

**SEQUESTRATION OF CONTAMINANTS BY  
MANGROVE (*Avicennia marina*) ECOSYSTEM FROM  
THE GULF COAST OF SAUDI ARABIA**

BY

**MD IQRAM UDDIN AL AMRAN**

A Thesis Presented to the  
DEANSHIP OF GRADUATE STUDIES

**KING FAHD UNIVERSITY OF PETROLEUM & MINERALS**

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the  
Requirements for the Degree of

**MASTER OF SCIENCE**

In

**ENVIRONMENTAL SCIENCE**

**APRIL 2019**

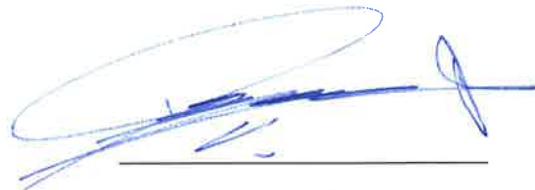
KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN- 31261, SAUDI ARABIA

**DEANSHIP OF GRADUATE STUDIES**

This thesis, written by **MD IQRAM UDDIN AL AMRAN** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of

**MASTER OF SCIENCE IN ENVIRONMENTAL SCIENCE**



Dr. Mohamed Ali B. Qurban  
(Advisor)



Dr. Abdullatif Al-Shuhail  
Department Chairman



Dr. Krishnakumar P.K.  
(Co-Advisor)

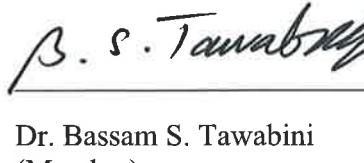
  
Dr. Salam A. Zummo  
Dean of Graduate Studies

Dr. Ronald Loughland  
(Member)

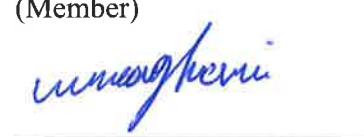
21/10/149

---

Date

  
B. S. Tawabini

Dr. Bassam S. Tawabini  
(Member)

  
Waleed Abdulghani

Dr. Waleed Abdulghani  
(Member)

© MD IQRAM UDDIN AL AMRAN

2019

| This Thesis is dedicated to my wife & only son Jawad, may Allah forgive their sins, have  
Mercy on them and grant them al-Jannat ul Firdaus, Ameen

“My Lord! Bestow on my parents your mercy as they did bring me up when I was small.”

Quran; Surah Al-Isra, Verse 24

|

## **ACKNOWLEDGMENTS**

In the name of Allah, the most gracious, most compassionate, most merciful and all the praises and thanks be to Allah who have given me the opportunity and capability to finish my studies at KFUPM.

I am deeply indebted, and my most sincere appreciation goes to my advisor (Dr Mohammad Qurban) and Co-advisor (Dr Krishnakumar P.K), for their knowledge, patience, encouragement, and guidance they extended to me over the past few years, be it scientifically, personally or academically.

I would like to thank my thesis committee members for their support and sharing their knowledge over the years: Dr Ronald Loughland (EPD-Saudi Aramco), Dr Bassam S. Tawabini and Dr Waleed M. Abdulghani from Geosciences Department.

The help from the center for Environment & Water under Research Institute, KFUPM professors, staff, friends and RI scientist (Dr Manikandan, Dr Shemsi, Dr Mazen, Dr Sajid, Dr Chandra Shekhor, Dr Joydas, Dr Masiur Rahman, Mr Abdul Hakeem, Mr Elias, Mr Premlal, Mr Jeff, Mr Azher, Mr Ibrahim, Mr Modasir, Mr Yaseer, Mr Hamid, Mr Hasan, Mr Kabir, Mr Masum Billah, Mr Usman and many more during my studies here are highly appreciated.

Thanks to my wife for her endless pray, love, and support for keeping my spirits high and encouraging me during this whole journey. Thanks also to the Bangladesh community: their encouragement and support has been most influential and inspiring. |

## TABLE OF CONTENTS

<b>ACKNOWLEDGMENTS .....</b>	<b>V</b>
<b>TABLE OF CONTENTS .....</b>	<b>VI</b>
<b>LIST OF TABLES.....</b>	<b>X</b>
<b>LIST OF FIGURES.....</b>	<b>XI</b>
<b>LIST OF ABBREVIATIONS.....</b>	<b>XIV</b>
<b>ABSTRACT .....</b>	<b>XV</b>
<b>ملخص الرسالة .....</b>	<b>XVII</b>
<b>CHAPTER 1 INTRODUCTION.....</b>	<b>1</b>
1.1 Introduction.....	1
1.2 Problem Statement .....	4
1.3 Significance of Study .....	4
1.4 The Research Objectives.....	5
<b>CHAPTER 2 LITERATURE REVIEW .....</b>	<b>6</b>
2.1 Mangroves.....	6
2.1.1 Species and distribution .....	6
2.1.2 Importance and contribution to ecosystem service .....	6
2.1.3 Losses and threats .....	7
2.2 The Arabian Gulf .....	8
2.2.1 Location .....	8
2.2.2 Climate and environmental Characteristics .....	8

2.2.3	Environmental degradation in Arabian Gulf.....	9
2.2.4	Mangroves in Arabian Gulf .....	10
2.3	Metal Pollution and Toxicity .....	11
2.3.1	Metals.....	11
2.3.2	Metals in Sediment .....	12
2.3.3	Metals in Mangrove Ecosystem.....	13
2.4	Oil Pollution and Toxicity .....	14
2.4.1	Poly Aromatic Hydrocarbons (PAHs) .....	14
2.4.2	PAHs in the Mangrove Sediment .....	15
2.4.3	Vertical profile of PAHs in the mangrove sediments .....	16
2.4.4	Historical PAHs Accumulation pattern in the mangrove sediments .....	17
2.4.5	Weathering of PAHs in the mangrove sediments .....	18
2.4.6	Investigation and sources of PAHs in the mangrove sediments .....	19
2.4.7	PAHs in the mangrove plants .....	21
<b>CHAPTER 3 METHODOLOGY.....</b>	<b>23</b>	
3.1	Study area.....	23
3.2	Collection and processing of sediment sample .....	29
3.3	Collection and preservation of mangrove samples .....	29
3.4	Experimental study .....	31
3.4.1	Contaminants and mangrove plant.....	31
3.4.2	Preparation of sediment .....	31
3.4.3	Plant materials and growing condition .....	33
3.4.4	Preparation of experimental set up .....	33

3.4.5 Experimental sample collection and analysis .....	35
3.5 Laboratory analysis .....	36
3.5.1 Metal analysis from sediment sample.....	36
3.5.2 Metal analysis from plant tissue .....	36
3.5.3 PAH and TPH analysis from sediment sample.....	38
3.5.4 PAH and TPH analysis from plant tissue .....	38
3.6 Quality control .....	40
3.7 Assessment of contamination in sediment sample.....	41
3.8 Assessment of contamination in plant sample .....	44
3.9 Data analysis .....	45
<b>CHAPTER 4 RESULTS AND DISCUSSION.....</b>	<b>46</b>
4.1 Summary of contamination in field sediment samples .....	46
4.2 The relation of metal concentration between sediment and plant tissue .....	48
4.3 Assessment of metal contamination in field sediment sample .....	54
4.4 Trends of metal concentration in plant tissue .....	56
4.5 Trends of Bioaccumulation Factor of metals in plant tissue.....	59
4.6 Trends of Translocation Factor of metals in plant tissue .....	62
4.7 The relation of hydrocarbon concentration between sediment and plant tissue .....	65
4.8 Trends of Hydrocarbon concentration in Plant tissue.....	68
4.9 Trends of Bioaccumulation Factor of hydrocarbon in plant tissue.....	70
4.10 Trends of Translocation Factor of hydrocarbon in plant tissue .....	72
4.11 Assessment of diesel oil contamination in experimental study .....	79
4.11.1 Concentration of hydrocarbon in experimental set up .....	79

4.11.2 Concentration of hydrocarbon in sediment sample .....	82
4.11.3 Hydrocarbon Removal Efficiency of sediment in experimental study .....	85
4.11.4 Kinetic evaluation .....	86
4.11.5 Assessment of biodegradation half times .....	89
4.11.6 Accumulation of hydrocarbon in leaf, bark and root tissue of <i>Avicennia marina</i> .89	
4.11.7 Bioaccumulation of hydrocarbon in plant tissue (leaf, bark and root) .....	96
<b>CHAPTER 5 CONCLUSION AND RECOMMENDATIONS.....</b>	<b>97</b>
5.1 Conclusions.....	97
5.2 Recommendations .....	98
<b>REFERENCES.....</b>	<b>99</b>
<b>APPENDIX .....</b>	<b>119</b>
<b>VITAE .....</b>	<b>127</b>

## LIST OF TABLES

Table 1	Descriptive statistics of selective contaminants concentration in the field sediment sample .....	50
Table 2	Enrichment factor, geoaccumulation index, pollution load index, potential ecological risk for the sediment in four mangrove area .....	58
Table 3	Comparative accounts on heavy metals (mg/kg) in mangrove tissue from study area with available literature on the Arabian Gulf and Red Sea.....	77
Table 4	US Environmental Protection Agency (US-EPA) top priority 16 PAHs & associated relevant information .....	78
Table 5	Global concentrations of PAHs (ng/g) in the mangrove sediments .....	79
Table 6	Physical and chemical characteristics of soil used in experimental study....	82
Table 7	Descriptive statistics of hydrocarbon concentration in experimental study.	84
Table 8	Kinetic expression and half times for bioremediation.....	92
Table 9	Concentrations (ng/g) and concentration factors (CFs) of $\Sigma$ PAHs in plant during 90 days of experiment.....	98
Table 10	Concentrations (mg/kg) and concentration factors (CFs) of TPH in plant during 90 days of experiment.....	99

## LIST OF FIGURES

Figure 1	Map of Arabian Gulf showing Mangroves area.....	24
Figure 2	Map of sample collection in Abu Ali Island.....	25
Figure 3	Map of sample collection in Tarut Bay.....	26
Figure 4	Map of sample collection in Rahima .....	27
Figure 5	Map of sample collection in Gurmah Island.....	28
Figure 6	(a) Sediment sample collection by using simple core sampler, (b) collection of plant sample by using ceramic knife, (c) dismember of plant sample, (d) drying of sample through freeze dryer.....	30
Figure 7	Mangrove ( <i>Avicennia marina</i> ) seedling collection for experimental study from Abu Ali Island, Saudi Arabia.....	31
Figure 8	Sediment collection for experimental study from Abu Ali Island, Saudi Arabia.....	32
Figure 9	(a) Structure of experimental set up, (b) Nursing of mangrove seedling with different concentration of diesel, (c) Flooding seedling daily with saline water, and (d) Setting Rainbird sprinkler timer for irrigating Plant.....	34
Figure 10	(a) Heating digested sample in a hot block, (b) metal analysis using ICP- OES to separate individual trace metals from mixture of compounds, and (c) mercury analysis by Nippon MA 3000 direct combustion analyzer.....	37

Figure 11 a) Saponification performed to separate individual chemical compounds from mixture, (b) Individual PAHs analysis using GC-MS, and (c) TPH analysis using GC-FID.....	40
Figure 12 Correlation between Cr concentrations in sediment vs. plant tissues.....	49
Figure 13 Correlation between Cu concentrations in sediment vs. plant tissues.....	50
Figure 14 Correlation between Ni concentrations in sediment vs. plant tissues.....	51
Figure 15 Correlation between Hg concentrations in sediment vs. plant tissues.....	52
Figure 16 Correlation between Zn concentrations in sediment vs. plant tissues.....	53
Figure 17 Trends of concentrations (mean $\pm$ standard deviation mgkg $^{-1}$ ) of metals (a) Cr, (b) Cu, (c) Ni, (d) Hg and (e) Zn in <i>Avicennia marina</i> growing in different mangrove areas.....	57
Figure 18 Trends of BAF (mean $\pm$ standard deviation mgkg $^{-1}$ ) of metals (a) Cr, (b) Cu, (c) Ni, (d) Hg and (e) Zn in <i>Avicennia marina</i> growing in different mangrove areas.....	60
Figure 19 Trends of TF (mean $\pm$ standard deviation mgkg $^{-1}$ ) of metals (a) Cr, (b) Cu, (c) Ni, (d) Hg and (e) Zn in <i>Avicennia marina</i> rising in different mangrove areas.....	66
Figure 20 Correlation between $\Sigma$ PAH concentrations in sediment vs. plant tissues.....	66
Figure 21 Correlation between TPH concentrations in sediment vs. plant tissues.....	67

Figure 22 Trends of concentrations (mean $\pm$ standard deviation $\text{mg kg}^{-1}$ ) of (a) $\sum\text{PAHs}$ and (b) TPH in <i>Avicennia marina</i> growing in different mangrove areas.....	69
Figure 23 Trends of BAF (mean $\pm$ standard deviation $\text{mg kg}^{-1}$ ) of hydrocarbons (a) $\sum\text{PAHs}$ and (b) TPH in <i>Avicennia marina</i> growing in mangrove areas.....	71
Figure 24 Trends of TF (mean $\pm$ standard deviation $\text{mg kg}^{-1}$ ) of hydrocarbons $\sum\text{PAHs}$ and (b) TPH in <i>Avicennia marina</i> growing in mangrove areas.....	73
Figure 25 Trends of degradation of (a) $\sum\text{PAHs}$ and (b) TPH in sediment with diesel contaminated soil growing for <i>Avicennia marina</i> .....	83
Figure 26 Biodegradation of (a) $\sum\text{PAHs}$ and (b) TPH from diesel contaminated soil as a function of time ( $n = 3$ ).....	85
Figure 27 Biodegradation kinetic evaluation of diesel oil for (a) $\sum\text{PAHs}$ and (b) TPH as a concentration of 75 ml/kg, 50 ml/kg and 25 ml/kg soil.....	87
Figure 28 Trends of accumulation of hydrocarbon (a) $\sum\text{PAHs}$ (b) TPH in leaf of <i>Avicennia marina</i> growing in diesel contaminated soil.....	91
Figure 29 Trends of accumulation of hydrocarbon (a) $\sum\text{PAHs}$ (b) TPH in stem of <i>Avicennia marina</i> growing in diesel contaminated soil.....	92
Figure 30 Trends of accumulation of hydrocarbon (a) $\sum\text{PAHs}$ (b) TPH in root of <i>Avicennia marina</i> growing in diesel contaminated soil.....	93

## **LIST OF ABBREVIATIONS**

ANOVA	: Analysis of Variance
BAF	: Bioaccumulation Factor
BDL	: Below detection limit
CF	: Contamination Factor
EF	: Enrichment Factor
ERL	: Effect Range Low
ERM	: Effect Range Medium
GC-MS	: Gas Chromatography Mass Spectrometry
GC-FID	: Gas Chromatography Flame Ionization Detector
GPS	: Global Positioning System
ICP-OES	: Inductively Coupled Plasma Optical Emission Spectrometer
I <sub>geo</sub>	: Geoaccumulation index
MDL	: Minimum Detection Limit
PAH	: Polycyclic Aromatic Hydrocarbons
PLI	: Pollution load index
PSU	: Practical Salinity Unit
SPP	: Suspended Particulate Phase
TDS	Total Dissolved Solids
TF	: Translocation Factor
TPH	: Total Petroleum Hydrocarbon
USEPA	: United States Environmental Protection Agency
WSF	: Water Soluble Fraction
WHO	: World Health Organization

|

## ABSTRACT

Full Name : [Md Iqram Uddin Al Amran]

Thesis Title : [Sequestration of Contaminants by Mangrove (*Avicennia marina*) Ecosystem from the Gulf Coast of Saudi Arabia]

Major Field : [Environmental Science]

Date of Degree : [April 2019]

Mangrove ecosystems act as natural filters for anthropogenic contaminants and support in keeping a healthy living condition for the marine environment. But contaminants like heavy metals and petroleum hydrocarbons represent a potential risk to the marine ecosystem. Studies on the toxicity of marine pollution on mangrove ecosystem are very limited. This study examines the potential of *Avicennia marina* for absorption, accumulation and partitioning of heavy metals and hydrocarbons in individual plant tissues (i.e., leaves, bark and root/pneumatophore) at four study sites along the Saudi coast of the Arabian Gulf. In addition, a three-month pot experiment was conducted in outdoor environment where seedlings of same plant species were transplanted into diesel contaminated soil at concentrations of 75, 50, and 25 ml diesel kg<sup>-1</sup> dry soil. All samples were analyzed for selected heavy metals using an inductively coupled plasma optical emission spectrometer (ICP-OES) and Hg was analyzed using a Nippon MA 3000 direct combustion mercury analyzer. A gas chromatograph-mass spectrometer (GC-MS) and a gas chromatography flame ionization detection (GC-FID) were used for analyzing aromatic and aliphatic hydrocarbon, respectively. According to the results of this study, the maximum concentrations of Cr, Cu, Ni, Hg and Zn in plant tissue were 12 (root), 102.5 (bark), 9 (leaf), 0.063 (leaf), 5, and 8.6 (root) mgkg<sup>-1</sup>, respectively. The mean values of total polycyclic aromatic hydrocarbons (PAHs) detected in the sediment, leaf, bark and root of mangroves were 44.26, 192.4, 258.4, and 511.7 ngg<sup>-1</sup>, respectively. The average trend of total petroleum hydrocarbon (TPH) concentration followed a descending order: sediment > bark > leaf > root. The observed removal percentages of PAHs and TPH were

92.91% and 96.15%, respectively. The maximum bioaccumulation factor (BAF) and translocation factor (TF) were 120 for root and 7.15 for leaf. The experiment results suggest that the *Avicennia marina* can be considered as an efficient plant species for the sequestration of petroleum hydrocarbons.

ملخص الرسالة

الاسم الكامل: محمد إكرام الدين آل عمران

**عنوان الرسالة:** عزل الملوثات بواسطة النظام البيئي (المانغروف) من ساحل الخليج في المملكة العربية السعودية

التخصص: علوم بيئية

تاريخ الدرجة العلمية: أبريل 2019

يعمل النظام البيئي لغابات المانغروف كمرشحات طبيعية للملوثات البشرية للحفاظ على الظروف المعيشية الصحية للبيئة البحرية. لكن الملوثات مثل المعادن الثقيلة والهيدروكربونات النفطية تمثل خطرًا محتملاً على النظام البيئي البحري. الدراسات على سمية التلوث البحري على النظام البيئي للمنغروف محدودة للغاية. أجريت هذه الدراسة للبحث في إمكانات وقدرة *Avicennia marina* على امتصاص وترامك وتقسيم المعادن الثقيلة والهيدروكربونات في الأنسجة النباتية الفردية (الأوراق واللحاء والجذور / المكورات الرئوية) في أربعة مواقع على طول الساحل السعودي للخليج العربي. بالإضافة إلى ذلك ، أجريت دراسة تجريبية لمدة ثلاثة أشهر في الهواء الطلق حيث تم زرع ستلات من نفس الأنواع النباتية في أوعية تحتوي على تربة ملوثة بالديزل بتركيز 75 و 50 و 25 مل ديزل كجم<sup>-1</sup> تربة جافة . وقد تم استخدام مطياف الانبعاث البصري للبلازما المقترنة بالبحث (ICP-OES) لتحليل جميع العينات الطشف عن بعض المعادن الثقيلة، بينما تم تحليل الزئبق باستخدام محل الزئبق 3000 Nippon MA. استخدم مطياف الكثلة الكروماتوجرافية الغازية (GC-MS) وجهاز كشف تأين لهب الغاز الكروماتوغرافي (GC-FID) لتحليل الهيدروكربونات العطرية والأليفاتية على التوالي. وفقاً لنتائج هذه الدراسة فإن التركيزات الفصوصى من الكروم والنحاس والنikel والزنك في الأنسجة النباتية كانت 12 (الجذر) ، 102.5 (اللحاء) ، 9 (الورقة) ، 0.063 (الورقة) ، 58.6 (الجذر) mgkg<sup>-1</sup> على التوالي. القيم المتوسطة للهيدروكربونات العطرية المتعددة الحلقات (PAHs) المكتشفة في روابض ، أوراق ، لحاء و جذور المنغروف هي 44.26 ، 192.4 ، 258.4 و 511.7 (ngg<sup>-1</sup>) ، على التوالي. بينما يتبع الاتجاه المتوسط للتركيز الكلى لهيدروكربون البترول (TPH) ترتيب تنازلي: الرواسب > اللحاء > جذر > جذر. كما لوحظ أن نسب الإزالة PAHs و TPH كانت 92.91 % و 96.15 % ، على التوالي. كان الحد الأقصى لعامل التراكم الأحيائي (BAF) وعامل الإزاحة (TF) لـ *Avicennia marina* 7.15 و 120 (TF) للأوراق. تشير نتائج التجربة إلى أن يمكن اعتباره من الأنواع النباتية الفعالة لعزل الهيدروكربونات البترولية.



# **CHAPTER 1**

## **INTRODUCTION**

### **1.1 Introduction**

Mangrove locates between terrestrial and aquatic zone and significantly contribute to the preservation of coastal shorelines [1][2][3][4][5] . As a highly prolific biological system, mangroves provides shelter for aquatic and earthy species [6], shields shore areas from natural calamities and sea level rise [7], and acts as a basin of carbon sequestration [8]. On the other hand, mangroves are considered as stressed ecosystem, decreasing globally with an annual rate of 2% due to deforestation, contamination, and adaptation [9][10][10][11][12]. It is considered as one of the most endangered ecosystems in the world because approximately one third of the global share became extinct since the second world war [13]. The levels of pollution have been increasing in the mangrove areas due to municipal and agricultural activities, manufacturing waste handling activities in coastal area, marine transportation and tourism, mining processes, and chemical and oil spills [14] .

Due to the presence along coastal shorelines, the majority of mangrove species are exposed to anthropogenic pressures including coastal pollution [15]. Therefore, dispersion, accretion, and segregation of contaminants in mangrove sediment have been examined in many countries including Australia [16], Brazil [17] [18], China [19][20][21], Hong Kong

[22][23][5][24]; Portugal [25] Puerto Rico [26], French [27], India [28][29][30] , Malaysia [31][32], Saudi Arabia [33], United Kingdom [34], and Bahrain [35]. The degree of contaminant accumulation varies from species to species, region to region, and even within same plant species.

The distribution of mangroves in the Arabian Gulf Coast is limited to few regions including Tarut Bay, Dammam, Gurmah Island, Abu Ali Island, and Khafji. Approximately 204 km<sup>2</sup> of mangrove areas exist in the Kingdom of Saudi Arabia, of which only 4 km<sup>2</sup> (2000 estimate) area is included in the Saudi coast of the Arabian Gulf [36]. *Avicennia marina* is the only mangrove species, grows in the intertidal zones along the eastern coastlines of the Arabian Peninsula [37][35] which is known to be tolerant to different contaminants [3] including petroleum hydrocarbons [38], extreme salinities, and high water temperature [39]. The mangroves of the Arabian Gulf Coast are extremely limited in extent of coverage and the area has been adversely affected during the last couple of decades [40][41][42]. On the other hand, several plantation activities have been developed as a mangrove restoration program in Tarut Bay, Abu Ali, and at Khafji, which were successful in some cases [41].

Recently, there has been quick and large marine expansion in the Arabian Gulf [42] , marked as one of the highest anthropogenically impacted zones in the world [43]. The future consequences of these development activities may significantly damage the mangrove areas, hamper their important ecological services, and stress the dependent habitat of this region. The pollution due to the release of petroleum products can adversely impact the mangrove by reducing the viability of seed, shortening life span, defoliating

leaf, and increasing leaf fall [44][45]. As sediments act as pollutant sinks, the contaminant analyses may reveal the historical differences and the impacts of anthropogenic and naturally occurring activities into the marine ecology [46][47].

Phytoremediation, a biological cleanup mechanism uses trees for removing, destroying or sequestering contaminants from the environment and recently, which has been receiving significant attention in the area of bioremediation [48][49][50][51]. There are several studies which used plants to remove inorganic pollutants, including heavy metals [49], polycyclic aromatic hydrocarbons [52], total petroleum hydrocarbon [53], crude oil [54], bunker fuel oil [55], a mixture of benzene, toluene and xylene (BTX) [56], and polychlorinated biphenyls (PCBs) [57]. The two major sources of pollution in mangrove swamps are toxic metals and petroleum products [58]. Mangrove swamps have intrinsic physical, biochemical, and natural adsorption characteristic which is active for wastewater-borne contaminants [59][5]. Kumar et al. [61] found the highest concentrations of pollutants (i.e., Pb and Zn) in the root of *Avicennia marina* compared to other body parts.

However, there is possibly no study investigated and reported the level of contaminants in the *Avicennia marina* available in the Saudi Coast of Arabian Gulf. Moreover, the contaminant sequestering levels of *Avicennia marina* in this region is also unknown. Hence, this study was carried out to (i) investigate the levels of selected contaminants in the mangrove ecosystems and (ii) examine the sequestration efficiency of *Avicennia marina* of this region under controlled laboratory conditions.

## **1.2 Problem Statement**

Although a few studies were conducted focusing on the levels of contaminants in the mangrove ecosystem of the Western Arabian Gulf coast, the role of mangrove as a sink for contaminants is not possibly studied significantly for the Saudi Coastline of the Arabian Gulf. Removal of the toxic contaminants from the marine environment is an important issue. Though mangroves can absorb contaminants, it is important to investigate the reaction mechanism of mangroves related to metallic toxins, and to what degree it can protect environment from contaminants. In order to the link between mangroves and pollutants, a few questions should be addressed, including: How does a plant react to contaminants in natural conditions? Are contaminants absorbed in mangroves and if so, where? Can mangroves be utilized for monitoring contaminants in its surroundings?

## **1.3 Significance of the study**

The observed ongoing development activities along the Saudi coast of the Arabian Gulf is expected to continue and could impact the mangrove ecosystem. Therefore, the analysis of the current status of contaminants in the mangrove swamps existing under harsh environment and the prospect of bioaccumulation by the mangrove are important for investigating the present and future challenges and opportunities pertinent to the mangrove ecosystem. This study focuses on the bioaccumulation and translocation efficiency of *Avicennia marina* exists along the Saudi coast of the Arabian Gulf for the removal of heavy metals and hydrocarbons. The importance of this study is to fill the gaps in the knowledge

pertinent to the survival of *Avicennia marina* under harsh environment to assess its ecological services such as bioremediation and contaminant accumulation and to serve as a basis to improve natural ecosystems. Hence, this study will depict the status of contaminants in the naturally growing mangrove swamps along the Saudi coast of the Arabian Gulf and the performance of using mangrove in contaminants sequestration. The outcomes of this study will be beneficial for different relevant agencies including Ministry of Environment, Water and Agriculture, the National Center for Wildlife, and Saudi Aramco.

