Chapter

Green Technology for Crude Oil Processed Water Treatment: A Practical Approach for Nigeria Petroleum Industry

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Abstract

Cleaner production is the key to environmental sustainability. Conversion of crude oil to various beneficial products is responsible for the contamination of air, water, and soil which are harmful to human, plants, animals, public health and the environment. Adequately treating produced water is beneficial for irrigation, wildlife consumption, industrial water and for domestic purposes. Therefore, green technology for treatment of crude oil processed water would provide the environmental friendliness needed for prolong utilization of our natural resources. Hence, the aim of this book chapter is to investigate the potentials of constructed wetland as a promising, effective and environmentally friendly alternative for secondary petroleum refinery wastewater treatment. Planted and unplanted mesocosm scale experiment with real secondary refinery wastewater was used for the purpose of the study. The parameters investigated were temperature, pH, dissolved oxygen, electrical conductivity, total suspended solids, carbon oxygen demand, total petroleum hydrocarbon and oil and grease. The results revealed that *Typha latifolia* planted VSSF CWs effectively treated organic contaminants in secondary refinery wastewater with a better performance than the unplanted control VSSF CWs. The chromatographs for wastewater and *T. latifolia* samples showed a hydrocarbon distribution between n-C_9 to n-C_{24} indicating abundance of lower weight hydrocarbon contamination.

Keywords: Approach, Crude oil, Green Technology, Processed Water, Nigeria, Treatment

1. Introduction

1.1 Importance of crude oil to the Nigeria economy

Crude oil is Nigerian's main source of revenue. The Federal Government of Nigeria derive about 90% of its revenue and 35% of its Gross Domestic Products from petroleum industry [1]. Nigeria has four refineries located in Kaduna, Warri and two in Port Harcourt with capacity of 438, 750 billion b/d along with 21 depots and about 5001 km of product pipelines [2]. The Federal Government of Nigeria has absolute ownership of its oil and gas resources, thus, exercises its rights through

concessions, joint venture, production sharing contracts and service contracts [3]. The Organization of Petroleum Exporting Countries (OPEC) ranked Nigeria as the sixth largest producer of oil [1]. Crude oil is essential for modern life for it provision of fuel and raw materials for an immense variety of useful products, from plastics to fertilizers, to pesticides, and medicines that facilitated unprecedented economic growth and improved human health around the world in the 20th century [4, 5]. Also, Globally, it is the most important source of power [5, 6], it represents about 40% of world total energy use [6]. Several nations are excessively reliant on petroleum for their main source of electricity and transportation fuel [7].

Olujobi et al. [1] described the Nigeria oil industry as consisting of three main streams: upstream petroleum sector (exploration, and production), downstream (crude oil refining for domestic consumption, marketing, and transportation) and the midstream (natural gas). The activities of the upstream and downstream sectors are interconnected and interdependent which is done through the establishment of an adequate regulatory framework consisting of laws and regulations setting out rights, obligations, procedures and standards, and regulatory institutions charged with responsibility for monitoring compliance as explained by Ambituuni et al. [2]. Nigeria has gained in economic and technological advancement through upstream and downstream activities and have posed human health, safety, and environmental risks [2]. Aside the gains of petroleum industry to the Nigeria economy, it is also faced with products theft, pipelines vandalism and cross-border smuggling, lack of capacity storage depots and substandard jetties [8]. Furthermore, Niger delta of Nigeria is a wetland consisting of mangroves, freshwater swamps, lowlands rainforest, salt water marshes and derived savanna vegetation covering about 12% (111, 020 km^2) of Nigeria's surface area, however, due to oil and gas exploration and development, Niger Delta is undergoing critical environmental threat, biodiversity extinction, and speedily growing human population [9]. It is important to be able to balance the derived economic and social merits from crude oil and the detrimental outcomes associated with ecotoxicological effects on soil and water environments [6].

1.2 Significant of crude oil processed water on the environment

Petroleum industries are a major source of environmental pollution. Conversion of crude oil to various beneficial products is responsible for the contamination of air, water, and soil. One of the major effects of oil exploration and exploitation activities is air pollution with the resultant negative effect of health such as exposure to ambient air levels of CO may result into the formation of carboxyhemoglobin and inhaled particles would increase blood viscousity which may hinder oxygen movement to the tissues [7]. The negative impact of contamination of the aquatic ecosystem on fishes was reported in a review on phytoremediation of crude oil spills by Yavari et al. [10] as abnormal neurone development, genetic damage, physical deformities, as well as changes in biological activities such as feeding, reproduction, and migration. Also, oil spills can suffocate aquatic life and renders water unfit for communal and domestic purposes [11]. Other resultant consequences as highlighted by Ite et al. [12] are atmospheric pollution associated with flaring and venting of natural gas, this act can contribute to global climate change, pollution of marine environment which often result in adverse impacts on wildlife and negative impact on tourism, and fishing and other businesses as well as water and soil pollution.

Produced water is a byproduct of oil and gas production and it is the largest wastewater produced by the petroleum industry [13]. Igunnu and Chen [14] estimated that about 250 million barrels of it is generated daily from oil and gas fields worldwide with 40% of it discharged into the environment. Similarly, Allison

and Mandler [4] stated that on the average, 10 barrels of wastewater is generated for each barrel of crude oil processed. These large volumes of wastewater produced during petroleum production is either discharged into the sea or re-injected into production or disposal reservoirs [15] or for reuse purposes. The contaminants in the produced water are harmful to human, plants, animals [16] as well as public health and the environment are threatened by its presence [17]. However, if produced water is adequately treated, it can be put to beneficial uses such as irrigation, wildlife consumption, industrial water and for domestic purposes [14].

Produced waters contain varying levels of organic and inorganic contaminants that can pose serious hazard to the environment when discharged untreated [18]. Accordingly, organic contaminants are classified as toxic, teratogenic, and carcinogenic [19]. The toxicity of petroleum wastewater depends on several factors including quantity, volume, and variability of discharge [20]. Thus, the effects of produced water on the environment cannot be overemphasized. Soil, an important medium for crop cultivation and habitat for living organisms is the most affected by the discharge of produced water [21]. The potential effects of produced water on soil quality and plants were reported by Pichtel [17] as low permeability of soil to air and water due to excessive sodicity, high accumulation of salts in soil causing plants to desiccate and die, and replacement of existing plant species by new species because of chemical changes in the soil. Contamination of soil by hydrocarbon can affect the physical, chemical and biological characteristics of the soil [10]. Also, reduction of dissolved oxygen in waterbodies as mentioned by Abbas [22] which is considered as detrimental to the aquatic ecosystem. Health hazards due to contaminants from petroleum wastewater may have short term (death at high concentrations of hydrogen sulphide gas) or long-term effects (cancer from benzene) [4].

