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Table of Content

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Full Length Research Paper

Modeling and simulation of reactors in plug flow reactor (PFR) and Packed Bed Reactor (PBR) series for the conversion of methanol into hydrocarbons

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Democratic Republic of the Congo.

The aim of this paper is to size the PFR reactor and to deduce the likely useful mass of the catalyst in the PBR for the production of hydrocarbons such as propane, butane and pentane from methanol via dimethyl ether (DME). The use of these reactors would require kinetic analysis, material balance, energy balance and then sizing. The interest in the chemical catalytic conversion of synthesis gas to gasoline suggests that the fuels industry may have come full circle from the time that synthesis gas from either natural gas or coal gasification were economic alternatives to crude oil. In this instance, cellulosic waste is the alternative raw materials that can be provided from DRCs logging waste and from agricultural activities. In the case of Muanda in the DRC, as in neighboring countries, the exploitation of black gold does not seem to have played any positive role in terms of development.

Key words: Packed bed reactor, plug flow reactor, modeling, simulation.

INTRODUCTION

Growth and development of population has led to increased demand for energy; forcing projected rise in overall energy demand by around 16% in the period 2015 - 2040, while gasoline demand is expected to grow by around 13%. Owing to its inherent contribution to a decrease in crude oil reserves, much focus has been on climate change; and its impact on greenhouse gas emissions in the environment, in particular CO_2, has led to the development and increasing use of alternative sources of energies as well as synthesis of biofuels (Rojas, 2018) as a sustainable approach for producing gasoline-range hydrocarbon biofuels. It can also mitigate the challenges associated with crude oil, such as

environmental pollution, scarcity and cost of fossil-derived fuels, as well as political instability in major crude oil-producing countries. MTG process begins with the production of syngas, followed by conversion of syngas to methanol and production of gasoline from methanol (Chakraborty et al., 2022).

As is often the case in oil extraction areas, crude oil leaks, gas flaring and toxic wastes are part of the daily life of Muanda's citizens. The authors of the report have gathered numerous textual and visual elements confirming the reality and extent of these pollution problems. Although residents have been complaining for many years about the severe degradation of all natural

environments (fresh water, sea water, soil, air) caused by drilling, their accusations have been confirmed on several occasions by experts or local officials (https://multinationales.org).

Biofuels are produced by various means such as the FischerTropsch method or by methanol. This relates to the production of synthesis gas (mixture of CO and H$_2$) from organic raw materials and its subsequent conversion to methanol, followed by dehydration to dimethyl ether and conversion to hydrocarbons. The final stage has attracted more attention in recent years, which is linked to the benefits that EMR comes from the upgrading of the feed stream of a low H$_2$/CO ratio, either from biomass or coal or natural gas. The EMR has proven its applicability both as an intermediate and as a final product. Indeed, the direct use of DME as a transport fuel has been put into practice and proven (Rojas, 2018). Syngas, which is derived from wood, waste wood, cellulose or lignin is a renewable fuel type. Depending upon the feedstock type, it typically begins as a blend of hydrogen, carbon monoxide, carbon dioxide, methane and nitrogen. These components can be separated and the methane purified to create bioSNG. Both syngas and bioSNG can be used as a fuel in gas engines (https:www.clarke-energy.com/applications/renewable-gas/).

The Democratic Republic of Congo (DRC) is the second largest country in Africa and the third most populous. It has immense resources - forests, water, fertile soils and high rainfall, plus considerable mineral reserves: copper, cobalt, coltan, diamonds, gold, zinc and other base metals as well as oil.

Forests cover about 60% of the national territory (or some 134 million hectares), including most of the rainforest of the Congo Basin, which is the second largest complex of tropical forests in the world after the Amazon. These forests are crucial for the subsistence of around 40 million Congolese, to whom they provide food, medicine, energy, building materials and a source of income (https://reliefweb.int/report/democratic-republic-congo).

The aim of this work is to perform the sizing of reactors series for the production of hydrocarbons from methanol, with methanol based syngas and BioSNG derived from wood, waste wood, cellulose or lignin for the yield of a renewable fuel type, as well as gasoline based on methanol. With adequate conservation and management, the forests of the DRC could bring long-lasting multiple benefits to the country and the planet (https://reliefweb.int/report/democratic-republic-congo). Indeed, the reactor constitutes a main element in the design of the process which requires kinetic analysis, material balance, energy balance and then dimensioning.

METHODOLOGY

The different solutions are obtained by digital simulation and modeling by implementing the different values obtained, the results of which follow linear and exponential trend curves. The parameters related to the geometry and operation of series reactors in continuous mode, in particular the plug flow reactor and the packed bed reactor (fixed bed reactor), were simulated to obtain the best dimensions and optimize the process from the degree of conversion of methanol.

Mathematical model

Material and thermal balance of the PBR

$$dQ = U(T_S - T)dA_p = \frac{4U}{D}(T_S - T)dV_r \qquad (1)$$

The following assumptions were made for the development of the dimensioning for which the PFR performance of the reaction rate equations is of the first order (Figures 1 and 2).

The various pre-requisites are such that: i) the reactor operates in a state of equilibrium ii) the reaction is in the liquid phase with constant density, and iii) the pressure drop along the reactor is negligible (Couper, 2012).

Modeling of PFR and PBR reactors in series and calculation of parameters

Considering the above relation, the equation giving the volume of the PFR is as follows (Diagbonia and Ehirim, 2019):

$$V_R = C_{A0}V_0 \int_0^{X_{AF}} \frac{dX_A}{-r_A} \qquad (2)$$

$$\frac{V_R}{V_0} = C_{A0} \int_0^{X_{AF}} \frac{dX_A}{-r_A} \qquad (3)$$

$$\tau = C_{A0} \int_0^{X_{AF}} \frac{dX_A}{-r_A} \qquad (4)$$

After adjusting the material balance from the differential elements to give an expression for the volume of the reactor, we have as follows (Couper, 2012):

$$V_R = F_{A0} \int_0^{X_{AF}} \frac{dX_A}{-r_A} \qquad (5)$$

$$C_A = \frac{P}{RT} \qquad (6)$$

$$-r_A = kC_A{}^2 \qquad (7)$$

Development of the dimensioning of the PBR

Firstly, for a heterogeneous reaction (e.g fluid-solid), the mass of the solid catalyst, W, is a bigger problem than that of determining the volume of the reactor (Rosen, 2014).

Thus, for the Packed Bed Reactor (PBR), if the pressure drop and the degradation of the catalyst are neglected for this purpose, its model will have been established (Rosen, 2014) (Figure 2).

$$W_{cat} = \frac{F_{A0} \int_0^x x_A}{-r_{oxy}} \qquad (8)$$

Where W, is the mass of the catalyst required to reduce the molar feed rate of A, F$_{A0}$ for a conversion x_A.

$$V_{cat} = \frac{W_{cat}}{\rho_{cat}} \qquad (9)$$

$$-\boldsymbol{r_{oxy}} = x_A \frac{WHSV}{Mm_A} \cdot \left(\frac{1h}{3600\,s}\right) \qquad (10)$$
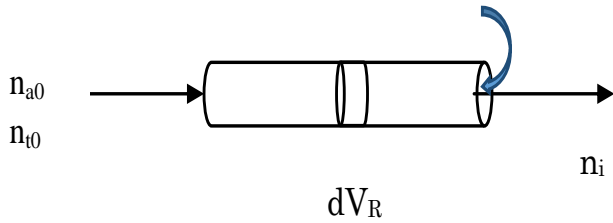
Figure 1. Representation of the PFR.

Knowing the residence time, the volume of the reactor is deduced by the following relation:

$$V_{PBR} = \tau \times V_0 \tag{11}$$

$$V_0 = F_A \times V_m \tag{12}$$

Thus, the volume of the reactor depends only on the feed rate.

Calculation of the reaction rate (kinetic analysis), material balance, residence time, and PFR volume

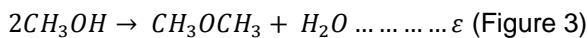Methoxymethane can be produced by the following reaction kinetics (Table 1):

2CH₃OH ↔ CH₃OCH₃ + H₂O
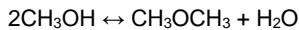
$$-r_A = k_0 e^{\left[\frac{-E_0}{RT}\right]} C_A$$

RESULTS AND DISCUSSION

The material balance in the plug flow reactor (PFR) is as follows:

Block diagram

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \dots\dots\dots\dots \varepsilon \text{ (Figure 3)}$$

For a molar flow rate of 1000 mol/h, the material balance is:

$$ACC = IN - OUT + GEN - CONS$$

$$CH_3OH: \quad 0 = 100 - n^{out}_{CH_3OH} + \varepsilon - 2\varepsilon \leftrightarrow n^{out}_{CH_3OH} = 1000 - 2\varepsilon \tag{13}$$

$$H_2O: 0 = 0 - n^{out}_{H_2O} + \varepsilon - 0 \leftrightarrow n^{out}_{H_2O} = \varepsilon \tag{14}$$

$$CH_3OCH_3: 0 = 0 - n^{out}_{CH_3OCH_3} + \varepsilon - 0 \leftrightarrow n^{out}_{CH_3OCH_3} = \varepsilon \tag{15}$$

For a conversion of 0.66:

$$0,66 = \frac{1000 - 1000 + 2\varepsilon}{1000} \rightarrow 660 = 2\varepsilon$$

$$\varepsilon = 330 \; mol/h$$

From where $\begin{cases} n^{out}_{H_2O} = n^{out}_{CH_3OCH_3} = 330 \frac{mol}{h} \\ n^{out}_{CH_3OH} = 340 \frac{mol}{h} \end{cases}$

Equilibrium constant

The equilibrium constant is given as follows:

$$[H_2O] = \frac{\varepsilon}{1000} P_t$$

$$[CH_3OCH_3] = \frac{\varepsilon}{1000} P_t$$

$$[CH_3OH] = \frac{100 - 2\varepsilon}{1000} P_t$$

$$K_{éq} = \frac{\varepsilon^2}{(1000 - 2\,\varepsilon)^2}$$

$$K_{éq} = 0,94$$

Determination of the temperature in the reactor

In chemistry, equilibrium constant characterizes the state of equilibrium of a chemical system, with the value of the latter dependent on the reaction considered and the temperature in order to predict the direction of evolution of the system (Table 2). It is noted that the progression of the reaction is effective at the temperature range going from 300 to 650K (Figure 4). Once exceeded, there is a regression of the reaction as indicated by the bending on the curve, which this time stabilizes and remains constant from 700K up to above 1000K.

Calculation of the volume of the PFR reactor

The volume of the reactor is obtained by the following relation:

$$V_R = F_{A0} \int_0^{X_{AF}} \frac{dX_A}{-r_A} \tag{16}$$

$$C_A = \frac{P}{RT} \tag{17}$$

$$-r_A = k C_A^{\,2} \tag{18}$$

where F_{A0} = 0.28 moles; P=1346.868 Pa; R=8.314 m³.Pa/mol.K; k=1.00; C_A= 0.27 mol/m³; T=600 K; $-r_A$=0.077 mol/m³.s; X_{AF}=0.67; and V_R=2.43 m³.
Hence to calculate the residence time in the reactor, the following relation was used:
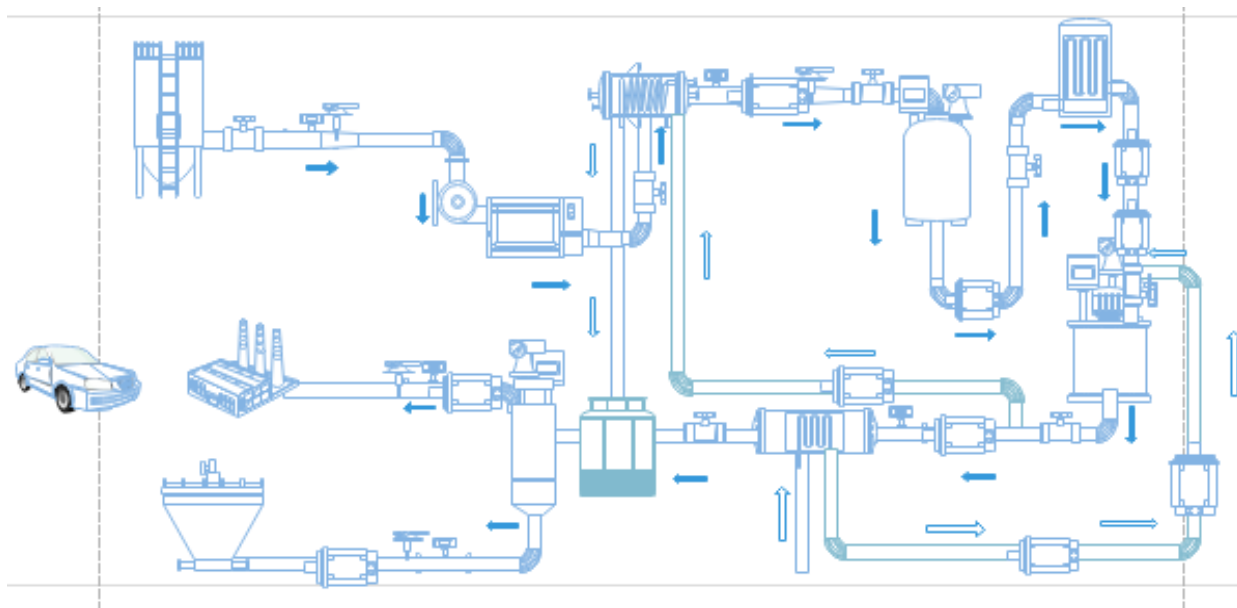
Figure 2. Industrial diagram of the installation.

Table 1. Calorific capacities, enthalpies and free energies of compounds formation involved in the synthesis of dimethyl ether.

Compounds	ΔH° (kJ/mol) at 298.14 K	ΔG° (kJ/mol) at 298.14 K	Cp (J/mol K)	ΔH° reaction (kJ/mol)	ΔG° reaction (kJ/mol)
CH₃OH	-201.54	-166.51	79.5		
CH₃OCH₃	-184.05	-112.93	64.4	-22.27	-8.51
H₂O (Gaseous)	-241.8	-228.6	33.6		
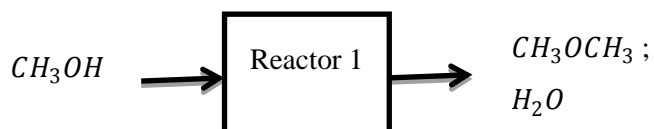
Figure 3. Block diagram.

$$\tau = \frac{V_R}{V_0} \tag{19}$$

$$V_0 = \frac{m}{\rho} \tag{20}$$

Having = 11.24 m³/s and the volume of the reactor, the residence time is = 0.22 s.

Calculation of the mass of the catalyst and the volume of the PBR

The mechanism involved in the methanol to gasoil process is quite complex. A simplified reaction scheme (proposed by Chang and Silvestri, 1977) is shown as follows:

$$2CH_3OH \underset{+H_2O}{\overset{-H_2O}{\longleftrightarrow}} CH_3OCH_3 \xrightarrow{-H_2O} C_2 - C_5 \text{ alkenes}$$
$$\rightarrow alkanes, cycloalkanes \text{ and } aromatics$$
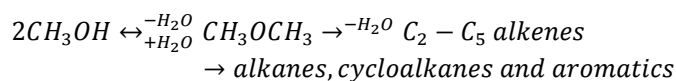
Figure 5 shows the product selectivity measured as a function of a wide range of contact time. The latter measures the contact time between the catalyst and the reagent molecules. At the smallest contact time, that is, in the order of 10^{-3} hours, water and dimethyl ether are the main products obtained. When the contact time increases, the production of dimethyl ether finally reaches a maximum and then decreases. From the methyl ether,

Table 2. Tables of different temperatures for the operation of the PFR reactor.

Chemical reaction	$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$
$\Delta H°RX$(kJ/mol)	-22.77
$\Delta G°RX$(kJ/mol)	-8.51
k_0	1,00
T (K)	K_{eq}
250-650	1.00
650-1000	**1.00**
350-1000	0.99
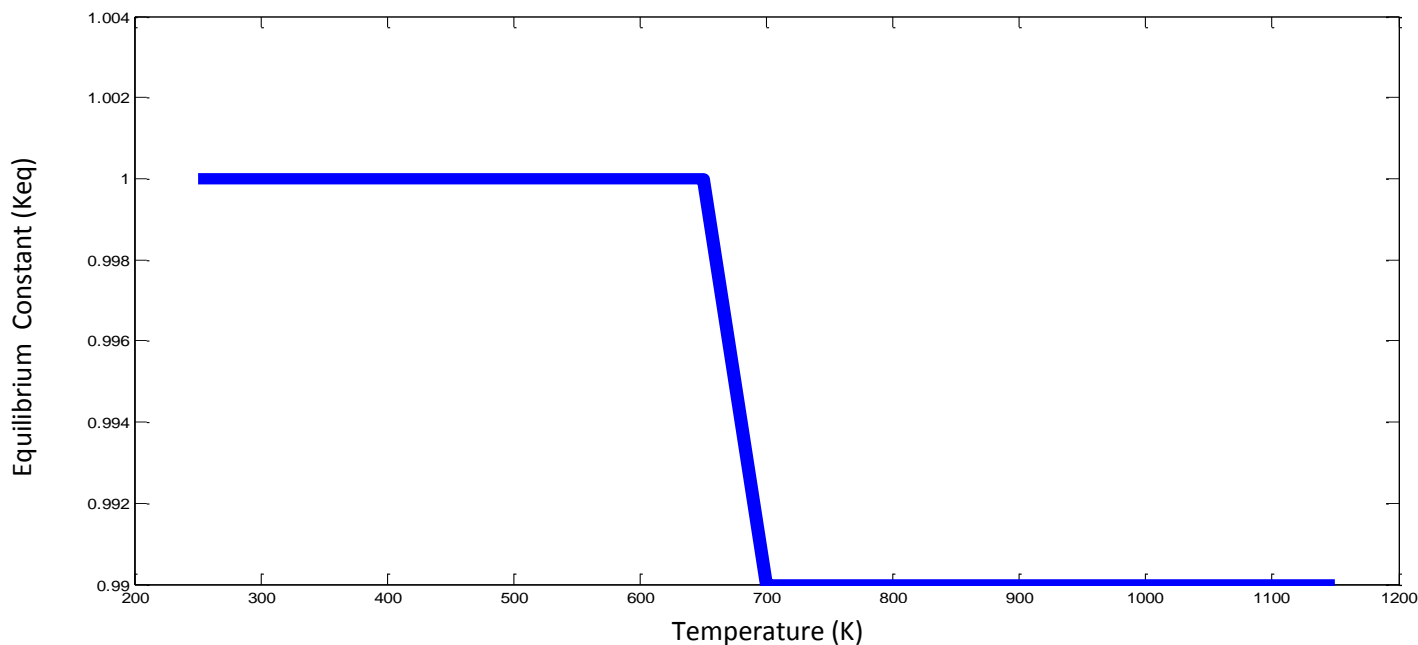
Figure 4. Graph of equilibrium constant as a function of temperature.

there is now a high probability of further dehydration to give the alken products. With further increase in contact time, alkanes / + alkenes and aromatics are obtained (Rosen, 2014) (Figure 6). Indeed

$$W_{cat} = \frac{F_{A0} \int_0^x x_A}{-r_{oxy}}$$ (21)

Where W, is the mass of the catalyst required to reduce the molar oxygenate feed rate Foxy for a conversion x_A.

$$V_{cat} = \frac{W_{cat}}{\rho_{cat}}$$ (22)

(Diagbonia and Ehirim (2019)

$$-r_{oxy} = x_A \frac{WHSV}{Mm_A} . \left(\frac{1h}{3600\,s}\right)$$ (23)

(Rosen, 2014)

Knowing the residence time and the space speed by analogy, the volume of the reactor is deduced by the following relation:

$$V_{PBR} = \tau \times V_0$$ (24)

$$V_0 = F_A \times V_m$$ (25)

Having considered $-r_{oxy}$= 0.00176 mol/kg$_{cat}$.s; $WHSV =$ 0.000278 s $- 1$; $F_{oxy} =$ 0.186 mol/s; $x_A =$ 0.43; $Mm_A =$ 0.068 kg/mol, we obtained W_{cat} =45.52 kg ; F_A=1000 mol/h; τ=1 h; V_{PBR}=24.4 m^3.