## **1.4 The Research Objectives**

The main objective of this study is to assess the role of mangrove (*Avicennia marina*) existing along the Arabian Gulf coast of Saudi Arabia in the sequestration of selected contaminants.

The Specific Objectives of my study are given below:

1. To study and compare the level of selected trace metals and hydrocarbons in sediment samples at mangrove and non-mangrove areas: observations from field investigation;
2. To study the accumulation of selected trace metals and hydrocarbons in different part of mangrove plants: observations from field investigation;
3. To study the accumulation of petroleum hydrocarbon from diesel contaminated soil by *Avicennia marina* based on an experimental study

## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.1 Mangroves**

##### **2.1.1 Species and Distribution**

Mangrove forests are found as an unique group of ecosystems along the intertidal regions of tropical and sub-tropical regions [62][63][64][65][1][3][4][5]. Mangrove flora consists of around 39 genera in 26 families [66][67]. *Avicennia spp.* is a widespread salt secreting genus of mangrove ecosystems present in tropical and subtropical regions [68]. Even though the mangrove coverage area varies in different published literatures, the distribution of the mangrove forests cover 15.2 million hectares dispersed in 123 countries of the world; Asia possesses the highest proportion of mangrove coverage among other major mangrove zones [69][70], covering approximately 75% of world coastlines [71][64]. The global coverage of mangrove ecosystems was estimated as 200,000 km<sup>2</sup> in 1997 [37] , 152,308 km<sup>2</sup> in 2010 [72], and 137,760 km<sup>2</sup> in 2011 [64].

##### **2.1.2 Importance and contribution to ecosystem service**

Mangroves are recognized as an economic and biological resources with a number of highly beneficial ecosystem services [73][74][2][75][76] . With a productivity of 2,500 mg

$\text{C m}^{-2}$  per day the mangrove ecosystem is considered as one of the most productive ecosystems of the world [77][78]. Mangrove plants have developed some special adaptation techniques such as air breathing roots (e.g., pneumatophores), salt excretion glands, prop roots and viviparous germinations of seeds [79]. The environmental and ecological services rendered by the mangrove cannot be underestimated. Mangrove swamps serve as highly productive habitat for diverse marine and terrestrial flora and fauna by providing a good sources of food, shelter and nursery areas, which represent relatively complex food webs with intricate relationships with neighboring habitats [6][80]. It also involved in regulating coastal zones from protecting natural calamities such as floods, cyclones, hurricanes and tsunamis [10][81][82][83][84], acting as an intense carbon sink [11][53][85][86], and provisioning timber, fuelwood and charcoal for human wellbeing [87].

### **2.1.3 Losses and threats**

Due to their location in the intertidal zone, mangrove forests are characterized by a high heterogeneity in soil and water salinity [68]. The reduction of global mangrove coverage is approximately 30% since 1980 mainly due to rapid costal urbanization [88], and one-third of the global mangrove area has been lost since the World War II [89]. This decline continues at an annual rate of about 2% [9][10][11]. Currently, less than 10% of the mangrove areas around the world are considered as protected areas [90][91]. Many national and international agencies and/or local governments have adopted management and conservation policies to protect these ecosystems [92] [93]. Although various ecosystems have been recognized, mangroves are one of the most threatened tropical environments [10][65][85] due to pollution, deforestation, fragmentation, and sea-level rise [64][87].

Some recent studies suggested that mangroves have been suffering from organic and inorganic contaminant including poly aromatic hydrocarbons (PAHs) [65][94]. The main drivers underlying these threats are increasing populations and development in coastal areas, aquaculture, shrimp culture and climate change, runoff from urban, and industrial and agricultural areas [95][63][96][97][90][87][93]

## **2.2 The Arabian Gulf**

### **2.2.1 Location**

The Saudi Arabian Gulf coastline extends about 400 km along the eastern edge of Arabia from approximately 25°N to 28°N latitude. The Gulf is shallow, with depths rarely exceeding 100 m and averaging around 35 m [98][99][43][100]. Due to its enclosed and shallow nature the Gulf is particularly subject to the accumulation of anthropogenic contaminants [101].

### **2.2.2 Climate and environmental characteristics**

High temperature and instable saltines make the marine life of Arabian Gulf more stressful than other areas. Salinity is considered one of the major significant ecological features regulating and restricting the abundance and dispersal of aquatic life in the Gulf [102]. The seawater characteristics of the Arabian Gulf are determined by the shallow depths, extreme air temperatures, high evaporation rates and restricted circulation [98]. The variety of living organism in the Gulf is normally low in compare to same species living under parallel situations to another place [102] . High evaporation rate, shortage of significant waterflow, and constrained amalgamation with the Bay of India increase the salinity level in the Western Arabian Gulf around 42% seaward and more than 60% in some confined

shallow seashore zones [103]. Throughout the most recent 50 years, climate change impacts have raised sea surface temperature up to  $0.2^0\text{c}$  for each decade and this ultimately reached to around  $0.45^0\text{c}$  every decade over the most recent 20 years [104]. Generally, the number of species decreases in the new ecological conditions with high temperatures [105].

### **2.2.3 Environmental degradation in the Arabian Gulf**

Seashore locations of Arabian Gulf are the superior part for infrastructure, recreational and financial development and that is the key focus for investor [106]. Development along the Arabian Gulf have increased at an alarming rate in the last couple of years to accommodate mega projects with artificial archipelago, seaside towns, harbors and marinas [107]. Ecological space reduction because of severe reclamation and digging exercises in marine areas is the major risk for both biodiversity and ecosystem degradation [108]. It is assessed that over 40% of the shorelines have already been industrialized in the Arabian Gulf [109]. New built up land through reclamation could also restrict the normal water flow and ultimately modify the salinity [110]. The marine species including coral reefs, seabirds etc. which need supports to survive in mudflats are decreased in number due to these development work, sediment runoff and high salinity [111]. The number of biodiversity is also decreased in the location adjacent to distillation plant because of brine waste which relate to high temperature, saltiness and a range of organic and inorganic contaminants [106]. Substantial amounts of residential effluents from sewage are released to beach front and waterbody of the Arabian Gulf [99] which contain harmful germs and heavy metals [112].

#### **2.2.4 Mangroves in Arabian Gulf**

In the Arabian Gulf, mangrove habitats play essential role in the sustenance of biological diversity to improve the marine efficiency [80]. The distribution of mangroves in Arabian Gulf coast are limited to only four regions including Tarut Bay, Dammam, Gurmah Island, Abu Ali Island, and Khafji. It is estimated that approximately 204 km<sup>2</sup> of mangroves in the Kingdom of Saudi Arabia, of which only around 4 km<sup>2</sup> (2000 estimate) exists in the Saudi coast of the Arabian Gulf [41] and overall 125-130 km<sup>2</sup> in whole Arabian gulf [39]. Historical accounts suggest that once the whole coast of the western Arabian Gulf was covered with *Avicennia* and *Rhizophora*, species of mangroves [113]. But the *Rhizophora* species of mangroves have already been extinct from these areas due to coastal development and industrial activities [114].

At present, the only dominant mangrove species in the Arabian Gulf coastlines is the *Avicennia marina* [36]. This is due to their special adaptation characteristics such as morphological structure which allow them to withstand the hyper environment of Arabian Gulf [115]. *Avicennia marina* has a complex root system, including four types of roots, i.e., cable roots, aerial roots (or pneumatophores), fine nutritive roots (or feeding roots) and anchor roots [116]. Mangrove (*Avicennia marina*) is the only mangrove species, grows in the intertidal zones along the eastern coastlines of the Arabian Peninsula [117][35] which is known to be tolerant to oil pollution [38], extreme salinities and water temperature [39]. There are two naturally occurring mangrove (a pure stand of *A vicennia marina*) plantations on the Saudi coast of the Arabian Gulf; Tarut Bay and Gurmah Island [113].

## **2.3 Metals Pollution and Toxicity**

### **2.3.1 Metals**

Metal contamination is globally recognized as an anthropogenic key pollutant for marine pollution [118][43][119][120] due to their toxicity, persistence, and bioaccumulation problems [100][121][122]. Heavy metals constitute an ill-defined group of inorganic chemical hazards, and the most commonly found metals at contaminated sites include lead (Pb), iron (Fe), aluminium (Al), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg), and nickel (Ni) [123]. Heavy metals cannot be degraded or destroyed, but the chemical form and their solubility in water can be changed which will affect their availability to plants [124]. Exact sources of trace metals in environmental samples are usually difficult to identify [65].

Heavy metals presence in earth's crust occurs naturally and can be introduced through anthropogenic activities [125]. The major sources responsible for the accumulation of heavy metals in marine environment include industry, waste water, agricultural runoff, petroleum, sewage, and municipal discharge [126][127][125] . When heavy metals enter the marine sediment, it can respond with water properties or slow down to the bottom and act in response with the bottom marine sediments. The evaluation of marine sediments with respect to the levels of contaminant content is challenging due to the association of multiple phenomena. As sediments are pollutant sinks, the contaminant analysis may reveal the historical differences and impacts of manmade and natural contributions into the marine ecology [128][129][46][47] .

### **2.3.2 Metals in Sediment**

Sediment is regarded as the ultimate sinks of heavy metals [130][5]. Besides mangrove ecosystem, sediments serve as a contaminant transport by adsorbing and holding trace metals [131][132][133][134]. The noxiousness and the movement of heavy metals in sediments depend on concentrations, chemical shape, binding state, metal properties, environmental variables, and physical and chemical characteristics of soil [135]. Bayen 2012 [65] described the global pollution status of mangrove ecosystems focusing on heavy metals and organic pollutions. Having situated adjacent to coastal shorelines, majority of the mangrove species have been exposed to anthropogenic pressure including coastal pollution [15]. Therefore, dispersion, accretion, and segregating of contaminants in mangrove sediment have been examined in many countries of the world including Australia [16], Brazil [17][18], China [19][136][1], Hong Kong [137] [138][24], Portugal [25] Puerto Rico [26], French [27], India [28] [60][30], Malaysia [31][32], Saudi Arabia [139], United Kingdom [34], and Bahrain [35].

In Arabian Gulf, the levels of metals in sediment is used as a monitoring tool to analyze marine environmental risk and the pollution in sediment was investigated in several times including 1991 oil spill from the near shore area between Kuwait and Qatar [140], land based industrial pollution in Bahrain [141], pollution from desalination effluents [142][143] etc.

### **2.3.3 Metals in Mangrove Ecosystem**

Mangrove ecosystems serve as physical and biogeochemical barriers to contaminant transport [144]. Chemical contaminants retained in mangrove ecosystems partition between sediment, suspended particulate matter, and biota [90]. Eventually, mangrove ecosystem may efficiently retain metals and prevent movement of metals to adjacent aquatic systems [73]. Therefore, metallic enrichment of mangrove environments should not be regarded alone as a proof of the proximity of a source, but the efficiency of the ecosystem to retain metals should also be taken into consideration [65].

Mangrove plants adapt different strategies to survive in high-salt and anoxic conditions and in high trace metal concentrations [145][5]. The concentrations of some of the heavy metal in plant tissues are influenced by metabolic requirements of essential micronutrients such as Cu and Zn [146]. The geochemical behaviors of metals, their spatio-temporal variability, and the sediment composition can influence the distribution of trace metals [22][147][148][18].

Studies have found that metals such as Cu, Zn, Pb, Cd, Cr, Mn, and Hg accumulate mainly in root tissue, rather than in foliage, in numerous mangrove species, including *A. marina* [22] [131][1] . Macfarlane et al. 2007[63] underlines that mangroves metals accumulation depends on metal ion, metal concentration, field conditions and/or experimental settlement. Accumulation of trace metals in mangroves mostly take place in the root zone and turnover of metals is limited to aerial parts of the plant, i.e., leaves, bark and flowers [62][63] [149] which is also similar for *Avicennia marina* [150][3]. Studies on the variety of mangrove

body part such as leaves [113][22][151], roots [152] bark, flower, fruits, twigs [153] [154] pneumatophore [155] and field and laboratory experiments showed that the trapping of heavy metals in mangrove ecosystems was a very efficient and fast phenomenon [73][156].

Heavy metals contamination in coastal and marine environments of the Arabian Gulf is becoming a threat to both the naturally stressed marine ecosystems and humans that rely on marine resources for food, industry and recreation [157]. In the Arabian Gulf region, the typical sources of metal contamination are represented by oil and gas industry, offshore platforms, housing projects, industrial cities, oil terminals, ships, stainless steel, and cement industries, and power stations [158] [120]. Mangrove ecosystem suffers from direct impacts of anthropogenic pollutants like heavy metals and organic contaminants [159] which are accumulating via the food chain to hazardous levels [160]. Today only a few hundred mangrove trees of *Avicennia* survive on the Saudi coast of the Arabian Gulf and these are threatened due to land reclamation and pollution [161]. Many studies related to metal contaminants in the Arabian Gulf are available in the literatures [140][141] [162].

## **2.4 Oil Pollution and Toxicity**

### **2.4.1 Poly Aromatic Hydrocarbon (PAH)**

Poly aromatic hydrocarbons (PAHs), a group of hydrophobic compounds consist with at least two benzene rings. These compound have especial importance in the field of ecotoxicology because of their carcinogenic, long lasting, mutagenic and toxic characteristics [163][164][165][23]. PAHs are considered as global contaminants, because

when released into the atmosphere these are transported over long distances [166] . The US environmental protection agency (USEPA) has classified PAH as one of the six priority pollutants and listed 16 most priority PAHs relative to carcinogenic and mutagenic potentials (Table 4). Several anthropogenic processes including oil spills, ship traffic and atmospheric precipitation of combustion derived particle are reported to be the major sources of PAHs in the marine and coastal environment [167]. Coastal wetlands such as mangrove system has been reported as one of the major accumulators of PAHs owing to their high productivity, rich in organic matter and abundance detritus materials [168].

#### **2.4.2 PAHs in the Mangrove Sediment**

Mangrove ecosystem is reported to be the most vulnerable tropical habitat due to the marine pollution caused by petroleum hydrocarbons [169] . It is well known that PAHs are the major composition of the oil. The occurrence, level, and fate of organic including PAHs in the mangrove systems have been reported in some recent literatures [90][65] . The striking features for the mangrove sediments include the low energy environment, anoxic condition of the epiploic sediments (1-3 cm from surface), and high proportion of organic carbon and sulfide. These special features of mangrove sediments favor the sink of accumulation and contamination by PAHs. Sediments in the mangrove systems are fine grained and therefore, have longer period of residence time; these characteristic favors the adsorption of high amount of PAHs [29] . Generally, the higher proportion of HMW (4 or more aromatic rings) PAHs than that of LMW (2-3 aromatic rings) PAHs is the characteristic of the mangrove sediments [170]. Because LMW PAHs can easily be degraded by physical (solubilization and volatilization) process during sediment

transportation [171]. Another possible reason for the relatively less amount of LMW PAHs is that microbial degradation most preferably favors the LMW PAHs. The high amount of organic carbon resulted mainly from the mangrove forest litter component [172] can elevate microbial activity in the mangrove sediments.

The determination of the concentration of PAHs in the mangrove sediments have been reported from many mangrove systems including China [173], Brazil [174][175], India [176][177][178], Indonesia [179] , Nigeria [180] and Malaysia [170] (Table 2). Most of these studies only determined 16 priority PAHs [181][180][178]. However, only few studies documented their alkylated homologs [175]. Relatively less is known for the seasonal profile of PAHs in the mangrove sediments [182][183][184]. Many studies focused on the spatial variation of PAHs in the surface sediments of mangrove systems [185][94][20][179][186][170]. These studies reported that number of factors associated with the spatial distribution of PAHs in the surficial sediments of mangrove include i) sedimentation rate and textural composition characteristics, ii) the input rate and source of the PAHs in the individual sediment core, iii) depositional pattern of sediment, and iv) abiotic and microbial process in the sediments [187][188]. According to the classification proposed by Baumard (1998)[189] , PAHs pollution level for most of the reported mangrove sediments falls under low to moderate category; Table 5).

#### **2.4.3 Vertical profile of PAHs in the mangrove sediment**

Reports are available for the vertical profile of PAHs in the mangrove sediments [190][174][191][192][193]. In the mangrove sediments vertical distribution of individual

PAHs generally do not exhibit any consistent trend like some other organic contaminants [176]. For example, in the mangrove systems of Sundarbans, India the level of ΣPAH was reported to be minimum (132 ng/g) in the depth of 28-30 cm, whereas the maximum concentration (2938 ng/g) was found at the 12-16 cm depth range. On the other hand, Cavalcante (2009)[192] reported that ΣPAH level indicated decreasing trend towards deeper layer in the sediment cores from the Fortaleza, Brazilian Mangroves. By comparison, Li (2009)[191] presented the increasing trend of PAHs with sediment depth from the mangrove systems of Hong Kong, South China. The reported values for the concentrations of PAHs were 1300 ng/g in the surface layer (0-2 cm) and 5000 ng/g in the deeper layer (10-15 cm). Ranjan (2012)[29] suggested that in the mangrove sediments distribution of the depth profile of the PAHs in the mangrove sediments may be influenced by some of the important factors such as 1) sediment granulometry that is regulated by the hydrological conditions of the wetlands as well as the seasonal pattern of fluctuation of the flocculation, and 2) in-situ bacterial degradation and metabolisms of benthic communities.

#### **2.4.4 Historical PAHs accumulation pattern in the mangrove sediments**

Sediments are the chief reservoir for the PAHs [194] and they are considered as one of the important compartment that may provide information related to historical pollution pattern [195][196] . ‘Fingerprints’ of PAHs in dated sediment cores from the mangrove systems provides useful information related to the sources and rate of deposition of PAHs [29] . Only few reports documented the historical accumulation pattern of PAHs in the mangrove systems. On Pichavaram mangroves in the southeastern India, investigated 16 PAH in the

dated sediment cores in order to trace their pattern of depositional flux via  $^{210}\text{Pb}$  dating. The rate of PAH flux in mangrove sediments was  $0.064 \pm 0.031 \mu\text{g}/\text{cm}^2/\text{yr}$ . The authors reported that before 1900s there was low PAH flux, from then onwards it was synchronously increasing and the greatest increase of PAHs flux was reported during the last 4 decades (i.e., after 1970s) [29]. The synchronous increasing of PAH in the sediment of the last four decades (i.e., after 1970s) was clearly indicating the recent pollution discharges include oil and grease from a variety of industries. Besides, the organic and inorganic contaminants from sea going vessels, fishing boats, combustion of biomass and aquaculture practice were also suggested for the additional pollution load in the study site. On Mai Po mangroves in Hong Kong, it was also investigated the historical depositional record of PAH by  $^{210}\text{Pb}$  isotope analysis; and relatively consistent pattern of PAH was documented for the past 41 years [197].

#### **2.4.5 Weathering of PAHs in the mangrove sediments**

Weathering of PAH is relatively less studied for the mangrove sediments. On Guanabara Bay, Rio de Janeiro, Brazil, the investigation of the weathering of oil over 4 years after an oil spill on January 17, 2000. The authors applied hopanes and steranes (molecular markers) in order to detect the presence of oil in the mangrove sediments. Their study demonstrated that one of the sampling sites have 70% weathering of the PAHs in the surface sediments during 4 yrs sampling time. The authors attributed this finding to the tidal regime, degradation by biological and physical agents, and bioturbation. The vertical migration of oil was also suggested to explain the high reduction of the PAHs in the surficial sediments [198]. It concluded that high percentage of coarse sediment and

activities of benthic communities may influence the vertical migration of oil in the mangrove sediments [192]. The degradation pattern of PAHs were investigated after 30 days of an oil spill in the Pearl estuarine mangroves [199]. The authors reported that there was a reduction in the level of PAH from  $2135 \text{ ng g}^{-1}$  (30 days after oil spill) to  $1196 \text{ ng g}^{-1}$  (120 days after oil spill) for the most contaminated sites. The authors explain the rapid weathering of PAHs in the sediments by tidal flushing in the mangrove systems and evaporation of the oil. During tidal cycles LMW and water-soluble PAH generally drained away from these ecosystems. What is more, the authors emphasized that the high weathering process must not due to microbial degradation.

#### **2.4.6 Investigation and sources of PAHs in the mangrove sediments**

Two main pathways are considered as the sources for PAH in the mangrove sediments; i) petrogenic; discharge of petro chemicals (e.g, oil spills) to the environments and ii) pyrogenic; this process include combustion of petroleum product and biomass burning. PAH from petrogenic sources are characterized with high proportion of LMW PAHs and alkylated PAHs, however the PAHs from pyrogenic source are characterized with low proportion of HMW PAHs [170]. Diagnostic ratio (the ratio of the particular PAH species in ambient samples) and isomer ratio have long been used to determine the source of the PAH [200][201][202] . It have been documented that diagnostic ratios are one of the most efficient method in order to investigate the pollution emission sources for PAHs [203]. The common PAH diagnostic ratios used in the literatures together with their typically reported values are presented in the review literature of [194].

The petrogenic source as the major source of PAHs in the mangrove sediments from Persian Gulf, Iran by several diagnostic ratios such as Ant/(Ant+Phe), Flu/(Flu+Pyr), BaA/(BaA+Chr) ,BaA/Chr, Chr/BaA, Methyl-phenanthrene /Phe and Phe/Ant [204]. Sediment PAHs were of pyrogenic origin in the mangrove systems of Malaysia (Tahir et al. 2011), North of Persian Gulf [184] and Deep Bay in China [185]. The identified biomass burning as the sources of PAHs in the mangrove sediments from Igbanko in Nigeria affected by forest fire. The ratio Fl/Py and  $\Sigma$  3-6 rings PAH/  $\Sigma$  5-alkylated PAH series were applied to assess the sources of PAHs in the mangrove sediments 10 months after oil spill in mangrove forests in Guanabara Bay, Brazil. The results showed clear evidence that mangrove sediments were affected by petrogenic source of pollution [180].

The author investigated several diagnostic ratios for assessing pyrogenic and petrogenic origins of PAHs in the mangrove systems of Malaysia. The diagnostic ratios such as Ant/(Ant+Phe), Flt/(Flt+Pyr), B[a]A/ (B[a]A+ Chry) and I[c,d]P/(I[c,d]P+B[g,h,i]P) indicate that pyrogenic source of PAHs, whereas MP/P and (3-MP + 2-MP)/(4/9-MP/1-MP) indicated the petrogenic origin of PAHs. The authors concluded that pyrogenic sources had major and petrogenic sources had relatively less contribution to the sedimentary PAHs of the studied mangrove systems [170]. The conclusion was drawn on the basis of the strong positive correlation ( $R^2=0.92$ ;  $p<0.05$ ) between total PAHs and combustion derived PAHs (fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzofluoranthenes, benzo[e]pyrene, benzo[a] pyrene, indeno[1,2,3-cd] pyrene and benzo[g,h,i]perylene), suggesting the major contribution of pyrogenic PAHs . However, weak correlations between total methylphenanthrenes and total PAHs ( $R^2=0.09$ ;  $p<0.05$ ) suggesting the less contribution of petrogenic PAHs. The application of BgP/IP and BaA/

$\Sigma 228$  ratios to the sediments from Malaysian mangrove systems showed that these PAHs were emitted during combustion of gasoline, diesel, grass wood or coal [181].

The application of LMW/HMW confirm the pyrolytic and petrogenic mixed origin of PAHs in the mangrove systems of the Sundarbans, India [193]. Calcavantae [205] studied the sediment PAHs in a urban mangroves of Fortaleza, Brazil. Based on Phen/Ant, Flr/Pyr, the authors concluded that over 90% of the sediments layers have pyrolytic sources of PAHs. The suggested sources of the PAHs include combustion of gasoline as well as oil, and combustion of biomass especially charcoal and wood.

Essien [183]investigated the origin of PAHs mangrove systems of Iko river estuary, in the Nigeria. They applied three diagnostic ratios- LMW/HMW, Phen/Anth, Flt/Pyr, indicated the predominance of combustion derived PAHs. However, diagnostic ratio such as Naph/Phen indicated the presence of fresh and unweathered petroleum. Doubt and difficulty in the explanation of the diagnostic ratios occurred if two or more ratios are considered to investigate the possible sources [206].

#### **2.4.7 PAHs in the mangrove plants**

For plants major proportion of PAHs can be accumulated by leaf [207]. The major pathway for the accumulation of PAHs is from the atmosphere to the epidermis of the leaf, although very less is known for the pattern of PAHs profile in mangrove plants [208][209], virtually no information available related to the differences of the accumulation pattern of PAHs profile among mangrove plant species.

Ke [199] documented the level of PAHs in the oil coated mangrove plant (*Aegiceras corniculatum*) leaves of from oil spill contaminated sites of Yi O mangrove swamp, Hong

Kong. 30 days after the oil spill the level of PAHs in the leave sample was  $16698 \pm 2135$  and after 126 days the reported level was  $24888 \pm 1196$ . Li [209] investigated the level of PAHs in the leaves and roots of the mangrove plant species (*Kandelia obovata*, *Aegiceras corniculatum*, *Bruguiera gymnorhiza* and *Avicennia marina*) from Shenzhen, China. The authors reported that the range for the values of  $\Sigma$  PAHs was 1389–7925 ng/g and 440–6882 for leaf and root, respectively. Bioconcentration factors relative to sediment (BCFs) were applied in order to investigate bioaccumulation pattern. It was found that BCFs in leaves (1.51) was higher than that of roots (1.03) because of the low concentrations of PAH in the roots. The BCFs of LMW PAHs was higher (2.71) than that of HMW PAHs (1.10) because of high bio-accessibility of LMW PAHs by mangrove plants. Further, concentrations of PAHs in the mangrove roots of the three-plant species (*Kandelia candel*, *Avicennia marina* and *Bruguiera gymnorhiza*) were investigated by Lu [208] from Jiulong River Estuary, Fujian, and China. The range of the total PAHs concentrations was 30.83 to 62.73 ng/g. It has been suggested that several factors determine the concentration of PAHs in the plants including species variations, initial PAHs content in the sediment and microbial activities in the sediments. In general, higher concentrations of PAHs is found in the plant tissues than that reported for sediments, besides, leaves always have higher concentrations than root [210].

## **CHAPTER 3**

### **METHODOLOGY**

#### **3.1 Study area**

In the Arabian Gulf, mangrove habitats play essential role in the sustenance of biological diversity to improve the marine efficiency [80]. The distribution of mangroves in the Arabian Gulf coast (Fig. 1) is limited to only four regions including: Abu Ali Island (Fig. 2), Tarut Bay- Dammam (Fig. 3), Rahima (Fig. 4), and Gurmah Island (Fig. 5). The mangrove area in the Kingdom of Saudi Arabia is approximately 204 km<sup>2</sup> and of around 4 km<sup>2</sup> (2000 estimate) of this area exists in the Saudi coast of the Arabian Gulf [41] . Historical information suggest that once the whole coast of the Western Arabian Gulf was covered with *Avicennia* and *Rhizophora*, species of mangroves [113]. But the mangrove forests are currently almost extinct in the Saudi Coast of the Arabian Gulf [100].

