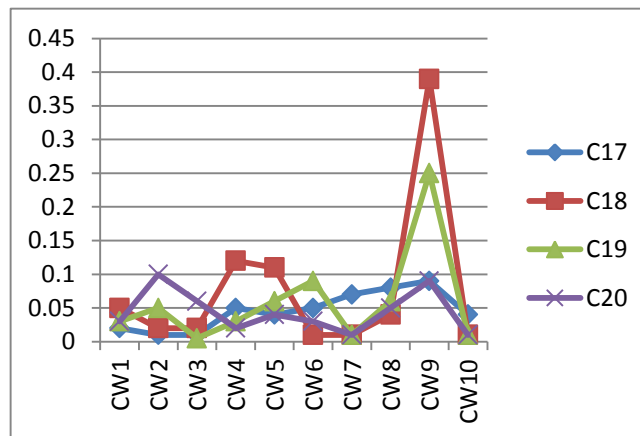


Fig. 4: Spatial variations in concentrations of aliphatic hydrocarbons (C17-C20) in Ekerekana Creek

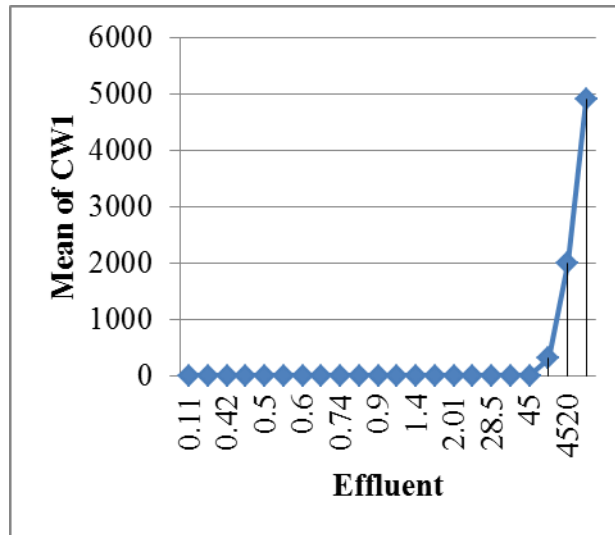


Fig. 5: Means plot between CW1 and Effluent samples

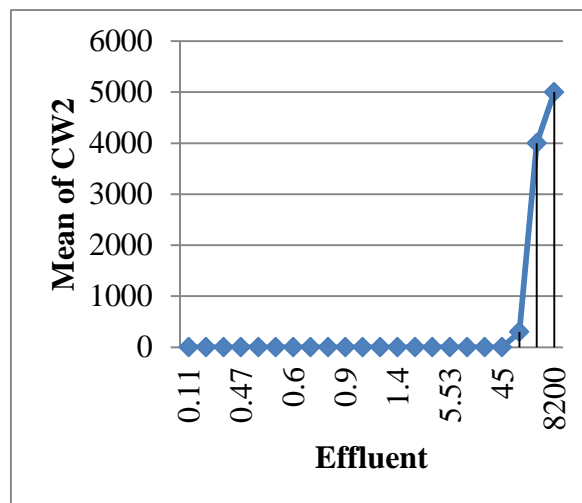


Fig. 6: Means plot between CW2 and Effluent samples

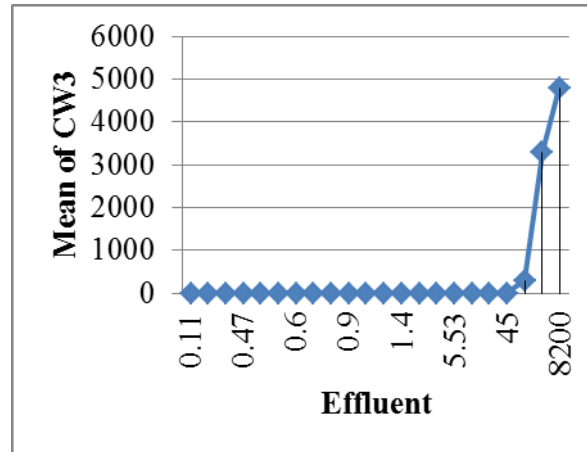