The quality of produced water varies from region to region depending on the type of extracted hydrocarbons, extraction methods and the minerals present in geologic formation [13, 14]. Lin et al. [13] also stated that produced wastewater is characterized by high TDS, oil and grease, benzene, toluene, ethylbenzene, and xylenes (BTEX), polycyclic aromatic hydrocarbons (PAHs); organic acids; and waxes as well as heavy metals, ammonia and hydrogen sulfide. Abbas et al. [22] reported the characteristics of produced water in varied ranges composing of 1220–2600 mg/L COD, 2–565 mg/L O&G, 0.026–778.51 mg/L BTEX, 1.2–1000 mg/L TSS, and metals ranging from 0 to 150, 000 mg/L. They however, stated that the composition was highly depended on the crude oil quality, origin of wastewater contaminants and operating conditions of the refineries. Similarly, Mustapha [23], characterized secondary refinery wastewater and found that the wastewater was composed of organic and inorganic compounds including salts, suspended solids and metals varying from 12.2 ± 0.3 to 253.0 ± 0.7 NTU, 146.7 ± 0.1 to 446.0 ± 0.4 mg/L TDS, 161.7 to 782.5 mg/L TS, 10.4 to 283.1 mg/L BOD, 40.2 to 520.8 mg/L COD, 0.01 to 3.4 mg/L Cr, 0.01 to 0.06 mg/L Pb0.01 to 1.16 mg/L phenol and 0.7 to 14.2 mg/L O&G, suggesting that the secondary wastewater can adequately be treated with CWs for reuse purposes or safely discharge into the environment. Consequently, Lin et al. reported that about 45% of produced water from onshore activities is reused for conventional oil and gas operations.

1.3 Green technology for wastewater treatment

Natural resources are valuable resources of the world. They represent vital resources for a variety of human activities and also provide a living environment for a range of aquatic organisms. The deterioration of our environment due to pollution is most pronounced in developing countries. This has become a persistent

problem that needs to be given priority attention. Thus, prolong utilization of water and soil resources would necessitate the application of sustainable techniques such as green technology. Green technology is a natural process that provide high quality outcomes without compromising on environmental sustainability [24]. They serve as alternative method for the treatment of wastewater. Several types of green technologies have been applied for the remediation of polluted sites. Examples include but not limited to phytoremediation, bioremediation, biostimulation, bioaugmentation, natural attenuation, constructed wetlands, vermifiltration, nanotechnology, membrane filtration, and microbial fuel cells [19, 21, 24–27]. Phytoremediation is a cost-effective, plant-based technique of environmental remediation that uses the ability of plants and indigenous microorganisms in the rhizosphere to treat different types of contaminants [26]. More advantages of phytoremediation include public acceptance and ability to simultaneously treat organic and inorganic contaminants [28].

Constructed wetlands (CWs) are man-made wastewater treatment facilities duplicating the processes occurring in natural wetlands. They consist of shallow ponds or channels, which have been planted with aquatic plants and rely on natural microbial, biological, physical and chemical processes to treat wastewater [23]. This process is a complex, integrated system in which water, plants, animals, and microorganisms and natural elements interact to improve water quality [29]. CWs are a promising green technology that can decrease the adverse effect brought about by anthropologic activities. This technology has been used extensively for petroleum wastewater treatment. They have however has been largely ignored in developing countries where effective; low-cost wastewater treatment strategies are critically needed. CWs are lower in energy consumption, cost of investment, cost of operation and maintenance [18]. They are also known for their effective treatment, simplicity, low sludge production, high nutrient absorption capacity, process stability and its potential for creating biodiversity [18, 30]. Constructed wetlands are used for all types of wastewater treatment around the world. If they are correctly built, operated, and maintained [23] they can effectively restore sites of a wide variety of contaminants ranging from BOD, suspended solids, nitrogen, phosphorus, heavy metals, volatile organics, semi-volatile organics, petroleum hydrocarbons, pesticides and herbicides, PAHs, chlorinated solvents, to non-chlorinated solvents in storm water or municipal, agricultural and industrial wastewaters. Paz-Alberto et al. [31] mentioned that the effectiveness of a green technology such as CW is dependent on sufficient biomass production and contaminant accumulations into its tissues. In addition, effective treatment is based on the characteristics of the wastewater and treatment methods [32]. Additionally, effectiveness of remediation is usually judged by the level of reduction of contaminants and degradation of organic contaminants [6]. Also, the use of CWs for wastewater treatment can revitalize the environment, generate a water source or restore a marsh habitat during the course of treatment [32].

There are several studies on the use of different types of CWs for petroleum wastewater in developed countries with few reported researches in the developing countries. These researches are focused on constituents and effective treatment of petroleum contaminated wastewater. For instance, Stefanakis et al. [33] used horizontal subsurface flow CWs to effectively treat groundwater containing influent quality of 0.009 ± 0.004 mg/L methyl *tert*-butyl ether (MTBE), 10.2 ± 3.8 mg/L benzene and 27.1 ± 8.0 mg/L ammonia. Alsghayer et al. [29] also used horizontal subsurface flow CWs to treat wastewater containing high concentrations of polycyclic aromatic hydrocarbons (PAHs) (Phenanthrene, Pyrene, and Benzo[a]Pyrene) with high removal efficiencies. Effective treatment of petroleum contaminated wastewater with VSSF CWs was also reported by Mustapha [25].

The objectives of the study in this book chapter are to showcase constructed wetland as a promising, effective and environmentally friendly alternative for petroleum refinery wastewater treatment, investigate the contaminant pathways using mass balance approach. The outcomes of the study can prove to be beneficial to petroleum industry especially for Nigeria, water resources departments, environmental managers and researchers in the field of environmental Engineering and management. The application of the study will ensure reduction of hazardous constituents into water bodies and soil and assure improved water quality by the discharge of treated wastewater into the environment. The adequately treated wastewater from constructed wetland systems can be reused and/or safely discharged into water bodies, this can drastically reduce the cost of production of potable water. Additionally, health problems and diseases associated with the discharge of untreated or inadequately treated wastewater can be minimized and treated water can also be reused. Thus, field experiment using mesocosm scale experiment with real refinery effluent collected from the effluent discharged point of the Kaduna refinery and petrochemical industry was conducted for the purpose of the study.