The only dominant mangrove species in the Arabian Gulf coastlines is the *Avicennia marina* [36]. This is due to its special adaptation characteristic such as morphological structure which allow to withstand the hyper environment of the Arabian Gulf [115]. There are two naturally occurring mangrove area on the Saudi coast of the Arabian Gulf includes Tarut Bay and Gurmah Island [113].

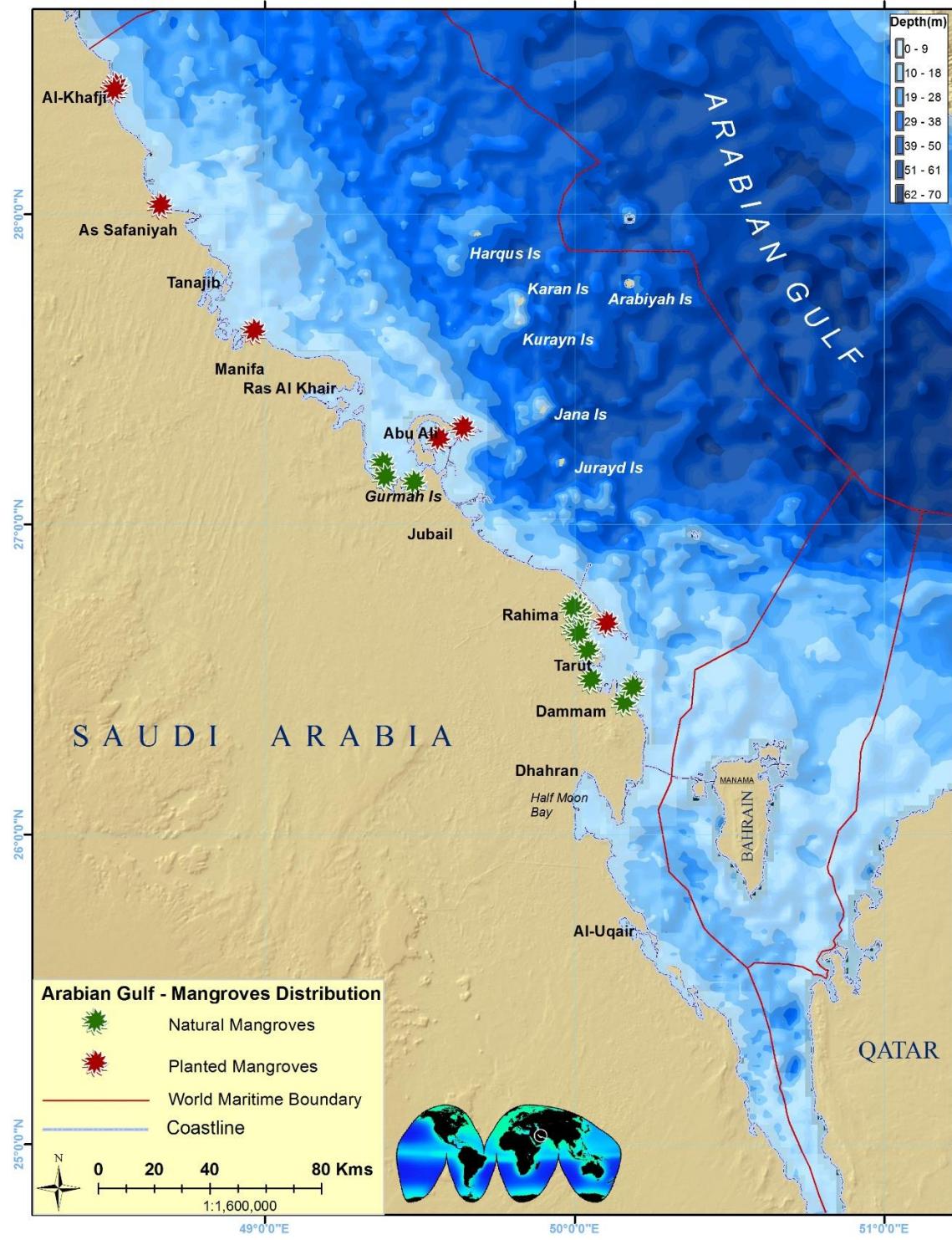


Figure 1 Map of Arabian Gulf showing Mangroves area

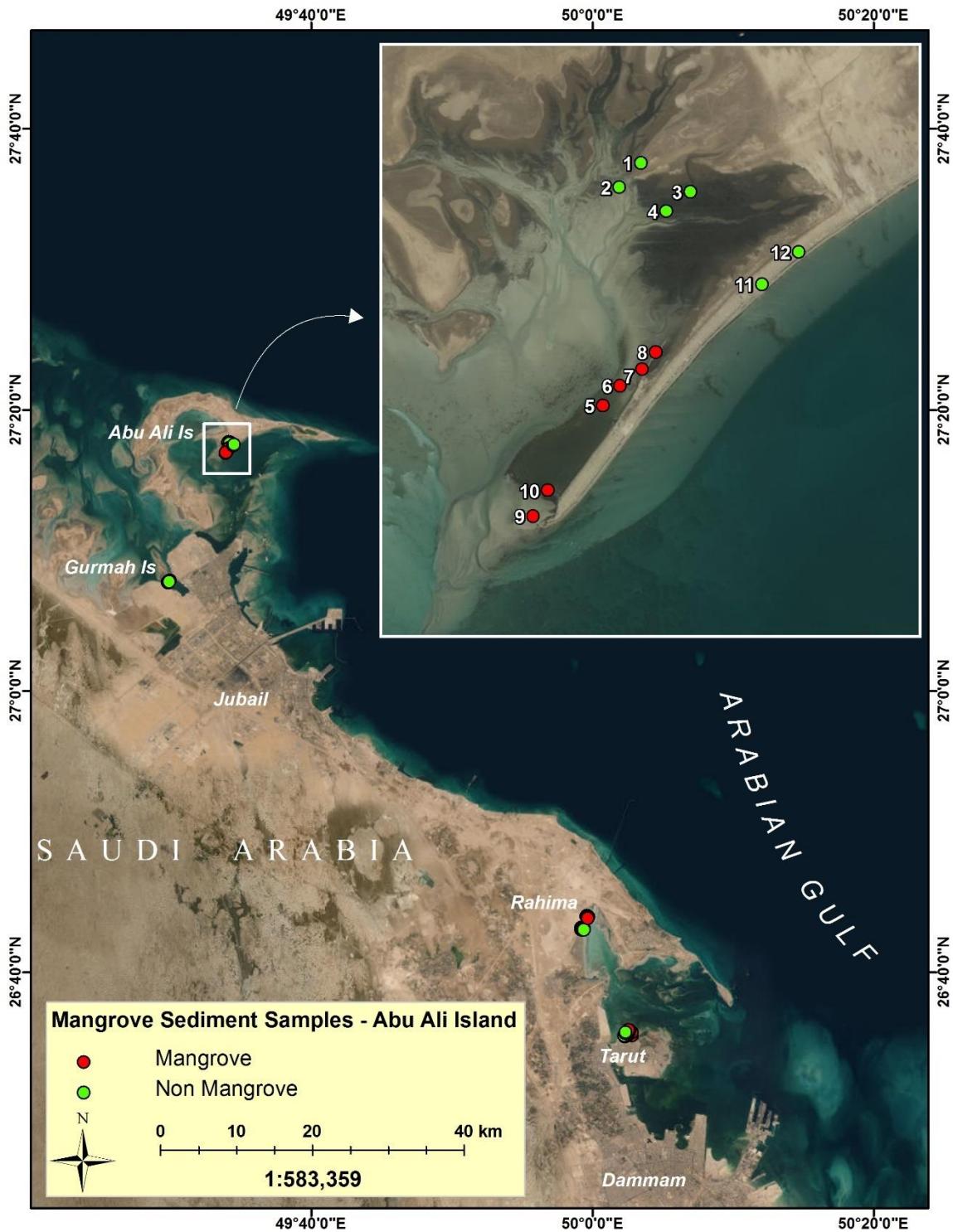


Figure 2 Map of sample location in Abu Ali island



Figure 3 Map of sample location in Tarut Bay



Figure 4 Map of sample location in Rahima

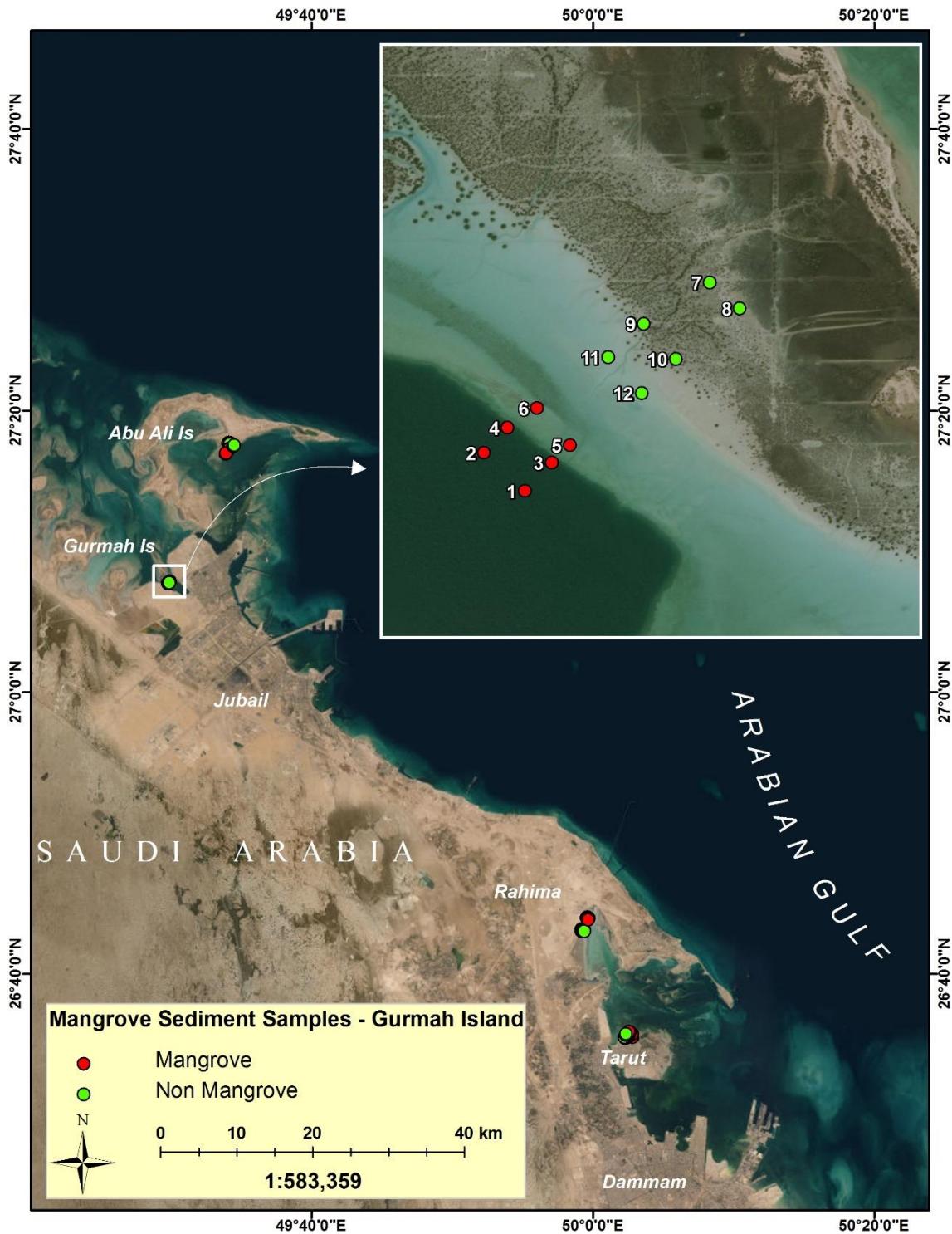


Figure 5 Map of sample location in Gurmah Island

### **3.2 Collection and processing of sediment sample**

Field surveys were conducted between April to May 2018 to determine the ecological status of the mangrove vegetation. Two sediment samples were collected from each selected station in the both mangrove and non-mangrove areas categorized by subtidal, tidal, and super tidal zones. A portable core sampler of 30 cm length with a cover lid was used to collect the sediment samples at three heights: top (0-10 cm), middle (11-20 cm), and bottom (21- 30 cm) (Fig. 6). A handheld Global Positioning System (GPS) Garmin® V was used for determining the geographical locations of the sample stations. Sediment samples were prepared for both metals and hydrocarbons analyses through air-drying, sieving, and digestion following the EPA Method 3050B.

### **3.3 Collection and preservation of mangrove sample**

The plant organs of *Avicennia marina* were collected from randomly selected trees from supra tidal, inter tidal, and sub tidal zones. The leaf, pneumatophore and bark from each plant sample were collected without uprooting the plant from the location close to the sediment sampling station (Fig. 6). The Sample organs were collected from the trees of similar health conditions which were taller than 1m with a girth greater than 2 cm. Soon after sampling, plant samples were washed in clean seawater, wrapped in polythene zip-locked bags and transported to the laboratory using ice chests. The collected samples were stored in a freezer to maintain the temperature at -20°C for further analysis. All samples were minced, homogenized, and freeze-dried. The freeze-dried samples were crushed to make a powder and homogenized before analysis.



Figure 6 (a) Sediment sample collection by using simple core sampler from mangrove area, (b) Collection of plant sample by using ceramic knife (c) Dismember of plant sample (d) drying of sample through freeze dryer

## **3.4 Experimental Study**

### **3.4.1 Contaminants and mangrove plant**

In this study, diesel fuel was purchased from local fuel filling station in Dhahran, Saudi Arabia. Local mangrove seedling of *Avicennia marina* plant was obtained from the in-situ nursery in Abu Ali Island which is maintained by the Ministry of Environment, Water and Agriculture (Fig. 7). The age of the seedlings were 2 years with mature shape, size, color, and average height of  $50 \pm 2$  cm. These seedlings were acclimatized for 15 days before treating with diesel fuel.



Figure 7 Mangrove (*Avicennia marina*) seedling collection for experimental study from Abu Ali Island, Saudi Arabia

### **3.4.2 Preparation of sediment**

The sediment used to grow the seedling in the pot experiment was collected randomly from the Abu Ali island, Saudi Arabia (Fig. 8). It was air-dried for 15 days and sieved through a 4 mm mesh sieve to eliminate the coarse rock and foreign materials. The soil has a  $p^H$  of 5.05 and its organic matter content is 1.45%. For grain size analysis, sediment samples

were kept at room temperature to dry and were wet-sieved and eventually pipette-analyzed to measure silt and clay ratios [211]. Sediment coarser than 4  $\Phi$  ( $>63 \mu\text{m}$  - sand fractions) were investigated at one-phi intervals (-2 to 4  $\Phi$ ) and fine grained at 8  $\Phi$  (silt) and 14  $\Phi$  (clay) classes. Sediment textural types were measured by Sheppard's (1954) classification. Mean grain size (MGS) was measured by the Folk and Ward [214] method. The organic matter was measured by the Nelson and Sommers [215]method. Total N was assessed by digestion and titration method [216] and the available P was determined by the Olsen extraction method [217]. For the preparation of contaminated soil, diesel was weighed and mixed to the sediment using three different concentrations such as 75, 50, and 25 ml per kg of soil. These mixed sediments were kept under room temperature for about fourteen days to remove the volatile components in the oil. The diesel contaminated soil was stabilized for 2 weeks to ensure the evaporation of the unstable components in the oil. The soil pH were measured before experimentation following Steed and Reed [218] method.



Figure 8 Sediment collection for experimental study from Abu Ali Island

### **3.4.3 Plant materials and growing condition**

*Avicennia marina* was grown on the contaminated soil for 90 days in pots having 14 cm diameter and 20 cm height. Each pot was filled with 3 kg of soil with different concentrations of diesel oil. The control plants were not provided with oil but all the remaining conditions were same as the treatment plants. Diesel oil was added one-time to the sediment in three different concentrations of 75, 50, and 25 ml per kg of soil for three treatment conditions. Potted seedlings (12 replicates per treatment and control) were maintained in approximately 35-40 cm of standing saline water to maintain the original environment.

### **3.4.4 Preparation of experimental set up**

The set up was built in front of the north compound and continued from September 2018 to December 2018. This experimental setup was prepared using four seedling trays ( $3.2 \times 1.5 \times 1$  ft) fitted parallelly on the top of a table ( $8 \times 4 \times 4$  ft). Similarly, four water reservoirs of 500 liter capacity) were attached with each individual seedling tray just beneath the level of table. Each reservoir contains a pump inside of it to simulate the tidal cycle from water tank to seedling tray (Fig. 9). The brackish water with 35 psu salinity was prepared synthetically using aquarium salt mix and reverse osmosis water in a marine aqua toxicology laboratory of the Center for Environment and Water, KFUPM.



(a)



(b)



(c)



(d)

Figure 9 (a) Structure of experimental set up in KFUPM, (b) Nursing of mangrove seedling with different concentration of diesel, (c) Flooding seedling daily with saline water, and (d) Setting Rainbird sprinkler timer for irrigating plant automatically

All the seedlings were irrigated twice daily with saline water by pumps to maintain 2 times ebb and 2 times flow. The pumps were running for 6 hours each regulated by a Rainbird sprinkler timer. The excess water was slowly poured back into the tanks located below the table (Fig. 9). We used 12 replicated seedlings per treatment in this experiment. This experiment was conducted under natural outdoor conditions. The experiment consisted of three replicates of each treatment and subsequent analyses of three samples from each repetition.

#### **3.4.5 Experimental sample collection and preparation**

TriPLICATE sediment samples from pots were collected at 0, 30, 60 and 90<sup>th</sup> days after the start of experiment. The samples were homogenized and passed through a 20 mm standard sieve. The plant samples were harvested including leaves, stems, and roots from the individual tree. Both soils and plants were destructively sampled from the pots. The plant tissues were washed with deionized water to remove soil particles, then the tissues were separated into different sub samples and stored in a refrigerator maintaining the temperature at 4<sup>0</sup> C. The stored samples were not kept more than 10 days in the refrigerator. At the end of the experiment, diesel concentrations were recorded in both sediment samples and plant tissues (TPH, and PAHs analysis). Survival percentage was calculated from the number of plants that were still alive after 90 days of experiment. Plant morphology including the change of leaves color was also recorded during the application of petroleum hydrocarbons.

## **3.5 Laboratory Analysis**

### **3.5.1 Metal analysis for sediment sample**

The total extractable metal content of the sediments was determined according to the US EPA Method 3050B. Approximately 0.5 g of a sample was digested in 5 ml of ultrapure HNO<sub>3</sub>. After thorough mixing the digestion, the glass tubes were capped with SC506 disposable reflux caps. The samples were refluxed at 95 °C ± 5 °C for 15 min without boiling on a hot block (Fig. 10). After cooling, 5 ml of concentrated HNO<sub>3</sub> was added, and the samples were refluxed for another half an hour. The samples were allowed to cool, and 2 ml of water and 3 ml of 30% H<sub>2</sub>O<sub>2</sub> was added. The total recoverable metal concentration of As, Cd, Cr, Cu, Fe, Pb, and Zn, was determined in triplicate with a Perkin Elmer DV 8000 inductively coupled plasma optical emission spectrometer (ICP-OES) according to US EPA Method 6010. The concentration of Hg was determined using Nippon MA 3000 direct combustion mercury analyzer (Fig. 10). The results were expressed as mg/kg dry tissue weight

### **3.5.2 Metal analysis from plant tissue**

0.5 g of freeze-dried tissue sample including leaves, barks and roots was weighed in a Pyrex flask. Ten ml ultrapure nitric acid plus 2 ml perchloric acid were added, and beakers covered with glass covers. Beakers were left to soak overnight. Samples were then digested to 100-110C (to brown fumes) for 3-hours. The lids were opened, and the digest was allowed to go to near dryness (2-3 ml). Another 5 ml nitric acid was added, and samples were further digested for 30 minutes, and again allowed to go to near dryness. At this stage copious fumes of perchloric acid would be starting to evolve.

Another 5ml nitric acid was added, and contents were further digested to white fumes of perchloric acid. Two ml nitric acid was further added and mixed. Then 15 ml distilled water was added, and contents warmed. The final digest should be very clear. The contents were filtered using ash less whatman 42 filter papers and volume made to 25 ml in clean PP/PE tubes or containers. Then took 2 ml from the digested solution and made it 10 ml by adding 2% HNO<sub>3</sub> in a 15ml vials which was finally ready for trace metal analysis by Perkin Elmer DV 8000 inductively coupled plasma optical emission spectrometer (ICP-OES) according to US EPA Method 6010. The concentration of Hg was determined using Nippon MA 3000 direct combustion mercury analyzer (Fig. 10). The results were expressed as mg/kg dry tissue weight.

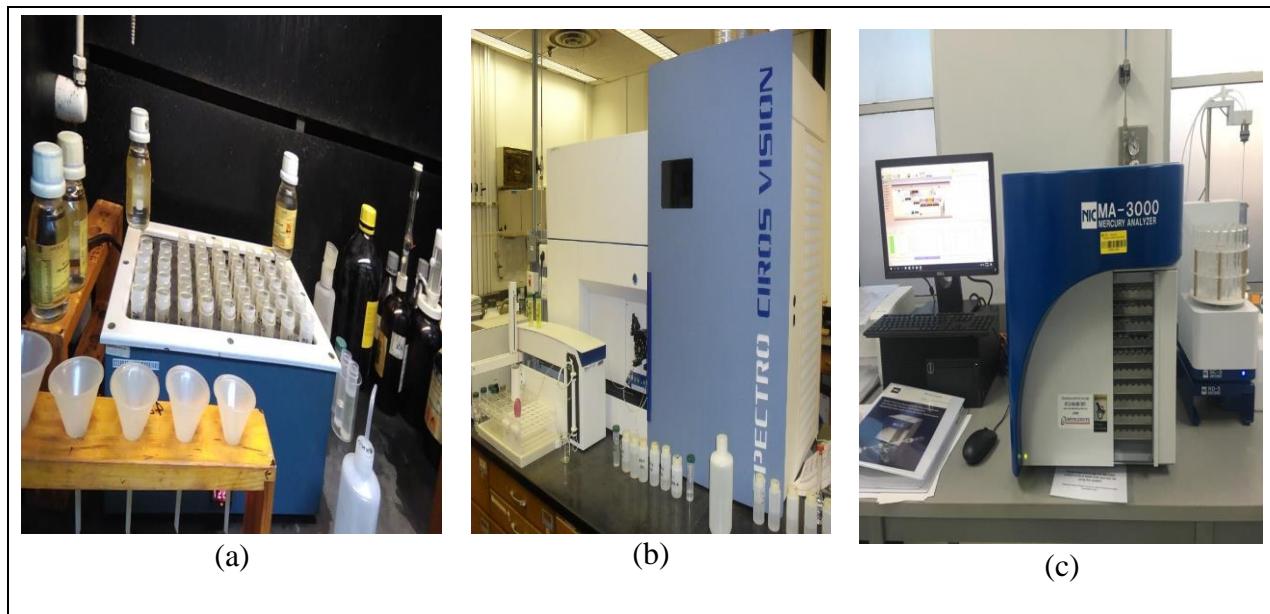


Figure 10 (a) Heating acid digested sample in a hot block, (b) metal analysis using ICP-OES to separate individual trace metals from mixture of compounds, and (c) mercury analysis by using Nippon MA 3000 direct combustion mercury analyzer

### **3.5.3 PAH and TPH analysis from sediment sample**

Weighed 5 g of sediment samples in a glass vial and covered it after adding 10 mL of dichloromethane: hexane (1:1) mixture. It was kept ultrasonic bath for 20 min and carefully decanted the extract into another vial (solvent on the top) and sediment left at the bottom of first vial. The whole process was repeated for three times to ensure that there were no fine solid particles in the solvent. Solid particle can be removed either by filtration or small pipette after settling down. It was kept for evaporation up to 1-2 ml volume by blowing air. Rinsed the vial with hexane to remove traces of sample and transferred all rinsing into the 2 ml GC vial. It was kept for sometimes to have final volume in 1ml for GC analysis. Then the extracts were injected to GC-MS and GC-FID separately for analyzing PAH and TPH respectively using USEPA method 8270C.

### **3.5.4 PAH and TPH analysis from plant tissue**

Plant samples involves various part of complex tissue because of having lignin, cellulose, chlorophyll etc which required several forms of clean up before injection. Therefore, EPA 3545A method was considered for the extraction while customized EPA 3611 and 4630 were considered for clean ups.

#### **Extraction**

Weighed 5 g of plant samples and extracted it by following the same procedure of sediment using ultrasonic bath and same concentration of mixture.

## **Saponification of the dichloromethane extract**

Poured the extract into separatory funnel and rinsed the vial 2-3 times with dichloromethane to take all samples out. 25 mL of 50% H<sub>2</sub>SO<sub>4</sub> was added to saponify the fats and shaken it for 3-5 minutes. H<sub>2</sub>SO<sub>4</sub> and dichloromethane layer were separated by gravity due to density difference ( $\rho_{\text{dichloromethane}} = 1.33 \text{ g/cm}^3$  and  $\rho_{\text{H}_2\text{SO}_4} = 1.84 \text{ g/cm}^3$ ) and stored in separate vials. Transferred the dichloromethane extract to cleaned separatory funnel, added 60 mL distilled water and shaken it about 3minutes. Kept it until a clear separation of layers of dichloromethane & water was formed. (Water was on the top and dichloromethane extract at the bottom, due to density difference). Concentrated dichloromethane extracts to around 2 mL by passing air and added 3 to 5 ml of hexane and blow down the mixture to about 1 ml (this was to change solvent from DCM to hexane) (Fig. 11).

## **Column separation**

A glass column was formed for separation by putting glass wool + anhydrous sodium sulfate+ silica + alumina + anhydrous sodium sulfate. placed about 0.5 to 1.0 cm layer of sodium sulfate on top of column. Silica and alumina were introduced into the glass column with use of solvent hexane. The column was ready for use after rinsing it with about 1.5 times the volume of the materials inside the column. The remnant water from the extract were removed by sodium sulfate while Silica removed some unwanted organics. Placed the concentrated 1 mL extract from the above into the glass column prepared earlier. Then poured 15 ml Hexane and 25 ml Dichloromethane: Hexane (30:70) through the column separately to collect aliphatic and aromatic component of the extract respectively. After collecting the aromatics and aliphatic solutions in separate vials, reduced the volume to 1

ml by air blowing. When the sample volume was reduced to 1 mL, transferred it into GC vial and washed the sample vial with Hexane to remove the traces of samples and taken the solvent in GC vial. It was kept for sometimes to have final volume in 1ml for GC analysis. Then the extracts were injected to GC-MS and GC-FID separately for analyzing PAH and TPH respectively using USEPA method 8270C (Fig. 11). Total PAHs concentration were determined as the summation of the individual concentration of the 16 PAHs compounds ( $\Sigma$ PAHs) nominated by USEPA as priority pollutants.