According to the graph in Figure 5, the hydrocarbons are obtained in a residence time of about one hour in the reactor from the experiments of Chang and Silvestri (1977).
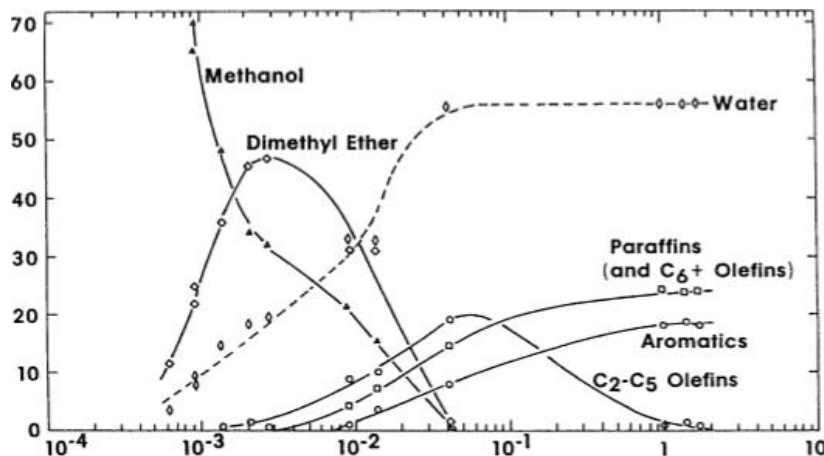
Figure 5. Fractional conversion of methanol to hydrocarbons by residence time on H-ZSM-5 (Keraron, 2010).
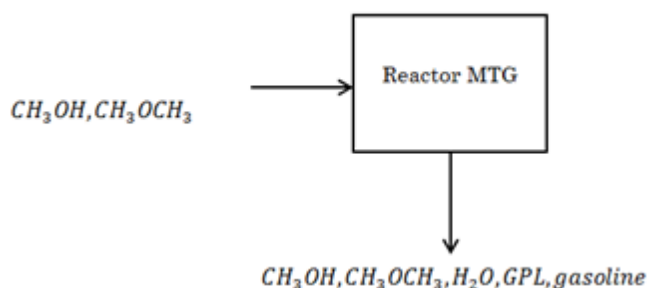
Figure 6. MTG process block diagram.

Figure 7 gives the volume of the PFR reactor as a function of the fractional conversion of methanol. The volume of the reactor is proportional to the fractional conversion whereas its growth is linear for the PFR. With a fractional conversion = 0.90, the volume of the PFR reactor = 3.28 m^3. However, for the feed equilibrium mixture, the desired fractional conversion = 0.67 and the reactor volume = 2.43 m^3, for a pressure of 1346.868 Pa and a temperature of 600K.

Figure 8 gives the effect of the concentration of methanol on the volume of the PFR. The change in the volume of the reactor is linear; the greater the concentration of methanol, the greater is the volume of said reactor; it has an optimum concentration = 0.27 mole/m^3 for which P = 1346.868 Pa and T = 600K; and the volume of the reactor is 2.43 m^3.

Figure 9 gives the mass of the catalyst as a function of the conversion of dimethyl ether and methanol to hydrocarbons. The mass remains constant with the variation of the oxygenate conversion rate. For example, for a conversion of 0.43, the mass of the catalyst remains

45.52 kg. his is also the case for a constant reactor volume of 24.4 m^3 and for a reaction rate of 0.00327 mol/kgcat.s.

As regards PBR where the reactions are complex with several kinds of mechanisms established by different authors, however, the model established by Rojas (2018) made the task simpler in terms of the reaction kinetics related to our second reactor.

The physicochemical analysis of the inputs of the PFR and the PBR provided several elements sufficiently necessary in the meticulous approach of the dimensioning, starting in fact, by the establishment of the material balance around the PFR. However, the fractional conversion of methanol into DME can reach 0.9, the feed into the PBR required equilibrium mixing of methanol/DME/water since for an infinitely small residence time the conversion of unconverted methanol into PFR continued in the PBR until an almost complete conversion is reached (Figure 5). Thus, for this process, therefore knowing the course in the reactors, the fractional conversion established was therefore 0.67 (which can
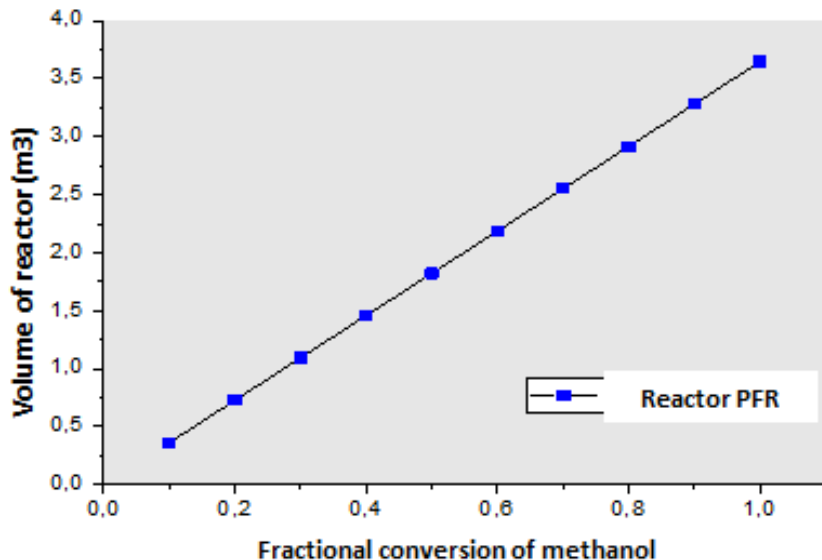
Figure 7. Graph showing the effect of the fractional conversion of methanol on the volume of the PFR reactor.
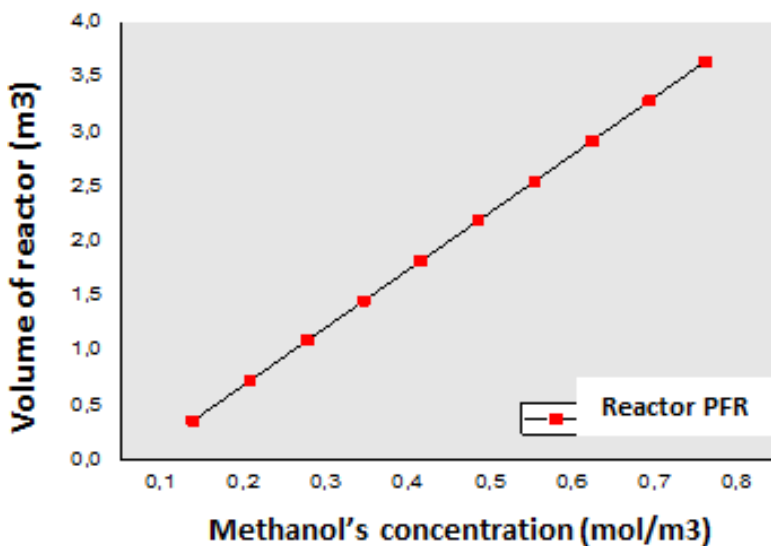
Figure 8. Graph showing the effect of the concentration of methanol on the volume of the PFR reactor.

also reach 0.75 for other authors) in the PFR reactor.

Here the considered fuel to the gasifier is of recent biological origin, such as wood or organic waste; the gas produced by the gasifier is a renewable fuel and the power produced by its combustion is renewable. When the fuel to the gasifier is a waste stream, its conversion to power in this manner has the combined benefit of the conversion of this waste into useful products as biofuel route of methanol to gasoline process (https:www.clarke-energy.com/applications/renewable-gas/ visited 04 march 2022 at 15h 57'). The wealth of the DRC in natural resources offers a striking contrast with the poverty of its population(https://reliefweb.int/report/democratic-republic-congo). With those DRC's forests, there is a big potential to improve social and human health by renewable energies industries that will contribute to enhancing the local economic situation.

Conclusion

The objective of this work was to size the reactors series
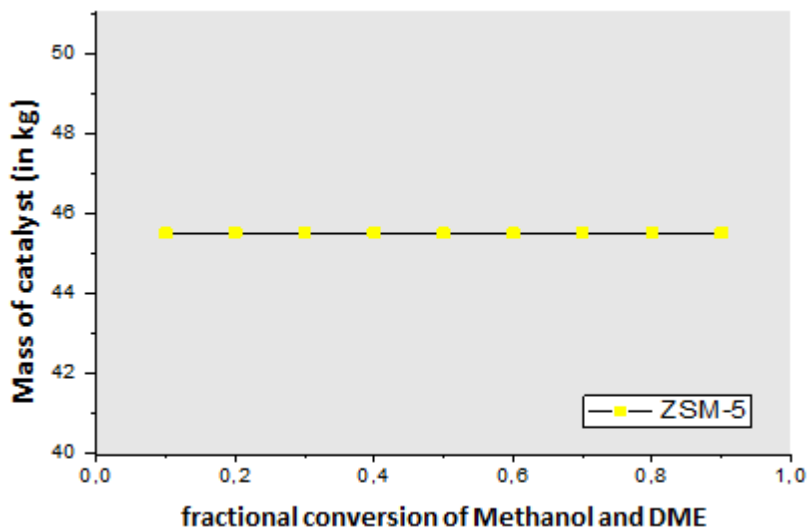
Figure 9. Graph showing the mass of the catalyst as a function of the conversion of dimethyl ether and methanol.

(plug flow reactor and packed bed reactor) for the production of gasoline (hydrocarbons). He revealed the importance of the process and various advantages of the latter, mainly from a technical point of view; in fact, the development of a process requires several prerequisites for highlighting the process from design to synthesis (Complete process). This approach helped to orient in a more objective sense what has been the aim of this work.

Determination of the volume of the PBR revealed that the latter depends on the molar feed rate when the molar volume is considered at the standard condition of temperature and pressure (CSTP.) The biggest problem was determining the reaction rate for the methanol / DME mixture conversion to hydrocarbons, in order to deduce the mass of the catalyst. The latter has been shown, to be independent of methanol / DME conversion.

The yield of the process was 43% of the methanol / DME mixture mass entering the PBR. Different topological optimization experiments could improve this efficiency since it is proportional to the conversion of the methanol / DME mixture.

Therefore, the narrow coastal strip of the Democratic Republic of Congo (DRC), at the mouth of the Congo River, is an area of oil extraction – as is off neighboring Angola, Congo-Brazzaville and Gabon, although on a smaller scale. In the DRC as in neighboring countries, the exploitation of black gold does not seem to have played any positive role in terms of development. On the contrary perhaps according to a report recently published by a group of French and Congolese non-governmental organizations, these extractive activities have a considerable environmental and social cost for local populations. In Muanda, a coastal town that is home to the deposits, oil exploitation is clearly not synonymous

with wealth, but, according to these NGOs, with human rights violations (https://multinationales.org/Perenco-en-RDC-quand-le-petrole).

Modeling and simulation of reactors in PFR and PBR series for the conversion of methanol into hydrocarbons is a route studied in this manuscript for solving this pollution, economic, social and human health problems as is often the case in oil extraction areas. Crude oil leaks, gas flaring and toxic wastes are part of the daily life of Muanda's citizens (https://multinationales.org/Perenco-en-RDC-quand-le-petrole).

Furthermore, Primus Green Energy who have constructed a 100,000-gallon demonstration plant at Hillsborough, NJ contemplates a variation of the ExxonMobil MTG process. The synthesis gas to be used is a combination of municipal solid waste and natural gas. Similarly, the proposed MTG plant of *Sundrop* Fuels will be based on gasification of forest wastes supplemented with hydrogen from natural gas. The interest in the chemical catalytic conversion of synthesis gas to gasoline suggests that the fuels industry may have come full circle from the time that synthesis gas from either natural gas or coal gasification were economic alternatives to crude oil. In this instance, cellulosic waste is the alternative raw materials which can be provided from DRCs agricultural activities and logging waste (https://www.sciencedirect.com/topic-engineering-methanol-gasoline-process/).

Finally, all the results shown in this paper had matched with others researches results that dimethyl ether is a building block for the production of green fuels of Ortega Rojas. This manuscript confirm also by sizing, modeling and simulation of PFR and PBR, the prefeasibility to use

this one process among economical alternatives to reach that goal or aim of the research, with particular attention on using the different basics reactors PFR and PBR.

NOMENCLATURE

F_{A0}, Molar flow rate of methanol considered constant (in moles); $k_0 e^{\left[\frac{-E_0}{RT}\right]}$, equilibrium constant of the reaction for the production of dimethyl ether; C_A, normal concentration of methanol (mol/m³); V_0, volume flow rate of feed to the reactor (m³/s); n_A, molar flow rate of methanol (mol/s); m, mass flow rate of methanol (kg/s); ρ, density of methanol (kg/m³); $-r_A$, reaction rate for the production of dimethyl ether (mol/m³.s); F_{oxy}, molar flow rate of oxygenates (mol/s); F_A, total molar feed rate in the reactor (mol/s); W_{cat}, mass of the catalyst (kg); V_{cat}, volume of the catalyst (m³); ρ_{cat}, density of the catalyst (kg/m³); $WHSV$, *weight hour space velocity* (s⁻¹); $-r_{oxy}$, reaction rate for converting oxygenates (DME and methanol) into hydrocarbons (mol/kg.s); x_A, fractionnal conversion of the reactants in the reactor (DME and methanol); Mm_A, molar mass of oxygenates (DME and methanol) (kg/mol); V_m, molar volume at CSTP (0.0244 m³/mol); **DME,** Dimethyl Ether; **ZSM-5,** Zeolite Socony Mobil-5; *MTG, methanol-to-gasoline*; *PBR, packed bed reactor*; *PFR, plug flow reactor*; **MTO,** Methanol-To-Olefins; **SAPO-34,** Silico-Alumino-Phosphate-34; **CSTP,** standard temperature and pressure conditions; ∆**H°rx,** enthalpy of the reaction; ∆**G°rx,** Gibbs free energy of the reaction.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

REFERENCES

Chakraborty JP, Singh S, Maity SK (2022). Advances in the conversion of methanol to gasoline. In Hydrocarbon Biorefinery (pp. 177-200). Elsevier.

Chang CD, Silvestri AJ (1977). The conversion of methanol and other O-compounds to hydrocarbons over zeolite catalysts. Journal of Catalysis 47(2):249-259.

Couper JR (2012). Chemical process equipment selection and design, third edition.

Diagbonia P, Ehirim OE (2019). Design flow reactors for production of Dimethyl ether. American Journal of Engineering Research 8(8):70-83.

Keraron M (2010). Conversion du méthanol en oléfines sur SAPO-34: modélisation cinétique et design de réacteur. Ecole Polytechnique, Montreal (Canada).

Rojas CEO (2018). Dimethyl ether as building block for the production of green fuels.

Rosen A (2014). Reactor Design. TUFTS Chemical Engineering Review Guide Available at: http://sites. tufts. edu/andrewrosen/files/2013/09/reactor_design_guide1. pdf.

https://multinationales.org/Perenco-en-RDC-quand-le-petrole

https://reliefweb.int/report/democratic-republic-congo

https://www.sciencedirect.com/topic-engineering-methanol-gasoline-process/

https:www.clarke-energy.com/applications/renewable-gas/ visited 04 march 2022 at 15h 57'

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Use of ciliated protozoans in the saprobic evaluation of hydrosystems in an equatorial zone (South region of Cameroon)

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Agriculture, which accounts for 70% of water abstractions worldwide, plays a major role in water pollution. Resulting pollution poses risks to aquatic ecosystems and humans. With the aim of evaluating the saprobic state of four hydro systems subject to pollution from intensive rubber cultivation, the present study was carried out within and around the Hevecam rubber plantation in Niete, South Region of Cameroon. The study was done from September 2019 to December 2020 with monthly sampling, physico-chemical water analysis and determination of ciliate diversity and distribution. Water in the study stations was acidic (6.40±0.31CU), with average temperature (25.20±0.56°C) and conductivity of up to 761.8 µs/cm. Conductivity values coupled with phosphates (up to 29.7 mg/L), herbicide residues are indicators of agricultural pollution on water quality. Station N2 showed the greatest ciliate abundance and species richness. The long dry season of 2020 showed the highest diversity and abundance. The saprobic index indicated moderate to high levels of organic pollution (2.16 to 3.67). Water quality was degraded with the impact of the agricultural pollution due to the presence of herbicide and fertilizer residues at stations N2 and N4. High levels of phosphates and nitrates have resulted in an increased organic load reflected in the saprobic indices; indicating average to high organic pollution.

Key words: Saprobic, Hevecam, organic pollution, anthropogenic, water quality.