2. Practical approach for petroleum wastewater treatment

2.1 Materials and methods

2.1.1 Description of the study area

This study was conducted offsite of the refinery (Minna, Nigeria) about 150 km from the Kaduna Refinery and Petrochemical Company which lies between latitude 10°31′35″ N and Longitude 7°26′19″ E and Minna is within 9° 36′ 54″ N and 6° 33′ 51″ E within the Northern guinea savannah ecological zone of Nigeria. Kaduna and Minna (Nigeria) have a tropical climatic condition with temperature ranging between 13 and 35°C and average accumulated rainfall of 306 mm and Minna with average high temperature of 34°C and low of 22°C with total rain accumulation of 256 mm (NIMET 2010). The Kaduna refinery and petrochemical (KRPC), Kaduna is the third largest refinery Nigeria with a capacity of 110, 000 barrels per stream day (BPSD). The type of crude oil processed by the refinery are Escravos light crude and Ughelli Quality Control Centre (UQCC) crude oil [25]. The refinery uses large volume of water for processing crude oil into its finished products and it discharges large quantities of wastewater into the environment. It discharges approximately 100, 000 m^3/day of secondary treated wastewater [23]. The discharged effluent is composed of oil and grease, hydrocarbons, phenols, nutrients, and heavy metals [34]. The refinery treats its effluents by chemical addition, clarification, oxidation, oil skimming, filtration and evaporation before being discharged via drainages into the Romi stream. More details on the process and characteristics of the petroleum refinery effluent are given in Mustapha et al. (2015).

2.1.2 Experimental setup of vertical subsurface flow constructed wetlands

The mesocosm-scaled subsurface flow constructed wetland (SSF) systems were composed of four VSSF constructed wetlands connected in parallel to each other. The VSSF wetlands were cylindrical in shape and made of plastic material (44 cm diameter and 88 cm height). The media type used for the VSSF CWs was gravel with coarse sand. Coarse size gravel of 25–36 mm was used near the middle and outlet of the VSSF CW cells and the inlet parts were filled with 6–10 mm gravel to support the plant roots. The bottom of the VSSF CWs were fitted with perforated

PVC pipes of diameter 50 mm about 10 cm above the media connected to the collection chamber. The VSSF wetland cells had an effective volume of 123 L with a porosity of 0.40. It has a designed flow rate of 0.0048 m^3/h, hydraulic loading rate of 0.0032 m^3/m^2 h and a theoretical hydraulic retention time of 48 hours. The VSSF CWs were planted with *T. latifolia* 10 cm below the media and the other two unplanted VSSF CWs served as the control to assess the performance of *T. latifolia*. The *T. latifolia* used in this study was collected from a swampy area outside the refinery. Refinery wastewater was discharged into a 5 m^3 collection tank, which subsequently flows gradually by gravity into the VSSF CW cells while the treated effluent was collected at the outlet. Influent and treated samples from the outlet of the wetland cells were collected every 2 weeks for both field and laboratory analysis to determine the performance of the *T. latifolia* in the remediation processes of electrical conductivity (EC), total suspended solids (TSS), carbon oxygen demand (COD), total petroleum hydrocarbon (TPH) and O&G. The temperature, pH and dissolved oxygen (DO) of the samples were also measured immediately on the site using handheld equipment (WTW Ph 340i, HM TDS-3 9001, WTW Cond, 3310 and OXi 340i). The analytical procedures used for influent and effluent samples were based on the Standard Methods for Examination of Water and Wastewater (2002). The method used for TPH determination was Gas Chromatography–Flame Ionization Detector (GC-FID) and Hexane Extractable Gravimetric method for O&G. The experiments were duplicated under the same conditions.

2.1.3 Typha latifolia, *an ideal wetland treatment plant*

Typha spp. is an aquatic, emergent monocotyledon plant species with linearly erect leaves and green stems extending well above the surface of the water as well as with an extensive rhizomes and roots systems, it also has a well-developed vascular system and supporting tissues [35]. This plant can be beneficial or nuisance in aquatic systems depending on the defined uses of the aquatic systems. There are reported researches on the beneficial uses of *Typha spp*. in constructed wetland treatment processes. Accordingly, Belmont et al. [36] testified on the effective performance of *Typha* spp. in wastewater improvement. Thus, *T. latifolia* was chosen for this study for its moisture tolerance, abundance, efficiency, fast growth and management.

The experiment started up by first counting and weighing *T. latifolia* before transplanting into the wetland cells. The plant height and number of live shoots of *T. latifolia* were recorded at the time of the transplant and subsequently every month after the transplant consecutively for a period of six months to monitor the growth rate of the *T. latifolia* in secondary treated refinery wastewater. The biomass was sorted into leaf, root and stem, washed under running tap and then rinsed with deionized water in order to remove any soil particles attached to the plant surface and their wet weight were determined, then oved dried at 105°C for 24 hours. The oven dried samples were grounded into powder, these were digested and analyzed for TPH and O&G determination.

2.1.4 Statistical analysis

Statistical analysis was performed using the IBM SPSS 20 (IBM SPSS Inc.). All experiments were performed in replicates. One way analysis of variance (ANOVA) at 95% ($p < 0.05$) was used to determine the significance of the data, multiple comparisons of means of the experimental parameters for the planted and unplanted VSSF CWs using Duncan multiple range test and Tukey honest significant difference. The treatment efficiency of the VSSF CWs were calculated as the percent of the contaminant removal, R and mass removal percent, M as presented below:

$$R = \frac{C_i - C_o}{C_i} \times 100 \quad (1)$$

$$M = \frac{C_i V_i - C_o V_o}{C_i V_i} \times 100 \quad (2)$$

Where R and M are contaminant removal percent and mass removal percent, C_i and C_o are influent and effluent concentrations and V_i and V_o are influent and effluent volumes of the *T. latifolia* planted and unplanted VSSF CWs.