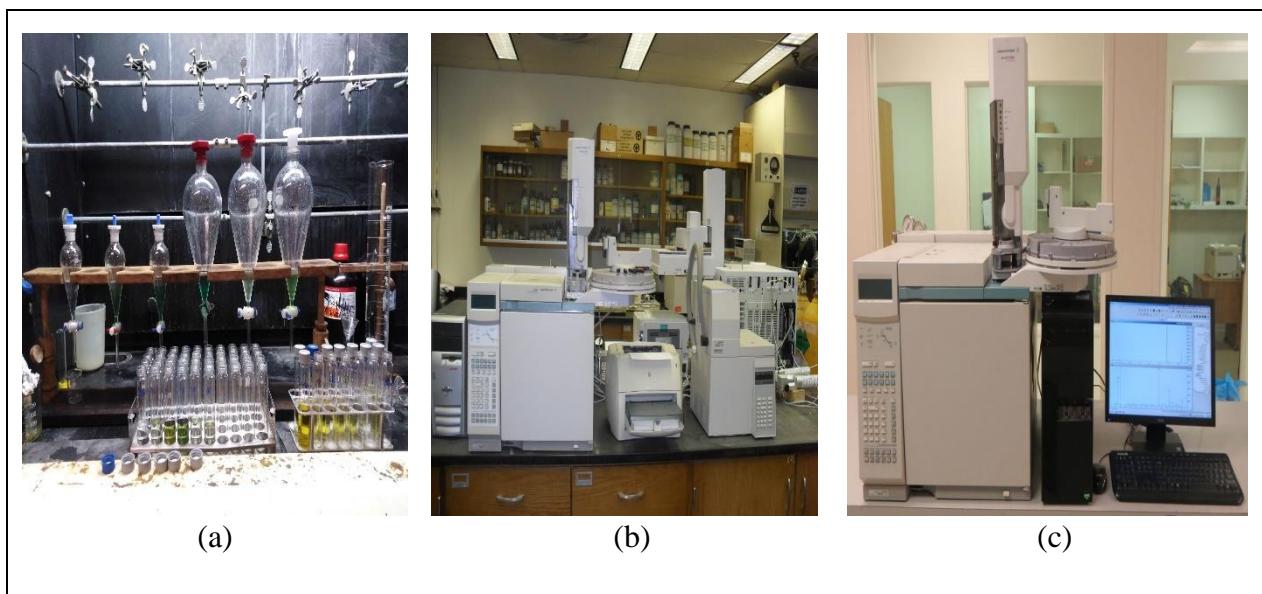


Figure 11 (a) Saponification performed to separate individual chemical compounds from mixture, (b) Individual PAHs analysis using GC-MS, and (c) Individual TPH analysis using GC-FID

### 3.6 Quality Control

Quality control was assured by running laboratory reagent blanks (LRBs) and initial calibration verification (ICV) and continuous calibration verification (CCV) standards. Internal standard (100ul of 1ppm of O-terphenyl and 40ppm of 5Alpha Androstan) was

added to the sample mixture for PAH and TPH analysis. Moreover, 10% of the samples were run in duplicate, and, for each batch of 20 samples, one sample was spiked and run in duplicate. All plastic, quartz, and glassware were soaked in HNO<sub>3</sub> (5%) for at least 24 hours and repeatedly rinsed with ultra-pure water prior to use.

### 3.7 Assessment of contamination in sediment sample

#### Enrichment factor (EF)

The enrichment factor (EF) is a helpful method as a pollution index in ecological media to evaluate the degree of soil pollution with regard to heavy metals by distinguishing their naturally occurring and anthropogenic sources. To assess the EF values for a certain metal, the intensity was stabilized to the textural attributes of the Earth's crust. In this study, iron was applied as the reference component for geochemical normalization. The EF values for heavy metals in soil samples were analyzed applying the subsequent formula:

$$EF = \frac{(M_{sed} / Fe_{sed})}{(M_c / Fe_c)}$$

where  $M_{sed}$  and  $M_c$  are the substances of the analyzed heavy metal in the soil and the Earth's crust, separately, and  $Fe_{sed}$  and  $Fe_c$  are the contents of Fe in the soil and the Earth's crust, respectively. Typical concentrations (mg kg<sup>-1</sup>) of metals in the Earth's crust were used to determine the EF values in this research [219][220]: 44900 for Fe, 0.098 for Cd, 83.0 for Cr, 25.0 for Cu, 44.0 for Ni, 17.0 for Pb, and 71.0 for Zn. According to Sakan [221], seven tiers of pollution levels were considered based on diverse EF values: EF < 1 indicates no enrichment; 1 < EF < 3 is minor enrichment; 3 < EF < 5 is moderate enrichment; 5 < EF < 10 is moderate to severe enrichment; 10 < EF < 25 is severe enrichment; 25 < EF < 50 is very severe enrichment; and EF > 50 is extremely severe enrichment.

### **Geoaccumulation Index ( $I_{geo}$ )**

The geoaccumulation index ( $I_{geo}$ ) is a pollution index which is specified by the subsequent equation:

$$I_{geo} = \log_2(C_n/1.5 B_n)$$

where  $C_n$  is the absorption of metals assessed in sediment samples and  $B_n$  is the geochemical background intensity of the metal (n) which is the same as those used in the above-mentioned enrichment factor computation. Factor 1.5 is the background matrix correction factor due to lithospheric effects [222]. The geoaccumulation index consists of seven classes:  $I_{geo} \leq 0$  (Class 0, practically uncontaminated);  $0 < I_{geo} \leq 1$  (Class 1, uncontaminated to moderately contaminated);  $1 < I_{geo} \leq 2$  (Class 2, moderately contaminated);  $2 < I_{geo} \leq 3$  (Class 3, moderately to heavily contaminated);  $3 < I_{geo} \leq 4$  (Class 4, heavily contaminated);  $4 < I_{geo} \leq 5$  (Class 5, heavily to extremely contaminated);  $I_{geo} > 5$  (Class 6, extremely contaminated) [223].

### **Pollution Load Index (PLI)**

The pollution load index (PLI) recommended by Tomlinson [224], it was used to evaluate PLI in the sediments. The PLI value for the various sites was computed using the following formula:

$$PLI = (CF_1 \times CF_2 \times \dots \times CF_n)^{(1/n)}$$

where n is the number of metals in the study (eight in this study) and CF is the pollution factor which is obtained as follows:

CF = metal concentration in sediment/background concentration (Average shale value).

PLI provides a simple, comparative means for assessing a site: a value of zero indicates perfection, a value of one indicates only baseline levels of pollutants present and values above one would indicate progressive deterioration of the site [224].

### **Potential Ecological Risk Factor (ER)**

ER is an index of ecological risk assessment developed by [225] and widely used to evaluate the degree of pollution of heavy metals in the sediments. The equations for calculating the ER are as follows:

$$ER_i^i = Tr^i \times C_f^i = Tr^i \times (C_s^i / C_n^i)$$

where  $ER_i$  is the potential ecological risk factor for a given element  $i$ ;  $Tr_i$  is the biological toxicity factor for element  $i$ , which is defined as Cd = 30, Cr = 2, Cu = Pb = Ni = 5, Zn = 1 [225];  $C_f$ ,  $C_s$  and  $C_n$  are the contamination factor, the concentration in the sediment, and the background reference value for element  $i$ , respectively. RI is the sum potential toxicity response index for various heavy metals in the sediments. According to [225], the ER index consists of five classes for ecological risk level of single-factor pollution as below:  $ER \leq 40$  (low risk);  $40 < ER \leq 80$  (moderate risk);  $80 < ER \leq 160$  (considerable risk);  $160 < ER \leq 320$  (high risk);  $ER > 320$  (very high risk). Corresponding to RI, four categories were defined for general level of potential ecological risk:  $RI \leq 150$  (low risk);  $150 \leq RI \leq 300$  (moderate risk);  $300 < RI \leq 600$  (considerable risk);  $RI > 600$  (very high risk).

### **Degradation of hydrocarbon**

Percent degradation was calculated using the following formula:

$$D = \frac{C_0 - C_r}{C_0} \times 100$$

where  $C_0$  and  $C_r$  are the initial and residual oil concentrations, respectively

### **3.8 Assessment of contamination in plant sample**

Bioaccumulation is the gradual buildup over time of a chemical in living organisms. Once a toxic pollutant is in the water or soil, it can easily enter the food chain and finally accumulate in large quantity among top predator organisms.

The accumulation potential of *Avicennia marina* was examined by the use of bioaccumulation factor. It was computed by the following formula

$$BAF \text{ or } CF = \frac{C_{biota}}{C_{Sediment}}$$

(here, BAF = Bioaccumulation Factor, CF = Contamination Factor)

Where,  $C_{biota}$  was the chemical concentration in plant sample and  $C_{Sediment}$  was the chemical concentration in sediment sample.

$$\text{Translocation Factor (TF)} = \frac{C_{leaf}/C_{stem}/C_{shoot}}{C_{root}}$$

### **3.9 Data analysis**

The basic statistical description of each parameter, based on the measures of central tendency, was calculated from the available data. When the readings were below the minimum detection limit (MDL) for a given parameter, the MDL value was adopted. Not

detected values were considered zero to avoid data void and thus facilitate the subsequent calculations. The data obtained from the various experiments were subjected to Analysis of Variance (ANOVA) using the Microsoft Excel 2019. A two-factor ANOVA was run at confidence level ( $\alpha = 0.05$ ) of 95% to (i) ascertain if there was significant difference among the phytoremediation ability in different plant body parts of *Avicennia marina*, (ii) ascertain if there was significant difference between the level of contaminants, and (iii) determine if there was significant interaction between each of these plants and the contaminants.

## **CHAPTER 4**

### **RESULTS AND DISCUSSION**

#### **4.1 Summary of contamination in field sediment samples**

The levels of contaminants in both mangrove and non-mangrove areas varied significantly in the sample locations. The measured selected contaminants in the collected samples during the field study are presented in table 1. The average concentrations of PAHs, TPH1, TPH2, and TOC are higher in the mangrove sediments than the non-mangrove sediments. The maximum concentrations of PAHs, TPH1, TPH2, and TOC are  $176.41 \text{ ng g}^{-1}$ ,  $610.94 \text{ mg kg}^{-1}$ ,  $9971.19 \text{ mg kg}^{-1}$ , and  $52873.04 \text{ mg kg}^{-1}$ , respectively in mangrove sediment samples. The average concentrations of Cr, Cu, Ni, and Hg were higher in the mangrove sediments than the non-mangrove sediments except the concentration of Zn (Table 1). According to the ecotoxicological valuation, the sediment in these areas are not expected to cause significant adverse effects due to low concentration. Similar results are reported for some mangrove marshes [23] [209] [226]. Based on the overall assessment, it is deduced that the sediment collected from the mangrove zones of the Western Arabian Gulf have low ecological risk and a low possibility of toxic pollution.

Table 1. Descriptive statistics of selected contaminants concentration in the field sediment samples (Abu Ali Island, Tarut Bay, Rahima and Gurmah Island)

<b>Metal</b>	<b>Unit</b>	<b>Sample</b>	<b>Mean</b>	<b>SD</b>	<b>Min</b>	<b>Max</b>
<b>Cr</b>	mgkg <sup>-1</sup>	Mangrove	11.40	4.10	5.3	19.2
<b>Cr</b>	mgkg <sup>-1</sup>	Non-Mangrove	8.87	3.91	2.5	18.9
<b>Cu</b>	mgkg <sup>-1</sup>	Mangrove	3.30	1.46	1	5.3
<b>Cu</b>	mgkg <sup>-1</sup>	Non-Mangrove	2.38	0.84	0.8	4.1
<b>Ni</b>	mgkg <sup>-1</sup>	Mangrove	8.36	4.03	2.7	17.7
<b>Ni</b>	mgkg <sup>-1</sup>	Non-Mangrove	6.31	3.83	0.63	17.2
<b>Hg</b>	mgkg <sup>-1</sup>	Mangrove	0.004	0.002	0.001	0.01
<b>Hg</b>	mgkg <sup>-1</sup>	Non-Mangrove	0.003	0.002	0.001	0.009
<b>Zn</b>	mgkg <sup>-1</sup>	Mangrove	11.40	13.65	3.1	52.5
<b>Zn</b>	mgkg <sup>-1</sup>	Non-Mangrove	11.61	13.87	1.06	60.1
<b>ΣPAHs</b>	ngg <sup>-1</sup>	Mangrove	26.46	27.86	1	176.41
<b>ΣPAHs</b>	ngg <sup>-1</sup>	Non-Mangrove	5.94	8.66	1.04	36.00
<b>TPH 1</b>	mgkg <sup>-1</sup>	Mangrove	47.20	104.15	1.9	610.94
<b>TPH 1</b>	mgkg <sup>-1</sup>	Non-Mangrove	30.00	83.39	0.6	432.07
<b>TPH 2</b>	mgkg <sup>-1</sup>	Mangrove	737.80	1727.36	2.2	9971.19
<b>TPH 2</b>	mgkg <sup>-1</sup>	Non-Mangrove	367.40	1006.78	1.4	4622.15
<b>TOC</b>	mgkg <sup>-1</sup>	Mangrove	15193.81	4918.36	2156.00	52873.04
<b>TOC</b>	mgkg <sup>-1</sup>	Non-Mangrove	10867.19	1012.72	298.92	44090.00

## **4.2 The relation of metal concentration between sediment and plant tissue**

The concentrations of Cr in the sediment and in the plant body parts are correlated. The concentrations in different plant tissues are also correlated (Fig. 12). The strong correlations (i.e.,  $R > 0.50$  and  $p$  values  $<0.005$ ) are observed between sediment and leaf ( $R = 0.529$ ), sediment and bark ( $R = 0.643$ ), sediment and root ( $R = 0.663$ ), root and leaf ( $R = 0.759$ ), and root-bark ( $R = 0.914$ ).

The Cu concentrations in the root and the bark tissues are correlated ( $R = 0.779$ ) whereas no strong correlation is observed between sediment and plant, and between different plant body parts (Fig 13). The concentrations of Ni in mangrove and non-mangrove sediment are strongly correlated ( $R = 0.59$ ). The correlation coefficients for the sediment and the root, and the sediment and the bark are 0.711 and 0.43, respectively. The correlation between the sediment and the leaf was weak (Fig 14).

The concentrations of Hg in the sediment and different plant body parts is weakly correlated. The correlation between the plant tissues of different body parts is weak (Fig 15). The correlation analyses for the Zn concentrations in the sediment, the plant body parts, and the plant tissues of different body parts followed similar trends (Fig 16). Most of the previous studies demonstrated weak correlations between the metal concentrations in soil and the metals in plant tissues which recommend that mangroves do not actively accumulate metals or most metals exist under the threshold limits [62]. This study also found that the metal concentrations in sediment are below the natural background levels and classified as less contaminated.