INTRODUCTION

Agriculture in modern times faces great challenges in terms of ecology, sustainability, and quantity of production, compared to a human population expected to continuously grow till the end of the present century (WPP, 2017). The solution has been seen to come from the intensification of agriculture. Intensive agriculture firstly aims at increasing production levels to the maximum, through the employment of chemical fertilizers and technology, and usually an extension of limited territory, as part of the optimization of the possible space (Lichtfouse et al., 2009). However, intensive agriculture has led to an increase in man's impact on water resources both quantitatively and qualitatively. Quantitatively, more water is being required for agricultural activities while
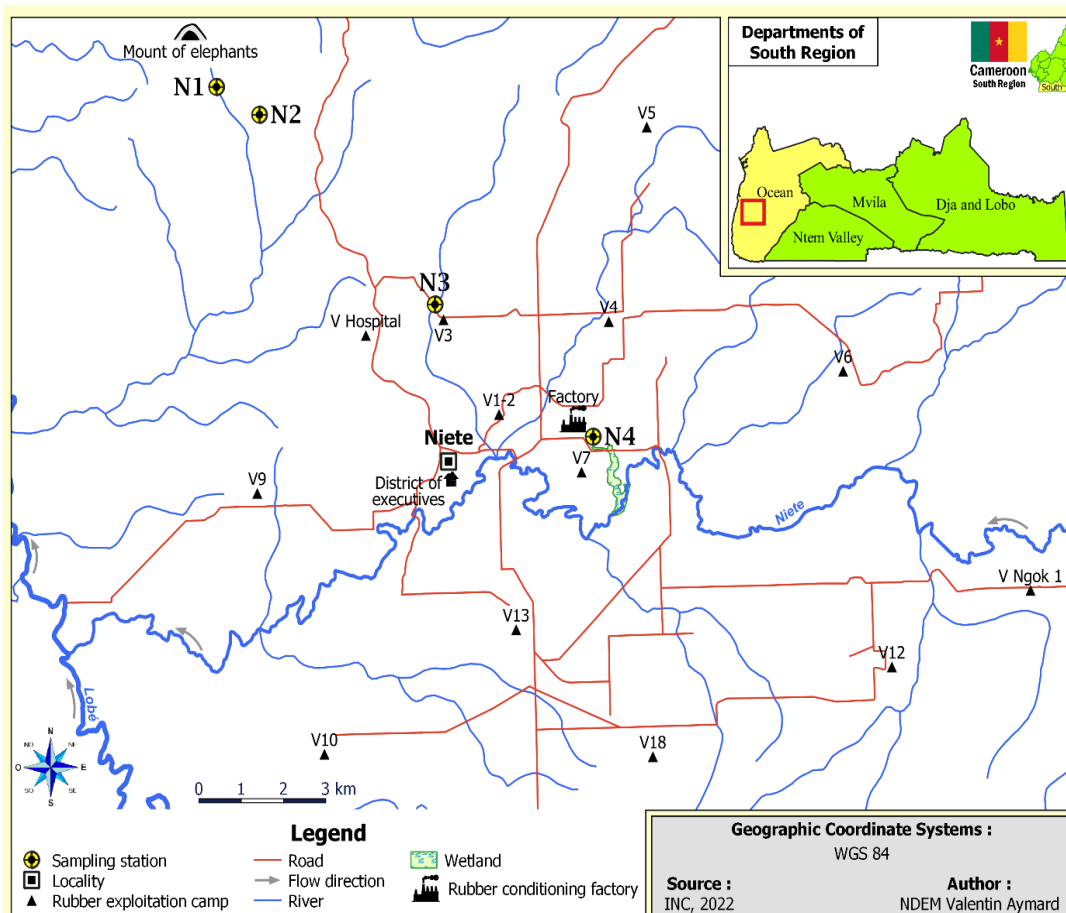
Figure 1. Hydrological map of Niete showing sampling stations.
Source: INC (2022)

qualitatively there is a degradation of water bodies due to the introduction of pollutants which arise from agricultural activities (Casey, 2017). Agriculture is responsible for 70% of water used for human activities. It is therefore a very important contributor to water pollution. Large volumes of agricultural pollutants enter water bodies where they pose serious problems to aquatic ecosystems, human health and water use for diverse human activities (Mateo-Sagasta et al., 2017). Such degraded waters are therefore of lower quality, unfit to satisfy man's diverse needs (Singh and Asha, 2016).

A continuous evaluation and monitoring of water quality is therefore necessary, in areas subject to intensive agricultural activities as this enables the rapid detection of perturbation and the implementation of sustainable solutions (Pratiksha and Vikram, 2022). Evaluation and monitoring are efficient when they involve the physical, chemical and biological characteristics of the water (Pooja, 2017).

Biological evaluation involves the use of living organisms present in the water to determine the water quality. It is based on the presence or absence of indicator organisms (bio indicators) but also their community structure (Trishala et al., 2016). It is in this light that ciliated protozoans are frequently used in the evaluation of organic pollution in water bodies (Antonija et al., 2021). They are very efficient in such studies given that they are usually present in numbers large enough to enable convincing statistical analysis, they are ubiquitous, they have very short generation times and are much more sensitive than metazoans to changes in their environment (Sparagano and Groliere, 1991).

The aim of the present work was therefore to evaluate using ciliated protozoans, the saprobic state of four contrasting hydro systems in an equatorial region subject to perturbations from intensive agriculture.

MATERIALS AND METHODS

Study site

The study was carried out in Niete, South region of Cameroon and its environs (Figure 1). Niete is an agro industrial locality covering a surface area of 2117 km^2 and with a population density of 19.31

inhabitats/km^2. It has as geographical coordinates 2° 40' 00'' N and 10° 03' 00'' E and is found between 20 and 200 m altitude with a relatively flat relief (3^e RGPH, 2005). The main economic activity is the cultivation of natural rubber. In Niete, the rubber plant (*Hevea brazilliensis*) is cultivated intensively over 40000 ha of land. The waste products from this cultivation are a potential source of pollution of air, land and water (Abhik et al., 2014). Niete has an equatorial climate with 4 seasons; a long dry season from November to mid-march, a short rainy season from mid-march to mid-June, a short dry season from mid-June to mid-August and a long rainy season from mid-August to ending October. Average temperature is 25°C, a relative air humidity of 75% and rainfall varying from 1800 to 2000 mm per year. In Niete, two main types of soils were found; Ferralitic soils which are poor in nutrients and inadequate for intensive agriculture except with the use of intrans and hydromorphic soils found mainly around wetlands and aquatic environments (CVUC, 2014).

Sampling period

Sampling was done from September 2019 to December 2020 (sixteen months) following a monthly sampling frequency. However, results obtained were summarized and presented in seasons: long rainy season 2019 (LRS 2019), long dry season 2019 (LRS 2019), short rainy season 2020 (SRS 2020), short dry season 2020 (SDS 2020), long rainy season 2020 (LRS 2020) and long dry season 2020 (LRS, 2020). This was done in order to determine any possible influence of seasonality on the physical and chemical properties of water and on the distribution of ciliated protozoa at the stations studied.

Sampling stations

Sampling was done on four stations showing contrasting ecological conditions, 3 within the Hevecam rubber plantation (N2, N3 and N4) and 1 out of it (N1).

N1 is a slow flowing stream situated outside the Hevecam rubber plantation, within the equatorial rainforest. The waters were poorly illuminated due to a dense vegetation cover. There was a total absence of any form of human activities around this station. This station served as the reference (control) station during the study.

N2 is a large pond situated at the periphery of Village 11 within the Hevecam rubber plantation. Evident signs of eutrophication could be observed at this station as seen by the marked presence of macrophytes in and around the pond, as well as abundant floating water plants. There was also an important presence of decaying organic matter resulting from dead leaves branches and stems. The pond was highly illuminated due to the absence of vegetation cover and was surrounded by rubber farms which used herbicides and fertilizers in large quantities.

N3 was a fast-flowing stream located very close to Village 3 within the Hevecam rubber plantation. It was characterized by the presence of macrophytes at its banks and few floating aquatic plants. Water illumination was high due to the absence of vegetation cover. The station was surrounded by rubber trees whose cultivation depended on the use herbicides and fertilizers.

N4 was an industrial effluent from the rubber processing factory. It was situated in Village 7 within the Hevecam rubber plantation very close to the rubber processing factory. Water from the effluent was dark in color with a pungent smell indicative of anoxic and reductive conditions. There was the presence of macrophytes around the banks of the station but no plant matter was observed on or in the water. The effluent flowed freely and emptied into a nearby river. Plate 1 (N1, N2, N3 and N4) shows the various sampling station.

Physico-chemical analysis

Determination of physico-chemical parameters

Physico-chemical analysis was carried out both on the field and in the laboratory of Hydrobiology and Environment of the University of Yaounde 1.

On the field, some physical and chemical water parameters were measured directly these included: temperature in degree Celcius (°C) using a 1/10°C graduated alcohol thermometer graduated, pH using a pH meter of mark HACH HQ11D, electrical conductivity in micro siemens per centimeter (µS/cm) and total dissolved solids in milligrams per liter (mg/L), using a multiparameter of mark HACK HQ14 and oxygen in percentage saturation (% sat) using a dissolved oxygen meter of mark AR8210. Water samples were collected using sterile double capped polyethylene bottles of 250 and 1000 mL bottles at the surface by directly filling, without bubbles, and transported to the laboratory in an insulated cooler. Back in the laboratory other parameters such as colour (Pt.Co), turbidity (FTU) suspended solids (mg/L), nitrates (mg/L), nitrites (mg/L) and phosphates (mg/L), using a spectrophotometer of mark HACH DR 1900. Heavy metals and herbicides were measured using a mass spectrometer of mark TSQ8000 and GC-MS/MS, respectively following standard methods (Rodier et al., 2009; APHA, 2017).

Measurement of biological parameters

Sampling of ciliates: Ciliates were sampled in 3 main ways: direct water sampling by collecting water from sampling stations from the water column without any form of filtration; sampling natural substrates by collecting dead leaves and branches on/in the water column; and sampling using artificial substrates consisting of 50 cm/50 cm/20 cm foam blocks placed at the bottom of each station and collected 5 to 7 days later (Dragesco et Dragesco-Kerneis, 1986).

Observation, identification and counting of ciliates: Water samples containing ciliated protozoa were homogenized and 1 mL was collected using a calibrated pipette and placed in a Petri dish. Observation, identification and counting were done both on living samples and after silver impregnations (silver carbonate and Klein Foisnner dry silver nitrate methods were used) (Foissner, 2014), using a binocular lens, a phase contrast light microscope and identification keys (Dragesco and Njine, 1971; Dragesco and Dragesco-Kerneis, 1986; Foissner et al., 1991, 1992, 1994, 1995). Three series of counts were carried out and their average recorded. This enabled the collection of abundance values for ciliated protozoans with reduced error linked to the random manner in which ciliates were distributed in water samples. Impregnations played a key role in identification by enabling the observation of taxonomically important cellular structures like the infraciliature, number, shape and position of nuclei (Foissner, 2014).

Data analysis

Data analysis was done using Microsoft Excel 2010, SPSS version 20.0 and PAST 3. It involved graphical representations of the results obtained, determination of diversity indices, significance difference tests (Tukey's range test) and correlation tests (Spearman's correlation coefficient). The monthly data obtained were used to calculate mean seasonal values. Tukey HSD post-hoc and Wilcoxons test were used to assess significant differences between stations and seasons for each physicochemical parameter.

Spearmann rank correlation coefficient (r) was calculated using

Plate 1. N1, N2, N3 and N4 showing the various sampling stations.
Source: Authors

the software SPSS version 17.0. This coefficient enabled the measurement of the strength and direction (either positive or negative) of association between two ranged variables. It was used in the present study to establish the correlations between the different parameters measured and also the evaluation of the level of dependence between the different variables of the ecosystem. Two variables are more or less correlated using the Spearmann's rank correlation (r) when their correlation coefficient is close to 1 (Jaber et al., 2018).

The Shannon and Weaver (H), Simpson's (1-D) and Margalef diversity indices were used to determine the community structure of ciliated protozoans. They accounted for both the abundance and the evenness of the species present.

Sorenson's Similarity Index (S) (Thorsvald, 1948) was used to determine the degree of similarity between the different sampling stations of the study.

The saprobic index (S) of Zelinka and Marvan (1961) was used in the biological assessment of organic pollution. Aquatic ecosystems are classified into 4 main classes (oligosaprobic, alpha mesosaprobic, beta mesosaprobic and polysaprobic).

The organic pollution index (IPO) (Leclercq, 2001) was determined in order to give a precise account on the degree of organic pollution across the different sampling stations during the period of study. The determination of this index was based on three parameters : NH_4^+ (mg/L), NO_2^- (µg/L) and PO_4^{3-} (µg/L). For each parameter, 5 classes of ecological significance were defined (Table 1). The OPI corresponds to the class mean for the 3 measured parameters. The values obtained were classified under 5 different levels of pollution (Table 2) (Enah, 2019)

RESULTS

Physical parameters

Temperature

Temperatures varied from 24.5 to 26.3°C with an average

of 25.2±0.56°C. The highest temperature was obtained at station N3 during the SRS 2020 and the least at N1 during the LRS 2020. Station, N4 recorded the highest temperatures with a mean of 25.61±0.61°C and N1 the least with an average of 24.93±0.33°C. Highest temperatures were recorded during the short rainy season of 2020 with a mean of 26.19±0.40°C, while the least during the short dry season of 2020 with a mean of 24.71±0.04°C (Figure 2).

Suspended solids

Suspended solids varied from 4.5 to 91.0 mg/L with a mean of 25.37±18.21 mg/L. The highest value was recorded at station N2 during the SDS (2020), and the least at station N1 during SRS (2020). Station N1 presented the lowest values with a mean of 9.46±2.44 mg/L while N4 had the highest values with a mean of 37.54±9.00 mg/L. Suspended solids were highest during the SDS 2020 with a mean of 36.42±32.48 mg/L and least during the SRS 2020 with a mean value of 14.25±8.89 mg/L (Figure 3).

Turbidity

Turbidity varied from 6.0 to 116.7 FTU with an average of 26.46±23.13. The highest value was obtained at station N2 during the SDS (2020) and the least at station N1 during LDS (2020). Turbidity values were highest at station N2 with a mean of 41.97±33.74 FTU and least at N1 with a mean value of 10.01±4.28 FTU. The SDS (2020) had the highest turbidity values with a mean of

Table 1. Classes of OPI with respect to the limiting values of each parameter.

Class	Parameters		
	NH_4^+ (mg/L)	NO_2^- (µg/L)	PO_4^{3-} (µg/L)
5	<0.1	≤5	≤15
4	0.1-0.9	6-10.0	16-75
3	1-2.4	11-50.0	76-250
2	2.5-6	51-150	251-900
1	>6	>150	>900

Source: Enah (2019)

Table 2. Classification of the degree of pollution with respect to the classe intervales of OPI.

Class mean	5.0 - 4.6	4.5 - 4.0	3.9 - 3.0	2.9 - 2.0	1.9 - 1.0
Level of organic pollution	Zero	Weak	Average	Strong	Very strong

Source: Enah, 2019
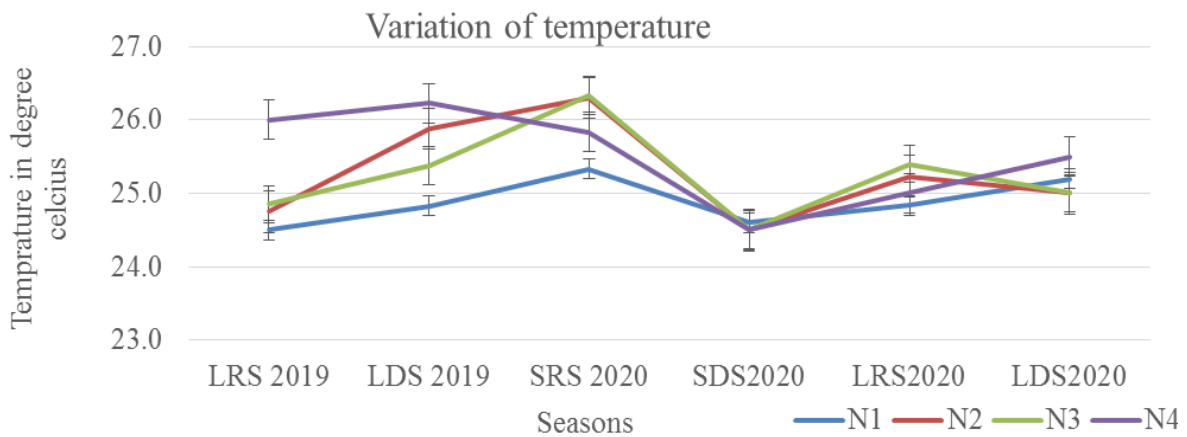
Figure 2. Variation of temperature.
Source: Authors
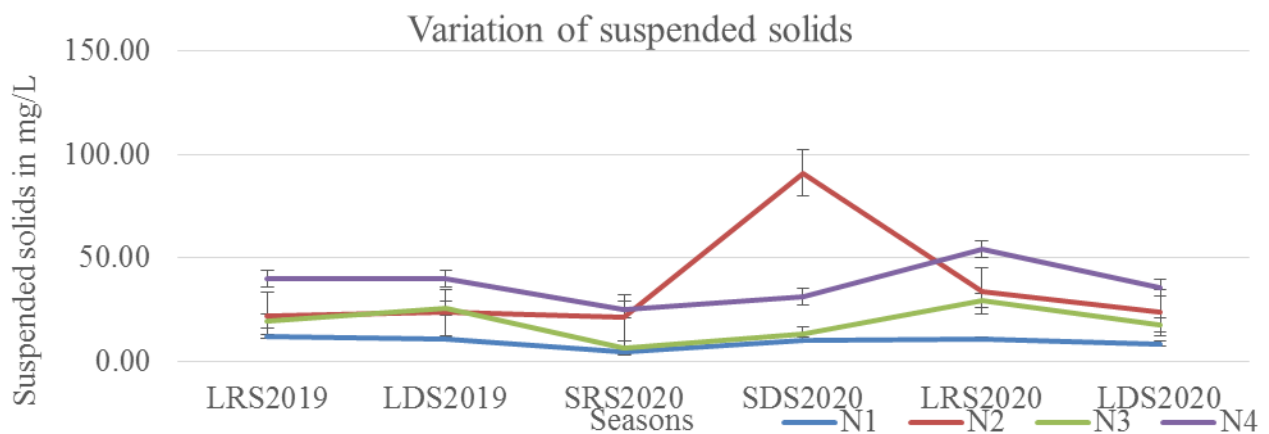
Figure 3. Variation of suspended solids.
Source: Authors
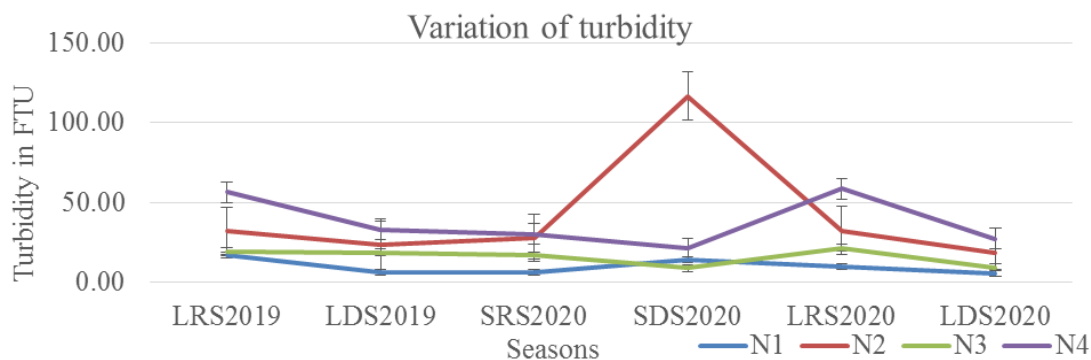
Figure 4. Variation of turbidity.
Source: Authors
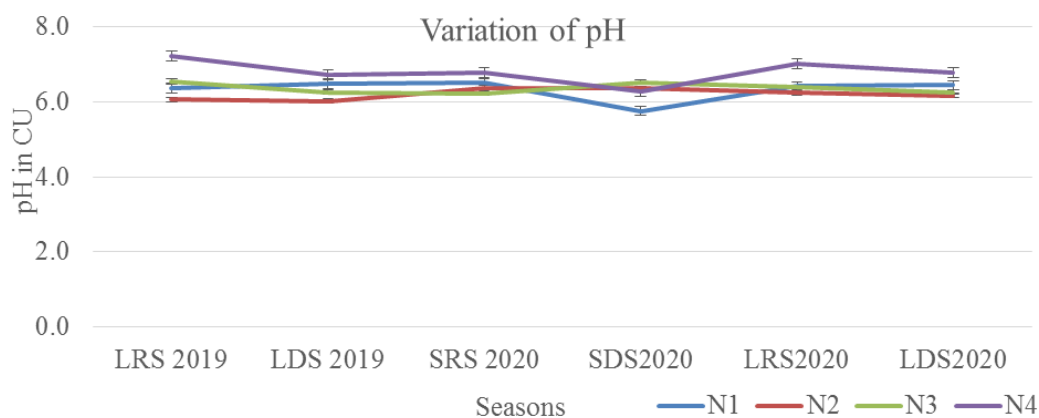
Figure 5. Variation of hydrogen potential.
Source: Authors

40.33±44.29 NTU while the LDS (2020) had the least values with a mean of 15.50±8.40FTU (Figure 4).