Fig. 7: Means plot between CW3 and Effluent samples

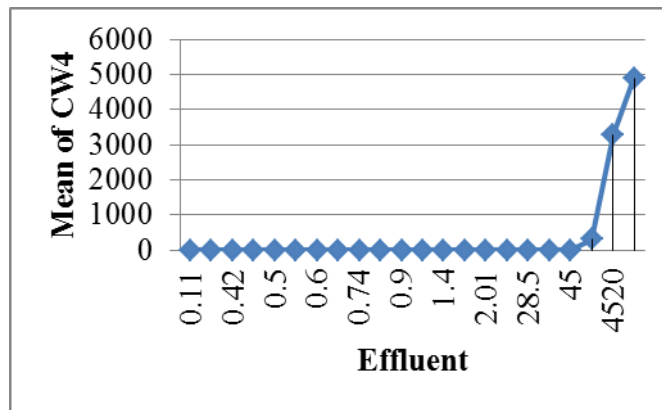


Fig. 8: Means plot between CW4 and Effluent samples

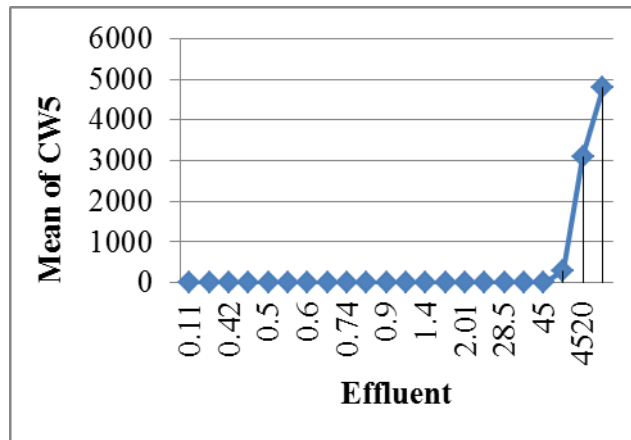


Fig. 9: Means plot between CW5 and Effluent samples

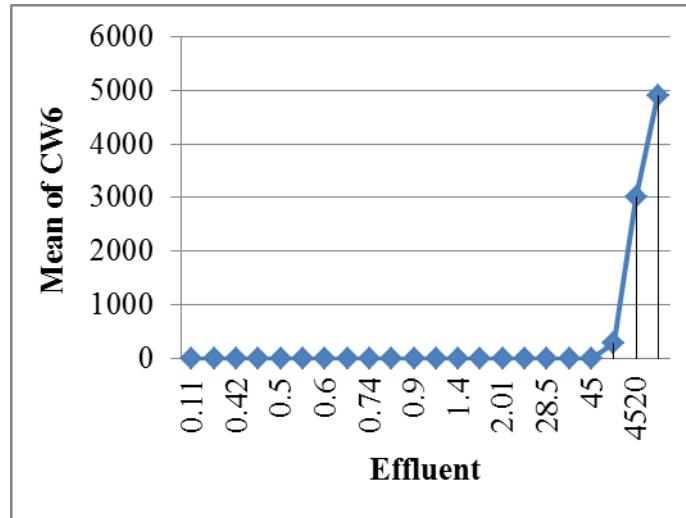


Fig. 10: Means plot between CW6 and Effluent samples