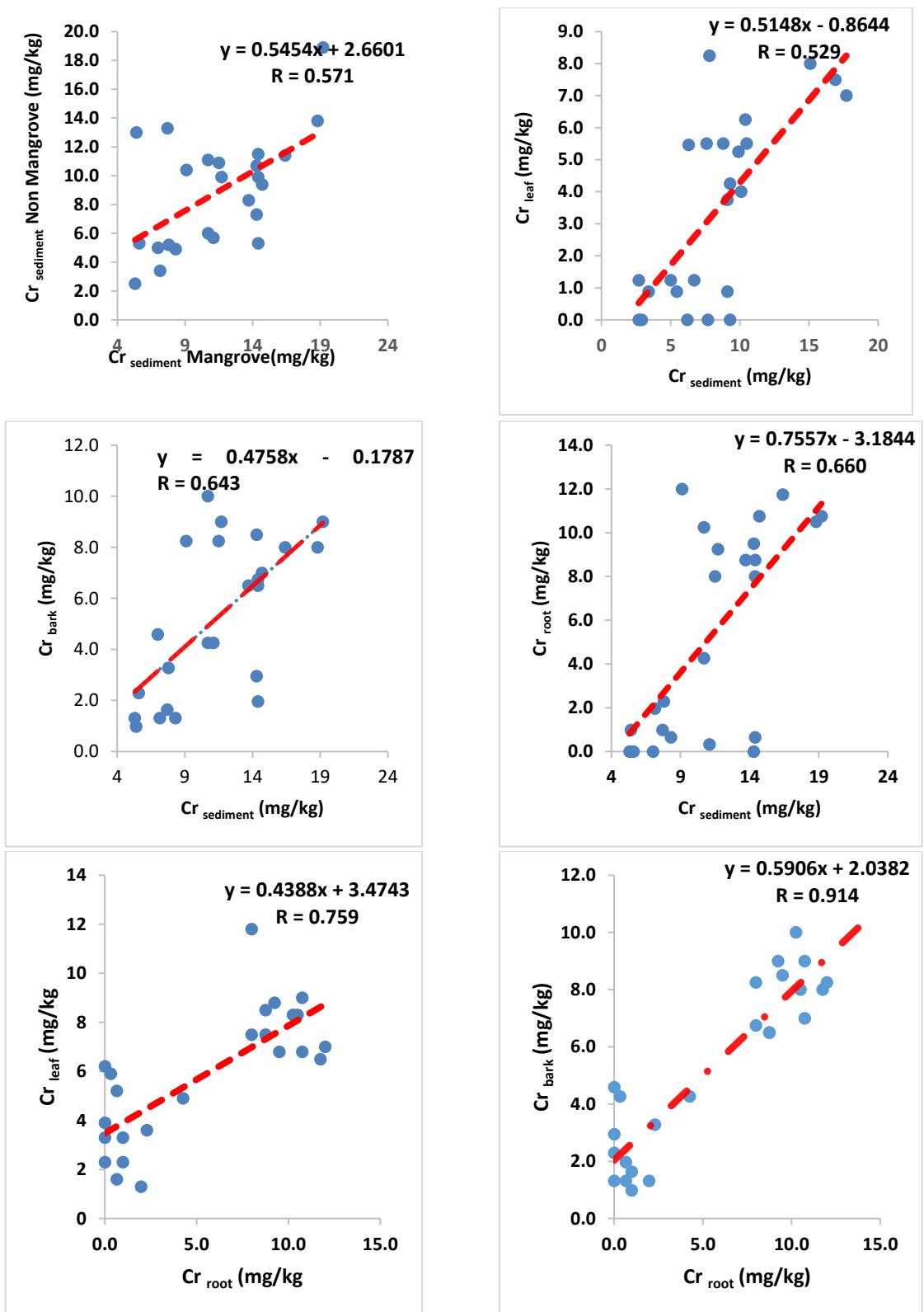


Fig 12: Correlation between Cr concentrations in sediment vs. plant tissues

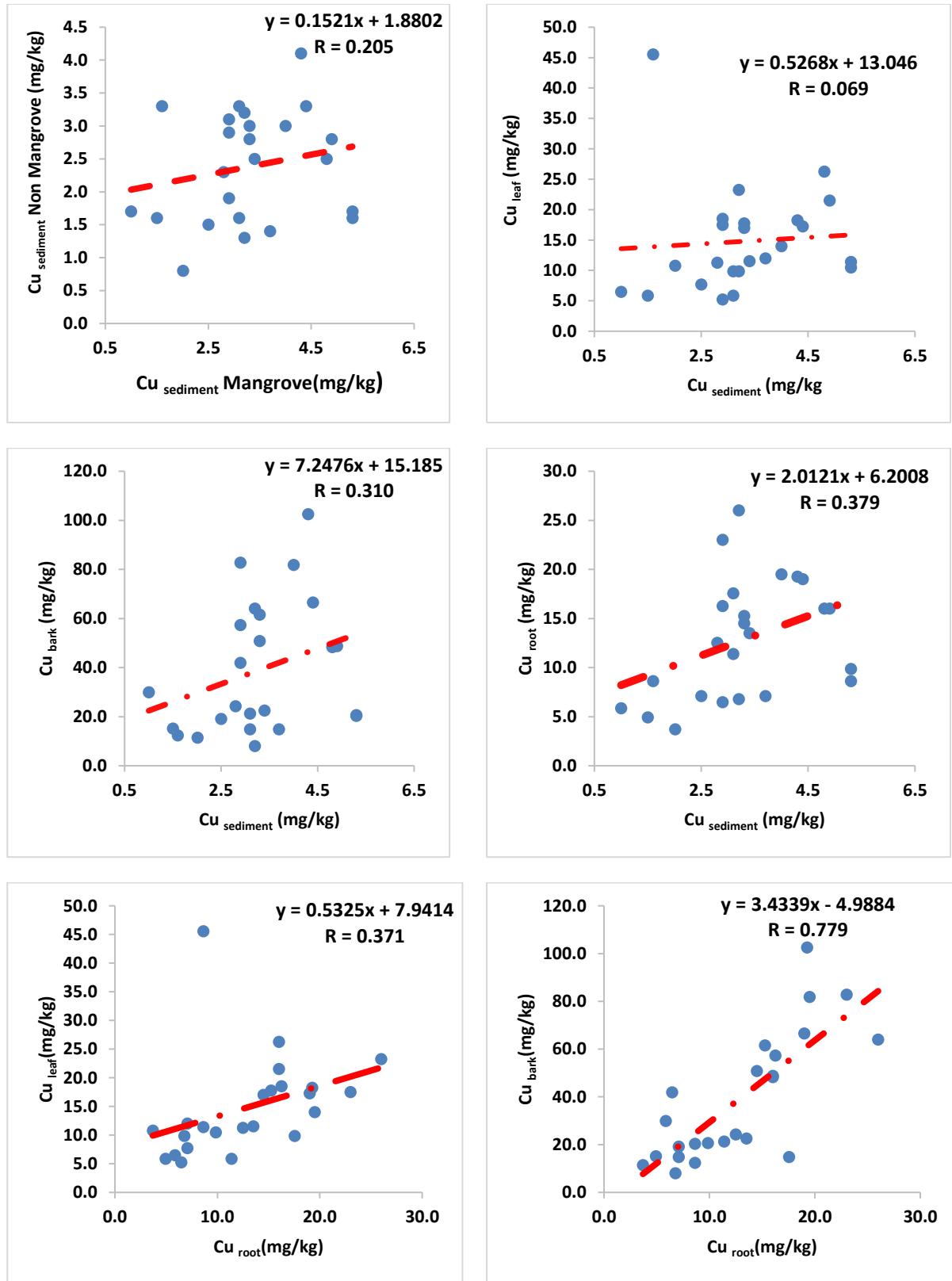


Fig 13: Correlation between Cu concentrations in sediment vs. plant tissues

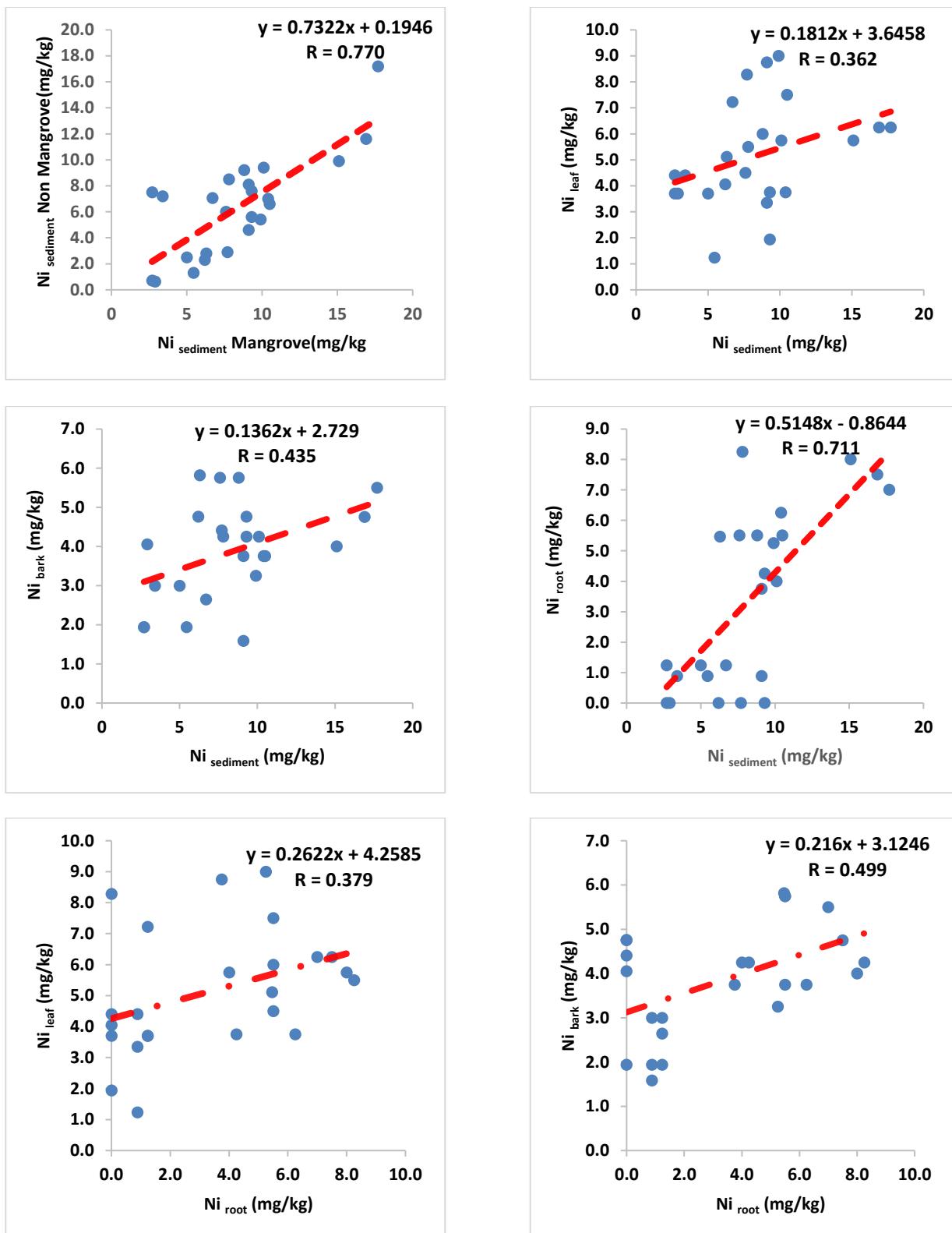


Fig 14: Correlation between Ni concentrations in sediment vs. plant tissues

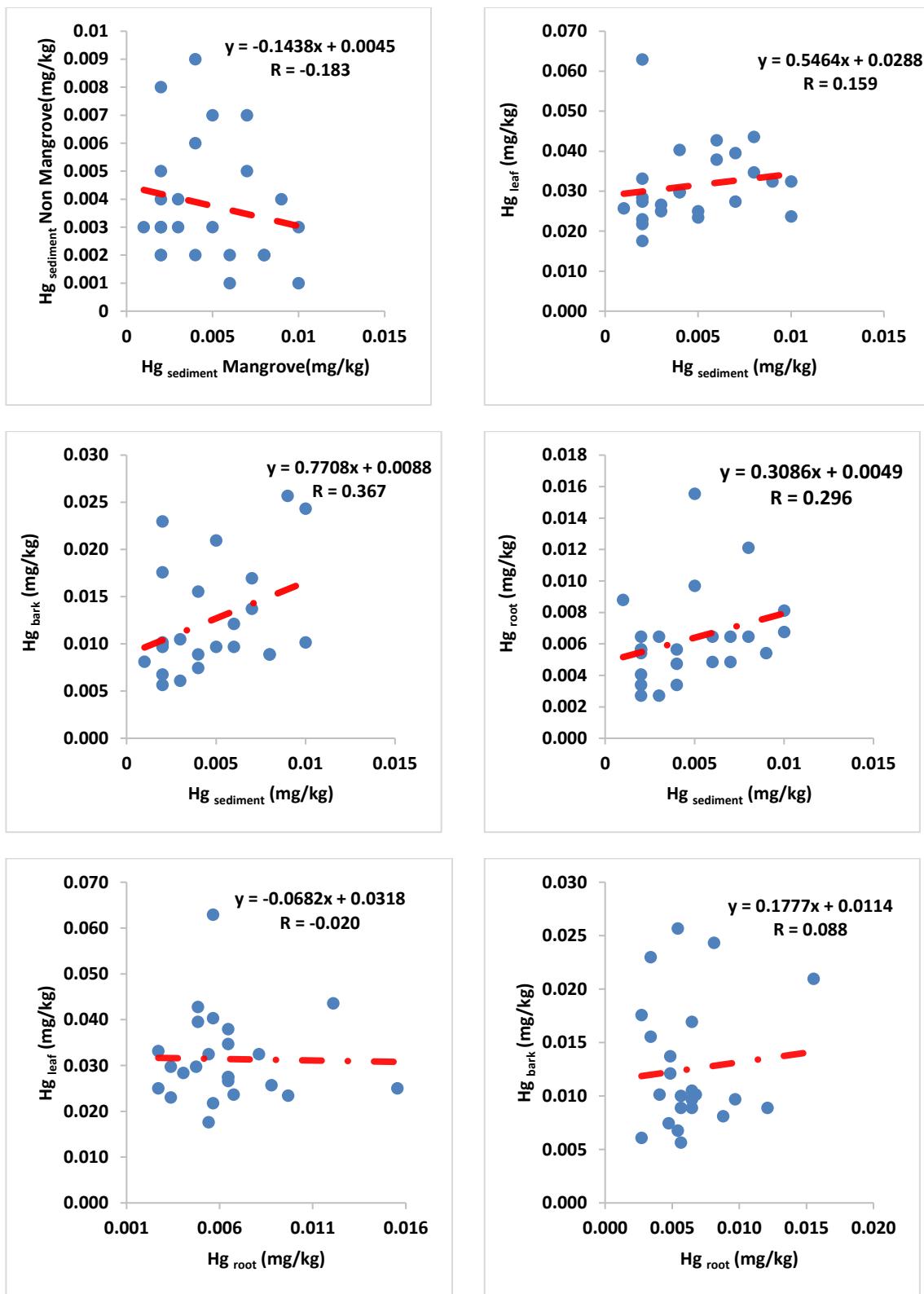


Fig 15: Correlation between Hg concentrations in sediment vs. plant tissues

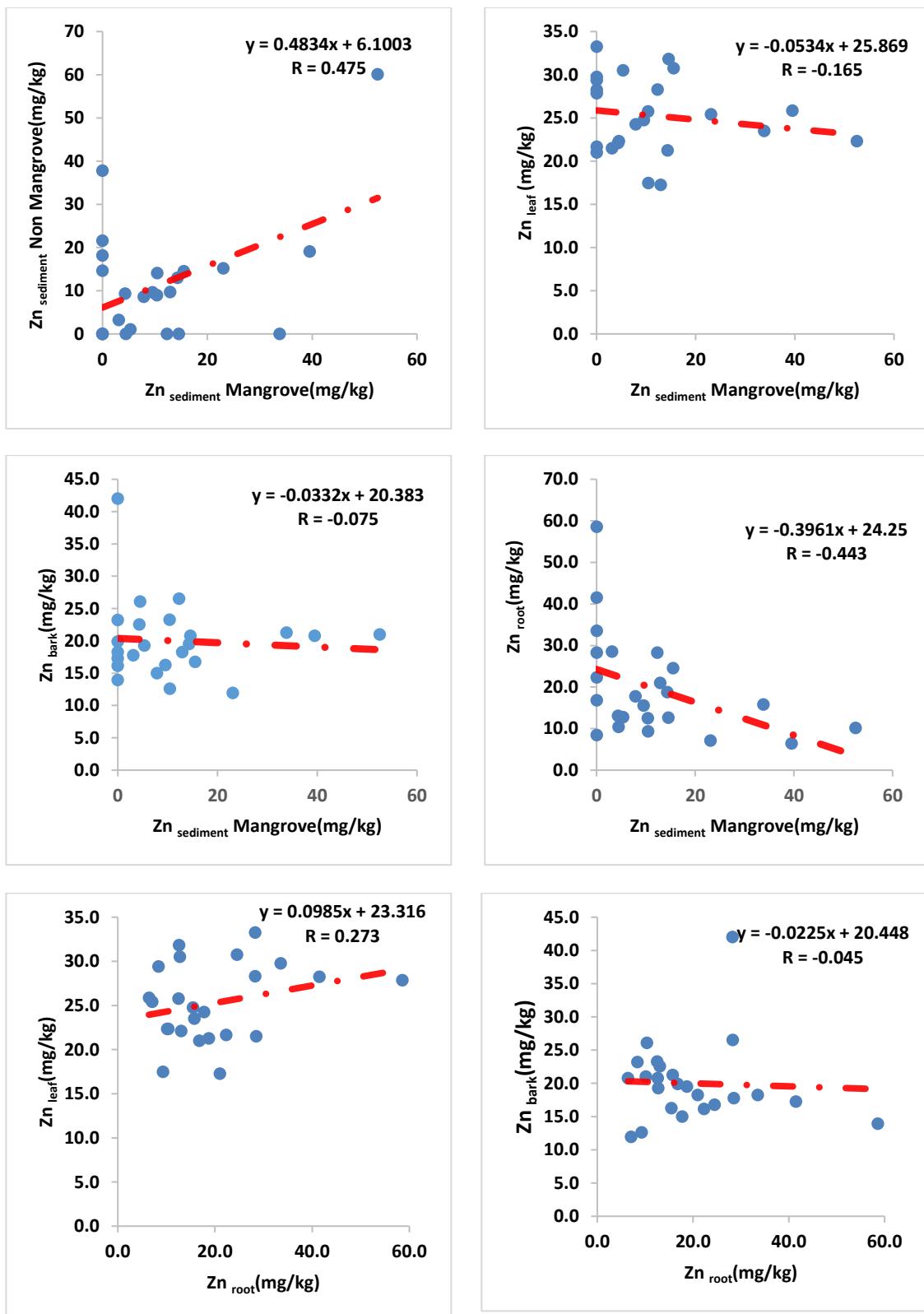


Fig 16: Correlation between Hg concentrations in sediment vs. plant tissues

#### **4.3 Assessment of metal contamination in field sediment sample**

Due to the rapid industrialization the Saudi coast of Arabian Gulf have been continuously contaminated. Seaside sediment are acknowledged as a large pool of contaminants including heavy metals. Bioavailable metals have the potential possibility to accumulate into marine organism from sediment and cause ecotoxicological effects. So, the enrichment factor, geoaccumulation index ( $I_{geo}$ ), pollution load index (PLI), and potential ecological risk (ER) were calculated (Table 2) to investigate the patterns of metal bioavailability in the sediment. The Enrichment Factor of both Cr and Cu were classified as minor enrichment in all mangrove areas including Abu Ali Island, Tarut Bay, Rahima, and Gurmah Island. There was no enrichment for Hg concentrations in all areas. The concentration of Zn was only moderate to severe in Abu Ali Island. The geoaccumulation index ( $I_{geo}$ ) for all metals in four different areas is classified as class 0 based on Varol (2011), particularly termed as non-contaminated. The pollution load index (PLI) values in all field samples are calculated as zero indicating perfection, suggested by Tomlinson [224]. Potential ecological risk (ER) is found as low risk following Hakanson (1980). Overall, in this study, the selected metal contaminants in all sediment samples fall below the ERL and ERM based on the guideline provided by Long [226].

Table 2. Enrichment factor, geoaccumulation index, pollution load index, potential ecological risk for the sediments in four mangrove area

Area	Contamination Factor	Cr	Cu	Ni	Hg	Zn
Abu Ali Island	Enrichment factor (EF)	2.36	2.05	2.89	0.06	6.7
	Classification	ME	ME	ME	NE	MDSE
	Geoaccumulation index	-3.88	-4.11	-3.61	-9.38	-2.86
	Classification	0	0	0	0	0
	Pollution Load Index			0.35		
	Potential Ecological Risk (ER)	1.32	2.86	4.10	0.66	1.89
	Classification	LR	LR	LR	LR	LR
Tarut Bay	Enrichment factor (EF)	2.47	3.33	3.01	0.08	3.52
	Classification	ME	ME	ME	NE	ME
	Geoaccumulation index ( $I_{geo}$ )	-3.95	3.54	3.73	9.06	2.99
	Classification	0	0	0	0	0
	Pollution Load Index			0.73		
	Potential Ecological Risk (ER)	1.19	4.18	3.55	1.38	1.12
	Classification	LR	LR	LR	LR	LR
Rahima	Enrichment factor (EF)	2.56	2.24	3.29	0.045	2.82
	Classification	ME	ME	MDE	NE	ME
	Geoaccumulation index ( $I_{geo}$ )	-3.17	-3.39	-2.80	-9.27	-3.69
	Classification	0	0	0	0	0
	Pollution Load Index			0.64		
	Potential Ecological Risk (ER)	2.05	4.40	6.45	0.71	0.59
	Classification	LR	LR	LR	LR	LR
Gurmah Island	Enrichment factor (EF)	2.03	1.82	3.38	0.051	3.52
	Classification	ME	ME	MDE	NE	ME
	Geoaccumulation index ( $I_{geo}$ )	-3.18	-3.35	-2.44	-8.51	-3.22
	Classification	0	0	0	0	0
	Pollution Load Index			0.54		
	Potential Ecological Risk (ER)	2.65	4.44	9	1	0.99
	Classification	LR	LR	LR	LR	LR

#### **4.4 Trends of metal concentration in plant tissue**

The concentrations of heavy metals Cr, Cu, Ni, and Hg are comparatively high in Gurmah island and Rahima compared to those of Tarut bay and Abu Ali Island. The level of Cr concentrations is found by the order Gurmah > Rahima> Tarut > Abu Ali for all plant parts including leaves, barks, and roots. The highest concentration of Cr was  $10.2 \text{ mgkg}^{-1}$  in Gurmah island and the lowest as  $1.9 \text{ mgkg}^{-1}$  in Abu Ali island. The concentration levels of Cu in leaf samples were Rahima > Gurmah > Abu Ali >Tarut ( $18.5 > 17.1 > 15.1 > 8.4 \text{ mgkg}^{-1}$ ); bark samples were Gurmah > Rahima > Abu Ali >Tarut ( $70 > 48.4 > 20.2 > 18.1 \text{ mgkg}^{-1}$ ); and root samples were Rahima > Gurmah > Tarut >Abu Ali ( $17.8 > 17.3 > 10.5 > 5.8 \text{ mgkg}^{-1}$ ). The levels of Ni concentration follow the order Gurmah > Rahima> Tarut > Abu Ali for all plant body parts. The highest and the lowest concentrations of Ni are  $6.7 \text{ mgkg}^{-1}$  and  $1.9 \text{ mgkg}^{-1}$ , respectively in root samples of Gurmah island. The concentrations of Hg in leaf samples follows the order Rahima > Gurmah > Abu Ali and Tarut and bark samples were Tarut > Abu Ali > Gurmah > Rahima. The highest concentration of Hg ( $0.036 \text{ mgkg}^{-1}$ ) is observed in root sample in Rahima while the lowest ( $0.04 \text{ mgkg}^{-1}$ ) value occurs in root samples of Abu Ali island. The concentrations of Zn in leaf samples, bark samples, and root samples follow the order: Rahima > Tarut > Gurmah > Abu Ali ( $27.79 > 26.66 > 24 > 22.57 \text{ mgkg}^{-1}$ ), Rahima > Tarut > Abu Ali > Gurmah ( $22.62 > 20.07 > 19.12 > 18.16 \text{ mgkg}^{-1}$ ), and Rahima > Tarut > Gurmah >Abu Ali ( $26.7 > 24.49 > 18.33 > 9.39 \text{ mgkg}^{-1}$ ), respectively. In general, a small percentage of metals accumulates in leaf tissues as the most of absorbed metals accumulates in root tissues [227].

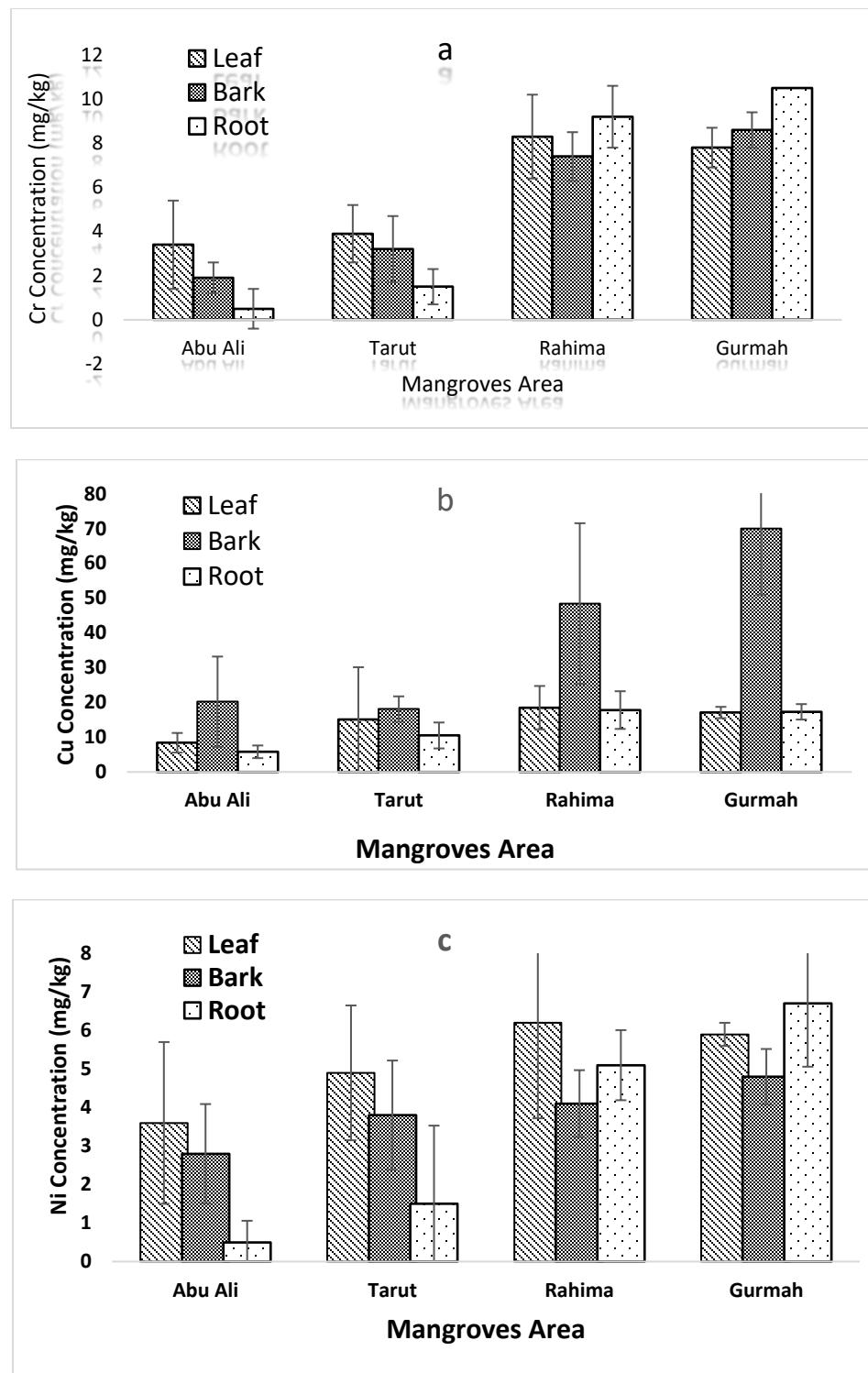


Fig 17: Trends of concentrations (mean  $\pm$  standard deviation  $\text{mg kg}^{-1}$ ) of metals (a)Cr, (b) Cu and (c)Ni in *Avicennia marina* growing in different mangrove areas

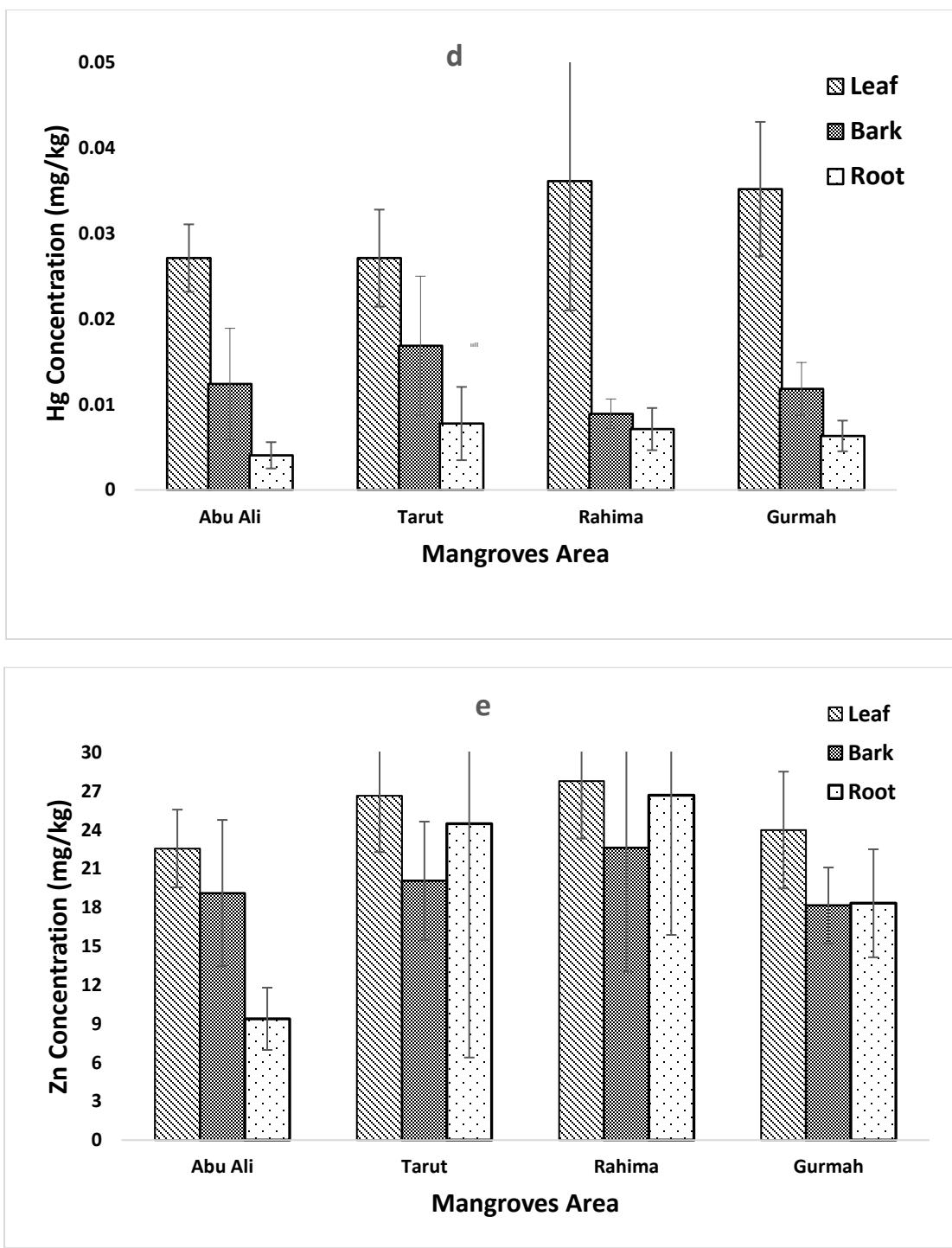


Fig 17: Trends of concentrations (mean  $\pm$  standard deviation  $\text{mg kg}^{-1}$ ) of metals (d) Hg and (e) Zn in *Avicennia marina* growing in different mangrove areas

#### **4.5 Trends of Bioaccumulation Factor of metals in plant tissue**

The BAFs of the heavy metals including Cr, Cu, Ni, Hg, and Zn in mangroves (Fig 18) are significantly different among different areas which indicated that the different ability of mangroves body parts to accumulate heavy metals from the environment. The BCF values of Cu, Hg, and Zn for all body parts of plant tissues exceed 1 which indicates that there is an efficient rate of transfer of metal from the sediment to the plant body parts. The range of BCF values of Cr, Cu, Ni, Hg, and Zn in leaf are 0.46 to 0.61, 4.03 to 6.8, 0.5 to 1, 5.72 to 12.44, and 2.15 to 33.22, respectively. The BAF values for both Cr and Ni are below 1 except in the leaf in Tarut bay for Ni. The range of BAF values for leaf, bark, and root are 5.72 to 12.44, 1.04 to 4.69, and 0.73 to 5.72. The observed highest concentration of BAF for Zn is 33.77 in Tarut bay and the lowest is 1.14 in Gurmah island. The results indicated strong linear connection between metal absorption in the plant body and the sediment as the corresponding  $BCF \geq 1$  showing hyperaccumulation capability.

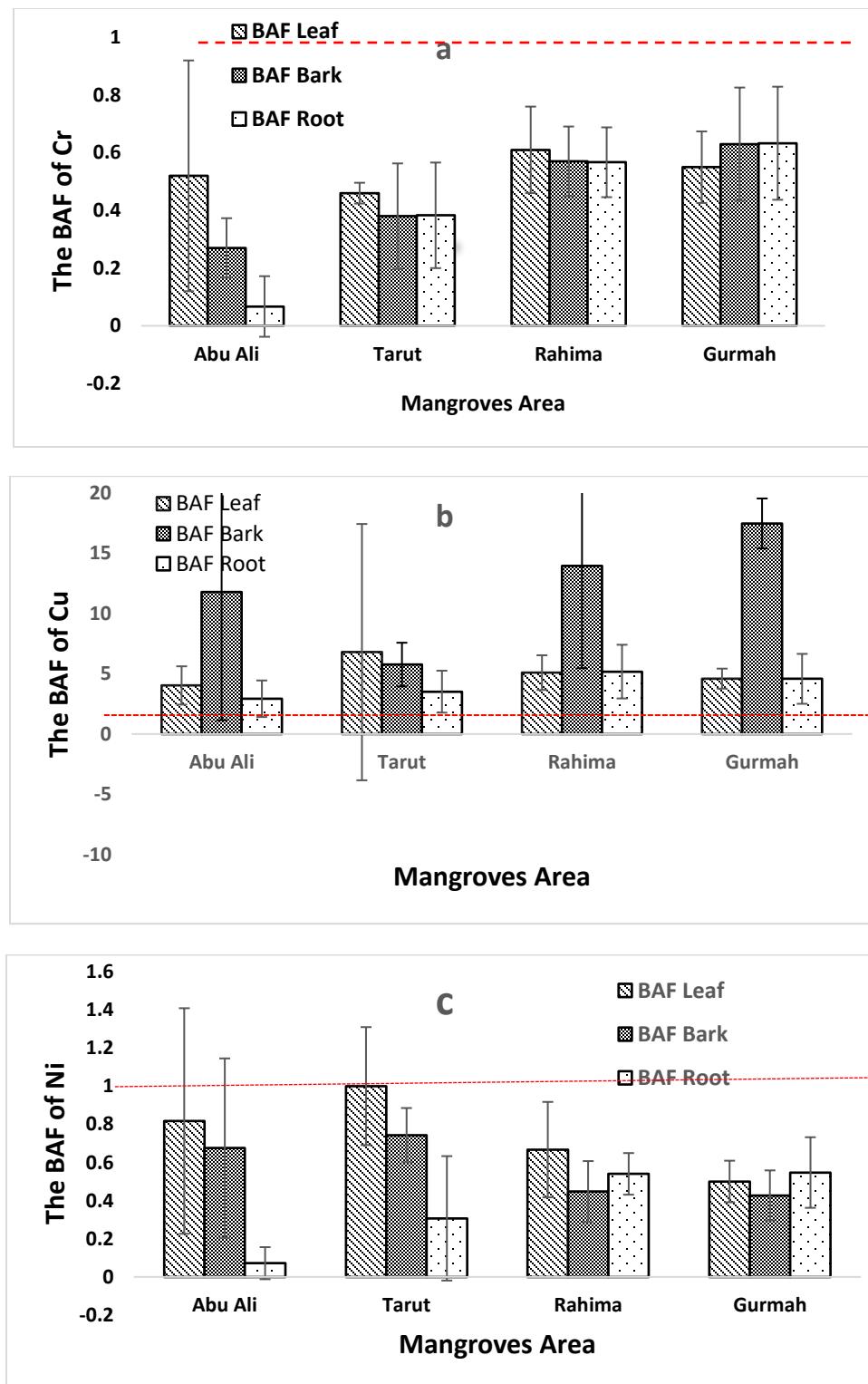


Fig 18: Trends of BAF (mean  $\pm$  standard deviation  $\text{mg kg}^{-1}$ ) of metals (a) Cr, (b) Cu and (c) Ni in *Avicennia marina* growing in different mangrove areas. Dashed line represents BAF  $\geq 1$ , called as hyperaccumulator [228]