Chemical parameters

Hydrogen potential (pH)

Hydrogen potential varied from 5.8 to 7.2 with a mean of 6.4±0.31. The least pH value was recorded in station N1 during the SDS (2020), and the highest at station N4 during the LRS 2019. The least pH values were recorded at station N3 with a mean of 6.18±0.1, while the least values were recorded at station N4 with a mean of 6.91±0.41 CU. Hydrogen potential was highest during the LRS (2019) with a mean value of 6.68±0.63 and least during the LDS (2019) with a mean value of 6.30±0.31 (Figure 5).

Electrical conductivity (EC)

Conductivity values varied from 25.67 µS/cm at station

N3 during the SDS of 2020 to 761.75 µS/cm at station N4 during the LDS 2020 with a mean value of 119.53±173.57 µS/cm. Station N4 recorded the highest values with a mean of 314.38±246.23 µS/cm while station N3 recorded the least with a mean of 32.94±6.2 µS/cm. Conductivity values were highest during the LDS 2019 with a mean value of 224.50±310.23 µS/cm and least during the SDS 2020 with a mean of 43.07±18.22 µS/cm (Figure 6).

Othophosphates

Orthophosphate varied from 0.4 mg/L at station N1 during the LRS 2019 to 29.7 mg/L at station N2 during the LDS 2020, with a mean of 15.45±8.97 mg/L. The SRS 2020 recorded the lowest phosphate values with a mean of 5.06±2.30 mg/L while the SDS 2020 recorded the highest with a mean of 22.99±3.55 mg/L. Station N2 recorded the highest levels of orthophosphates with a mean of 21.21±10.30 mg/L while station N1 recorded the least with a mean of 8.43±6.85 mg/L (Figure 7).
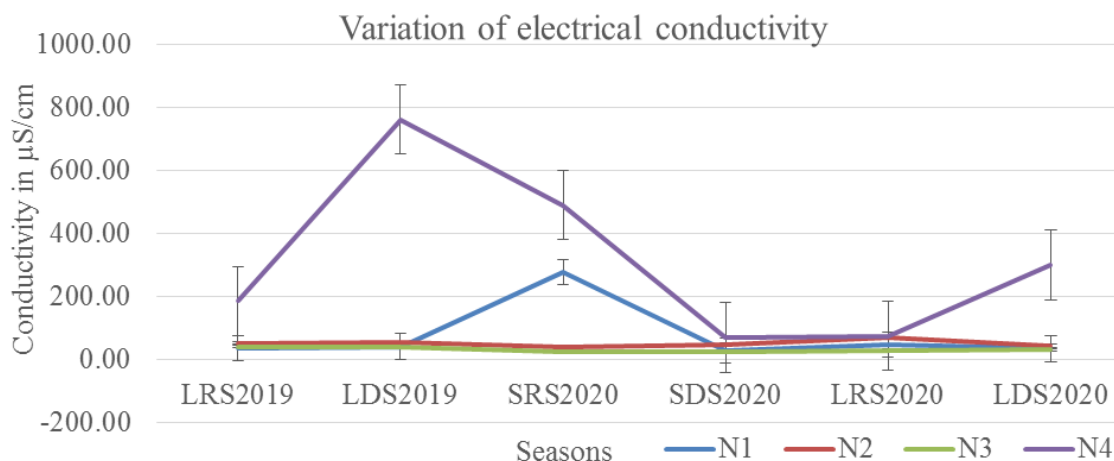
Figure 6. Variation of conductivity.
Source: Authors
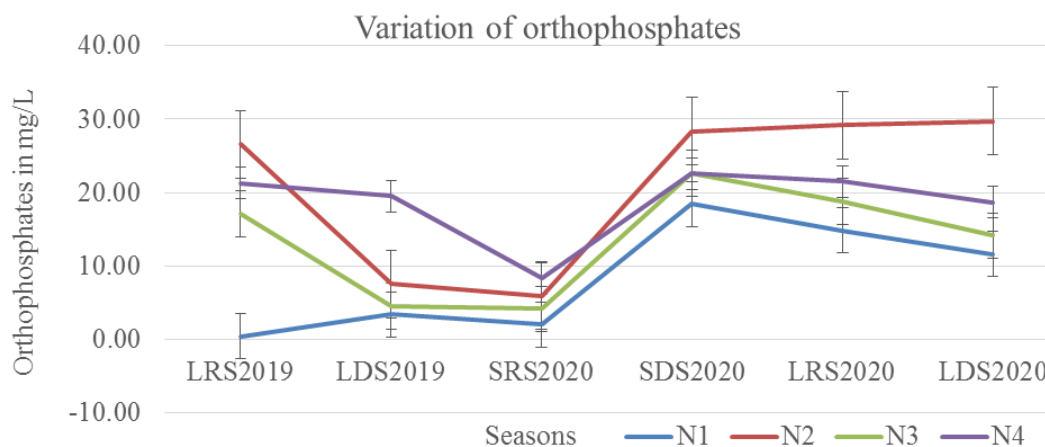
Figure 7. Variation of orthophosphates.
Source: Authors

Nitrates

A mean nitrate value of 1.70±0.88 mg/L was recorded, with maximum and minimum nitrate values of 4.05 mg/L recorded at station N4 during the SRS 2020 and 0.50 mg/L recorded at station N1 during the LRS 2019, respectively. Highest values were recorded at station N4 with a mean of 2.51±0.96 mg/L and the least at N1 with a mean of 0.87±0.22 mg/L. Nitrates were most abundant during the LRS 2020 with a mean of 2.04±0.90 mg/L and least during the SDS 2020 with a mean of 1.38±0.53 mg/L (Figure 8).

Nitrites

Nitrites varied from 0.009 to 0.170 mg/L with a mean of 0.03±0.04 mg/L. The least values of nitrites were recorded at the station N1 during the LDS 2019 and the highest at the station N4 during LDS 2019. Station N4 recorded the highest nitrite values while N1 recorded the least with mean values of 0.07±0.06 mg/L and 0.01±0.002, respectively. Nitrites were highest during the LRS 2019 and least during the LDS 2019 with mean values of 0.06±0.06 and 0.02±0.01 mg/L, respectively (Figure 9).

Ammonium

Ammonium varied from 0.02 to 0.33 mg/L with a mean of 0.13±0.11 mg/L. The highest ammonium value was recorded at station N4 during the LRS 2019, while the least was recorded at station N1 during the SRS, SDS and SDS of 2020. Ammonium was most abundant at station N4 with a mean value of 0.17±0.10 mg/L and least
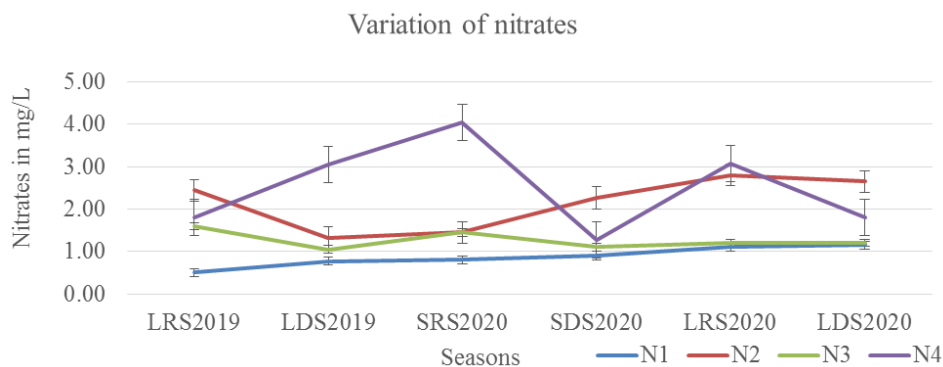
Figure 8. Variation of nitrates.
Source: Authors
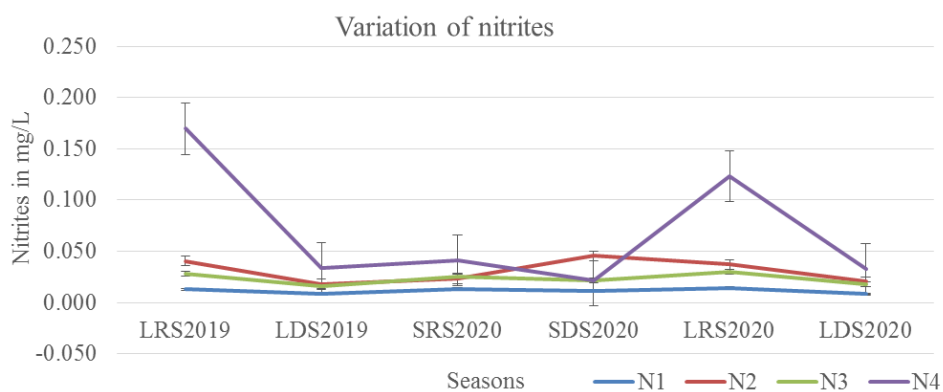
Figure 9. Variation of nitrites.
Source: Authors

at station N1 with a mean of 0.10±0.11 mg/L. Ammonium values were highest during the LRS 2019 with a mean of 0.30±0.03 mg/L and least during the SDS and LDS 2020 with a mean of 0.05±0.05 mg/L (Figure 10).

Dissolved oxygen

Dissolved oxygen varied from 42.5 to 80.50% sat with a mean of 67.09±12.25%. The least value was recorded at station N4 during the LDS 2019 while the highest value was recorded at station N1 during the LRS 2019. Station N4 recorded the least saturation in dissolved oxygen with a mean of 49.22±5.40% while station N1 recorded the highest with a mean of 78.31±1.86%. Dissolved oxygen levels were highest during the LRS 2019 with a mean of 70.25±10.67% and least during the LDS 2019 with a mean of 63.06±13.01% (Figure 11).

Metallic elements

Several metallic elements were found in water samples. The most abundant being Zn, Mg, Na and Mn while the

least being Cd and Ni. Metallic elements were highest at station N4 and least at station N3 and N4 (Figure 12).

Pesticides (Herbicides)

Several herbicide residues were present in water samples. Station N4 had the highest concentrations while N1 had the least (Figure 13).

Biological parameters

Ciliate composition

Five thousand seven hundred ciliates belonging to 57 species and 9 classes were recorded in the 4 stations. Marked domination of oligohymenophoreans was observed in both diversity (28%) and abundance (51%) (Table 3).

Ciliate species richness and abundance

Ciliate species richness and abundance varied from one
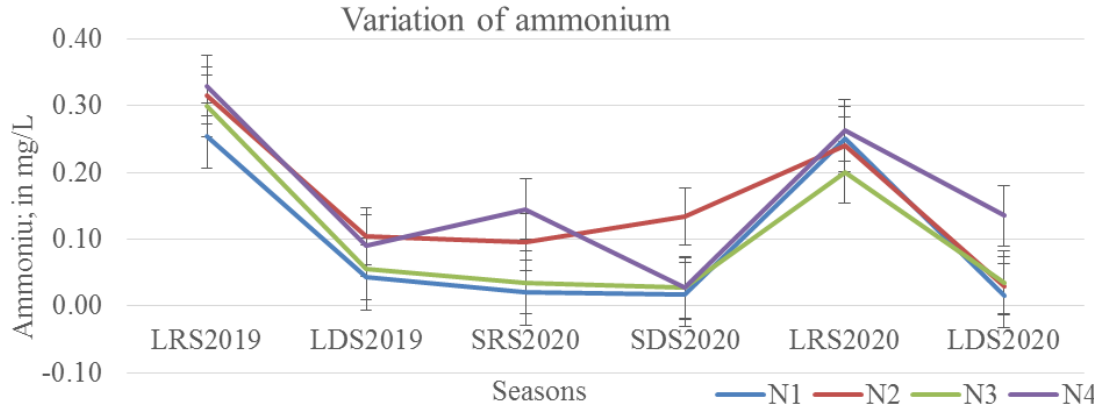
Figure 10. Variation of ammonium.
Source: Authors
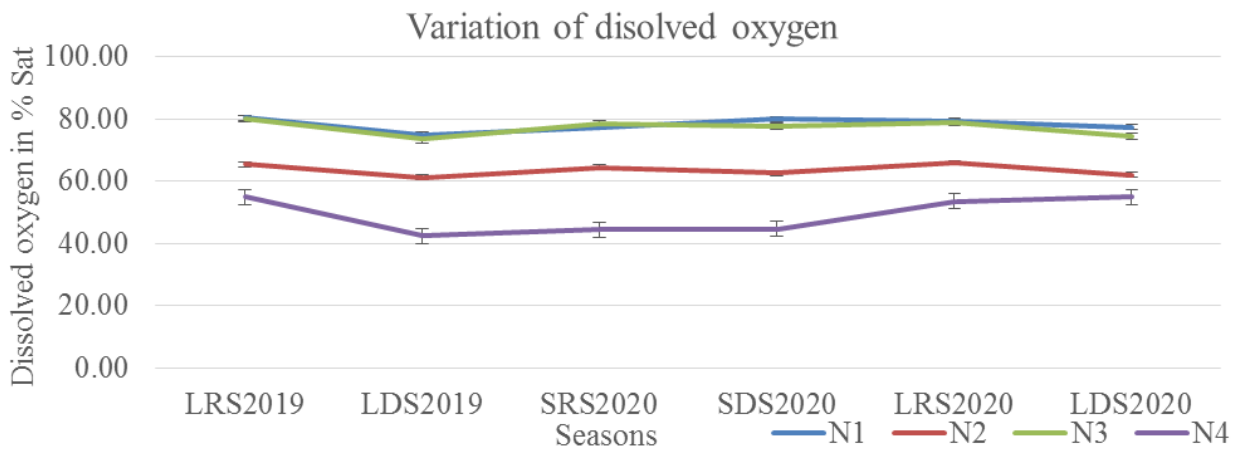
Figure 11. Variation of dissolved oxygen.
Source: Authors
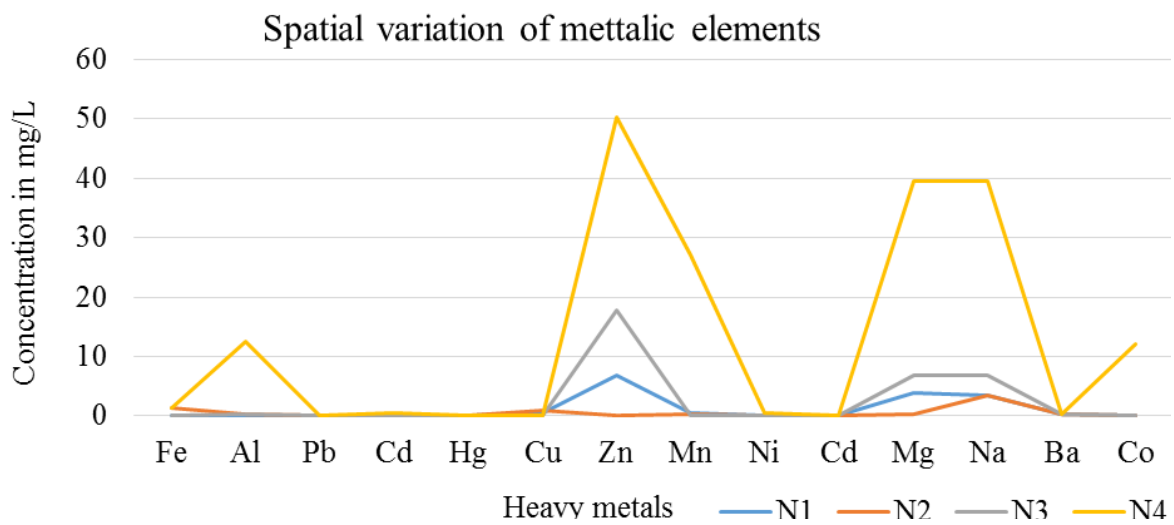
Figure 12. Spatial variation of metallic elements in water.
Source: Authors
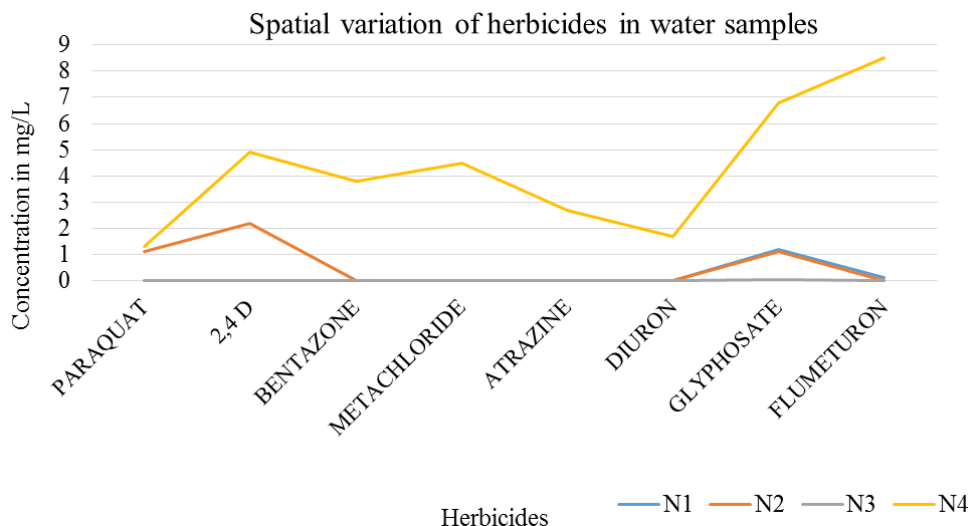
Figure 13. Spatial variation of herbicide residues in water.
Source: Authors

Table 3. Sorenson's similarity index.

Index	N2	N3	N4
N1	50	49	33
N2	-	73.2	56.3
N3	-	-	55.4

Source: Authors

station to the other and from one season to another. The highest species richness and abundance were recorded at station N2 with a total of 2305 ciliates belonging to 39 species. The LDS 2019 recorded the highest species richness and abundance with 1521 ciliates belonging to 47 ciliate species recorded. Station N1 recorded the least species richness and abundance with just 375 ciliates belonging to 21 species recorded and the LRS 2019 recorded the least abundance with 555 ciliates belonging to 26 ciliate species recorded. The long dry season 2020 recorded the least species richness with only 25 ciliate species recorded (Figures 14A and B and 15A and B).

Ciliate diversity

Station N2 recorded the greatest diversity with Simpson 1-D and Shannon H diversity indices of 0.88 and 2.50, respectively. Station N1 showed the diversity with Simpson 1-D and Shannon H diversity indices of 0.72 and 1.49, respectively (Figure 16).