3. Results and discussions

3.1 Presentation of results

Constructed wetlands are a promising and suitable technology for wastewater treatment. This is evident from the results collated from the field analysis conducted in a 184-day experiment using secondary refinery wastewater from Kaduna refinery, Nigeria. Thus, **Table 1** present the qualities of secondary refinery wastewater before and after treatment with vertical subsurface flow constructed wetlands (VSSF CWs). The secondary refinery wastewater, the treated wastewater (*Typha latifolia* planted VSSF CWs) and the effluent from the control (unplanted VSSF CWs) were characterized with varied concentrations of physicochemical and organic parameters. The water temperatures ranged from 31.08 ± 3.41 to 27.13 ± 1.71°C with an observed significance difference ($P > 0.05$) among the variables. The pH values for both effluents from the *Typha latifolia* planted and unplanted VSSF CWs showed no significance difference among them. Similarly, there were no significant difference in the oily content and total suspended solids (TSS) from both effluents though the effluents were significantly different from the influent concentrations. In contrast, electrical conductivity (EC) and carbon oxygen demand (COD) contents of the influent and effluent samples showed high significant differences among themselves. Comparing the effluent values to allowable

Parameter	Influent	*Typha latifolia*	Control	Allowable limits
Temp (°C)	31.08^{b} ± 3.41	27.13^{a} ± 1.71	29.13^{ab} ± 2.10	30–36
pH	7.48^{b} ± 0.14	7.19^{a} ± 0.06	7.32^{a} ± 0.122	6.0–9.0
DO (mg/L)	1.13^{a} ± 0.46	2.53^{b} ± 0.88	1.70^{ab} ± 0.67	<0.2
EC (μs/cm)	1350.17^{c} ± 182.43	998.00^{a} ± 113.56	1176.50^{b} ± 81.28	1000
TSS (mg/L)	66.17^{b} ± 18.92	30.83^{a} ± 8.45	46.17^{a} ± 16.92	30–50
COD (mg/L)	310.67^{c} ± 111.07	67.00^{a} ± 27.55	204.50^{b} ± 55.15	60–100
TPH (mg/L)	1.19^{b} ± 0.87	0.18^{a} ± 0.17	0.74^{ab} ± 0.79	—
O&G (mg/L)	3.91^{b} ± 1.22	2.01^{a} ± 0.71	2.84^{a} ± 0.47	10.0

Mean ± standard deviation. Values are means of two replicates (n = 2). Values on the same row with different superscript are significantly different ($P \leq 0.05$) while those with the same superscript are not significantly different ($P \geq 0.05$) as assessed by Tukey (HSD) and Duncan's Multiple Range Test.

Table 1.
One-way ANOVA for influent and effluent constituent of Typha latifolia *planted vertical subsurface flow constructed wetlands treating secondary refinery wastewater.*

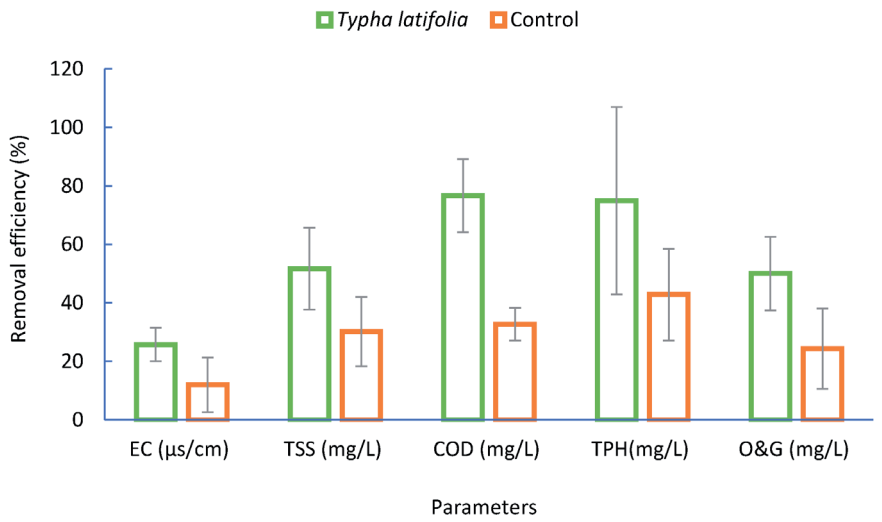


Figure 1.
Performance evaluation of T. latifolia *planted and control (unplanted) VSSF CWs.*

standards, temperature, pH, dissolved oxygen (DO), total petroleum hydrocarbon (TPH) and Oil and Grease (O&G) were within the limits of discharged while the effluents from *Typha latifolia* planted VSSF CWs met the discharge limits for EC, TSS and COD and the unplanted VSSF CWs had values above the allowable limits.

The treatment performance of *Typha latifolia* planted VSSF CWs for secondary treated refinery wastewater is presented in **Figure 1**. The removal efficiencies were determined for EC, TSS, COD, TPH and O&G contents. The *Typha latifolia* planted VSSF CWs showed a better performance than the unplanted VSSF CWs indicating that macrophytes have a significant role to play in constructed wetlands treatment process. The removal performance ranged from 25.71 ± 5.73 to 76.72 ± 12.51% and 11.94 ± 9.31 to 42.81 ± 15.71%, respectively for *Typha latifolia* planted and unplanted VSSF CWs. The *Typha latifolia* planted VSSF CWs showed highest removal efficiency for COD and the lowest for EC content while TPH content was most removed and similarly EC content the least removed in the unplanted VSSF CWs.

Constructed wetlands uses natural processes in plants, soil, and organisms for the removal of contaminants in wastewater [32]. It is composed of complex biogeochemical mechanisms and the removal processes of the different types of CWs varies and could be attributed to the difference in loading rate, nutrient species and abiotic environment [32]. Hence, in order to determine the removal pathways for the contaminants removal in VSSF CW treatment system mass balance approach was used. CWs can identify the potential sources and sinks of contaminants through the transfer and transformation of the contaminants in the

Sample	Contaminant	Influent	Root	Stem	Leaf	Sediment	Input
T. latifolia	TPH	568.72	0.085	0.010	0.023	0.000	568.84
Control		568.72	0.000	0.000	0.000	0.000	568.72
T. latifolia	O&G	1874.16	0.126	0.005	0.080	0.000	1874.37
Control		1874.16	0.000	0.000	0.000	0.000	1874.16

Table 2.
Mass balance approach for input parameters in mg.