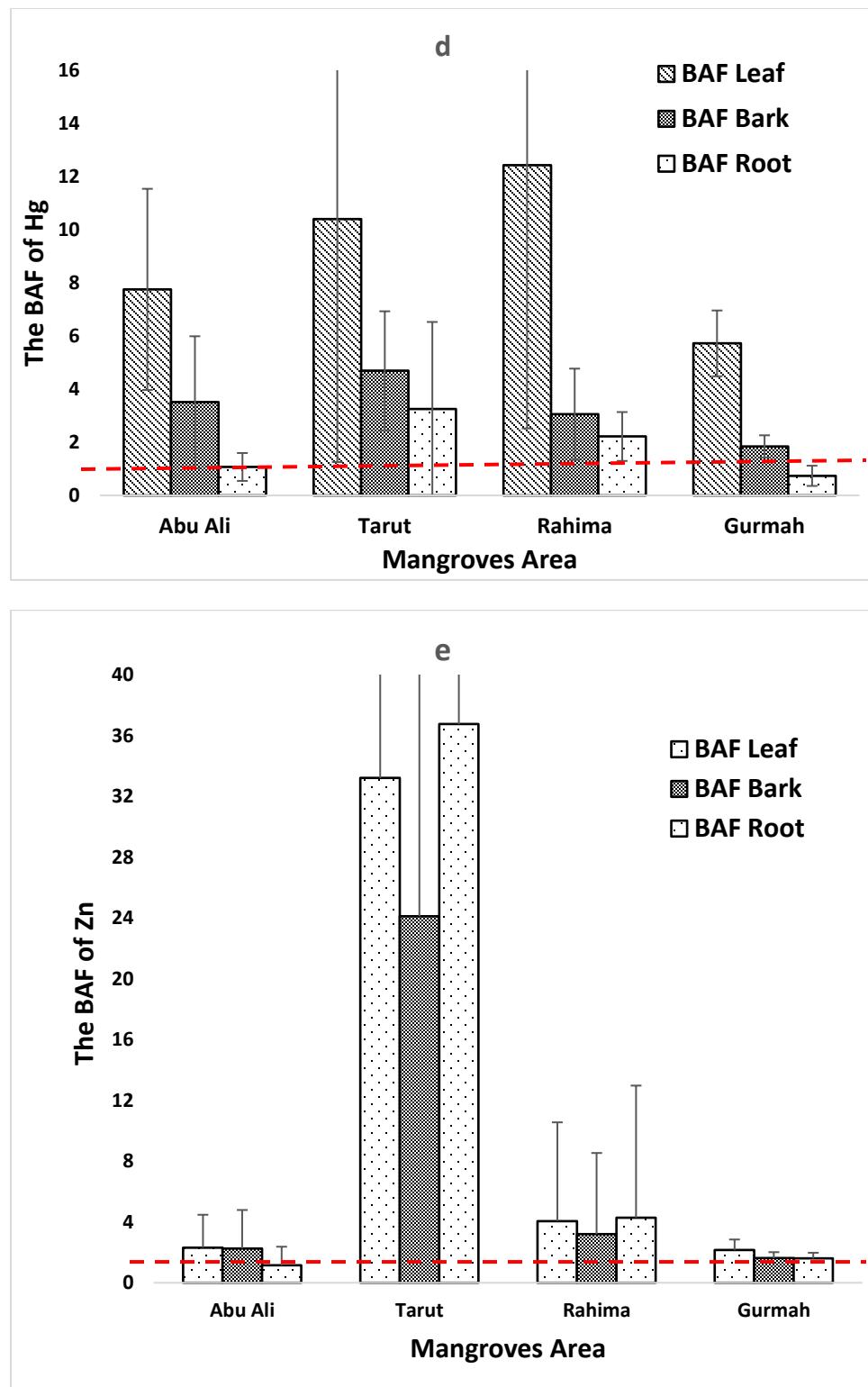


Fig 18: Trends of BAF (mean  $\pm$  standard deviation  $\text{mg kg}^{-1}$ ) of metals (d) Hg and (e) Zn in *Avicennia marina* growing in different mangrove areas. Dashed line represents BAF  $\geq 1$ , called as hyperaccumulator [228]

#### **4.6 Trends of Translocation Factor of metals in plant tissue**

The ability of phytoextraction capacity can be expressed by a translocation factor (TF), which is defined as the ratio of the metal concentration in the leaf/shoots/barks to that in the roots. Generally, the plant species with TF values greater than 1 are classified as high-efficient plants for metal translocation from the roots to above ground parts of plants. Therefore, our findings suggest that *Avecinnia marina* can be classified as a potential accumulator of Cr, Cu, Ni, Hg, and Zn. The TF value for Hg was greater than one in all leaves, barks, and root samples. The TF value for the translocation from root to leaf for Hg follows the trend 7.51 (Abu Ali) > 6.18 (Rahima) > 6.11 (Gurmah)> 4.43 (Tarut), whereas root to bark follows the trend 3.52 (Abu Ali) > 2.64 (Tarut) > 2 (Gurmah)> 1.33 (Rahima). The highest and the lowest TF values for root to leaf translocation is 1.99 in Tarut and 0.94 in Gurmah island, respectively. The highest and the lowest TF values of Ni for root to bark is 2.44 in Abu Ali and 0.75 in Gurmah island. The order of TF values of Cu for root to leaf is found as 1.0 > 1.06 > 1.53 > 1.76 (Gurmah > Rahima > Abu Ali > Tarut) and the order to bark to leaf is found as 1.87 > 2.61 > 3.49> 4.01 (Tarut > Rahima > Abu Ali > Gurmah).

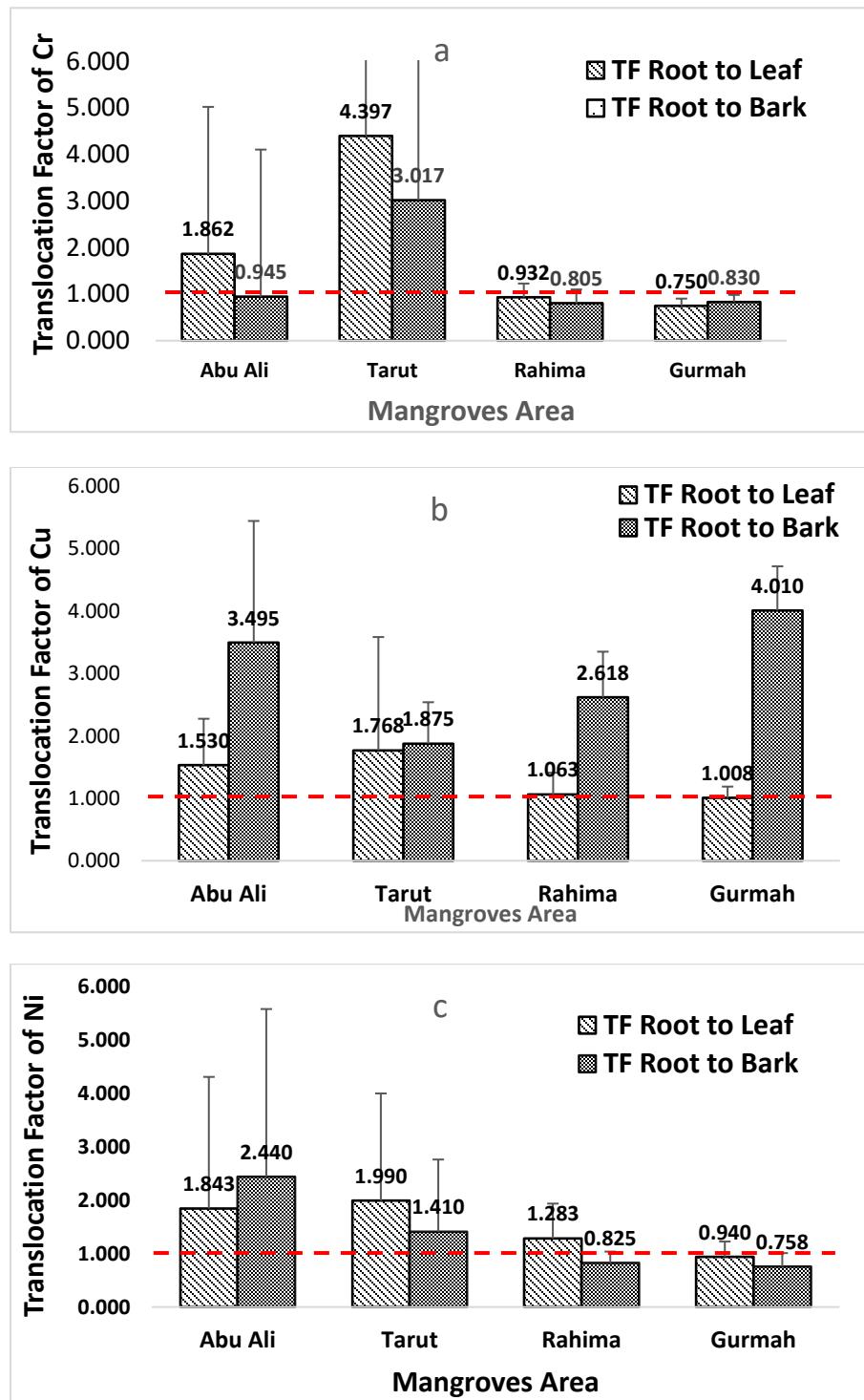


Fig 19: Trends of TF (mean  $\pm$  standard deviation  $\text{mgkg}^{-1}$ ) of metals (a) Cr, (b) Cu and (c) Ni in *Avicennia marina* growing in different mangrove areas. Dashed line represents  $\text{TF} \geq 1$ , called as Phytostabilization [229]

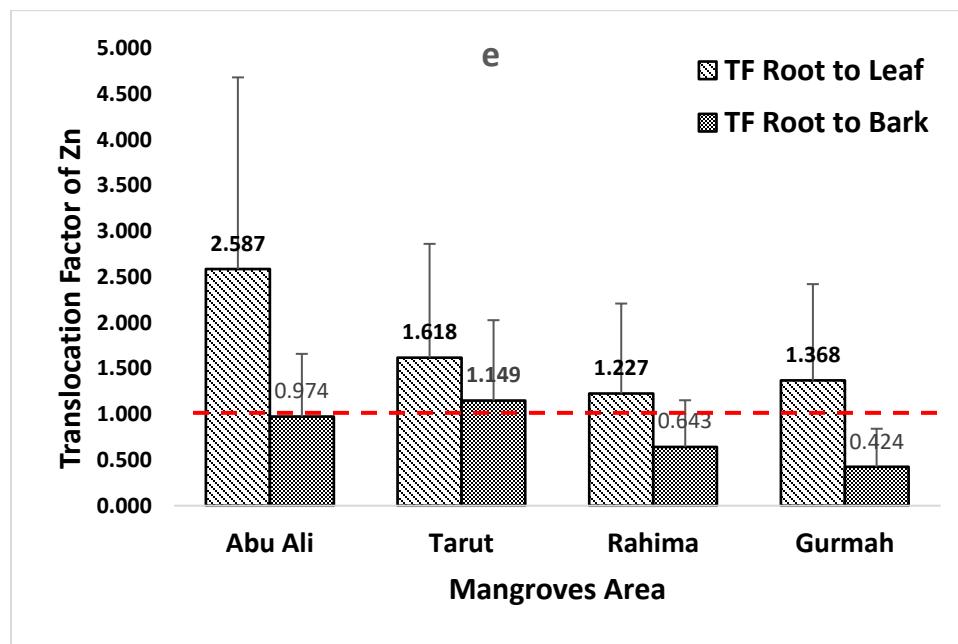
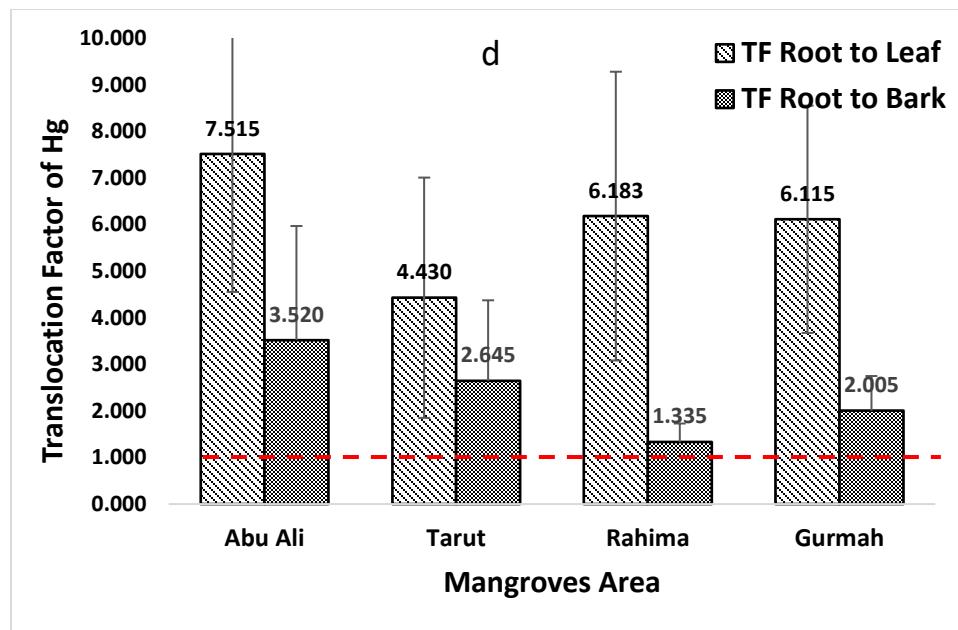


Fig 19: Trends of TF (mean  $\pm$  standard deviation  $\text{mgkg}^{-1}$ ) of metals (d) Hg and (e) Zn in *Avicennia marina* growing in different mangrove areas. Dashed line represents  $\text{TF} \geq 1$ , called as Phytostabilization [229]

#### **4.7 The hydrocarbon concentration in the sediment and plant tissues**

The concentrations of  $\Sigma$ PAHs in the sediment and the plant body parts and in the plant tissues of different body parts are weakly correlated (Fig 20). The correlation coefficients for the concentrations of TPH in the sediment and the plant body parts and in the plant tissues of different body parts are insignificant (Fig 21). The correlation between sediment to leaf and sediment to root were negative for the total PAHs. The distribution and concentration of petroleum hydrocarbon depends on the chemical composition and organic matter of the sediment [192]. In our study, there was no strong correlation for both PAHs and TPH concentration in the sediment and the surrounding mangrove plant body, which is concluded by other similar studies including Tam [23].

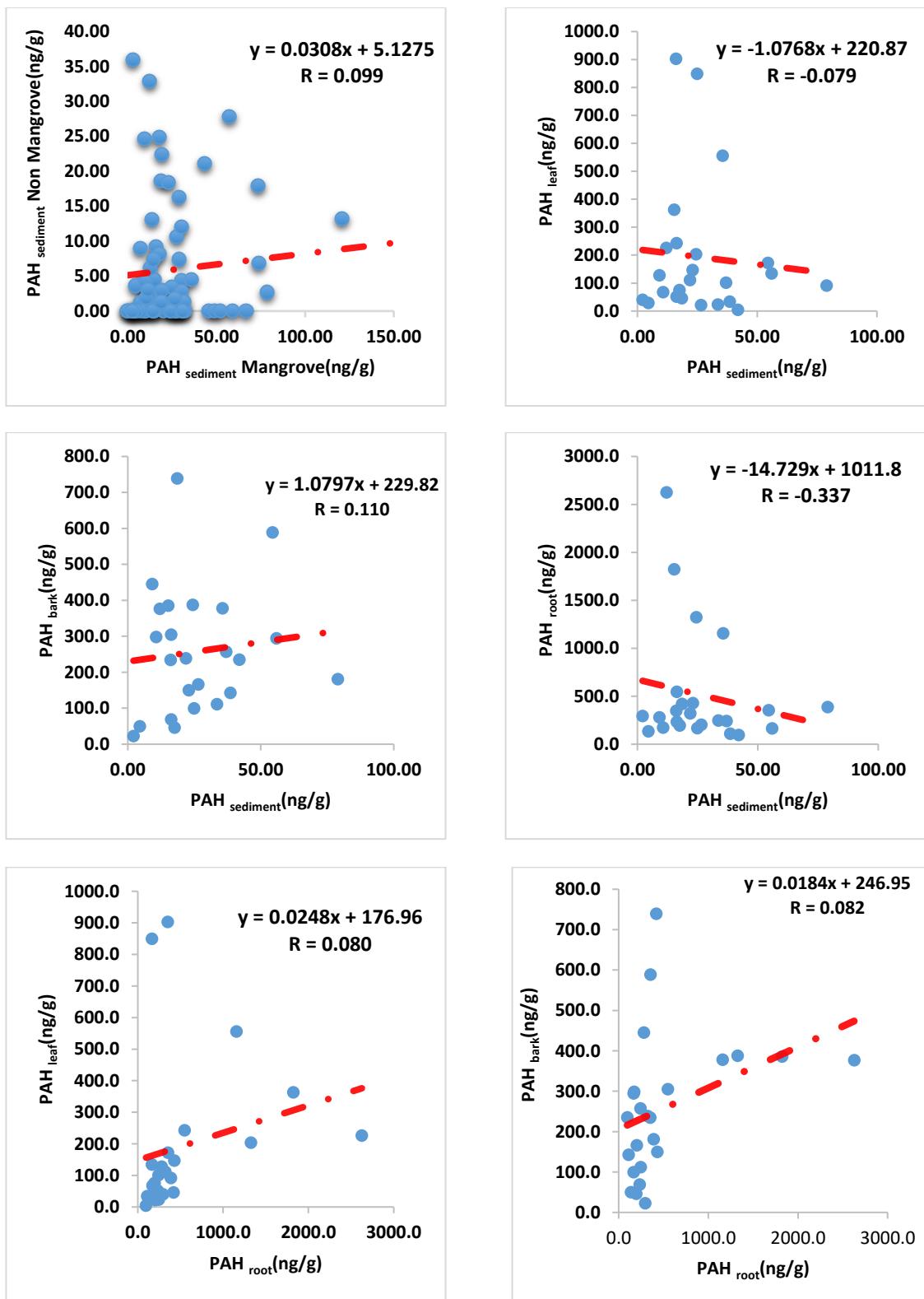


Fig 20: Correlation between  $\Sigma$ PAHs concentrations in sediment vs. plant tissues

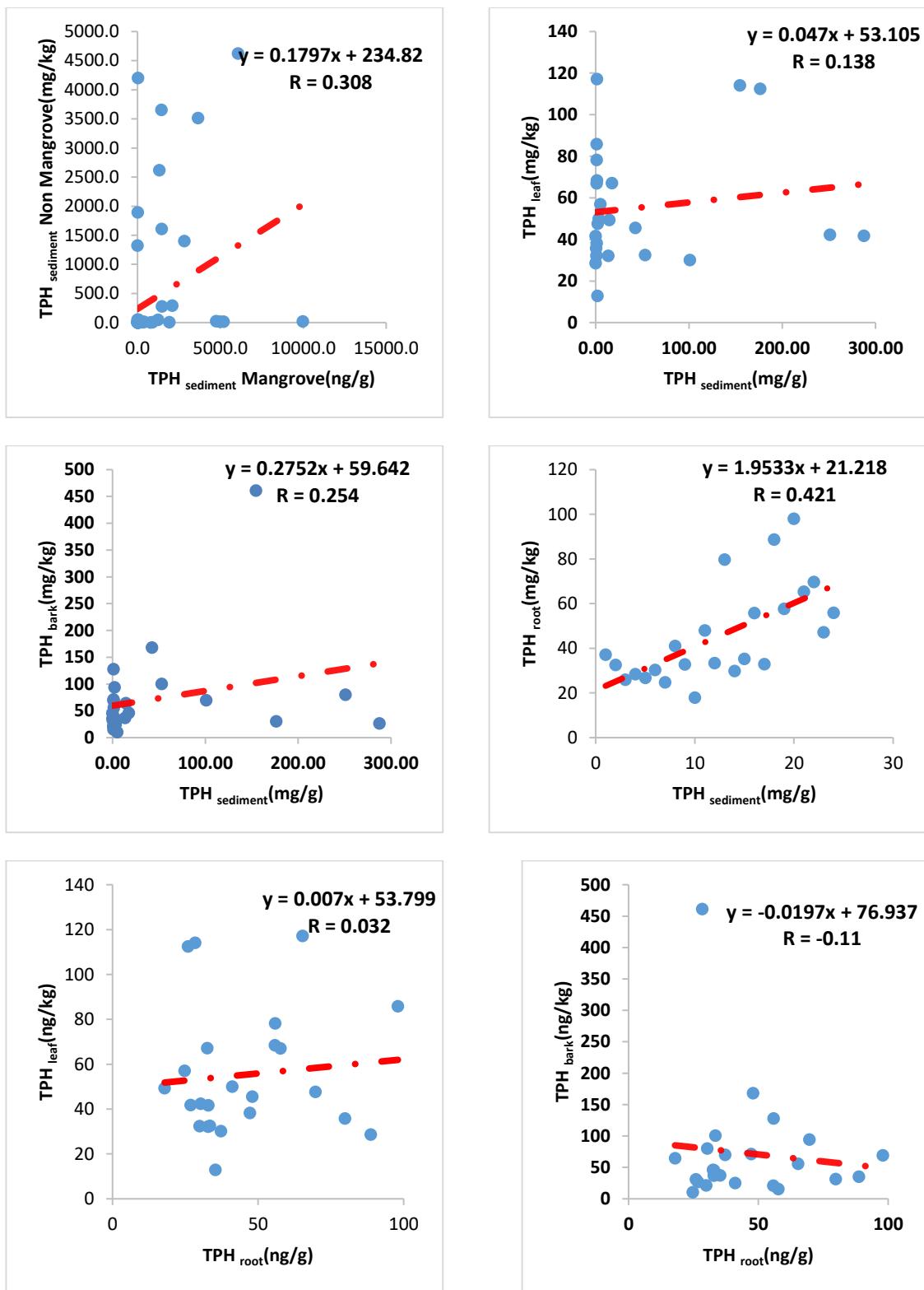


Fig 21: Correlation between TPH concentrations in sediment vs. plant tissues

#### **4.8 Trends of Hydrocarbon concentration in Plant tissue**

The concentration of the 16 USEPA priority polycyclic hydrocarbons ( $\Sigma$ PAHs) contamination in plant roots, bark and leaves were measured for the samples collected from four mangrove zones of the Saudi Coast of the Arabian Gulf including Abu Ali island, Tarut Bay, Rahima and Gurmah. In all of our field sample, the concentration of hydrocarbon in plant sample is comparatively high in the sediment. The values also varied within the same sampling area. The concentration of  $\Sigma$ PAHs was high in Gurmah island for all plant parts such as leaves, barks, and roots. The highest concentration of  $\Sigma$ PAHs in leaf, bark, and root samples were 396.21, 367.85 and 1260.35 ng/g, respectively in Gurmah island. The average lowest concentrations in both leaf and bark of the collected samples from Tarut are 35.9 and 131.01 ng/g, respectively. For TPH, the maximum value is observed in Gurmah for both leaf and root samples (72.31 and 350.83 mg/kg). The highest concentration of TPH in bark samples is observed in Abu Ali as 119.03 mg/kg. The trend of total  $\Sigma$ PAHs concentration in all sites followed the descending order: roots > leaf > bark > sediment. The detected accumulation trend of  $\Sigma$ PAHs in this study is comparable with the mangrove swamps in Red Sea [230] ; Arabian Gulf [231]; and Shenzhen [209]. Based on the guidelines proposed by Massoud [232], the present study area falls under “unpolluted” category .

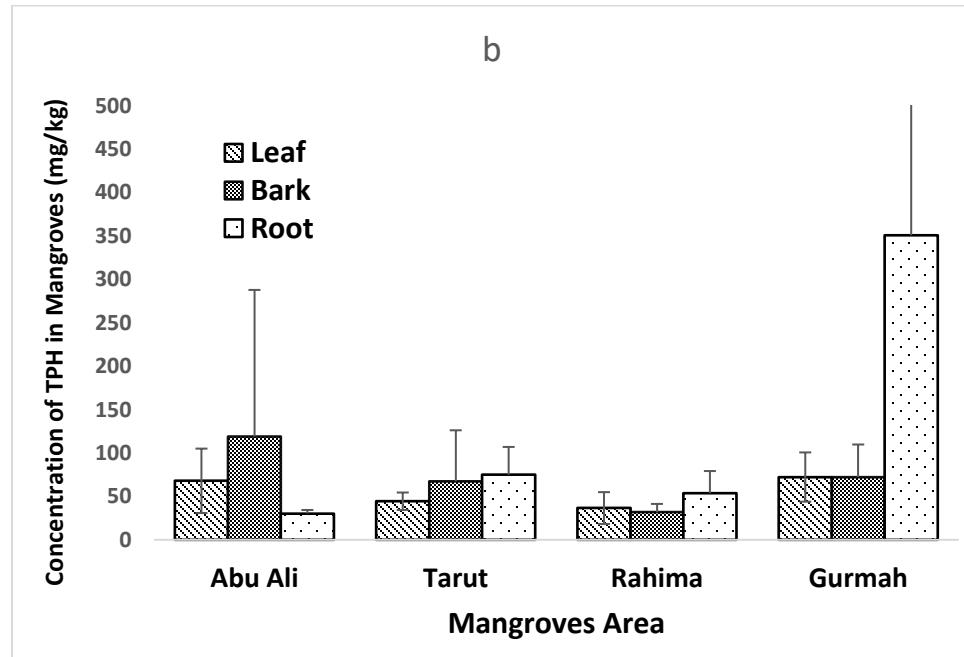
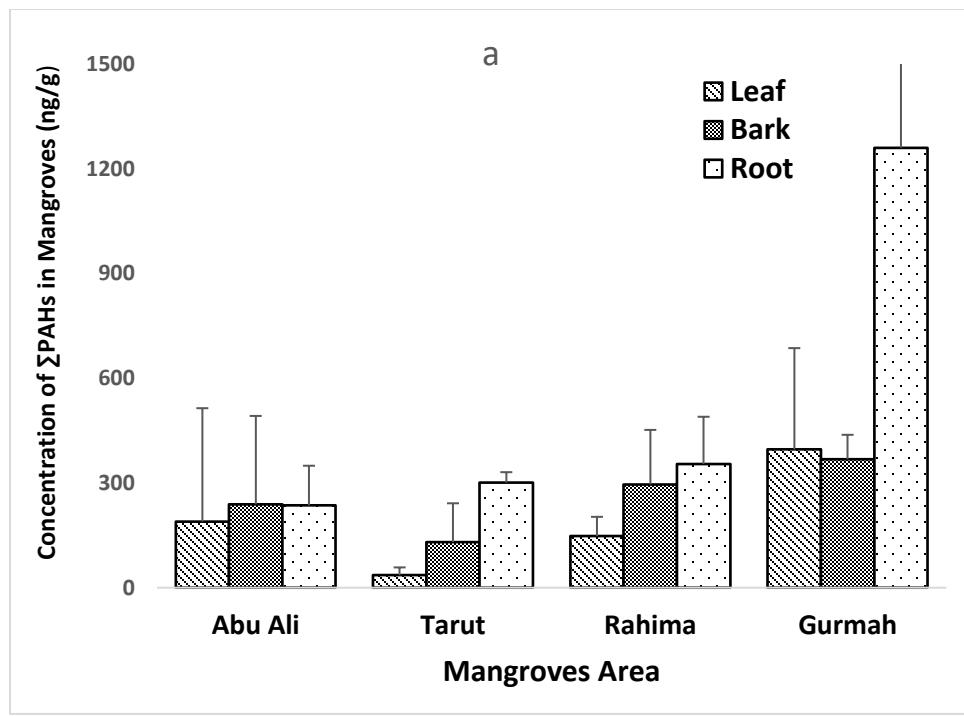


Fig 22: Trends of hydrocarbon concentrations (mean  $\pm$  standard deviation  $\text{mg kg}^{-1}$ ) (a) PAHs and (b) TPH in *Avicennia marina* growing in different mangrove areas

#### **4.9 Trends of Bioaccumulation Factor of hydrocarbon in plant tissue**

The BAFs of the  $\Sigma$ PAHs and TPH in mangroves (Fig 23) are significantly different among different areas which indicated that the different ability of mangroves body parts to accumulate hydrocarbons from the environment. The BCF values of both PAHs and TPH in all plants exceed 1 which showed that there was an efficient rate of transfer of metal from the sediment to the plant body. From the obtained data, the BCF values PAHs in leaf, bark and roots were as follows: 5.12-22.78, 8.43- 24.41 and 10.91-79.62 respectively. The BAF for TPH were as leaf (0.98 – 62.76), bark (1.12 – 45.16) and root (0.46 - 120). The highest concentration of BAF for both PAH and TPH were found in Gurmah island.