Sorenson's similarity index

Sorenson's similarity index stations in stations N2 and N3

showed the greatest similarity in ciliate community while stations N1 and N4 show the least with similarity indices of 73.2 and 33%, respectively (Table 4).

Data analysis and biological indices

Data analysis

Several parameters measured indicated significant differences from one station to another. Hydrogen potential was significantly higher at station N4 compared to N1, N2 and N3 with p values of 0.007, 0.001 and 0.01, respectively. Suspended solids also varied significantly between N1 and N2 (p=0.002), N2 and N3 (p=0.02) and between N2 and N4 (p=0.02). As for turbidity, a significant difference was noted only between N1 and N2 (p=0.03). Nitrates, nitrites and orthophosphates also recorded differences from one station to another. Nitrate values at station N2 were significantly different from those at N1 and N3 with p values of 0.001 and 0.02, respectively. Phosphate values recorded a significant difference only between stations N1 and N2 (p=0.02). As for nitrites significant differences were recorded between stations N1 and N2 (p=0.004), N1 and N4 (p=0.003) and between N1 and N3 (p=0.004). Significant differences were also recorded between temperature values in the SDS 2020 and those of LDS 2019 and SRS 2020 with p values of 0.003 and 0.03, respectively.

The abundance of ciliated protozoa differed significantly between the LDS 2019 and the LRS 2019 (p=0.004). Ciliate abundances also varied significantly between stations N1 and N2 (p= 0.02), but also between N1 and N4 (p=0.01). Several hysic chemical parameters showed either positive or negative correlations with ciliated protozoa recorded. Temperature had positive correlations
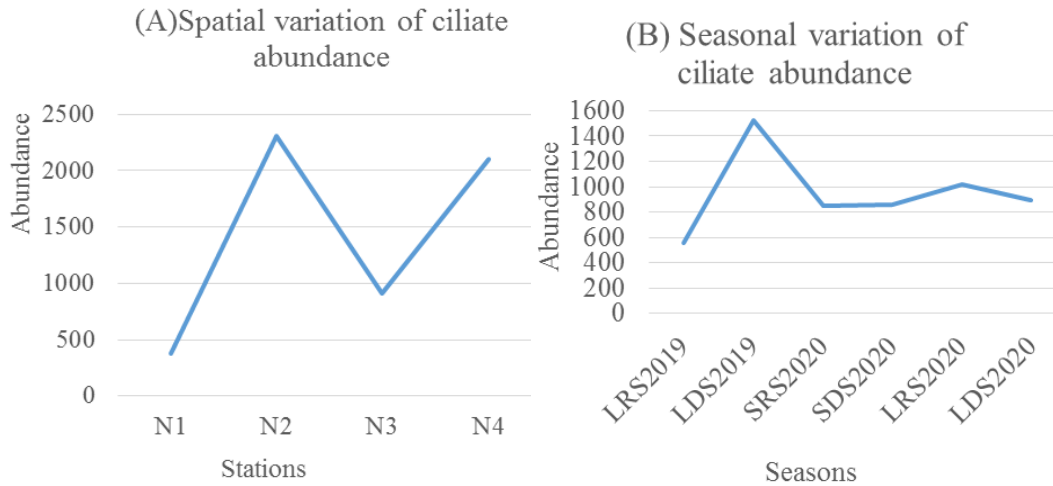
Figure 14. A and B: Variation of ciliate abundance.
Source: Authors
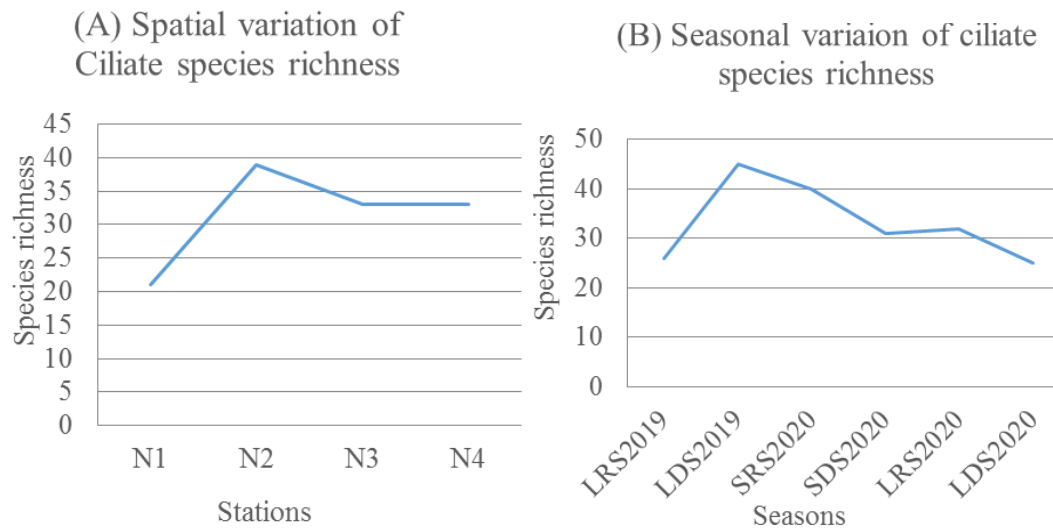
Figure 15. A and B: Variation of ciliate species richness.
Source: Authors
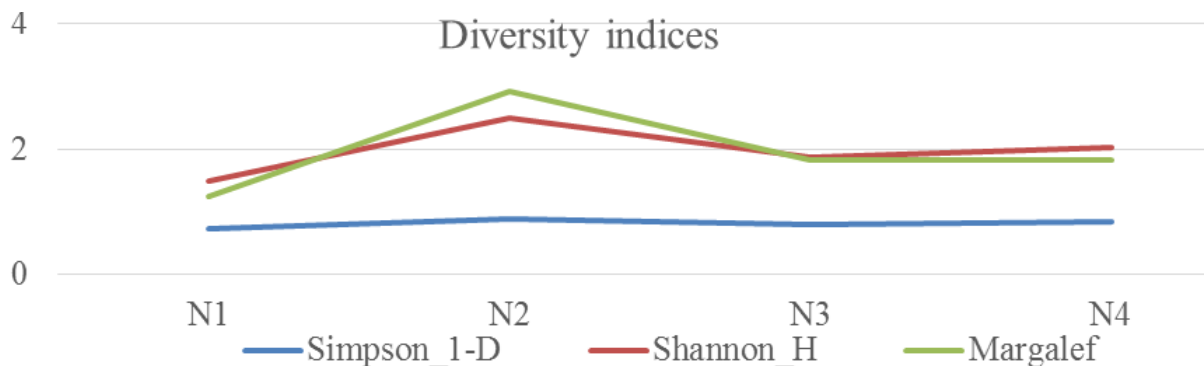
Figure 16. Diversity indices.
Source: Authors

Table 4. Distribution of ciliate species at different sampling stations.

Station N1	No.	Station N2	No.	Station N3	No.	Station N4	No.
Blepharisma species	6	*Amphileptus pleurosigma*	12	*Amphileptus pleurosigma*	18	*Amphileptus pleurosigma*	30
Chilodonella species	25	*Blepharisma* species	40	*Blepharisma* species	65	*Anigsteinia* species	105
Coleps hirtus	36	*Bursaria truncatella*	54	*Bursaria truncatella*	90	*Brachonella spiralis*	144
Colpidium species	8	*Cinetochilum* species	12	*Chilodonella* species	20	*Caenomorpha medusala*	32
Euplotes patella	10	*Climacostomum virens*	15	*Climacostomum virens*	25	*Cinetochelum* species	40
Frontonia atra	10	*Colpidium* species	20	*Colpidium* species	30	*Colpidium colpoda*	50
Frontonia leucas	15	*Euplotes patella*	25	*Euplotes patella*	40	*Frontonia leucas*	65
Halteria grandinella	137	*Frontonia atra*	253	*Frontonia atra*	390	*Frontonia* species	643
Holophrya discolor	5	*Frontonia leucas*	10	*Frontonia leucas*	15	*Lacrymaria olor*	25
Holophrya ovum	10	*Halteria grandinella*	15	*Halteria grandinella*	25	*Lembadion lucens*	40
Holosticha species	16	*Holophrya discolor*	24	*Holophrya discolor*	40	*Lembadion* species	64
Kerona pediculus	8	*Kerona pediculus*	12	*Holosticha* species	20	*Litonotus* species	32
Lembadion lucens	61	*Lacrymaria olor*	107	*Lacrymaria olor*	168	*Loxophylum* species	275
Lembadion magnum	85	*Lembadion lucens*	160	*Lembadion lucens*	245	*Metops* species	405
Paramecium caudatum	16	*Lembadion magnum*	24	*Litonotus cygnus*	40	*Metopus es*	64
Spirostomum minus	10	*Litonotus cygnus*	15	*Litonotus* species	25	*Neobursaridium gigas*	40
Stentor igneus	22	*Loxodes* species	39	*Loxodes* species	61	*Oxytricha chlorelligera*	100
Stichotricha secunda	10	*Loxophylum meleagris*	20	*Loxophylum* species	30	*Oxytricha* species	50
Thrithigmostoma cucullus	5	*Oxytricha chlorelligera*	10	*Oxytricha chlorelligera*	15	*Paramecium africanum*	25
Urocentrum turbo	6	*Oxytricha* species	9	*Oxytricha* species	15	*Paramecium bursaria*	24
uroleptus rattulus	10	*Paramecium bursaria*	20	*Paramecium africanum*	30	*Paramecium caudatum*	50
		Paramecium caudatum	0	*Paramecium bursaria*	0	*Pleurotricha* species	0
		Paramecium species	0	*Paramecium caudatum*	0	*Spirostomum* species	0
		Phascolodon vorticella	0	*Spirostomum ambiguum*	0	*Stentor igneus*	0
		Spirostomum ambiguum	32	*Spirostomum minus*	32	*Stentor* species	64
		Spirostomum minus	15	*Stentor igneus*	15	*Stichotricha secunda*	30
		Stentor amethystinus	246	*Stentor* species	246	*Stylonicha putrina*	492
		Stentor igneus	5	*Stylonicha* species	5	*Stylonicha* species	10
		Stentor species	145	*Trachelius ovum*	145	*Thritigmostoma cucullus*	290
		Stichotricha secunda	86	*Urocentrum turbo*	86	*Urocentrum turbo*	172
		Strombidium viride	30	*Uronema negricans*	30	*Uronema negricans*	60
		Stylonicha putrina	78	*Vorticella campanula*	78	*Vorticella* species	156
		Stylonicha species	49			*Vorticella campanula*	49
		Thritigmostoma cucullus	199				
		Trachelius ovum	27				

Table 4. Contd.

Urocentrum turbo	30
Uroleptus rattulus	35
Vorticella campanulla	80
Vorticella species	20

Source: Authors

with: *Blepharisma hyalinum* (p=0.03), *Oxytricha chlorelligera* (p=0.02) and *Vorticella chlorelligera* (0.02). Dissolved oxygen also had negative correlations with *Brachonella spiralis* (p= 0.013), *Caenomorpha medusala* (p=0.003) and *Metopus es* (p=0.00). Orthophosphates had significant positive correlations with *Paramecium bursaria* (p=0.012) and *Stentor igneus* (p=0.044). Suspended solids had a negative correlation with *Chilodonella minuta* (p=0.02) and positive correlations with *Colpidium campylum* (p=0.029), *Frontonia* species (p=0.015).

Biological indices

Saprobic index: Saprobic indices varied from one station to the other with station N1 having the least mean saprobic index during the various seasons of 2.16 and the station N4 having the greatest index of 3.67 as mean for the various seasons (Figure 17).

Organic pollution index: N1 had the least organic pollution index with a mean value of 3.00 indicative of moderate organic pollution while the rest had organic pollution indices indicative of strong organic pollution (Figure 18).

DISCUSSION

Water quality can be seen to vary greatly from one sampling station to another. It is evident that water quality in some of our stations notably N2 and N4 is of poor ecological quality. The relatively high (>20°C) and fairly constant water temperatures are typical of the tropical environment in which our study was carried out (Richter, 2016). These values are however similar to the 22 to 24°C recorded by Gwos et al. (2022), in streams in the Eastern region of Cameroon. These high temperatures speed up several chemical and biochemical processes in aquatic media (De villers et al., 2005). With the predominance of acidic ferralitic soils in the study area, the pH was averagely acidic except at the station N4. This modification of pH could be linked to infiltration of runoffs from nearby agricultural exploitations and effluents from the rubber conditioning factory which discharges at station N4 (Mitra et al., 2010). The influence of runoff rich in agricultural intrans such as fertilizers and herbicides can equally be shown by the relatively high values of parameters such as phosphates, nitrates, nitrites and ammonium. Results for these parameters were very similar to values recorded by Santza (2022) working in the Menoua basin in west Cameroon; an important agricultural zone in the country. The presence of phosphates and nitrates in water leads to an excessive growth of aquatic vegetation (Beniah and Ebere, 2020).

The excessive plant development notably at stations N2 and N4 might explain the high turbidity and suspended solids values recorded in these stations. These values were significantly higher than the maximum values of 20 mg/L and 23.5 FTU for suspended solids and turbidity, respectively recorded by Biram à Ngon et al. (2020) in Abouda forest stream, central region of Cameroon. Values for turbidity are also higher than the maximum value of 22.4 FTU recorded by Ndjama et al. (2017) in the Nkolbisson artificial lake in Yaounde. Campbell (2021) reported that suspended solids may decrease water's natural dissolved oxygen levels and increase water temperature. This may prevent organisms living in the water, such as small fish, from being able to survive. TSS may also block sunlight, which may halt photosynthesis, decreasing the survival of plants and further decreasing water's oxygen levels. Organic matter arising from the rubber conditioning factory present at station N4 might also explain the higher turbidity and suspended solids values recorded in the station (Arimoro, 2009).

The relatively high dissolved oxygen levels recorded in the various stations except station N4 are typical of forests environments and are similar to results recorded in Nsapè, Douala (Tchakonte et al., 2014) and Mefou, Yaoundé (Foto et al., 2013). Low dissolved oxygen levels at station N4 however, are indicative of oxygen consumption by microorganisms during the degradation of organic matter present in industrial influents. Filter et al (2017) reported that due to microbial transformation of particulate and dissolved
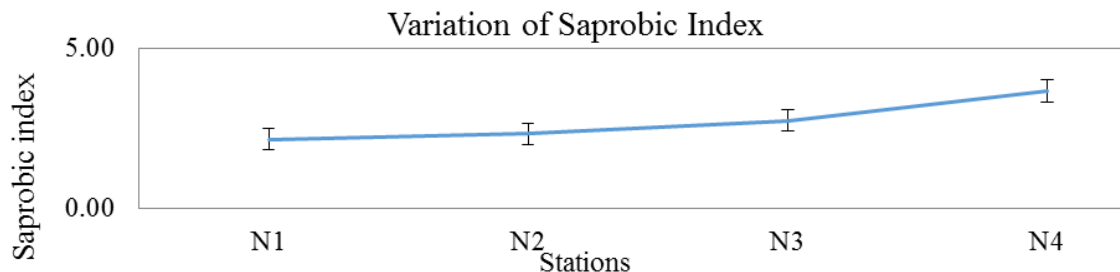
Figure 17. Saprobic indices of various stations.
Source: Authors
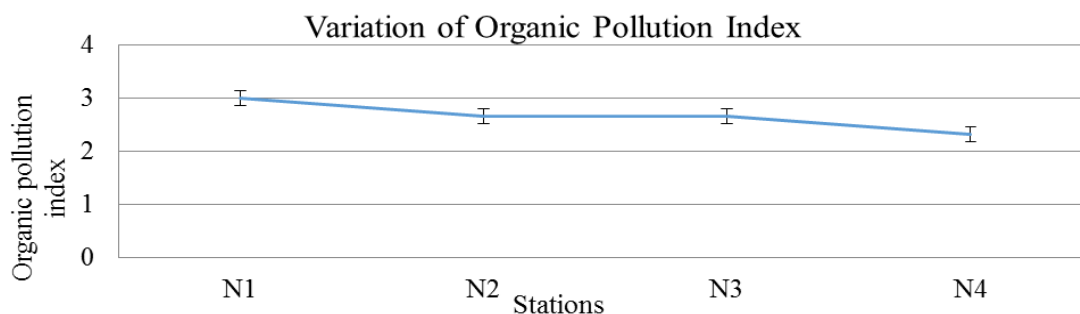
Figure 18. Organic pollution indices of various stations.
Source: Authors

organic constituents, oxygen can be consumed within short flow distances and induce anoxic and anaerobic conditions. These results are concordant with those recorded by Omoigberale et al. (2021) on the impact of rubber effluent discharges on the water quality along a stretch of the Oken River, situated in the southern part of Edo State in Nigeria.

Higher conductivity values of up to 761.75 µS/cm recorded in station N4 were close to the mean value of 615.7 µS/cm recorded by Efiong and Eze (2004) in an effluent drain 50 m away from the rubber conditioning factory in Odukpani, Cross River State (Nigeria). This high conductivity values are linked to the decomposition of organic matter in the effluents and the presence of inorganic salts involved in rubber processing (Omoigberale et al., 2021).

Relatively high values of metallic elements and herbicide residues such as glyphosate, atrazine, metachlorine and flumeturon at concentrations not usually found naturally in surface waters in some stations and the proximity of these stations to agricultural production centers involving intrans on one hand and the insufficient treatment of industrial wastes by HEVECAM before discharging into the environment on the other hand (Mereta et al., 2020).

Ciliate species richness (57 species) is much higher than 34 species recorded by Ajeagah and Acha (2021) in the Mingoa drainage basin in Yaounde (Cameroon) and 43 species recorded by Djeufa (2008) in River Nga located in a peri urban zone (Cameroon). The highest species richness and abundance of ciliated protozoa was recorded in N2 while the least was in N1. The variation in ciliate species richness and abundance is linked to variations in values of various hysic-chemical parameters such as nitrates and phosphate. High levels of phosphates and nitrates promote the development of phytoplankton and other plant matter whose decomposition upon death serves as an abundant source of food (Dias et al., 2008). The ciliate community consisting mainly of heterotrophic, predatory carnivorous, algivorous or omnivorous ciliates. According to Madoni and Braghiroli (2007), food is a very important factor in the distribution of ciliates in an ecosystem. Low levels of dissolved oxygen in station N4 is seen to favor the development of microaerobic ciliates such as *Brachonella, Metopus* and *Caenomorpha* which are indicators of the polysaprobic state of this station. Low oxygen levels also explain the lower ciliate diversity observed in station N4, which not all species can accommodate. This result is concordant with those reported by Udyog and Gupta (2001).

The organic pollution indices recorded in the stations indicated moderate to high levels of organic pollution. This concord with the values of saprobic indices recorded indicative of moderate to high organic load (Thorp and Covich, 2015). Station N1 located outside of the rubber

plantation recorded the lowest level of pollution and station N4 which is an industrial effluent, the highest. Organic pollution in the study area is therefore clearly seen as resulting directly from intensive agriculture involving intrans and industrial effluents which were poorly treated before being discharged into the environment. This resulted in the proliferation of plant material, which is a consequence of a drastic increase in nutrients (notably phosphates and nitrates) in the environment (Mateo-Sagasta et al., 2017). The presence in surface waters of saprobelic ciliates such *Metopus, Brachonella* and *Caenomorpha* otherwise present mainly in anaerobic sediments and household sewage effluents (Foissner, 1999) is indicative of the state of organic pollution of this aquatic environments. It is therefore necessary for special care to be taken in monitoring water pollution in this area.