Sample	Contaminant	Effluent	Root	Stem	Leaf	Sediment	Output	Removal, %
T. latifolia	TPH	19.570	2.576	0.526	0.382	17.40	40.45	92.89
Control		88.82	0.000	0.000	0.000	21.60	110.42	80.58
T. latifolia	O&G	235.430	3.801	0.918	0.444	21.00	261.59	86.04
Control		340.420	0.000	0.000	0.000	34.80	375.22	79.98

Table 3.
Mass balance approach for output parameters in mg.

wetland cells [32]. **Tables 2** and **3** present the fate of TPH and O&G in water, plants and sediment loads. **Table 2** showed the input variables and **Table 3** showed the output variables and mass removal percentage of the CW treatment systems. The input variables ranged from 1874.16 (O&G) to 568.84 (TPH) mg. The tissues of *T. latifolia* were segregated into root, stem and leaf parts, results showing that the root and leaf of *T. latifolia* accounted for the highest and least accumulation of TPH and O&G contents. However, higher contents were retained in the soil. Generally, the mass removal performance was high for both the planted and unplanted VSSF CWs although the planted (86.04 and 92.89%) showed a higher removal than the unplanted (79.98 and 80.58%).

The contaminant removal pathways were segregated into plant parts, sediment and other sources. The results are presented in **Table 4**. The plant contribution to the removal process was approximately 8 and 2% TPH and O&G and sediment exhibited the highest percent. Removal pathways by other sources that were not determined in the experiment also showed high removal performance.

The health of the plants used in constructed wetlands is reflected in its growth. The *T. latifolia* used for this study showed a continuous growth in height and increased canopy. The average results recorded from the startup of the experiment, from transplant (day 0) to the termination of the experiment are presented in **Figure 2**. The plant average canopy height ranged from 15 to 165 cm and density ranged from 25 planted *T. latifolia* to over 140 live stands of *T. latifolia* each in the two planted VSSF CW cells.

The environment will continuously be polluted with TPHs and the content will depend on the source of contamination be it crude oil itself or it finished or by-products. **Figures 3** and **4** presents the chromatographic profile of TPHs content in the secondary refinery wastewater used for the field experiment. The chromatography for wastewater sample showed a hydrocarbon distribution between n-C_9 to n-C_{24} with a hump between n-C_{19} and n-C_{24} (**Figure 3**). **Figure 4** presents the chromatograph for root sample of *T. latifolia* used for secondary refinery wastewater treatment. The hydrocarbon content of the root sample contained n-C_9 to n-C_{22}

Sample	Contaminant	Total input, mg	Total output, mg	Plant removal, %	Sediment, %	Other sources, %
T. latifolia	TPH	568.84	40.45	8.32	43.01	41.56
Control		568.72	110.42	0.00	8.03	72.55
T. latifolia	O&G	1874.37	261.59	1.89	19.02	65.13
Control		1874.16	375.22	0.00	9.28	70.70

Table 4.
Removal pathways for contaminants in vertical flow constructed wetlands.

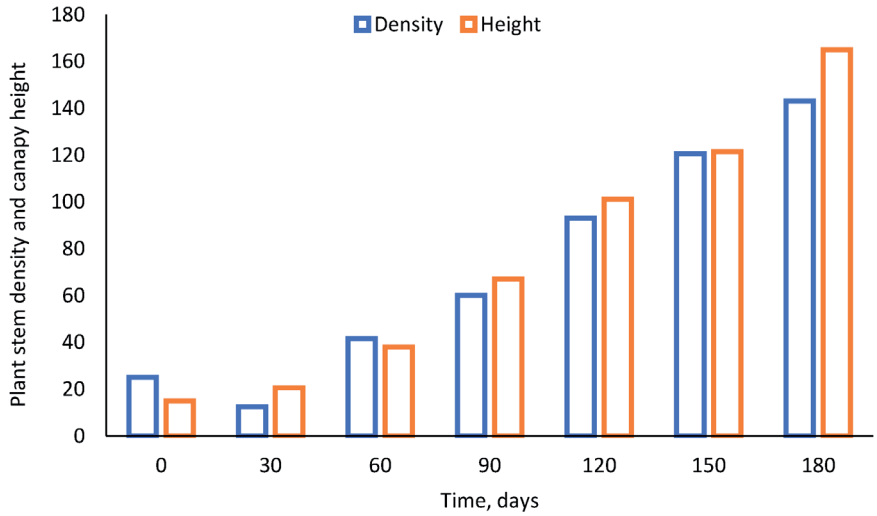


Figure 2.
Plant stem and canopy height for Typha latifolia *planted constructed wetlands.*

with a hump between n-C_{20} and n-C_{22}, the hydrocarbon content in the leaf sample ranged from n-C_{12} and n-C_{22} and stem sample contained ranged of n-C_9 to n-C_{20} (**Figure 4**) hydrocarbons.

3.2 Discussion of results

3.2.1 Physio-chemical properties of wastewater in treatment wetland

Physical, chemical and biological processes are used in subsurface flow CW treatment systems. Garcia et al. [37] mentioned physical factors as filtration and sedimentation, chemical factors include oxidation and sorption to organic matter while biological mechanisms include oxygen release and bacterial activity in the rhizosphere [37]. The planted system showed a high mean treatment performance for all the measured parameters (COD, TPH, O&G, TSS and EC) (**Figure 1**). Wastewater treatment occurs as the water flows gradually through the wetlands, consequently, temperature was reduced by 4°C, pH by 0.29 units, DO increased by 1.4 mg/L and EC decreased by 352 µs/cm for the *Typha latifolia* planted CWs and 2°C, 16 units, 0.57 mg/L and 174 µs/cm, respectively by the unplanted CWs. The observed oxygen in the CW treatment system may be attributed to water flowing vertically into the system, through the plant into the sediment and transfer through atmosphere to the water surface [32, 38]. Additionally, oxygenation of the treatment wetlands by continuous flow of water through the wetlands was supported by [39], favored by sedimentation, precipitation, absorption of soil particles, assimilation for the plant tissues and microbial transformations. Also, a reduction in the concentrations of the contaminants in the wastewater can increase the aerobic condition of VSSF CWs. This finding is in agreement with Al-Mansoory et al. [26]who observed higher gasoline concentrations with lower DO concentrations. Furthermore, increased DO in the *T. latifolia* planted VSSF CWs can aid biological pathway for removal of organic contaminants in secondary petroleum refinery wastewater. In this study, low removal of suspended solids was observed for both the planted and the unplanted VSSF CWs (**Figure 1**). This is in contrast to other studies. For instance, Mustapha [23] reported 60% TSS removal efficiency by VSSF CWs planted with *Cyperus alternifolius* and *Cynondon dactylon* and attributed