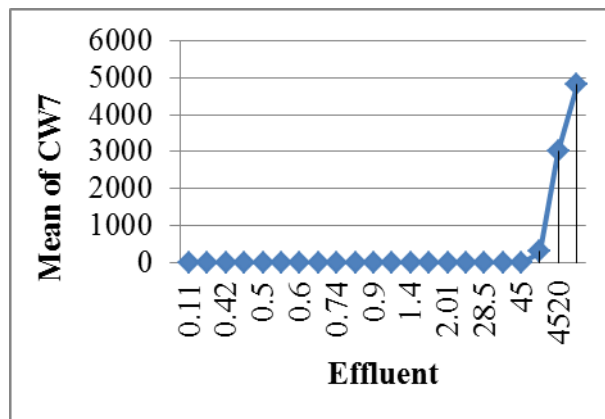


Fig. 11: Means plot between CW7 and Effluent samples

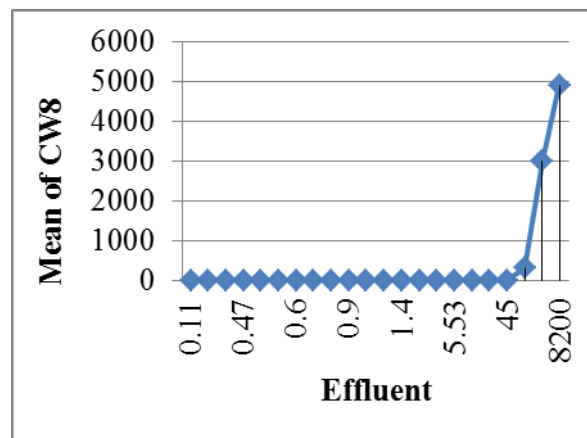


Fig. 12: Means plot between CW8 and Effluent samples

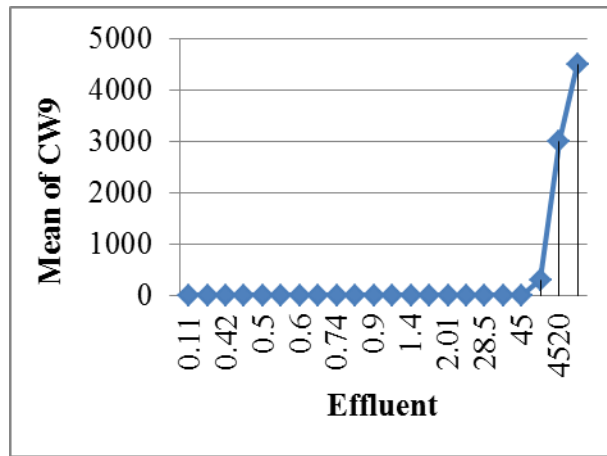


Fig. 13: Means plot between CW9 and Effluent samples

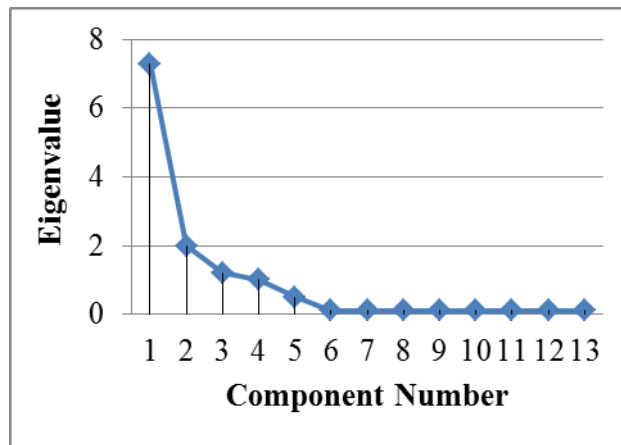
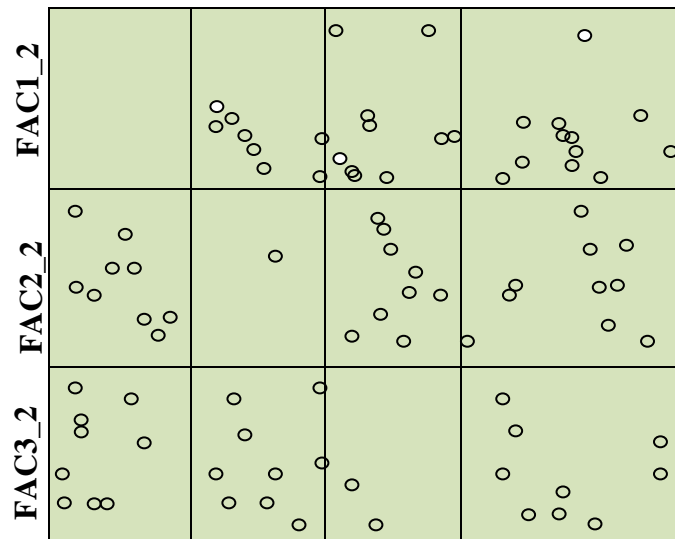