CONCLUSION AND RECOMMENDATIONS

Water from most of the study stations was degraded and of poor ecology. The presence of herbicides residues, heavy metals and high levels of phosphates and nitrates is indicative of pollution by agricultural intrans and industrial effluent. Clear correlations between hysic-chemical parameters and ciliate distribution suggest influence of these factors on ciliate diversity and distribution. Excessive nutrient enrichment has resulted in an increased organic load of water with saprobic indices indicating moderate to high levels of organic pollution which explains the presence of saprobelic ciliates such *Metopus, Brachonella* and *Caenomorpha* in some stations. It is therefore necessary for urgent measures to be taken to stop the ongoing pollution of these aquatic ecosystems and put in place restoration mechanisms to ensure better water quality. It is also necessary to reinforce surveillance of aquatic ecosystems especially in pollution prone environments and also ensure the respect of norms with regards to treatment of industrial wastes before release into the environment.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

REFERENCES

Abhik M, Sadrita D, Bal KC, Koushik M (2014). Do Extensive Rubber Cultivation Influence Local Environment ? A Case Study From Tripura, Northeast India. Current World Environment 9(3):768-779.

Ajeagah GA, Acha YA (2021). Diversity of Infusorian Community Structure in an Equatorial Hydro system: Influence of Environmental Factors. Cameroon Journal of Biological and Biochemical Sciences 29(2):31-47.

Antonija K, Vesna G, Renata MK, Petar Ž. Mirela SP, Sandi O, Katarina K, Thorsten S, Guillaume L, Ivan Č, Ivan M, Marija GU (2021). Ciliates (Alveolata, Ciliophora) as Bioindicators of Environmental Pressure : A Karstic River case. ELSEVIER : Ecological Indicators 124(107430).

APHA, AWWA, WEF (2017). Standard Method for Examination of Water and Waste Water, 20th edition. American Public Health Association 1150 p.

Arimoro FO (2009). Impact of Rubber Effluent Discharges on the Water Quality and Macroinvertebrate Community Assemblages in a Forest Stream in the Niger Delta. Chemosphere 77(3):440-449.

Beniah OI, Ebere CE (2020). Pollution and Health Risks Assessment of Nitrate and Phosphate Concentrations in Water Bodies in South Eastern, Nigeria. Environmental Advances. DOI :100018. www.elsevier.com/locate/envadv.

Biram ANEB, Foto MS, Ndjama J, Mbohou NZ, Mboye BR, Dzavi J, Oumar MO, Tarkang C, Nyame MD, Mbondo BS, Ngalamou C (2020). Water Quality Assessment in a Less Anthropogenic Forest Stream in the Centre Region of Cameroon. Haya: The Saudi Journal of Life Sciences. 5(1):1-8.

Campbel B (2021). What is Total Suspended Solids (TSS). Water and Waste Digest (WWD). https://www.wwdmag.com/

Casey KN (2017). Agriculture and Water Pollution Risks. UTAR Agriculture Science 3:34-44.

Communes et villes unies du Cameroun (CVUC) (2014). Niete. https://cvuc-uccc.com

De Villers J, Squilbin M, Yourssowsky C (2005). Physico-Chemical and Chemical Quality of Surface Waters: Generale Framework. Bruxelles Institute for Environmental Managment. Environmental data Observatory.

Dias RJP, Wieloch AH, D'Agosto M (2008). The Influence of Environmental Characteristics on the Distribution of Ciliates (Protozoa, Ciliophora) in an Urban Stream of Southeast Brazil. Brazilian Journal of Biology 68(2):287-295.

Djeufa HG (2008). Community Structure of Ciliated Protozoans in the Nga Water Body. DEA dissertation. University of Yaounde 1. 73 p.

Dragesco J, Njine T (1971). Complement to the Knowledge of Cameroonian Free Living Ciliates. Annales de la Faculté des sciences du Cameroun 7(8):79-140.

Dragesco J, Dragesco KA (1986). Free Filiates of Inter Tropical Africa: Introduction to the Knowledge of the Study of Ciliates. ORSTOM, Faune Tropical XXVI, Paris, 559 p.

Enah DA (2019). Characterasation of Benthic Macro-Invertebrates : Indicators of Organic Pollution in an Urbanized Area of North West Cameroon. Ph.D Thesis. University of Yaounde, Cameroon 242p.

Filter J, Jekel M, Ruhl AS (2017). Impacts of Accumulated Particulate Organic Matter on Oxygen Consumption and Organic Micro-Pollutant Elimination in Bank Filtration and Soil Aquifer Treatment. Water 9:349.

Foissner W (1999). Soil Protozoa as Bioindicators: Pros and Cons, Methods, Diversity, Representative Examples. Agriculture, Ecosystems and Environment 74:95-112.

Foissner W (2014). An Update of Basic light and Scanning Electron Microscopic Methods for Taxonomic Studies of Ciliated Protozoa. International Journal of Systematic and Evolutionary Microbiology 64(Pt_1):271-292.

Foissner W, Blatterer H, Helmut B, Kohmann F (1991). Taxonomische des Saprobien Systems. Band I :Cyrtophorida, Oligotrichida, Hypotrichida and Colpodea : Informationsberitchte Des Bayer Landesamtes Für Wasserwirtschaft. Heft 1/91, 478 p.

Foissner W, Helmut B, Kohmann F (1992). Taxonomische des Saprobien Systems. Band II : Peritrichida, Heterotrichida and Odontostomatida : Informationsberitchte Des Bayer Landesamtes Für Wasserwirtschaft 5(92):1-502.

Foissner W, Helmut B, Kohmann F (1994). Taxonomische des Saprobien Systems. Band III : Hymenostomata, pProstomatida, Nassulida: Informations Berichte des Bayer Landesamtes Für Wasserwirtschaft Heft 1/94, 548 p.

Foissner W, Helmut B, Kohmann F. (1995). Taxonomische des Saprobien Systems. Band IV : Gymnostomatae, Loxodes, Suctoria : Informationsberitchte Des Bayer Landesamtes Für Wasserwirtschaft Heft 1/95, 540 p.

Foto MS, Tchakonté, S, Ajeagah, GA, Zébazé TSH, Bilong BCF, Njine T (2013). Water Quality Assessment Using Benthic Macroinvertebrates in a Periurban Stream (Cameroon). International

Journal of Biotechnology 2(5):91-104.

Gwos NSR, Foto MS, Nyame MD, Betsi WCN, Biram ANEB, Disso E, Mboyé BN (2022). Characterisation of Benthic Macroinvertebrates and Some Environmental Factors of Streams in Cameroon East Region. World Journal of Biology Pharmacy andHealth Science 11(01):5-17.

Jaber A, Odeh A, Elayyan, Haifaa O (2018). Towards Quality Assurance and Exellence in Higher Education. River Publishers 284 p. ISBN 978-87-93-93609-54-9.

Leclercq L (2001). Interest and Limits of Water Quality Estimation Methods. Scientific Station of Upper –Fagnes Belgium, Work document 44 p.

Lichtfouse N, Mireille D, Philippe S, Véronique A (2009). Sustainable Agriculture. Dordrecht. Springer P 5.

Madoni P, Braghiroli S (2007). Changes in the Ciliate Assemblage Along a Fluvial System Related to Physical, Chemical and Geomorphological Characteristics. European Journal of Parasitology 43(2):67-75.

Mateo-Sagasta J, Marjani SZ, Turral H (2017). Water Pollution from Agriculture : A Global Review, the Food and Agriculture Organization of the United Nations Rome 35 p.

Mereta ST, Ambelu A, Ermias A, Abdie Y, Moges M, Haddis A, Hailu D, Beyene H, Kebede B, Mulat WL (2020). Effects of Untreated Industrial Effluents on Water Quality and Benthic Macroinvertebrate Assemblages of Lake Hawassa and its Tributaries, Southern Ethiopia, African. Journal of Aquatic Science 45(3):285-295.

Mitra M, Hasfalina CM, Mohd AH, Phang LY (2010). Treatment of Waste Water from rubber Industry in Malaysia. African Journal of Biotechnology. 9(38):6233-6243.

Ndjama J, Ajeagah GA, Nkoue GRN, Wirming J, Biram ANEB, Eyong EGT, Ako AA, Mohamadou B, Tchouya RVN, Hell JV (2017). Physico-Chemical and Biological Characteristics of the Nklobisson Artificial Lake in Yaounde, Cameroon. Journal of Water Resource and Protection 9(12):1547-1563.

Omoigberale MO, Ezenwa IM, Biose E, Okoye C (2021). The Impact of Rubber Effluent Discharges on the Water Quality of a Tropical Rain Forest River in Nigeria. African Journal of Aquatic Science pp. 1-12.

Omorusi VI (2013). Evaluation of Waste Water (Effluent) from Rubber Latex Concentrate for Microbiological and Physcio- Chemical Properties. Researcher 5(5):60-63.

Pooja A (2017). Physical, Chemical and Biological Characteristics of Water. Pathshala 16 p.

Pratiksha S, Vikram G (2022). Artificial Intelligence and Data Science in Environmental Sensing. Elsevier Inc. 978-0-323-90508-4. 305 p.

Richter M (2016). Temperatures in the Tropics. In: Pancel, L., Köhl, M. (eds) Tropical Forestry Handbook. Springer, Berlin, Heidelberg. https://doi.org/10.1007/978-3-642-54601-3_38.

Rodier J, Legube B, Marlet N, Brunet R (2009). Analysis of water. 9th edition. Dunod, Paris 1579 p.

Santza CV, Ndjouenkeu R, Ngassoum MB (2022). Water from the Menoua Watershed (Cameroon) and Agricultural Pollution : the Chemical Risks Inherent in its Consumption. Environnement, Risques et Santé. 21(2):157-168.

Singh RM, Asha G (2016). Water Pollution: Sources, Effects and Control. https://www.researchgate.net/publication/321289637. 16 p.

Sparagano O, Groliere CA (1991). Evaluation of Water Quality of a River with Ciliates as Bioindicators of Pollution. Comparism with Physico-Chemistry. Applied Hydro Ecology 1:43-62.

Tchakonté S, Ajeagah GA, Dramane D, Camara A, Konan KM, Ngassam P (2014). Impact of Anthropogenic Activities on Water Quality and Freshwater Shrimps Diversity and Distribution in Five Rivers in Douala, Cameroon. Journal of Biodiversity and Environmental Sciences 2(4):183-194.

Third Census on the Population and Habitat (RGPH) (2005). Bureau Centrale des Recensements et des Etudes de Population du Cameroun (BUCREP). http://www.bucrep.cm

Thorp JH, Covich AP (2015). Ecology and General Biology, Fourth Edition. Elsevier Inc. pp. 225-271. ISBN 978-0-12-385026-3. DOI: https://doi.org/10.1016/C2010-0-65590-8.

Thorsvald S (1948). A Method of Establishing Groups of Equal Amplitude in Plant Sociology Based on Similarity of Species Content. Limnology and Oceanography 5:1-3.

Trishala KP, Deepak R, Agrawal YK (2016) Bioindicators : The Natural Indicator of Environmental Pollution, Frontiers in Life Science 9(2):110-118.

Udyog S, Gupta PK (2001). Assemblage of Ciliated Protozoan Community in a Polluted and Non-Polluted Environment in a Tropical Lake of Central Himalaya: Lake Naini Tal India. Journal of Plankton Research 23(6):571-584.

World Population Prospects (2017) Revision : Key Findings and Advance Tables » (PDF). United Nations Department of Economic and Social Affairs, Population Division P 2.

Zelinka M, Marvan.P (1961). Zur Präzisierung derbiologischen Klassifikation der Reinheit Fliessender Gewässer.Archiv für Hydrobiologie 57:389-407.

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Review

An appraisal of phytoremediation as an alternative and effective remediation technology for crude oil-contaminated soils: A review

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The review investigates phytoremediation as an alternative environmentally-friendly method of cleaning and restoring hydrocarbon contaminated soils. Phytoremediation is a 'green' technology that exploits the natural ability of green plants to remove, degrade or suppress contaminants in soils, sludges, sediments, surface-water and ground-water in an ecologically-friendly manner. Its processes are stimulated by sunlight and microbial biota in the contaminated medium. The use of various mechanisms of phytoremediation is reviewed along with the criteria used in the selection of plant species for phytoremediation exercises. The importance of soil amendments in phytoremediation experiments is also considered. The usefulness of phytoremediation as a viable tool for the remediation of contaminated soils in the crude oil bearing regions of the world, and particularly in Nigeria, have been assessed through the work of previous authors to verify its suitability for the remediation and restoration of contaminated soils.

Key words: Crude oil, phytoremediation, pollution, plant species, soil.

INTRODUCTION

Pollutants are often released into the environment (such as the atmosphere, soil and water) through human actions, such as agricultural and industrial activities, and these substances cause environmental pollution (Ikhuoria and Okieimen, 2000; Erakhrumen, 2007; Jadia and Fulekar, 2008; 2010; Oyedeji et al., 2015). The remediation of such environments after pollution incidents is often necessary and can be effectively achieved using phytoremediation (Erakhrumen, 2007). Phytoremediation

is the methodology that exploits the natural ability of green plants to remove, degrade or suppress contaminants in soils, sludges, sediments, surface-water and ground-water in an ecologically-friendly manner and it is stimulated by sunlight. This technology operates on the concept of using 'nature to cleanse nature' following contamination of the environment (Osam et al., 2011).

Some plant species are capable of tolerating a wide range of environmental conditions and this ability can be

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used to modify these conditions (Susarla et al., 2002).

Phytoremediation technology enhances the amelioration and restoration of contaminated environments, such as soils and waters, by growing green plants that have the ability to tolerate and/or remove contaminating substances, thereby restoring the soil and its functions (Peer et al., 2006). It is a non-destructive, cost-effective *in situ* technology that utilizes plants and their associated micro-organisms to remediate contaminated soils. Cunningham et al. (1996) described it as an *in situ* use of plants and their associated micro-organisms to degrade, contain or render harmless, contaminants in soil or ground-water. The use of phytoremediation techniques can either be through naturally growing plants in the contaminated soil or by artificial cultivation of selected plant species (Erakhrumen, 2007) and has emerged as a viable option for the remediation of petroleum hydrocarbon polluted sites (Frick et al., 1999; Tanee and Kinako, 2008). A considerable number of regions in the global community continue to record substantial economic growth. In the clean-up of contamination by petroleum hydrocarbons, plants enhance the microbial degradation of contaminants in the rhizosphere (Merkl et al., 2004a, b, 2005; Atagana, 2011).

The use of phytoremediation as a remediation option may not only be to degrade contaminants but can also be used to enhance habitat recovery through the stimulation of vegetative plant growth. Plants can enhance bioremediation processes by absorbing, translocating or sequestering the organic contaminant and removing them from the soil system (Cunningham et al., 1995; Glick, 2003). In a situation where the contaminant, in its present concentration, is not phyto-toxic, the cultivation of plants can be a valuable tool in soil remediation. The mechanism and efficiency of phytoremediation technology depend on the type of contaminant, its bioavailability and the surrounding soil properties (Cunningham and Ow, 1996).

Although the phytoremediation of contaminated soil may be moderately slow, it is, however, environmentally-friendly, inexpensive, requires little equipment and or labour, is easy to perform, and has the benefit that the contaminated sites can be cleaned without removing the polluted soil. The key factor for successful phytoremediation practise is the identification of a plant species that is tolerant of the contaminated site, and can tolerate high concentrations of contaminant(s) in the polluted site. Bamidele and Agbogidi (2006) described an effective phytoremediation plant species as one that thrives well in a contaminated habitat. Some plant species of the families Poaceae, Brassicaceae, Fabaceae, Euphorbiaceae, Asteraceae and Lamiaceae have been identified, and considered as being able to remediate contaminants, due to their extensive root systems and presence of root nodules which house microbes that help in degrading hydrocarbons (Jadia and Fulekar, 2009; Hall et al., 2011).

Phytoremediation technology presents considerable potential for the treatment of contaminated soils and has proved successful in several studies. For instance, Merkl et al. (2004b) reported that the grass, *Brachiaria brizantha* (Hochst ex A. Rich.) Stapf. and the legumes *Centrosema brasilianum* (L.) Benth. and *Calopogonium mucunoides* Desv. are good plant species for phytoremediation because in crude oil contaminated soil they combined high seedling emergence with good biomass production.

White et al. (2006) investigated phytoremediation of alkylated polycyclic aromatic hydrocarbons in a crude oil-contaminated soil and reported that there was enhanced degradation of complex aromatic hydrocarbons attributable to the phytoremediation process. Agbogidi et al. (2007) investigated the use and effectiveness of *Tectona grandis* (Linn.) and *Gmelina arborea* (Roxb.) forest tree species of family Lamiaceae for phytoremediation of crude oil contaminated soils and reported that the two plant species are good candidates for phytoremediation, especially when the concentration of the crude oil is low in the contaminated soil. Atagana (2011) reported the bioremediation of co-contamination of crude oil and heavy metals in soil by phytoremediation using *Chromolaena odorata* (L) King & H.E. Robins of the family Asteraceae in a pot experiment. At the end of the experiment, crude oil was reduced in the soil and the reduction was attributed to natural attenuation and microbial action in the root system (rhizosphere) of the plant. It was also observed that C. *odorata* (L) has the capability of thriving and remediating crude oil contaminated soil.

Allowing polluted soil to undergo natural self-remediation takes some time (Kinako, 1981). Therefore, polluted soil needs human intervention to accelerate its recovery process after a pollution incident. Pollution is a serious environmental problem in the oil-bearing region of Nigeria (Figure 1). The practise of phytoremediation in developed and developing countries (such as Nigeria) could offer a feasible and economic alternative to achieve the remediation of petroleum hydrocarbon contaminated soils.

MECHANISMS OF PHYTOREMEDIATION

Remediation of soils contaminated with organic substances, including petroleum hydrocarbons, occurs through one, or more, of the following primary mechanisms: phytostabilization, phytoextraction, phytodegradation, phytovolatilization, and rhizodegradation (Figure 2).