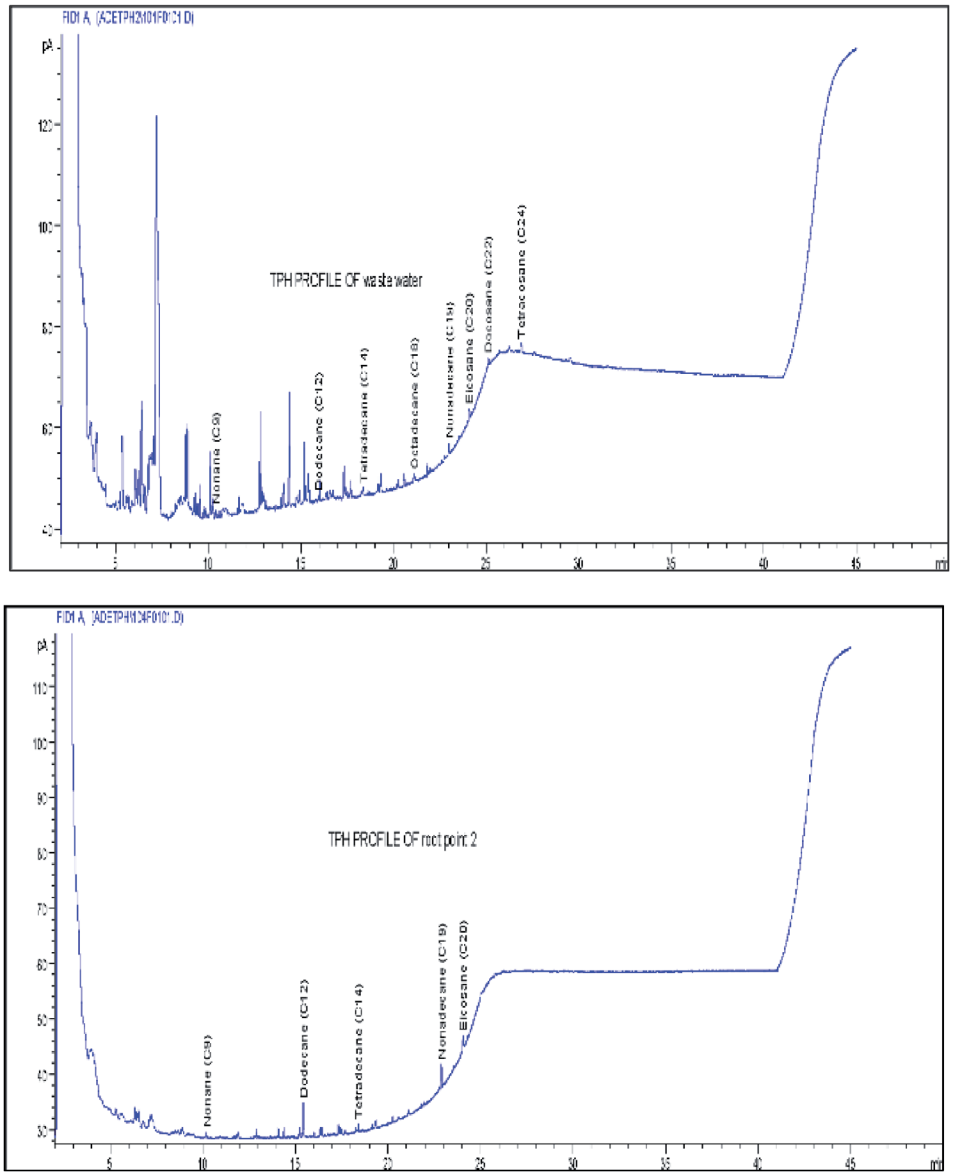


Figure 3.
Chromatographic profile of secondary wastewater (a), and root of T. latifolia *(b) for TPH contents.*

physical processes as the main pathway for the removal of suspended solids. Skrzypiec and Gajewska [40] reported 59 to 99% TSS removal in a VSSF CWs, stating that the decomposition of organic matter in CWs is by aerobic and anaerobic microbial processes and physical processes of sedimentation and filtration of particulate organic matter. Rios and Aizaki [39] and Wagner et al. [41] described the significant effects of salinity on plant growth with higher levels affecting the development of the plants. In this present study, *T. latifolia* was able to tolerant the EC values of the secondary refinery wastewater with its growth rate response (**Figure 2**).

Organic contaminants such as COD, TPH and O&G removal are favored by VSSF CWs due to it aerobic conditions. These contaminants were effectively removed in this study (**Figure 1**), suggesting aerobic biodegradation as a removal