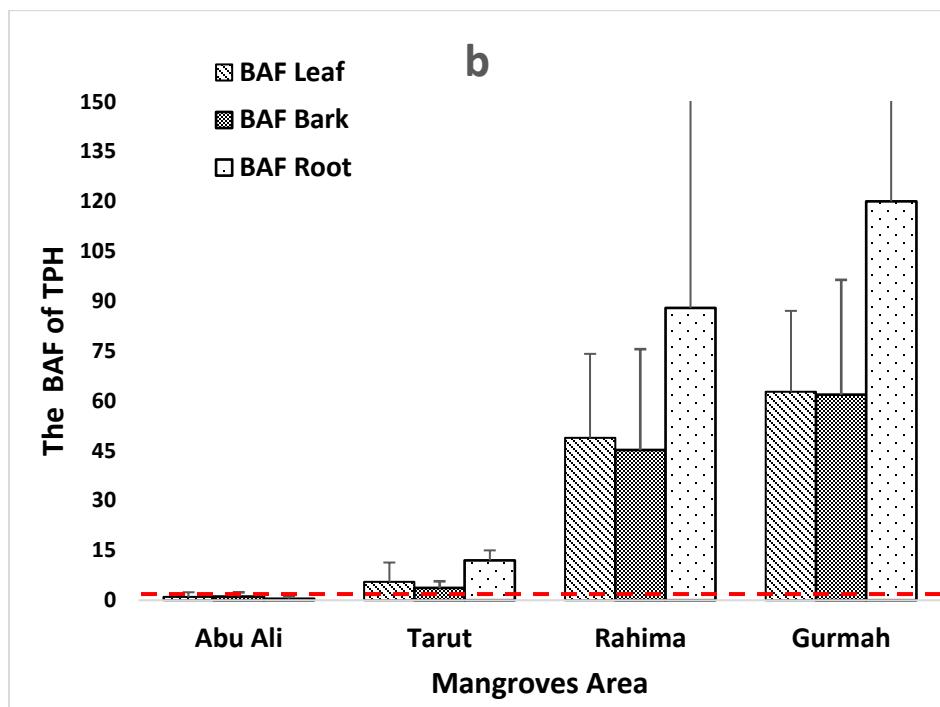
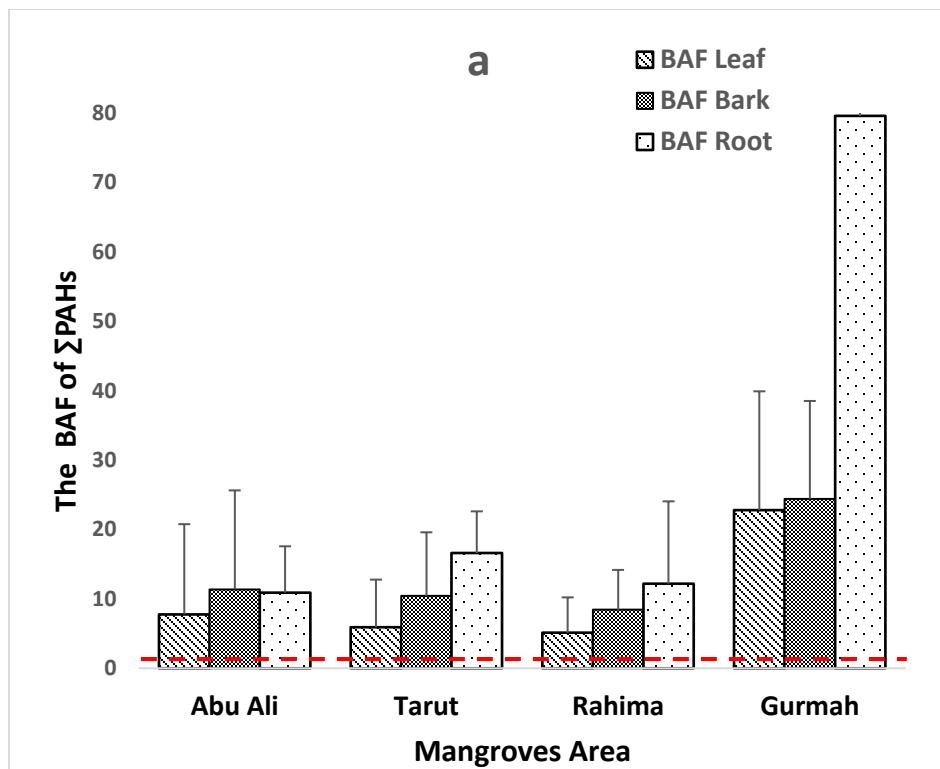


Fig 23: Trends of BAF (mean  $\pm$  standard deviation  $\text{mg kg}^{-1}$ ) of hydrocarbons (a)  $\Sigma\text{PAHs}$  and (b) TPH in *Avicennia marina* growing in different mangrove areas. Dashed line represents BAF  $\geq 1$ , called as hyperaccumulator [228]

#### **4.10 Trends of Translocation Factor of hydrocarbon in plant tissue**

The ability of phytoextraction capacity has also been expressed by a translocation factor (TF), which is defined as the ratio of the hydrocarbon concentration in the leaf/shoots/barks to that in the roots. Generally, plant species with TF values >1 are classified as high-efficient plants from the roots to above ground parts of plants. Therefore, our findings suggest that *Avecinnia marina* may be classified as potential accumulator for both  $\Sigma$ PAHs and TPH (Fig 24). The TF root to leaf for  $\Sigma$ PAHs were followed the trends 1.05 (Abu Ali) > 0.65 (Gurmah) > 0.45 (Rahima) > 0.16 (Tarut), whereas root to bark were 3.38 (Gurmah) > 3.10 (Tarut) > 1.64 (Abu Ali) > 1.48 (Rahima). TF value from root to leaf for TPH were found as 2.35 > 1.14 > 0.97 > 0.78 (Abu Ali > Tarut > Gurmah > Rahima) and  $TF_{bark}$  were found as 4.5 > 3.5 > 1.8 > 0.58 (Gurmah > Tarut > Rahima > Abu Ali).

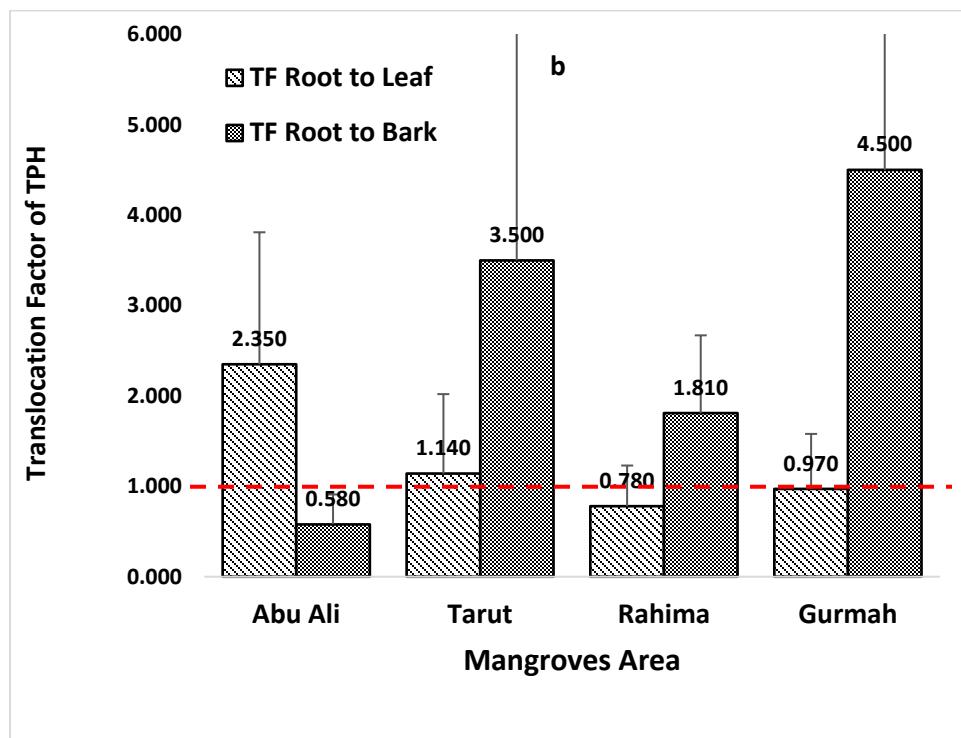
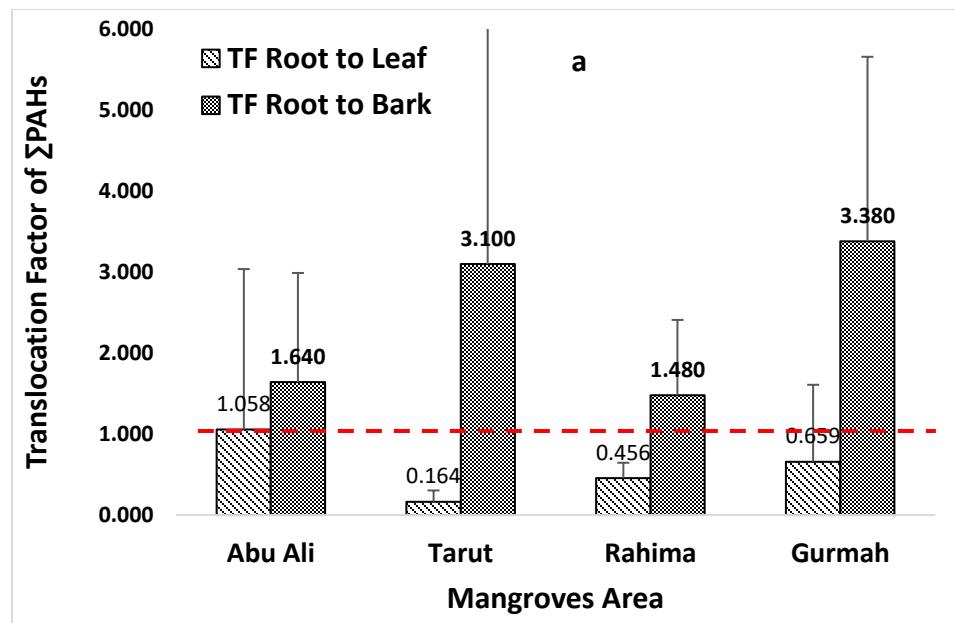


Fig 24: Trends of TF (mean  $\pm$  standard deviation  $\text{mg kg}^{-1}$ ) of hydrocarbons (a)  $\Sigma\text{PAHs}$  and (b) TPH in *Avicennia marina* growing in different mangrove areas. Dashed red line represents  $\text{TF} \geq 1$ , called as Phytostabilization [229]

Table 3. Comparative accounts on heavy metals (mg/kg) in mangrove tissue from study area with available literature on Kingdom of Saudi Arabia

<b>Area</b>	<b>Tissue Type</b>	<b>Cr</b>	<b>Cu</b>	<b>Ni</b>	<b>Hg</b>	<b>Zn</b>	<b>References</b>
Arabian Gulf, Saudi Coast	leaves	1.38	4.42	2.08	---	11.38	[233]
Arabian Gulf, Saudi Coast	leaves	2.2	18.4	6.5	---	41.4	[35]
Read Sea, Saudi Arabia	Leaves	14.96	13.24	7.56	---	---	[234]
	Pneumatophore	17.46	9.82	7.58	---	---	
Read Sea, Saudi Arabia	Leaves	3.84	247	3.1	---	38.4	[235]
Read Sea, Saudi Arabia	Leaves	9.3	356	2.3	---	29.5	[33]
	Branches	8.15	256	1.37	---	34.9	
	Pneumatophore	14.9	270	4.02	---	36.8	
Read Sea, Saudi Arabia	Leaves	2.37	6.38	21.10	---	4.23	[236]
	Pneumatophore	11.94	6.79	3.64	---	1.63	
	Leaves	3.4	8.4	3.6	0.03	22.6	
Arabian Gulf, Abu Ali Island	Barks	1.9	20.2	2.8	0.01	19.2	Present study
	Pneumatophore	0.5	5.8	0.5	0.004	9.4	
	Leaves	3.9	15.1	4.9	0.03	26.7	
Arabian Gulf, Tarut Bay	Barks	3.2	18.1	3.8	0.01	20.1	Present study
	Pneumatophore	1.5	10.5	1.5	0.01	24.5	
	Leaves	8.3	18.5	6.2	0.04	27.2	
Arabian Gulf, Rahima	Barks	7.4	48.4	4.1	0.01	22.6	Present study
	Pneumatophore	9.2	17.8	5.1	0.01	26.7	
	Leaves	7.8	17.1	5.9	0.04	24.0	
Arabian Gulf, Gurmah Island	Barks	8.6	70.0	4.8	0.01	18.2	Present study
	Pneumatophore	10.5	17.3	6.3	0.01	18.3	

Table 4. US Environmental Protection Agency US-EPA top priority 16 PAHs and associated relevant information

PAHs designation	Abbreviation	Conformation		Physico-chemical properties			Pollution criteria		Biodegradation	
		No of rings	MW	<sup>a</sup> Water solubility (mg l <sup>-1</sup> ) at 25° C	<sup>b</sup> log K <sub>ow</sub> at 25°	<sup>c</sup> log K <sub>oA</sub> at 25°C	<sup>d</sup> ERL (mg/kg)	<sup>e</sup> ERM (mg/kg)	<sup>f</sup> Estimated half-lives (days)	<sup>f</sup> Measured half-lives (days)
<b>Naphthalene</b>	Nap	2	128.17	31	3.37	5.1	0.16	2.10	5.56	n.d
<b>Acenaphthylene</b>	Acy	3	152.19	16	4	6.36	0.044	0.64	30.7	n.d
<b>Acenaphthene</b>	Ace	3	154.21	3.8	3.92	6.3	0.016	0.50	18.77	n.d
<b>Fluorene</b>	Flo	3	166.22	1.9	4.18	6.7	0.019	0.54	15.14	n.d
<b>Phenanthrene</b>	Phe	3	178.23	1.1	4.46	7.5	0.240	1.50	14.97	5
<b>Anthracene</b>	Ant	3	178.23	0.04	4.49	7.3	0.853	1.10	123	2.7
<b>Fluoranthene</b>	Flu	4	202.25	0.2	8.9	8.6	0.60	5.10	19.14	9.2
<b>Pyrene</b>	Pyr	4	202.25	0.13	8.8	8.6	0.665	2.60	283.4	151
<b>Benzo[a]anthracene</b>	BaA	4	228.29	0.011	5.8	9.5	0.261	1.60	343.8	>182
<b>Chrysene</b>	Chr	4	228.29	0.001	5.73	10.4	0.384	2.80	343.8	n.d
<b>Benzo[b]fluoranthene</b>	BbF	5	252.31	0.0015	5.78	-	NA	NA	284.7	n.d
<b>Benzo[k]fluoranthene</b>	BkF	5	252.31	0.0008	6.5	11.2	NA	NA	284.7	n.d
<b>Benzo[a]pyrene</b>	BaP	5	252.31	0.0015	6.35	10.8	0.43	0.001	421.6	11
<b>Dibenz[a,h]anthracene</b>	DahA	5	278.35	0.0005	6.5	-	0.063	0.260	511.4	n.d
<b>Benzo[g,h,i]perylene</b>	BghiP	6	276.33	0.00014	6.63	-	NA	NA	517.1	n.d
<b>Indeno[1,2,3-c,d]pyrene</b>	IcdP	6	276.33	0.00019	6.7	-	NA	NA	349.2	n.d

<sup>a</sup> [166]

<sup>b</sup> Octanol/Water Partition Coefficient, log K<sub>OW</sub>; [166]

<sup>c</sup> Octanol/Air Partition Coefficient, log K<sub>oA</sub>; [166]

<sup>d</sup> ERL, effects range low; [183]

<sup>e</sup> ERM, effects range medium; [183]

<sup>f</sup> [237]

Table 5. Global concentrations of PAHs (ng/g) in the mangrove sediments (pollution status; low: 0–100 ng/g; moderate: >100–1000 ng/g; high: >1000–5000 ng/g and very high: >5000 ng/g; [189])

<b>Areas</b>	<b>Sampling stations</b>	<b>No. of sampling stations.</b>	<b>ΣPAH</b>	<b>Mean/range</b>	<b>Pollution status</b>	<b>References</b>
Hong Kong	Mai Po (review)	-	-	178–4,842	moderate to high	Zhang et al. (2014); Zheng et al. (2000); Tam et al. (2001); Tam et al. (2002); Zhao et al. (2012)
	Ma Wan (review)	-	-	791–5,041	moderate to very high	Zhang et al. (2014); Tam et al. (2002); Li et al. (2009); Ke et al. (2005)
	Yio (review)	-	-	73–2,135	low to high	Zhang et al. (2014); Ke et al. (2002); Ke et al. (2005)
	Ho Chung (review)	-	-	1,162–11098	moderate to very high	Zhang et al. (2014); Tam et al. (2001); Yu et al. (2005)
	Sai Keng (review)	-	-	839–2,140	moderate to high	Zhang et al. (2014); Tam et al. (2001); Tam et al. (2002)
	Sheung Pak Nai (review)	-	-	59–241	low to moderate	Zhang et al. (2014); Tam et al. (2002); Ke et al. (2005)
	Tolo (review)	-	-	1,041	high	Zhang et al. (2014); Tam et al. (2001)
	Ting Kok (review)	-	-	56–172	low to moderate	Zhang et al. (2014); Ke et al. (2005)
	Shenzhen(review)	-	-	237–726	low to moderate	Zhang et al. (2014); Vane et al. (2008); Zhang et al. (2004)
Guangdong	Shantou (review)	-	-	15–238	low to moderate	Zhang et al. (2014); Cao et al. (2009b); Wu et al. (2009)
	Zhanjiang (review)	-	-	31–242	low to moderate	Zhang et al. (2014); Tang et al. (2008); Vane et al. (2008)
	Xiamen (review)	-	-	171–223	moderate	Zhang et al. (2014); Tian et al. (2008); Vane et al. (2008)
Fujian	Jiulong River Estuary (review)	-	-	193–1,074	moderate to high	Zhang et al. (2014); Zhang et al. (2004); Lu et al. (2005,2007); Tian et al. (2008)
	Beihai(review)	-	-	24	low	Zhang et al. (2014); Vane et al. (2008)
Guangxi	Haikou (review)	-	-	31–63	low	Zhang et al. (2014); Vane et al. (2008)
	Wenchang (review)	-	-	75	low	Zhang et al. (2014); Vane et al. (2008)

Table 5. Continued.....

Areas	Sampling stations	No. of sampling stations.	$\Sigma$ PAH	Mean/range	Pollution status	References
Shenzhen, China		12	16	313-5168	low to very high	Li et al. (2014)
Sunderban wetlands	India	7	19	9.39-4249.71	low to high	Binelli et al. (2008)
Sunderban Mangrove	India	3	16	121-533	Moderate	Zuloaga et al. (2009)
Sunderban Mangrove	India	4	16	132-2938	moderate to high	Domínguez et al. (2010)
Sunderban Mangrove	India	7	19	9.4-4222.8	low to high	Sarkar et al. (2012)
Hugly Esturine Mangrove	India	9	16	0-1839.5	low to high	Zuloaga et al. (2013)
Sunderban Mangrove	India	4	19	9.4-4222.8	low to high	Sarkar et al. (2012)
Thane Creek, Maharashtra,	India	10	15	902.58- 1643.60	moderate	Sukhdhane et al. (2015)
Martaja Estuarine, Mangrove	Bangladesh	9	16	0-641	low to moderate	Zuloaga et al. (2013)
Anakan Lagoon, Java	Indonesia	5	24	0-122120	moderate to very high	Dsikowitzky et al. (2011)
Peninsular Malaysia	Malaysia	9	17	20-112	low to moderate	Raza et al., 2013
Pulau Cik Wan Dagang, Kemaman	Malaysia	15	16	120-1420	low to moderate	Tahir et al. (2011)
Igbankoko mangrove	Nigeria	3	16	62.5-188 (108)	low to moderate	Sojinu et al. (2011)
Guadeloupe	French West Indies (FWI)	7	11	103-1656	low to moderate	Bernard et al. (1996)
	island					

Table 5. Continued .... ....

<b>Areas</b>	<b>Sampling stations</b>	<b>No. of sampling stations.</b>	<b>ΣPAH</b>	<b>Mean/range</b>	<b>Pollution status</b>	<b>References</b>
Guadeloupe	French West Indies (FWI) island	10	26	49-1065	low to moderate	Ramdine et al. (2012)
Qeshm Island and Khamir Port— Iran	Persian Gulf,	42	22	259- 5,376	moderate to very high	Ebrahimi-Sirizi et al. (2013)
North of Persian Gulf	Iran	9	16	75.24-581.94	low to moderate	Mohebbi-Nozar et al. (2015)
Guanabara Bay	Brazil	5	38	83-2430000	low to very high	Luz et al. (2010)
Guanabara Bay- Rj-Brazil	Brazil	4	16	1232-28278	moderate to very high	Maciel-Souza et al. (2006)
Rio de Janeiro, Brazil	Brazil	5	16	66-8435	low to high	Farias et al. (2008)
Fortaleza, Brazil	Brazil	6	17	3.04-2234.76	low to high	Cavalcante, et al. (2009)
Guanabara Bay	Brazil	5	37	10-33082	low to very high	Nudi et al. (2007)
Guanabara Bay	Brazil	4	16	4300-1387000	high to very high	Fontana et al. (2012)
Abu Ali Island	Arabian Gulf	18	16	7.61- 58.98	low	Present study
Tarut Bay	Arabian Gulf	18	16	0 – 52.20	low	Present study
Rahima	Arabian Gulf	18	16	4.48 – 176.41	low to moderate	Present study
Gurmah Island	Arabian Gulf	18	16	2.26 – 73.65	low	Present study

#### **4.11 Assessment of diesel oil contamination in experimental study**

Beside field study, an experimental work was done to see the uptake and accumulation of petroleum hydrocarbon by same mangrove plant species (i.e., *Avicennia marina*) which was considered for field study. In this study, we investigated the sequestration efficiency of plant from diesel contaminated soil through a pilot-scale pot experiment for 0-3 months duration. Diesel oil spill as four levels of concentration (75ml, 50 ml, 25ml and 0 ml of diesel per kg of soil) exposed to 2-year old seedlings in outdoor condition. The random collected sediment to grow the seedling in the pot experiment were air-dried, and characteristics of the soil were analyzed before mixing different concentration of contaminants (Table 6).

Table 6. Physical and chemical characteristics of soil used in experimental study

Parameters	Value
Textural Class	Sand
Particle size distribution	
Pebble	2.36
Granule	4.49
Coarse Sand (%)	61.79
Fine sand (%)	26.59
Silt (%)	3.70
Clay (%)	1.07
Total Organic Content (%)	1.45
Field N (%)	0.11
Available P mgkg <sup>-1</sup>	1.8
Soil pH	5.05

#### **4.11.1 Concentration of hydrocarbon in experimental set up**

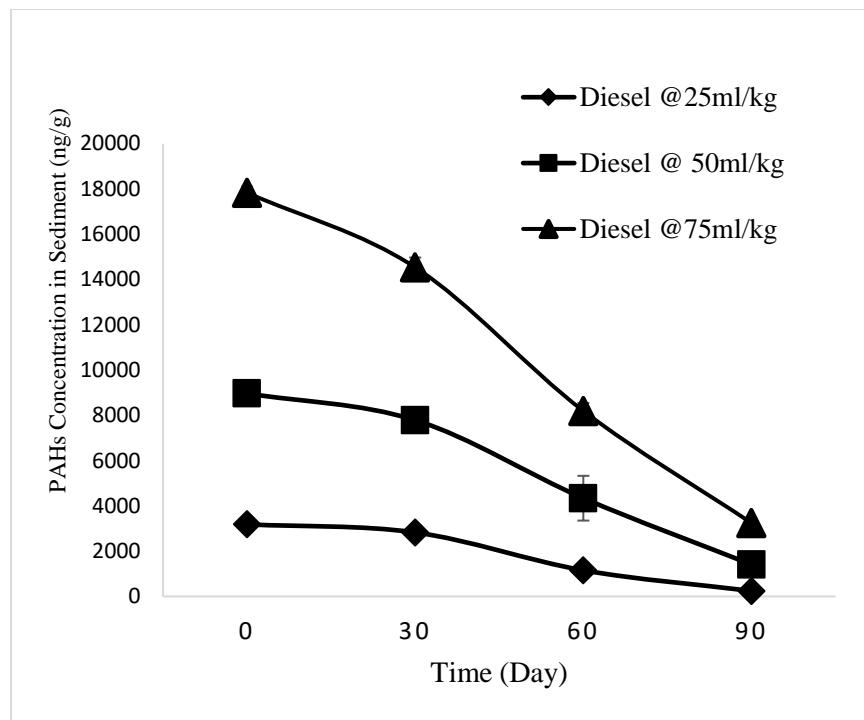
The status of USEPA priority PAHs and TPH, on a dry weight basis, in *Avicennia marina* roots, stems, and leaves were shown in table (table 7). At the initial condition of the experiment, under the different contamination level (25 ml/kg, 50 ml/kg and 75 ml/kg), the mean concentration of PAHs were 3186.09, 5781.1, and 8867.68 ppb which was degraded continuously and finally found as 242.65 ppb (25 ml/kg), 1166 ppb (50 ml/kg), and 1833.94 ppb (75 ml/kg) respectively at the end of 90 days experiment. For TPH, average concentration was 2084.6 ppm (25 ml/kg), 3620 ppm (50 ml/kg), and 4783.3 ppm (75 ml/kg) respectively at the beginning and after 3 months bioremediated as 188.94 ppm (25 ml/kg), 707.75 ppm (50 ml/kg), 1125.15 ppm (75 ml/kg). Major loss of hydrocarbon was made during the middle of the experiment, most likely for evaporation and aging effect. The existence of PAHs in control sediment were not noticeable, whereas aboveground accretion is detectable. This study confirmed that *A. marina* can absorb and accumulate petroleum hydrocarbon from oil polluted sediment. A significant portion of the hydrocarbons were absorbed in roots with small percentage of translocation to stems, while a considerable portion translocated to leaves. Similar result also found with same species for aboveground accumulation of PAHs from the surrounding air, which probably volatilized from the contaminated soil [238].