Phytostabilization

Phytostabilization is often referred to as the on-site
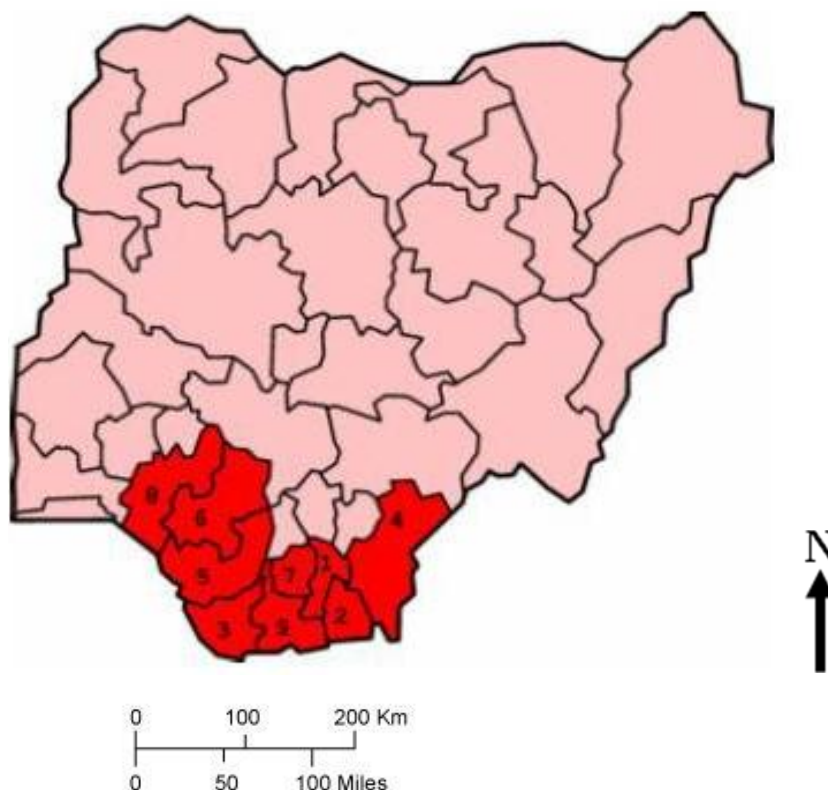
Figure 1. Map of Nigeria showing the Niger Delta oil-bearing region and numerically indicating the location of its member states Abia[1], Akwa Ibom[2], Bayelsa[3], Cross River[4], Delta[5], Edo[6], Imo[7], Ondo[8], and Rivers[9].
Source: Erakhrumen (2007).

activation of contaminants and is employed in the remediation of soil, sediment and sludges (Eapen and Dsouza, 2005; USEPA, 2000). In this process, plant roots limit contaminant mobility and availability within soils (Jadia and Fulekar, 2009; Mukhopadhyay and Maiti, 2010). The mechanisms involved may include absorption and accumulation by roots, adsorption onto root surfaces, or chemical precipitation within the root zone (Ghosh and Singh, 2005). Plant uptake and accumulation of petroleum hydrocarbons from contaminated soil, however, is generally quite small. Thus, in the case of petroleum hydrocarbons, phytostabilization may simply be involved in the establishment of vegetative cover to minimize potential migration of the contaminant through erosion, leaching or soil dispersion (Jadia and Fulekar, 2009; Raskin and Ensley, 2000). Plants (especially trees) can also act as organic pumps, transpiring water, and in turn retaining the contaminant in the root zone which helps prevent inter-site mobility (Berti and Cunningham, 2000). Phytostabilization has proved successful with low concentrations of contaminants in soil (Jadia and Fulenkar, 2009). It involves accumulation of the contaminants in the root zone. The plants harbour and tolerate the contaminants within the root system and this

is one of the major advantages of this process (USEPA, 2000).

Phytovolatilization

Phytovolatilization refers to the use of plants for the uptake of contaminants. The contaminants are taken up by plants, converted into volatile, less chemically toxic substances and transpired into the atmosphere (Jabeen et al., 2009; Jadia and Fulekar, 2009) through the open stomata on the leaf surface and some radial diffusion from the stem tissues and plant bark (Kamath et al., 2004). Some plants have the ability to absorb heavy metals and convert them to a gaseous form in plant tissues and thereafter release them into the atmosphere (Ghosh and Singh, 2005).

Phytoextraction

Phytoextraction involves the extraction of contaminants by plants through their root system and its subsequent accumulation in the harvestable aerial parts of the plant
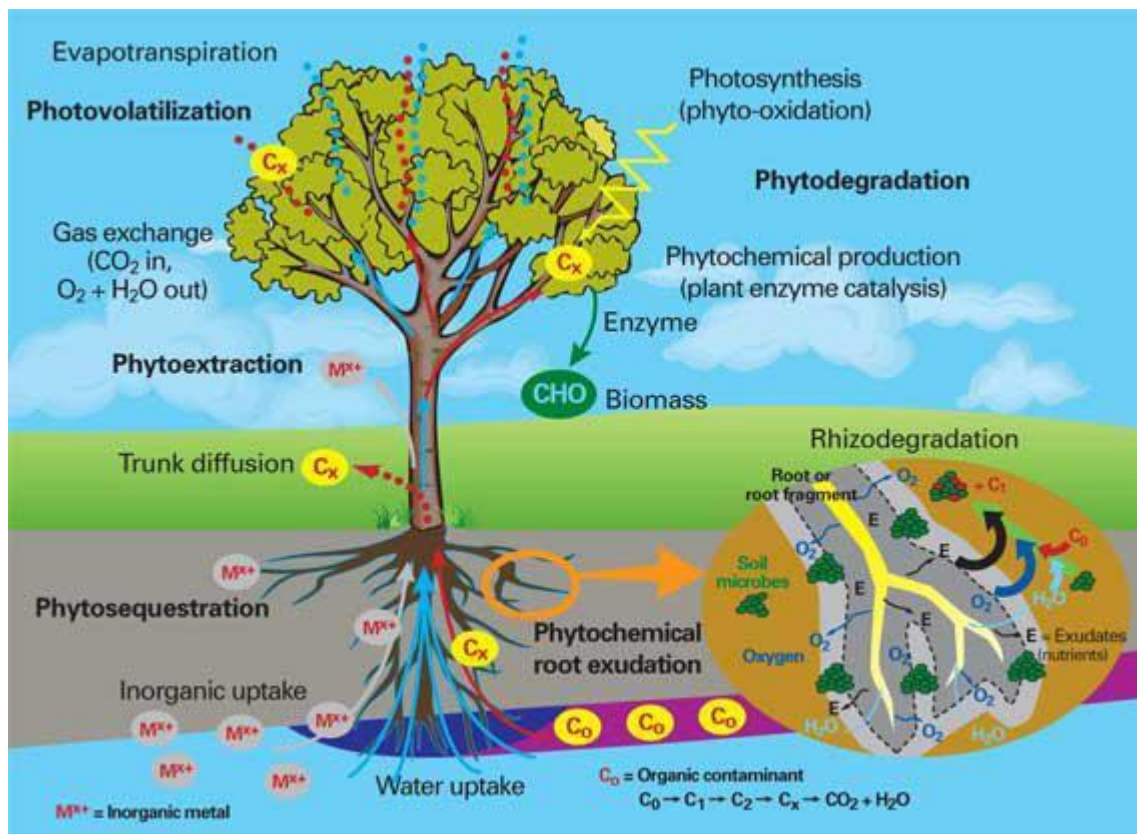
Figure 2. Mechanisms of phytoremediation.
Source: Seslar (2005).

(Erakhrumen, 2007). This is followed by harvesting and appropriate disposal of the plant biomass. The contaminant-accumulating plants are usually cultivated by agricultural practises (Jabeen et al., 2009). In the phytoextraction process, the roots of the cultivated plant species help absorb contaminants from the supporting soil, thereby reducing concentrations in the soil. With successive cropping and harvesting of plants from such contaminated soil, the concentration and level of the contaminants in the soil can be reduced (Vandenhove et al., 2001). It has been reported that the cost implication of a phytoextraction process is lower as compared to conventional soil remediation techniques.

Rhizofiltration

Rhizofiltration relies on the capability of the plant root system to take up and sequester contaminants, or nutrients, in excess quantities from aqueous waste streams (Erakhrumen, 2007). This process has the ability to remediate metals including lead (Pb), cadmium (Cd), nickel (Ni), vanadium (V) and chromium (Cr) (Jabeen et al., 2009). Plants suitable for this technique should produce extensive root systems, root biomass and surface area. The plant species should have the

capability to accumulate and tolerate substantial amounts of contaminants (Dushenkov and Kapulnik, 2000). Terrestrial plants are very appropriate for rhizofiltration. Plants such as *Helianthus annuus* (L.) of the family Asteraceae, *Brassica juncea* (L.) (Brassicaceae), *Nicotiana tabacum* (L.) (Salicaceae), *Spinacia oleracea* (L.) (Amaranthaceae) and *Zea mays* (L.) (Poaceae) have been investigated for their suitability to remove pollutants (Raskin and Ensley, 2000). Rhizofiltration can also be conducted both *in situ* and *ex situ* to remediate contaminated water bodies. This method can be used to remediate many metal contaminants. Dushenkov et al. (1995) recommended its commercialization and public acceptance for phytoremediation works.

Phytodegradation (sometimes referred to as phytotransformation)

Phytodegradation involves the breakdown of contaminants either internally, through metabolic processes, or externally, through the release of plant-produced enzymes into the soil using the relationship between plants and their associated micro-organisms in the rhizosphere (Jabeen et al., 2009; Oyedeji, 2016). Some plants are capable of detoxifying contaminants

(such as hydrocarbons) and transforming them into non-phytotoxic metabolites. These contaminants are detoxified in three phases: conversion, conjugation and compartmentalization (Kamath et al., 2004). Plants and micro-organisms are involved, both directly and/or indirectly, in the degradation of complex petroleum hydrocarbons into products that are generally simple, less toxic and less persistent in the environment than the parent compounds. Phytodegradation may occur internally in the rhizosphere (Mukhopadhyay and Maiti, 2010) and it is referred to as rhizodegradation or rhizoremediation. It is applied in the remediation of petroleum hydrocarbon contaminated soils.

Rhizodegradation or rhizoremediation

Rhizodegradation, otherwise referred to as rhizoremediation, is applied in the remediation of pollutants such as petroleum hydrocarbon contaminated soils. This process involves the use of tolerant plant species, and associated micro-organisms, in the rhizosphere to accelerate the remediation processes (Pajuelo et al., 2011). The root systems of plant species that are suitable for rhizodegradation support adequate microbial growth due to their ability to offer their root nodules as a habitat (for microbes, enzymes, nutrients and oxygen) as well as a large surface area for microbes to colonize in the soil layers (Anderson et al., 1993). The roots are capable of releasing 'degradative enzymes' to promote degradation of petroleum hydrocarbons (Wenzel, 2009). The root systems also play significant roles in transferring the contaminants to the degrading microbes and for the production of oxygen, either by transferring oxygen or creating a vacuum in the soil's sub-surfaces that permit diffusion of atmospheric oxygen (Van Epps, 2006) to increase the degradation of contaminants in the remediation processes.

In the rhizosphere, a much higher microbial density (which could enhance rhizodegradation) is present in the surface soil layer than in deeper layers (Hinsinger et al., 2005, 2006) and this is associated with higher microbial numbers, diversity and bioactivity (Boopathy, 2000). Availability of numerous degrading microbes in the soil significantly determines their potential for remediation (Mikkonen et al., 2011). Bacteria in the soil rhizosphere are increased by organic contaminants (Chaineau et al., 2003; Chaudhary et al., 2012). This increased microbial population, and its availability, promote plant growth through the degradation of organic contaminants. The *Rhizobium* population helped increase the growth performance of *Trifolium* species (L.) Fabaceae on hydrocarbon contaminated soil (Chiapusio et al., 2007). Rhizoremediation can be employed in the treatment of soil contaminated by petroleum hydrocarbons, but the choice and tolerance of plant species also influence its effectiveness.

TOLERANCE MECHANISMS OF PLANTS AND THEIR SUITABILITY FOR REMEDIATION

The physiological and molecular mechanisms of a plant species determine the suitability of such plants for remediation processes. A plant's tolerance to a particular contaminant is governed by its ability to tolerate an increasing level of the contaminant (Jabeen et al., 2009). Kamath et al. (2004) identified some criteria for selecting plant species. This should follow the needs of the application, the contaminants concerned and the potential of such plants to thrive well on contaminated soil. It is preferable to use native plant species for remediation purposes to support soil ecosystem restoration (Pilon-Smits and Freeman, 2006), as introduced, or exotic species, may become invasive during, or after, the clean-up exercise which give rise to other associated ecological problems.

SELECTION OF PLANT SPECIES FOR PHYTOREMEDIATION

Some researchers (Merkl et al., 2004a, b, 2005; White et al., 2006; Agbogidi et al., 2007; Atagana, 2011) have investigated and reported on the selection of plants for the remediation of soils contaminated with hydrocarbons. It was observed that there was enhanced degradation of complex hydrocarbons within the root rhizosphere (Merkl et al., 2004b; Atagana, 2011). This suggests that a good plant candidate for phytoremediation must have an extensive root system.

The selection of suitable plant species is a fundamental step to be considered in the phytoremediation processes. Some plants do not tolerate the presence of contamination, while others do and effectively enhance the remediation of hydrocarbons within soil. This may be due to variation in plant morphology (e.g. roots), physiology and biochemistry (e.g. root exudates) and interactions between microbes and the plants in the rhizosphere (Walker et al., 2003). Some grasses, herbs, shrubs and trees are good candidates for phytoremediation as listed (Table 1) and some of these plants have extensive branched fibrous roots that are more likely to provide large surface areas for interaction (Yateem et al., 2007). The rhizospheres of certain trees (e.g. *Populus deltoides x nigra*) have the capability to enrich hydrocarbon degrading micro-organisms more than the soil outside the root zone (Hutchinson et al., 2003). To achieve maximum hydrocarbon reduction in soil, and to successfully establish a stable vegetation cover, various criteria must be considered. Any ideal plant species candidate for the phytoremediation of hydrocarbon contaminated soil should be selected to provide a large surface area per unit volume of soil (Aprill and Sim, 1990; Smith et al., 2006) which thus permits rhizosphere-contaminant-microbe interactions. Due to the

Table 1. Some plant species with demonstrated potential to phytoremediate petroleum hydrocarbons.

Common name	Scientific name	Family	Source
Alfalfa	*Medicago sativa* L.	Fabaceae	Nichols et al. (1997)
Alpine blue grass	*Poa alpina* L.	Poaceae	Nichols et al. (1997)
Bermuda grass	*Cynodon dactylon* (L.) Pers.	Poaceae	Reynolds and Wolf (1999)
Bush bean	*Phaseolus vulgaris* L.	Fabaceae	Frick et al. (1999)
Carpet grass	*Axonopus compressus* (Sw.) P.Beauv	Poaceae	Efe and Okpali (2012); Efe and Elenwo (2014)
Cow pea	*Vigna unguiculata* L.	Fabaceae	Tanee and Kinako (2008)
Tall Fescue	*Festuca arundinacea* Schreb	Poaceae	Reynolds and Wolf (1999)
Little bluestem	*Schizachyrium scoparium* (Michx.) Nash	Poaceae	Pradham et al. (1998)
Miracle tree	*Leucaena leucocephala* (Lam.) de Wit	Fabaceae	Osam et al. (2011)
Nut sedge	*Cyperus rotundus* L.	Cyperaceae	Efe and Okpali (2012)
Eastern cottonwood	*Populus deltoides × nigra* L.	Salicaceae	Frick et al. (1999)
Rattle weed	*Crotalaria retusa* L.	Fabaceae	Osam et al. (2011)
Italian Rye-grass	*Lolium multiflorum* Lam.	Poaceae	White et al. (2006)
Sorghum	*Sorghum bicolour* (L.) Moench	Poaceae	Frick et al. (1999)
Sudan grass	*Sorghum vulgare* (L.) Moench	Poaceae	Frick et al. (1999)
Switch grass	*Panicum virgatum* L.	Poaceae	Pradham et al. (1998)
Vetiver	*Vetiveria zizanioides* (L.) Nash	Poaceae	Brandt et al. (2006)
Yellow flame tree	*Peltophorum pterocarpum* (DC.) K. Heyne	Fabaceae	Osam et al. (2011).

Source: Authors Survey.

frequent poor nutrient availability in contaminated sites (Kirkpatrick et al., 2006; Wenzel, 2009), they should be able to tolerate and thrive with low nitrogen (N) and phosphorus (P) availability.

SUITABILITY OF FABACEAE FOR PHYTOREMEDIATION OF HYDROCARBON CONTAMINATED SOILS

The Fabaceae family is made up of plant species commonly referred to as legumes and consists of ~18,000 species across the world and grow in diverse terrestrial habitats. The potential and suitability of Fabaceae for phytoremediation of hydrocarbon polluted soil, with its unique adaptation and rhizodegradation mechanisms, is well known (Merkl et al., 2004b; Tanee and Akonye, 2009; Osam et al., 2011; Atagana, 2011; Hall et al., 2011). There are a number of reports on the use of legumes in hydrocarbon contaminated soils remediation and their ability to fix N (Nichols et al., 1997; Dzantor et al., 2000; Osam et al., 2011) has been known for some time.

Contaminated soils are usually particularly deficient in N and P (Wenzel, 2009) and competition for nutrients among the soil biota reduce nutrient availability. N fixing plant species, such as   legumes, can be used in rhizoremediation work (Miller and Cramer, 2005). Microbes, such as *Rhizobium* species, can penetrate the root systems of leguminous plant species and form symbiotic interactions in their root nodules with which they are able to fix atmospheric N in the form of ammonium compounds (Suominen et al., 2000) and have also been found to increase potassium (K) and phosphorous (P) uptake in plants (Vershinina, 2012). Some of the common N-fixing microbes in soil include *Azotobacter* species, *Azospirillum brasilense*, *Rhizobium* spp. and Actinomycetes (Havlin et al., 2005) and these micro-organisms play vital roles in remediation work by degrading the contaminants. The amount of N fixation by microbes in plant root nodules is substantial, often >100 kg ha^{-1} year^{-1} (Vitosek et al., 2002). The interaction between microbes and leguminous plant species, such as alfalfa (*Medicago sativa*) and red clover (*Trifolium pratense*), have proven successful in the remediation of petroleum hydrocarbon contaminants (Frick et al., 1999). The use of woody leguminous plant species for phytoremediation in tropical areas is a reflection of their prevalence and abundance (Vitosek et al., 2002) and they can stimulate microbial growth, which increases oxidation of organic chemical substances (Peer et al., 2006).

THE USE OF PLANT SPECIES OF OTHER FAMILIES FOR REMEDIATION OF HYDROCARBON CONTAMINATED SOILS

Plant screening experiments have shown that some plant species, such as *Lolium multiflorum* Lam. and *Festuca arundinacea* Schreb are tolerant of hydrocarbon contamination (Frick et al., 1999). *B. juncea* L. is a useful plant species for phytoremediation and has been successfully used   to remediate a   3 km Bulgarian

ecological zone contaminated with Pb (Simeonova and Simeonov, 2006). Pb can be one of the impurities in crude oil. The results of their one season planting showed a decrease between 0 and 25.9% in the initial Pb concentrations at various sample locations.

Günther et al. (1996) found that soils planted with Italian rye-grass (*L. multiflorum* Lam.) had reduced hydrocarbons than soil that was unplanted. In their 22 weeks phytoremediation experiment, the initial extractable hydrocarbon concentration of 4330 mg total hydrocarbon/kg soil was decreased to <120 mg/kg soil (97% decrease) in planted soil.

The examination of the phytoremediation potential of two cold-hardy grass species, Tall fescue (*F. arundinacea* Schreb) and annual Italian rye grass (*L. multiflorum* Lam.) planted together in potted soils contaminated with crude oil, found that the contaminated soils had significantly lower concentrations of total petroleum hydrocarbon compared to unplanted controls (Reynolds and Wolf, 1999). The initial crude oil concentration for planted treatments and unplanted controls was ~6200 mg TPH per kg soil. After 640 days, crude oil-contaminated soils planted with both species had 1400 mg TPH per kg soil (77% decrease), while the unplanted control contained 2500 mg TPH per kg soil (60% decrease).