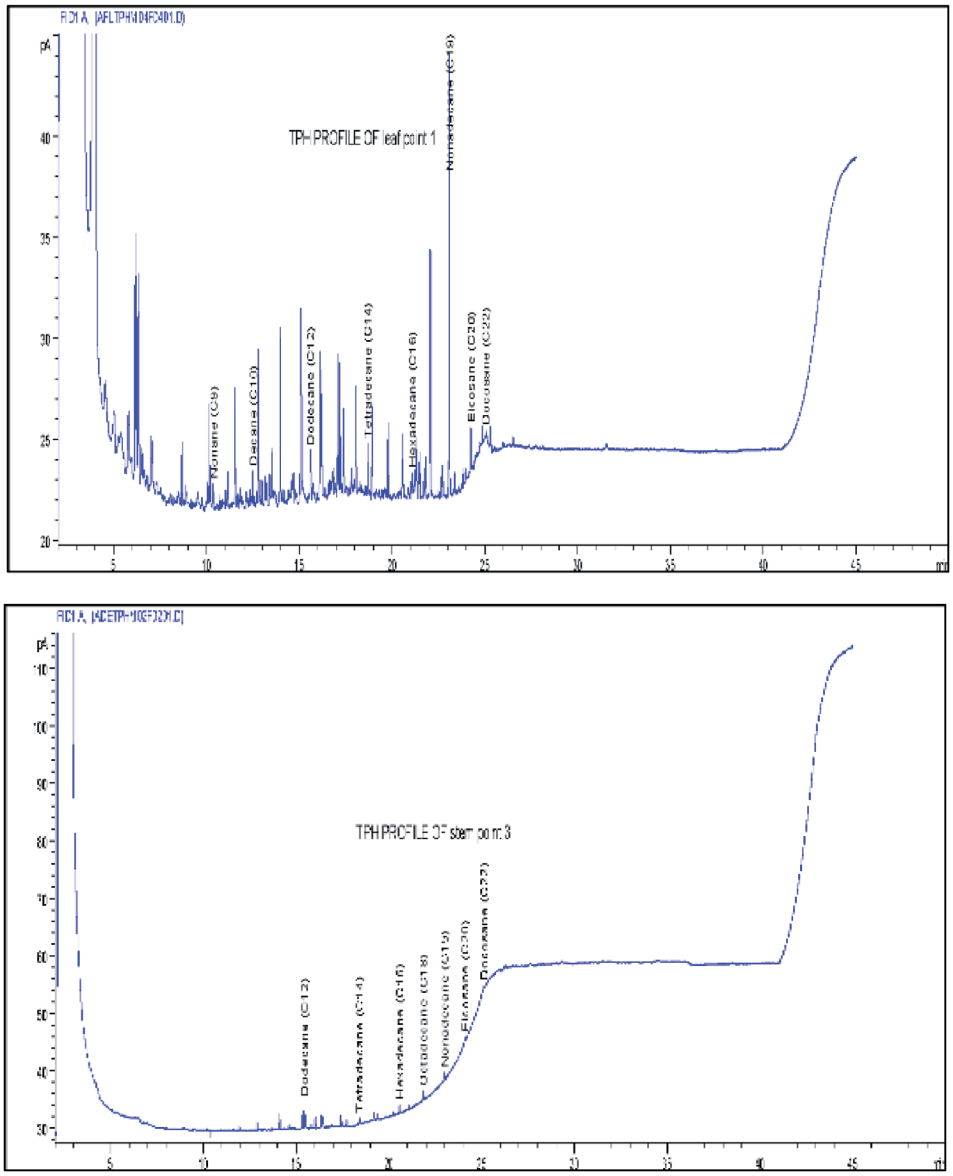


Figure 4.
Chromatographic profile of leaf (a) and stem (b) of T. latifolia *for TPH contents.*

pathway [37]. High COD removal in this study (**Figure 1**) is similar to the results reported by Mustapha [23] for *T. latifolia* planted VSSF and those reported by Kulshrestha and Khalil [42] for COD 77.28% and Skrzypiec and Gajewska [40] for TPH (97%) and COD (51 and 49%) in VSSF CWs and a COD removal of 39 to 69% in HSSF CWs was reported by [43]. They attributed removal mechanisms to filtration and sedimentation of suspended solids, organic matter mineralization within the wetlands and microbial degradation. Furthermore, Skrzypiec and Gajewska [40] reported that degradation of organic contaminants in CWs were dependent on pH, temperature, DO, hydraulic load, feeding mode, hydraulic retention time, depth of bed, plant species and harvesting.

Machado et al. [44] explained that substrate types can affect removal efficiency of a CW. A gravel substrate CW achieved 95.5% COD removal while a gravel-sand

substrate achieved a 99% in a VSSF CW planted with *Zizaniopsis bonarienses*. Li et al. [45] also reported the efficiency of organic contaminant removal in CW was highly dependent on oxygen concentration within the matrix in the bed and wetland design. They achieved a COD removal of >80% in horizontal subsurface flow CWs suggesting that the supplied artificial aeration may have enhanced the treatment process.

3.2.2 Functions of T. latifolia *in the processes of remediation*

Wetland plants are the most conspicuous component in the wetlands [18]. They have been reported to significantly contribute to the treatment processes. Al-Mansoory et al. [26] identified two major ways for effective treatment by plants namely creating favorable conditions for complex interactions involving rhizobacteria and root exudates to degrade contaminants in the soil. Also, Moubasher et al. [46] have attributed effective remediation to plants, its fibrous root system and rhizosphere. Hence, both plant and microorganisms have key role to play in phytotechnological processes of contaminant removal although, the rhizosphere is the most influential [28]. In this present study, the significant role of *T. latifolia* and its associated microorganisms was illustrated in reduction of the TPH and O&G in the planted VSSF CWs as compared to the unplanted control VSSF CWs (**Figure 1**). The significance of plants and microorganisms in the degradation of petroleum hydrocarbons was investigated by Moubasher et al. [46] who explained that presence of plants may greatly enrich the rhizosphere microbial flora by providing exudates, enzymes, and oxygen through its roots.

However, the plant contribution as shown by the theoretical mass removal percent were observed to be low for TPH and O&G compared to contribution by sediment and other sources (**Table 4**). The likely pathway removal of TPH and O&G in the unplanted VSSF CWs be explained by the processes of volatilization, eluviation and photolysis as suggested by Al-Mansoory et al. [26]. This is also in agreement with the findings by [46], as they also added the activity of its original microflora. In that case, the indigenous microorganisms in the soil of the VSSF CWs maybe responsible for the high contaminant degradation as presented in **Table 4**. In support of this argument, Alsghayer et al. [29] reported that microbial activities are increased in the soil as plant roots provide readily degradable carbon resulting into higher organic contaminant degradation through direct metabolism or a combined metabolism. In addition, Imfeld et al. [38] stated that the removal of toxic organic compounds in CWs are microbially mediated through aerobic and anaerobic microbial degradation processes. TPH are considered as water soluble compounds that display a sorption potential, generally more easily degraded and more readily mineralized under aerobic conditions [38]. This characteristics of TPH may explain its high removal rate in *Typha latifolia* planted VSSF CWs. In this study, TPH had a 93% mass removal rate, 8 and 43% are by plant uptake and sorption in soil and 42% assigned to volatilization and microbial degradation. In comparison to the study conducted by Ekperusi et al. [11] who assessed the transport and fate of hydrocarbons in *Lemna paucicostata* observed a < 1% (6.49 ± 0.66 mg/kg) accumulation in its tissues and 97.74% biodegradation of TPH, while *T. latifolia* accumulated higher percent (8%) in its tissues. The treatment of organic compounds by plants includes accumulation, sequestration, degradation, and metabolism of contaminants [11]. This is also supported by Azubuike et al. [47] who reported that the major removal pathway for organic contaminants is by degradation, rhizoremediation, stabilization, volatilization and mineralization in the presence of plants. This is in agreement with Eke et al. [48] stating that removal pathway in CWs is by volatilization, aerobic degradation and metabolic activity of microorganisms.