Fig. 14: Scree plot of eigenvalue of component numbers



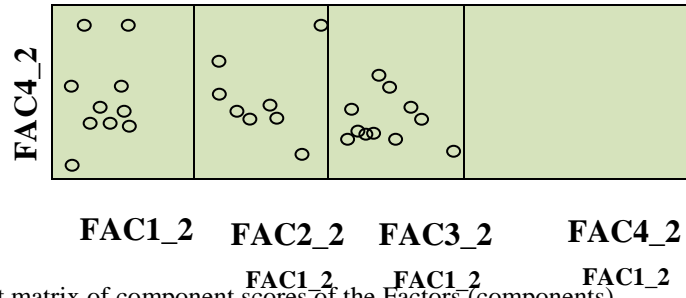


Fig. 15: Scatteredplot matrix of component scores of the Factors (components)

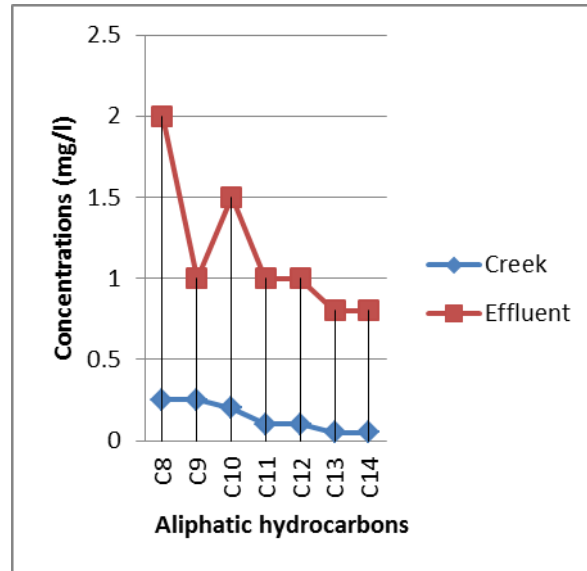


Fig. 16: Variations in mean concentrations of aliphatic hydrocarbons (C8-C14) in Ekerekana creek and effluent samples of the PHRC

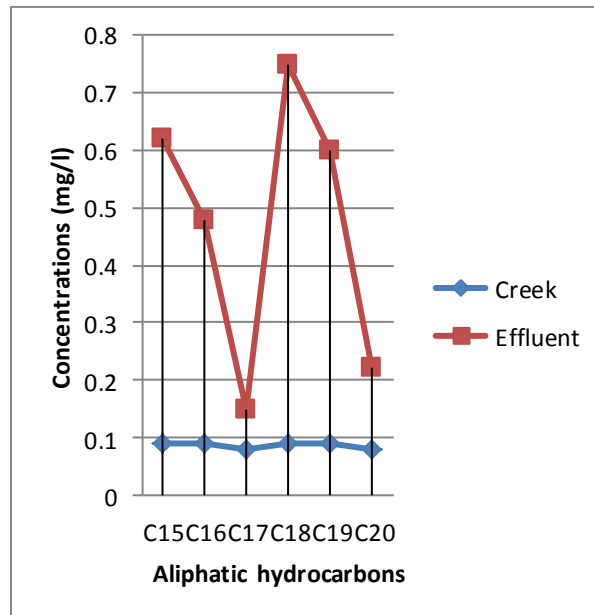


Fig. 17: Variations in mean concentrations of aliphatic hydrocarbons (C15-C20) in Ekerekana creek and effluent samples of the PHRC