In a 6-month laboratory study, switch grass (*Panicum virgatum*) and little blue stem *Schizachyrium scoparium* (Michx.) Nash were capable of decreasing the concentration of total Petroleum Aromatic Hydrocarbons (PAHs) in contaminated soil collected from a manufacturing gas plant (Pradham et al., 1998). The initial soil concentration of total PAHs for the three plant treatments and an unplanted control was 184.5±14.0 mg total PAHs per kg of soil. After 6 months, the concentration in the unplanted control soil was 135.9±25.5 mg/kg, while the concentration in planted treatments was much lower (*P. virgatum*, 79.5±3.7 mg/kg and *S. scoparium*, 97.1±18.7 mg/kg).

THE ROLE OF SOIL AMENDMENTS IN PHYTOREMEDIATION PROCESSES

Fertilizers and natural zeolites can play vital roles in phytoremediation processes. White et al. (2003, 2006) and Tanee and Kinako (2008) reported the importance of fertilization in phytoremediation protocols. Chaineau et al. (2003) suggested that the addition of fertilizer (as a soil amendment) and periodic tillage are useful in the degradation of petroleum hydrocarbons in contaminated soil. However, excessive use of nitrogenous fertilizer can damage the environment and to avoid this problem, N-fixing plant species supplemented with soil amendments are encouraged in remediation work (Miller and Cramer, 2005). The environmental applications of natural zeolites such as clinoptilolite as a viable soil amendment has also been reported for contaminated soils (Ming and Allen,

2001; Bowman, 2003; Chmielewska, 2003; Tian et al., 2004; Englert and Rubio, 2005; Leggo et al., 2006; Misaelides, 2011) and for the restoration of soil nutritional qualities. Adebowale et al. (2005) reported environmental significance of Nigerian kaolin for adsorption and remediation of Pb^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} metal ions in media. Trckova et al. (2004) affirmed that kaolin is effective in the amelioration of adverse effects of contaminants from both the living organisms and the environment.

COMPARISON OF PHYTOREMEDIATION WITH ALTERNATIVE REMEDIATION STRATEGIES

Phytoremediation has shown remarkable cost effectiveness and recent societal acceptance. Its advantages include low costs, according to various authors who have conducted a series of experiments (Frick et al., 1999; Macek et al., 2000; Glick 2003). Other advantages compared with other remediation processes include: Can be applied *in situ*; Cost-effective and, therefore, economically viable; Offers less disruption to the natural environment compared with mechanical methods; Avoids excavation and heavy damage to soils; Can be applied to large areas of terrestrial contamination; Relatively easy to apply; Preserves soil structure; Potentially quick to apply to the contaminated sites; No disposal site(s) is required; Can be applied to a diverse range of hazardous materials; Plants act as indicators of contamination; Plants help contain contaminants; Plants transfer oxygen and nutrients to the rhizosphere; Other additional advantages of providing plant cover are soil conservation, landscape aesthetics, improved habitat for fauna, carbon-sequestration, etc. (Frick et al., 1999; Oyedeji, 2016).

DISCUSSION

The use of phytoremediation as an alternative environmentally-friendly method of cleaning and restoring contaminated soils has been reviewed. The success of previous phytoremediation works conducted by different authors (Nichols et al., 1997; Dzantor et al., 2000; Tesar et al., 2002; Merkl et al., 2004b; Bamidele and Agbogidi, 2006; Osam et al., 2011; Atagana, 2011) using a range of plant species has shown that research on this emerging technology should be encouraged, strengthened and applied where applicable. This is especially the case in areas prone to hydrocarbon contamination such as the Niger Delta region of Nigeria. The findings of this work have revealed that phytoremediation, particularly rhizodegradation or rhizoremediation, could be employed in the remediation of hydrocarbon contaminated soils (Atagana, 2011; Osam et al., 2011; Oyedeji, 2016) and it also revealed that plants in the family Fabaceae have

been used for phytoremediation and found to be good candidates because of their extensive root system and ability to fix N within their root nodules. It is, therefore, hoped that land owners, farmers and governments at all levels will gain awareness of this viable ecosystem remediation technology for our ecosystems and support research on phytoremediation as a practical and effective technology for soil remediation.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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REFERENCES

Adebowale KO, Unuabonah IE, Olu-Owolabi BI (2005). Adsorption of some heavy metal ions on sulfate- and phosphate-modified kaolin Applied Clay Science 29:145-148.

Agbogidi MO, Dolar ED, Okechukwu EM (2007). Evaluation of *Tectona grandis* (Linn) and *Gmelina arborea* (Roxb) for phytoremediation in crude oil contaminated soils Agriculturae Conspectus Scientificus 72(2):149-152.

Anderson T, Guthrie E, Walton B (1993). Bioremediation in the rhizosphere Environmental Science and Technology 27:2630-2636.

Aprill W, Sims RC (1990). Evaluation of the use of prairie grasses for stimulating polycyclic aromatic hydrocarbon treatment in soil Chemosphere 20(1):253-265.

Atagana HI (2011). Bioremediation of co-contamination of crude oil and heavy metals in soil by phytoremediation using *Chromolaena odorata* (L) King & HE Robinson Water Air and Soil Pollution 215:261-271.

Bamidele J, Agbogidi O (2006). The effect of soil pollution by crude oil on seedling growth of *Machaerium lunatus* (L) GFW Meg Discovery and Innovation 18(2):104-108.

Berti WR, Cunningham SD (2000). Phytostabilization of metals – In: Raskin I Ensley B (eds) Phytoremediation of toxic metals: Using plants to clean up the environment Wiley Interscience New York pp. 71-88.

Boopathy R (2000). Factors limiting bioremediation technologies Bioresource Technology 74(1):63-67.

Bowman RS (2003). Applications of surfactant-modified zeolites to environmental remediation Microporous and Mesoporous Materials 61(1):43-56.

Brandt R, Merkl N, Schultze-Kraft R, Infante C, Broll G (2006). Potential of Vetiver (*Vetiveria zizanioides* L Nash) for phytoremediation of petroleum hydrocarbon-contaminated soils in Venezuela. International Journal of Phytoremediation 8:273-284.

Chaineau C, Yepremian C, Vidalie J, Ducreux J, Ballerini D (2003). Bioremediation of a crude oil-polluted soil: biodegradation leaching and toxicity assessments Water Air and Soil Pollution 144(1):419-440.

Chaudhary P, Singh SB, Chaudhry S, Nain L (2012). Impact of PAH on biological health parameters of soils of an Indian refinery and adjoining agricultural area - a case study Environmental Monitoring and Assessment 184(2):1145-1156.

Chiapusio G, Pujol S, Toussaint ML, Badot PM, Binet P (2007). Phenanthrene toxicity and dissipation in rhizosphere of grassland plants (*Lolium perenne* L and *Trifolium pratense* L) in three spiked soils Plant and Soil 294(1):103-112.

Chmielewska E (2003). Remediation of specifically polluted waste effluents using natural zeolites Environment Protection Engineering 29(1):35-44.

Cunningham SD, Ow DW (1996). Promises and prospects of phytoremediation Plant Physiology 110(3):715

Cunningham SD, Anderson TA, Schwab PA, Hsc FC (1996) Phytoremediation of soils contaminated with organic pollutants Advances in Agronomy 56:55-114.

Cunningham SD, Berti WR, Huang JW (1995). Phytoremediation of contaminated soils Trends in Biotechnology 13(9):393-397.

Dushenkov S, Kapulnik Y (2000). Phytofiltration of metals. In: Raskin I and Ensley BD (Eds) Phytoremediation of Toxic Metals: Using Plants to Clean-up the Environment New York: Wiley pp. 89-106.

Dushenkov V, Kumar PBAN, Motto H, Raskin I (1995). Rhizofiltration: the use of plants to remove heavy metals from aqueous streams Environmental Science and Technology 29(5):1239-1245.

Dzantor EK, Chekol T, Vough L (2000). Feasibility of using forage grasses and legumes for phytoremediation of organic pollutants Journal of Environmental Science and Health Part A 35(9):1645-1661.

Eapen S, D'Souza S (2005). Prospects of genetic engineering of plants for phytoremediation of toxic metals Biotechnology Advances 23(2):97-114.

Efe SI, Okpali AE (2012). Management of petroleum impacted soil with phytoremediation and soil amendments in Ekpan Delta State Nigeria Journal of Environmental Protection 3(5):386-393.

Efe SI, Elenwo EI (2014). Phytoremediation of crude oil contaminated soil with *Axonopus compressus* in the Niger Delta region of Nigeria Natural Resources 5:59-67.

Englert A, Rubio J (2005). Characterization and environmental application of a Chilean natural zeolite International Journal of Mineral Processing 75(1):21-29.

Erakhrumen AA (2007). Phytoremediation: an environmentally sound technology for pollution prevention control and remediation in developing countries Educational Research and Reviews 2(7):151-156.

Frick CR, Farrell RE, Germida J (1999). Assessment of phytoremediation as an in situ technique for cleaning oil-contaminated sites Petroleum Technology Alliance of Canada (PTAC) Calgary pp. 1-88.

Ghosh M, Singh S (2005). A review on phytoremediation of heavy metals and utilization of its by-products Applied Ecology and Environmental Research 3(1):1-18.

Glick BR (2003). Phytoremediation: synergistic use of plants and bacteria to clean up the environment Biotechnology Advances 21(5):383-393.

Günther T, Dornberger U, Fritsche W (1996). Effects of ryegrass on biodegradation of hydrocarbons in soil Chemosphere 33(2):203-215.

Hall J, Soole K, Bentham R (2011). Hydrocarbon phytoremediation in the family Fabaceae- A review International Journal of Phytoremediation 13:317-332.

Havlin JL, Beaton JD, Tisdale SL, Nelson WL (2005). Soil Fertility and Fertilizers: An Introduction to Nutrient Management Pearson Prentice Hall Upper Saddle River NJ.

Hinsinger P, Gobran GR, Gregory PJ, Wenzel WW (2005). Rhizosphere geometry and heterogeneity arising from root-mediated physical and chemical processes New Phytologist 168(2): 293-303.

Hinsinger P, Plassard C, Jaillard B (2006). Rhizosphere: A new frontier for soil biogeochemistry Journal of Geochemical Exploration 88(1):210-213.

Hutchinson S, Schwab A, Banks M (2003). Biodegradation of petroleum hydrocarbons in the rhizosphere Phytoremediation: Transformation and Control of Contaminants 3:557-386.

Ikhuoria EU, Okieimen F (2000). Scavenging cadmium copper lead nickel and zinc ions from aqueous solution by modified cellulosic sorbent International Journal of Environmental Studies 57(4):401-409.

Jabeen R, Ahmad A, Iqbal M (2009). Phytoremediation of heavy metals: physiological and molecular mechanisms The Botanical Review 75(4):339-364.

Jadia CD, Fulekar M (2008). Phytotoxicity and remediation of heavy metals by fibrous root grass (sorghum) Journal of Applied

Biosciences 10:491-499.

Jadia CD, Fulekar M (2009). Phytoremediation of heavy metals: Recent techniques African Journal of Biotechnology 8(6):921-928.

Kamath R, Rentz J, Schnoor JL, Alvarez P (2004). Phytoremediation of hydrocarbon-contaminated soils: principles and a: lications Studies in Surface Science and Catalysis 151:447-478.

Kinako PDS (1981). Short-term effects of oil pollution on species numbers and productivity of a simple terrestrial ecosystem Environmental Pollution Series A Ecological and Biological 26(2):87-91.

Kirkpatrick WD, White P Jr., Wolf D, Thoma G, Reynolds C (2006). Selecting plants and nitrogen rates to vegetate crude oil-contaminated soil International Journal of Phytoremediation 8(4):285-297.

Leggo PJ, Ledésert B, Christie G (2006). The role of clinoptilolite in organo-zeolitic-soil systems used for phytoremediation Science of the Total Environment 363(1):1-10.

Macek T, Mackova M, Kas KJ (2000). Exploitation of plants for the removal of organics in environmental remediation Biotechnology Advances 18(1):23-34.

Merkl N, Schultze-Kraft R, Infante C (2004a). Phytoremediation of petroleum-contaminated soils in the tropics: Pre-selection of plant species from eastern Venezuela Journal of Applied Botany and Food Quality 78(3):185-192.

Merkl N, Schultze-Kraft R, Infante C (2004b). Phytoremediation of petroleum-contaminated soils in the tropics - The effect of crude oil on the growth of tropical plants Bioremediation Journal 8(3-4):177-184.

Merkl N, Schultze-Kraft R, Infante C (2005). Assessment of tropical grasses and legumes for phytoremediation of petroleum-contaminated soils Water Air and Soil Pollution 165(1):195-209.

Mikkonen A, Kondo E, Lappi K, Wallenius K, Lindström K, Hartikainen H, Suominen L (2011). Contaminant and plant-derived changes in soil chemical and microbiological indicators during fuel oil rhizoremediation with *Galega orientalis* Geoderma 160(3): 336-346.

Miller A, Cramer M (2005). Root nitrogen acquisition and assimilation Plant and Soil 274:1-36.

Ming DW, Allen ER (2001). Use of natural zeolites in agronomy horticulture and environmental soil remediation Reviews in Mineralogy and Geochemistry 45(1):619-654.

Misaelides P (2011). Application of natural zeolites in environmental remediation: A short review *Microporous* and *Mesoporous* Materials 144(1):15-18.

Mukhopadhyay S, Maiti SK (2010). Phytoremediation of metal mine waste Applied Ecology and Environmental Research 8(3):207-222.

Nichols T, Wolf D, Rogers H, Beyrouty C, Reynolds C (1997). Rhizosphere microbial populations in contaminated soils Water Air and Soil Pollution 95(1):165-178.

Oyedeji AA (2016). Impacts of selected leguminous tree species and kaolinite pre-amendment on oil-contaminated soil for bioremediation in the oil-bearing region of Nigeria PhD thesis of the University of Wolverhampton Wolverhampton UK.

Oyedeji AA, Kayode J, Besenyei L, Fullen MA (2015). Germination of seeds of leguminous tree species moistened with varying concentrations of crude oil-contaminated soil water extracts American Journal of Plant Sciences 6:1575-1580.

Osam MU, Wegwu MO, Ayalogu EO (2011). Biochemical and physico-chemical assessment of the efficacy of some wild-type legumes in the remediation of crude-oil contaminated soils Archives of Applied Science Research 3(6):247-256.

Pajuelo E, Rodríguez-Llorente ID, Lafuente A, Caviedes MÁ (2011). Legume-rhizobium symbioses as a tool for bioremediation of heavy metal polluted soils Biomanagement of Metal-Contaminated Soils Environmental Pollution 20:95-123.

Peer W, Baxter I, Richards E, Freeman J, Murphy A (2006). Phytoremediation and hyperaccumulator plants Molecular Biology of Metal Homeostasis and Detoxification 14:299-340.

Pilon-Smits EAH, Freeman JL (2006). Environmental cleanup using plants: biotechnological advances and ecological considerations Frontiers in Ecology and the Environment 4(4):203-210.

Pradham SP, Conrad JR, Paterck JR, Srivastava VJ (1998). Potential of phytoremediation for treatment of PAHs in soil at MGP sites. Journal of Soil Contamination 7(4):467-480.

Raskin I, Ensley BD (2000). Phytoremediation of toxic metals: using plants to clean up the environment John Wiley & Sons Inc New York 352 p.

Reynolds CM, Wolf DC (1999). Microbial based strategies for assessing rhizosphere enhanced phytoremediation Proceedings of the Pytoremediation Technology Seminar May 31-June 1 1999 Calgary Alberta Environment Canada: Ottawa pp. 125-135.

Seslar T (2005). Natural remedies Frontiers: The BP Magazine of Technology and Innovation 14:18-21.

Simeonova BG, Simeonov LI (2006). An application of a phytoremediation technology in Bulgaria-The Kremikovtzi Steel Works experiment Remediation Journal 16(2):113-123.

Smith M, Flowers T, Duncan H, Alder J (2006). Effects of polycyclic aromatic hydrocarbons on germination and subsequent growth of grasses and legumes in freshly contaminated soil and soil with aged PAHs residues Environmental Pollution 141(3): 519-525.

Suominen L, Jussila M, Mäkeläinen K, Romantschuk M, Lindström K (2000). Evaluation of the Galega–Rhizobium galegae system for the bioremediation of oil-contaminated soil Environmental Pollution 107(2):239-244.

Susarla S, Medina VF, McCutcheon SC (2002). Phytoremediation: an ecological solution to organic chemical contamination Ecological Engineering 18(5):647-658.

Tanee F, Kinako P (2008). Comparative studies of biostimulation and phytoremediation in the mitigation of crude oil toxicity in tropical soil Journal of Applied Sciences and Environmental Management 12(2):143-147.

Tanee FBG, Akonye LA (2009). Effectiveness of Vigna unguiculata as a phytoremediation plant in the remediation of crude oil polluted soil for Cassava (*Manihot esculenta* Crantz) cultivation Journal of Applied Science and Environmental Management 13(1):43-47.

Tesar M, Reichenauer TG, Sessitsch A (2002). Bacterial rhizosphere populations of black poplar and herbal plants to be used for phytoremediation of diesel fuel Soil Biology and Biochemistry 34(12):1883-1892.

Tian W, Wen X, Qian Y (2004). Using a zeolite medium biofilter to remove organic pollutant and ammonia simultaneously Journal of Environmental Sciences 16(1):90-93.

Trckova M, Matlova L, Dvorska L, Pavlik I (2004). Kaolin bentonite and zeolites as feed supplements for animals: health advantages and risks Vet Med-Czech 49(10):389-399.

United States Environmental Protection Agency (USEPA) (2000) Introduction to phytoremediation EPA 600/R-99/107 US Environmental Protection Agency Office of Research and Development Cincinnati Ohio.

Vandenhove H, Van Hees M, Van Winkel S (2001). Feasibility of phytoextraction to clean up low-level uranium-contaminated soil International Journal of Phytoremediation 3:301-320.

Van Epps A (2006). Phytoremediation of petroleum hydrocarbons Technical publication report environmental careers organization for US Environmental Protection Agency Washington DC.

Vershinina ZR, Baymiev AK, Blagova DK, Chubukova OV, Baymiev AK, Chemeris AV (2012). Artificial colonization of non-symbiotic plants roots with the use of lectins Symbiosis 56:25-33.

Walker TS, Bais HP, Grotewold E, Vivanco JM (2003). Root exudation and rhizosphere biology Plant Physiology 132(1):44-51.

Wenzel WW (2009). Rhizosphere processes and management in plant-assisted bioremediation (phytoremediation) of soils Plant and Soil 321(1):385-408.

White PM Jr., Wolf DC, Thoma GJ, Reynolds CM (2003). Influence of organic and inorganic soil amendments on plant growth in crude oil-contaminated soil International Journal of Phytoremediation 5(4):381-397.

White PM Jr., Wolf DC, Thoma GJ, Reynolds CM (2006). Phytoremediation of alkylated polycyclic aromatic hydrocarbons in a crude oil-contaminated soil Water Air and Soil Pollution 169(1):207-220.

Yateem A, Al-Sharrah T, Bin-Haji A (2007). Investigation of microbes in the rhizosphere of selected grasses for rhizoremediation of hydrocarbon-contaminated soils Soil and Sediment Contamination 16(3):269-280.

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