T. latifolia is a good phytoremediator since it was found growing freely in polluted site. This ideal was based on the report by Azubuike et al. [47] in their review on bioremediation techniques that most plants growing in polluted site can be considered as good phytoremediator. For instance, in this present study *T. latifolia* was able to tolerate the secondary refinery wastewater they were fed with in the course of the experiment. Thus, the increased density and canopy height is an indication of its ability to tolerate organic contaminants in the wastewater. This is in agreement with studies conducted by Alsghayer et al. [29] who used *Phragmites* and *Vetiver* to treat PAHs. They reported that increasing plant growth indicates increased plant biomass, shoot elongation and its adaptive characteristics. The presence of plants in CWs are reported to produce higher contaminant removal efficiency of planted systems and their ability to promote biodegradation [33]. It was also observed that the *T. latifolia* planted VSSF CWs had less residual TPH and O&G compared to the content in the unplanted control VSSF CWs. This study is also a confirmation of the positive role of plants in CWs. Increased treatment rate is observed in planted system due to presence of root, shoot biomass and microorganisms enhancing the rhizosphere effects [29]. Furthermore, overtime, there was increase in removal of contaminants in the secondary refinery wastewater, this increase may be related to plant growth and plant growth also results into increased root length which is expected to increase microbial degradation of organic compounds giving raise to effective biodegradation process [26]. Effects of plant root growth on microbial growth and corresponding increase in biodegradation of organic contaminants is also supported by Moubasher et al. [46]. They explained that microbes can secrete compounds that favors oil-degraders, restore the function of microbial community and increase phytoremediation efficiency.

Sediment or substrates compartment of CWs also have special role in its treatment processes. This could be through precipitation, filtration of suspended solids, sorption of heavy metals and organic matter as well as adhesion of microorganisms and support to root system [49]. The mechanisms for petroleum hydrocarbons in sediment include volatilization, photodegradation, leaching, plant uptake, biodegradation, and abiotic losses according to Al-Mansoory et al. [26]. Supply of oxygen into the substrates favor ideal conditions for the development of important microorganisms that plays vital role in the process of contaminant removal [50]. From the results of the mass balance, TPH and O&G were largely retained in the substrates of both the *T. latifolia* planted and unplanted control VSSF CWs suggesting that the mass removal pathway for these organics is as suggested by Hussain et al. [49]. Tropical climatic temperatures can play a significant role in biodegradation of hydrocarbons. The temperatures for the *T. latifolia* planted and the unplanted VSSF CWs were within the optimum temperature (20-30°C) required for biodegradation of hydrocarbons [26]. Therefore, significant mass removal of TPH occurred in the unplanted control VSSF CWs (**Table 2**). The high temperature in unplanted control VSSF CWs (**Table 1**), may have aided in the high treatment rate (**Tables 2–4**). Since temperature can determine the nature and extent of microbial hydrocarbon metabolism that affect biodegradation rate and physio-chemical behavior of oil hydrocarbons (viscousity, diffusion and volatilization) [51]. Coulon et al. [51] observed in their study that temperature had significant effect on TPH biodegradation regardless of bioaugmentation, although, the addition of nitrogen and phosphorus enhanced the biodegradation rate at 20°C. The functions of microbial species in sediment compartment are to metabolize organic contaminants to carbon dioxide and water [11].

3.2.3 Chains of hydrocarbon in secondary refinery wastewater

The hydrocarbon chains (C9 – C24) of this present study is similar to those identified by Ekperusi et al. [11] in their study (C8 – C40) which is consistent

with the hydrocarbons chain present in light crude oil associated with the Niger Delta oil fields, Nigeria. The wastewater, leaf, stem and root samples showed higher rate of lower molecular weight hydrocarbons (<n-C_{23}), this is an indication that all the samples contained light crude oil or by-product of gasoline diesel or jet fuel as suggested by Cortes et al. [52]. Similarly, Khudur et al. [6] also reported diesel as relatively low molecular weight hydrocarbons with typical carbon number of C8 – C28 and they are readily degraded by microorganism. Additionally, the presence of low molecular weight hydrocarbons in the plant tissues of *T. latifolia* is an indication of its translocation from the soil. This finding is in agreement with Al-Mansoory et al. [26] who stated that lower molecular weight hydrocarbons can be transported across plant membranes from the soil and released through the process of phytovolatilization [26]. In addition, lower molecular weight aromatic hydrocarbons known to be easily taken up by plants roots [46]. Khudur et al. [27] stated that readily uptake of lower molecular weight hydrogen compounds may indicate its toxicity. The suggested high toxicity of lower molecular weight hydrocarbon may not be applicable to *T. latifolia* growth rate and performance (**Figure 2**) in VSSF CWs. Again, toxicity may depend on several factors including quantity, concentrations, and bioavailability of contaminants [20]. The translocation of TPH into part tissues indicates the contribution of *T. latifolia* (plants) to contaminant removal processes in CWs.

4. Conclusions

The role of green technology for petroleum wastewater treatment specifically for Nigeria Petroleum industry was investigated and presented in this book chapter. Constructed wetlands served as the green technological approach for petroleum wastewater treatment. In conclusion,

- *Typha latifolia* planted VSSF CWs effectively treated organic contaminants in secondary refinery wastewater with a better performance than the unplanted control VSSF CWs.

- Tropical climatic temperatures significantly impacted TPH degradation rate in the unplanted control VSSF CWs.

- The wastewater contained higher lower molecular weight hydrocarbons (<n-C_{23}), these were translocated into leaf, stem and root samples.

- The pathways for TPH in *T. latifolia planted* VSSF CWs include volatilization, photodegradation, plant uptake, biodegradation, rhizodegradation, while rhizodegradation is assumed to be the main mechanism.

- Finally, constructed wetland treatment system planted with *T. latifolia* is a simple, ecologically safe approach characterized with low maintenance and operational system was able to effectively treat petroleum contaminated soil.

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Conflict of interest

The author declares no conflict of interest.

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List of abbreviations

COD	Carbon oxygen demand
CWs	Constructed wetlands
EC	Electrical conductivity
HSSF	Horizontal subsurface flow
O&G	Oil and grease
TPH	Total petroleum hydrocarbon
TSS	Total suspended solids
VSSF	Vertical subsurface flow

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