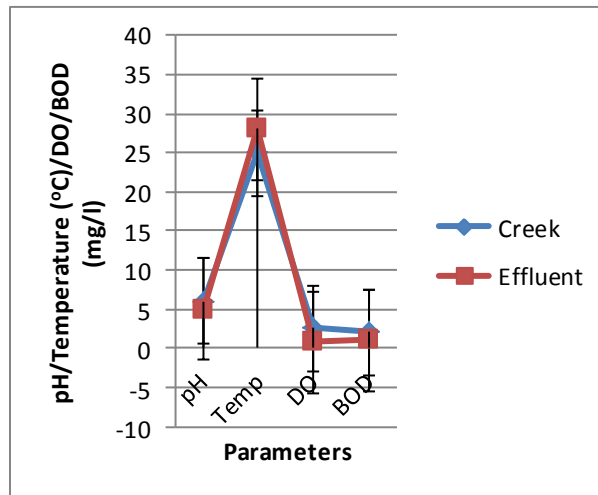


Fig. 18: Variations in mean pH, temperature, dissolve oxygen (DO) and biological oxygen demand (BOD) in Ekerekana creek and effluent samples of the PHRC

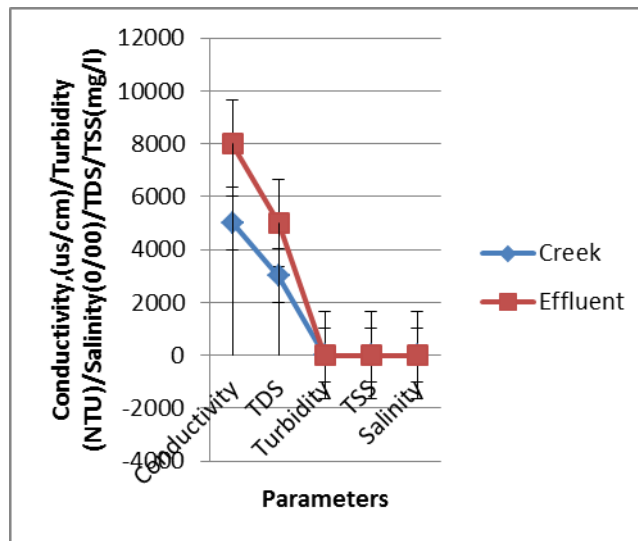


Fig. 19: Variations in mean Conductivity, total dissolved solids (TDS), total suspended solids (TSS) and salinity in Ekerekana creek and effluent samples of the PHRC

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Appendix

Table 5: Correlations (r) between the physicochemical parameters and petroleum aliphatic hydrocarbons in Ekerekana Creek

	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20
Ph	.056	-.35	-.043	-.101	-.090	.350	.034	.055	.597	.012	.771**	-.081	-.093
TDS	-.105	.049	-.004	.077	.491	-.125	-.123	-.135	-.539	-.138	-.567	-.032	-.320
Temp	-.220	-.424	-.165	.140	.036	-.031	.086	-.100	-.094	.355	.228	-.247	-.472
Conductivity	-.521	-.406	-.574	-.437	.481	-.132	.202	-.470	.026	-.362	.126	-.599	-.203
DO	.28	.094	.057	-.132	.146	.133	.081	-.005	-.083	-.013	-.061	.227	.281
BOD	-.385	-.079	-.367	.057	.306	-.015	.644*	-.315	.083	-.167	.331	-.365	.083
TSS	-.647*	-.798**	-.722	-.714*	.051	-.501	-.146	-.568	-.167	-.416	-.066	-.802**	-.423
Turbidity	.473	.202	.333	-.037	-.239	.367	-.600	.208	.341	.227	.119	.146	-.380
Salinity	.406	.416	.409	.288	.552	.699	-.122	.475	.587	.118	.492	.499	-.178