Table 7. Descriptive statistics for hydrocarbon concentration in experimental study

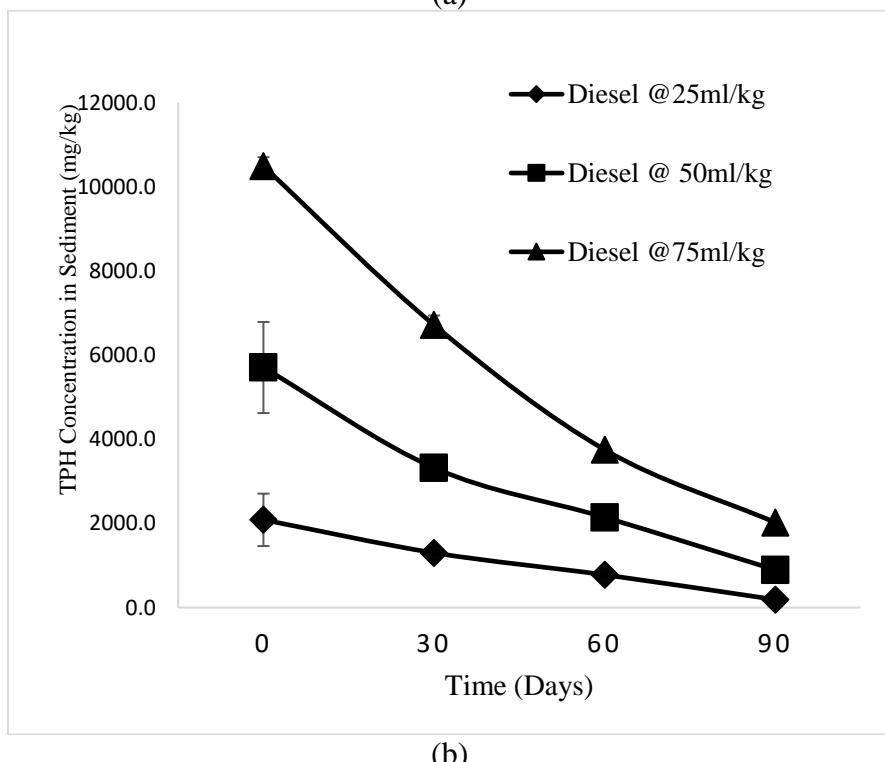
	Sediment			Leaf		Stem		Root		
Days	PAHs	TPH 1	TPH 2	PAHs	TPH	PAHs	TPH	PAHs	TPH	
	Min	bdl	bdl	bdl	27.5	43.5	4.3	20	14.7	31.4
<b>Control</b>	Max	bdl	bdl	bdl	70.4	73.5	9.3	13.8	27.2	79.2
	Mean	bdl	bdl	bdl	42.8	54.3	6.8	11.1	22	50.2
	SD	bdl	bdl	bdl	23.9	16.6	2.5	10.2	6.5	25.5
	Min	6398.3	3182	36527.8	387.5	160.9	111.2	81.8	2255.2	802.7
<b>30 days</b>	Max	7234.7	3632	39835.1	682.9	309.2	162.7	194.5	2669.7	1338.1
	Mean	6750.1	3395.8	38631.5	537.9	252.1	128.8	136	2450.7	990.1
	SD	433.7	225.8	1828.2	147.8	79.8	29.4	56.5	208.2	301.7
	Min	3584.6	1577.9	12189	798.9	418.5	453.9	135.8	2178.9	863.6
<b>60 days</b>	Max	4254.6	1641.9	13482.8	1229.4	808.1	470.7	138.3	3415.6	1317.8
	Mean	3853.6	1605.9	12826	1046.3	600.5	463.6	137.06	2700.9	1062.1
	SD	353.99	32.74	647.12	222.35	196.05	8.69	1.25	640.45	232.415
	Min	1751.16	1107.76	8227.57	837.8	539.2	1137	180.4	3894.3	1627.4
<b>90 days</b>	Max	1893.78	1138.9	8458.08	2224	807.1	1205	220.4	4091.3	2386.5
	Mean	1833.9	1125.15	8379	1597.7	670.73	1166.9	206.5	4009.8	1921.63
	SD	74.02	15.91	131.19	702.69	134.01	34.73	22.61	102.8	407.3

#### **4.11.2 Concentration of hydrocarbon in sediment sample**

The concentration of both PAH and TPH were degraded in the experiment (Fig 25). Both of the cases there was a significant degradation in sediment within these 90 days period and strongly correlated with each other. After the experiment, it was found that the concentration of both  $\Sigma$ PAHs and TPH were degraded in the experiment (Fig 25). The baseline concentration of PAHs was 8867, 5781 and 3423  $\text{ng g}^{-1}$  for 75ml/kg, 50 ml/kg and 25 ml/kg respectively. The baseline concentration of TPH were 68295, 31853 and 25780  $\text{ml kg}^{-1}$  for 75ml/kg, 50 ml/kg and 25 ml/kg respectively. Both of the cases there was a significant degradation in sediment within these 90 days period and strongly correlated with each other.



(a)



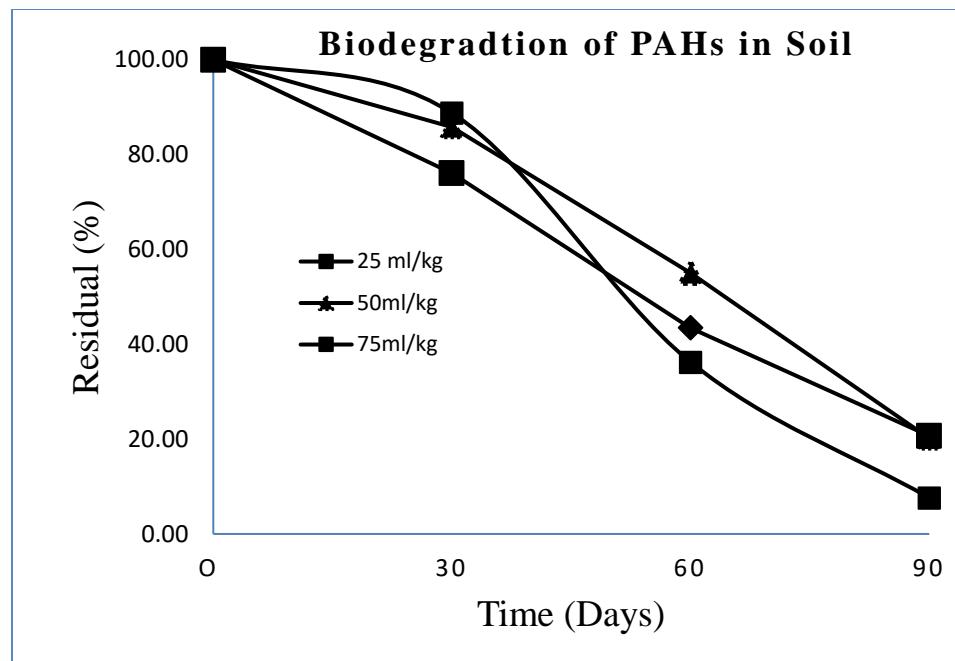
(b)

Fig 25: Trends of degradation of (a)  $\Sigma$ PAHs and (b) TPH in sediment with diesel contaminated soil growing for *Avicennia marina*

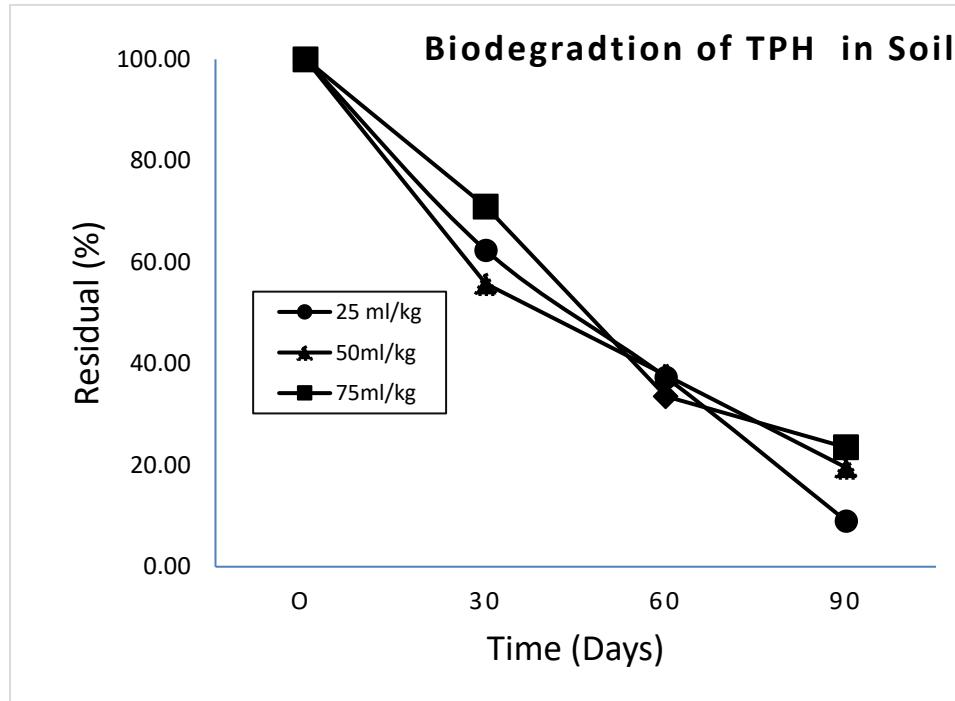
#### **4.11.3 Hydrocarbon Removal Efficiency**

The removal efficiency of polycyclic aromatic hydrocarbon from diesel contaminated soil is presented in Fig 26 (a). After 90 days, the result showed that the bioremediation with *A. marina* degraded approximately 79%, 79% and 92% respectively for  $75 \text{ mlkg}^{-1}$ ,  $50 \text{ mlkg}^{-1}$  and  $25 \text{ mlkg}^{-1}$ , representing a statistically significant percentage. For all the concentration, bioremediation was fast in the early stage and low concentration exhibit comparatively high removal efficiency than high concentration. As the use of mangroves for soil remediation, accretion of some toxic compounds, for example PAHs in plant tissues, has raised significant public concern. With regard to removal efficiency data in Fig 26 (a), it is notable that most of the PAHs degradation was achieved in the middle of the experiment. According to this figure low and medium concentration ( $25 \text{ ml/kg}$  and  $50 \text{ ml/kg}$ ) showed good PAHs removal.

The removal efficiencies of TPHs from soil after three months remediation is shown in Fig 26 (b). Soils samples were collected for TPH analysis at 0, 30, 60, and 90th days during the experiment. The average soil TPH removal percentage for diesel contaminated soils with *Avicennia marina* were 76%, 80% and 91%, respectively for  $75\text{ml/kg}$ ,  $50\text{ml/kg}$  and  $25 \text{ ml/kg}$  of soil. Therefore, it appears that the mangrove plant significantly enhances the removal of total petroleum hydrocarbons from soil. TPHs can be segregated into saturated hydrocarbons, aromatic hydrocarbons, asphaltene and polar portions [239]. High rate of total petroleum hydrocarbon was observed in between 30 and 60 days. Many published literatures indicate that using phytoremediation increases the bioremediation of TPH contaminants [240][241][242].



(a)



(b)

Fig 26: Biodegradation of (a) Polycyclic Aromatic Hydrocarbon and (b) Total Petroleum Hydrocarbon from diesel contaminated soil as a function of time ( $n = 3$ )

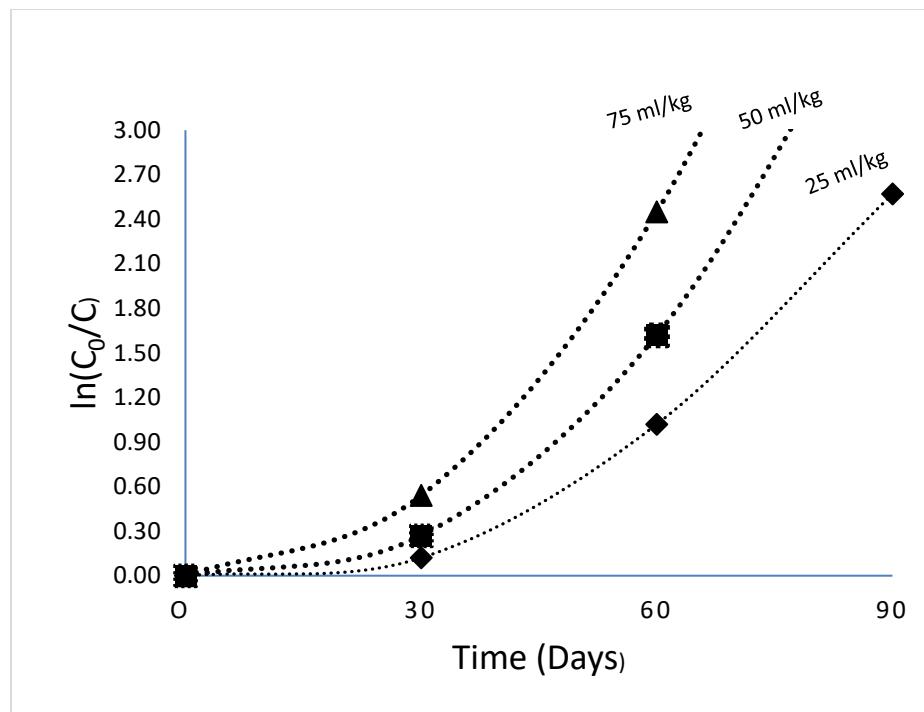
#### **4.11.4 Kinetic evaluation**

The application of first order kinetics describes the diesel oil biodegradation over a three-month period is the main focus of the present investigation. The experimental results confirmed that the use of plant improved the rate of bioremediation. A significant correlation between initial oil concentration and the concentration of PAHs and TPH reduction were observed: lower concentration exhibits higher removal efficiencies in all experiments.

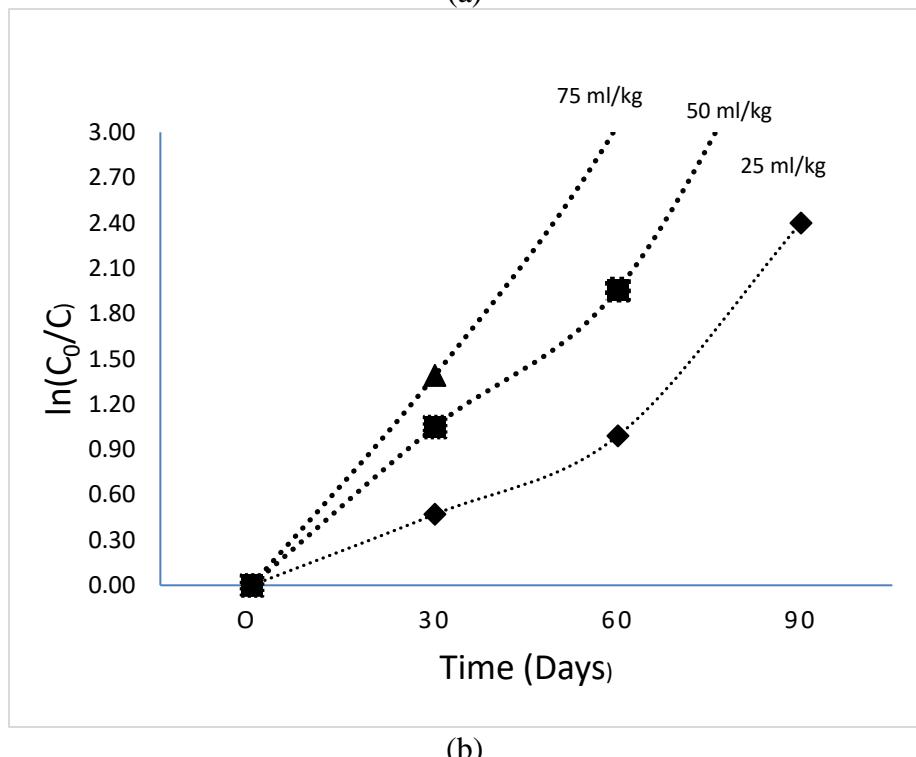
Kinetic analysis is a key factor for bioremediation process which is usually described by first order kinetic equations [243][244][245][246].

$$C = C_0 e^{-kt}$$

Where C is the concentration of hydrocarbon (mg/kg) at time t, t refers to the study time (day),  $C_0$  is the preliminary concentration of hydrocarbon (mg/kg) and k is the rate constant of the change in the diesel hydrocarbon content (day<sup>-1</sup>)



(a)



(b)

Fig 27: Biodegradation kinetic evaluation of diesel oil for (a)  $\Sigma$ PAHs and (b) TPH as a concentration 75 ml/kg, 50 ml/kg and 25 ml/kg soil

#### **4.11.5 Assessment of biodegradation half times**

The time required to degrade half of its actual quantity of an element is considered biodegradation half time which are needed for many chemical applications. Biodegradation half times are calculated by Eq. [247][243][248] .

$$C = \frac{1}{2} C_0 , \text{ after a period of one half-life}$$

$$t = t_{1/2} = C_0 / \frac{2}{C_0 = \frac{1}{2}} = e^{-kt} \frac{1}{2}$$

Taking log of both sides,

$$t_{1/2} = \frac{\ln(2)}{k} = \frac{0.693}{k}$$

where k means the rate constant which is measured by Eq. and tabulated in table 8

All of the biodegradation from both PAHs and TPH were fitted properly ( $R^2 = 0.93 - 0.99$ ) with the first order kinetic equation (table 8). The maximum biodegradation half times  $t_{1/2}$  of 81 days observed for polycyclic aromatic hydrocarbon at a concentration of 50ml/kg soil that was reduce to 80 days and 55 days for 25ml/kg and 75 ml/kg soil respectively. Similarly, for total petroleum hydrocarbon, 47 days was highest for 75ml/kg, and eventually reduced to 39 days and 37 days for 50 ml/kg and 25 ml/kg of soil.

Table 8. Kinetic expression and half times for bioremediation

No	Remediation strategy	Chemical Compounds	Oil (ml/kg)	Kinetic expression <sup>a</sup>	R <sup>2</sup>	T <sub>1/2</sub> (days)
1	Bioremediation	PAHs	25	y = 1.225x - 1.2133	0.9771	80
2	Bioremediation	PAHs	50	y = 0.725x - 0.6667	0.9542	81
3	Bioremediation	PAHs	75	y = 0.655x - 0.4167	0.9930	55
4	Bioremediation	TPH	25	y = 0.965x - 0.6433	0.9338	37
5	Bioremediation	TPH	50	y = 0.525x + 0.01	0.9748	39
6	Bioremediation	TPH	75	y = 0.555x - 0.15	0.9605	47

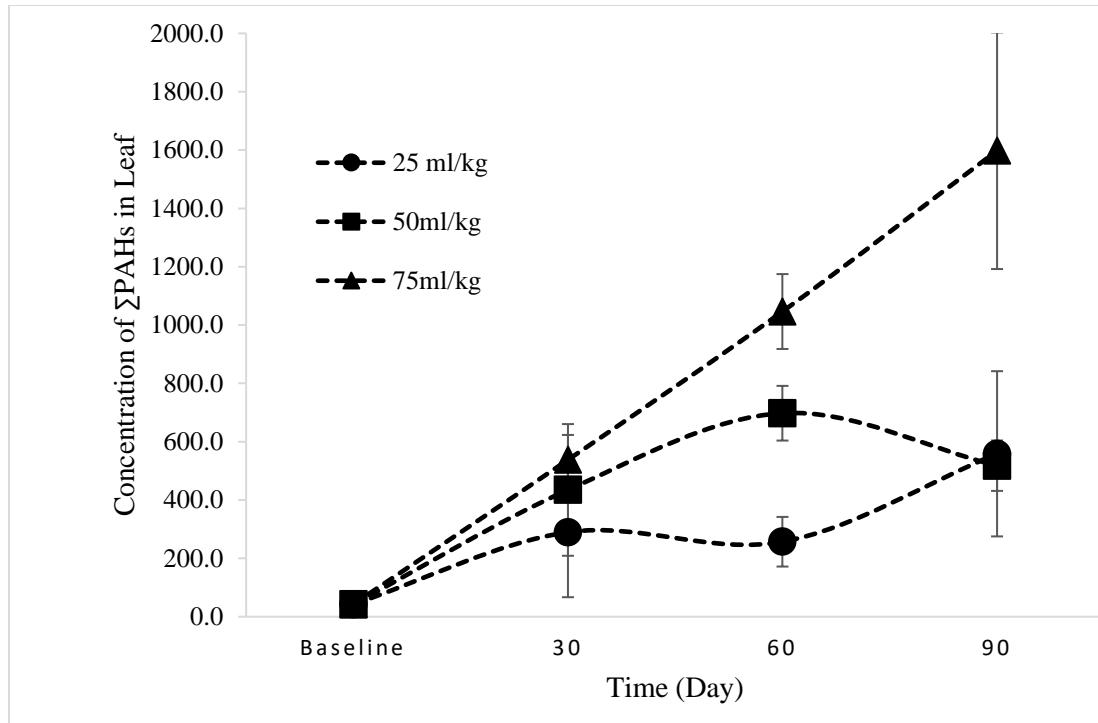
<sup>a</sup>Y = ln C<sub>o</sub>/C, x = t (days)

#### **4.11.6 Accumulation of hydrocarbon in leaf, bark and root of *Avicennia marina* from diesel contaminated sediment**

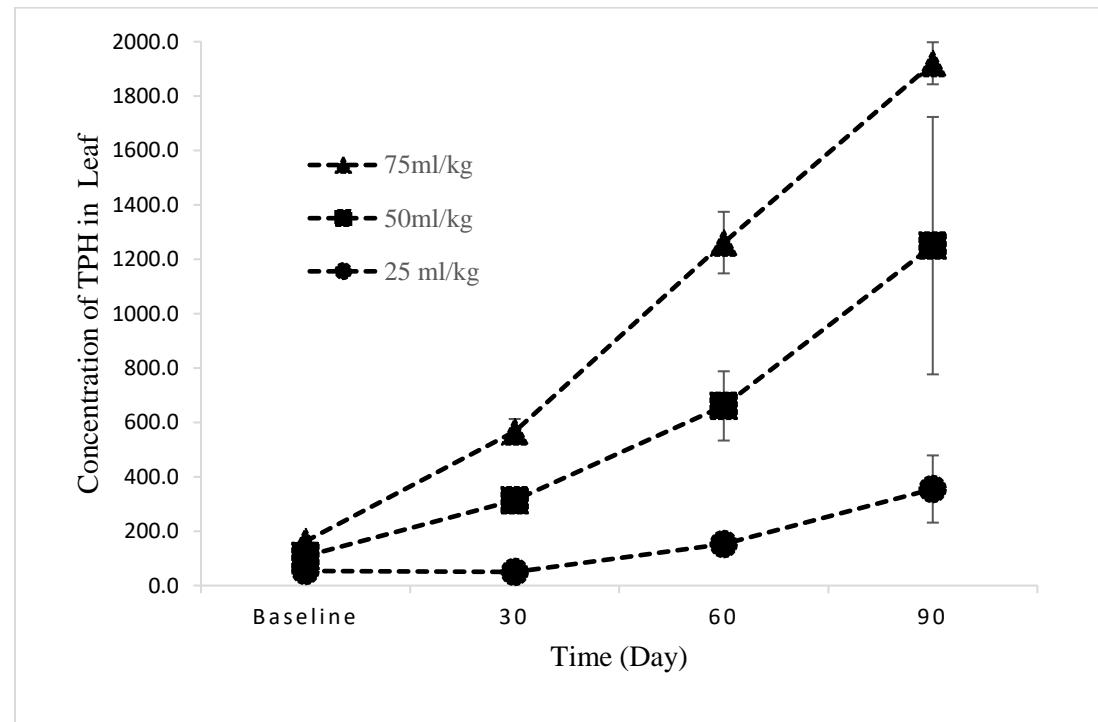
Plants can uptake PAHs from a contaminated environment through the deposition on leaf cuticle or stomata [207][249][209], from contaminated sediment by root, subsequently transfer them to aboveground body parts [250][251]. The levels of accumulation depends on type of plant, concentration of contamination in sediment, and microbiological activity [252]. There is a significant correlation on the levels of hydrocarbon accumulated by the plant leaf tissue (Fig 30). The trend of accumulation is upward, and it increases day by day which is true for every concentration and sample type even though the plant contains a considerable level of PAHs and TPH during baseline samples. Similarly, petroleum hydrocarbon residues in the stems and leaves were also raised up by enhancing their sediment concentration. Therefore, it can be inferred that *Avicennia marina* was able to

uptake and accumulate hydrocarbon through roots and move them to aboveground body part.

The concentration of PAHs and TPH in plant stem were comparatively low than roots and leaves although it showed similar increasing trend with time (Fig. 29). At the first month of experiment, the level of PAHs in the leaves were 289-257-558 ng/g with three different concertation, increased to 434—697- 517 ng/g during second moth, and eventually reached to 537- 1046-1597 ng/g at the end of experiment (third month). At the same time the concentration of diesel was 25-50-75 ml/kg in soil. All of the cases the concentration of PAHs was increased except 50ml/kg in third month (dropped 558 to 517 ng/g from previous month). The major pathway for the accumulation of PAHs is from the atmosphere to the epidermis of the leaf, although very less is known for the pattern of PAHs profile in mangrove plants [209]. Again, the accumulation TPH in plant leaves were also gradually increased from 50-264-252 mg/kg to 152-507-600 mg/kg in the second month, and finally found to 355 – 894 – 670 mg/kg having oil concentration of 25-50-75 ml/kg in soil (Fig. 28). Lotfinasabasl [221] stated that high TPH concentration of the leaves indicating high uptake capability by leaves of the *Avicennia marina*. The concentration of hydrocarbon (both PAHs and TPH) in roots were upwardly augmented with increasing time and concentration of diesel on sediment (Fig. 30). A high percentage of added diesel oil lead to the enhancement of PAHs and TPH in plant root. In specific, the concentration of hydrocarbon in roots expressively accumulated from 1020 to 2700 ng/g for PAHs and 462 to 1921 mg/kg for TPH, with the increase of oil concentration in soil (from 25 to 75 ml/kg), respectively (Fig. 30).

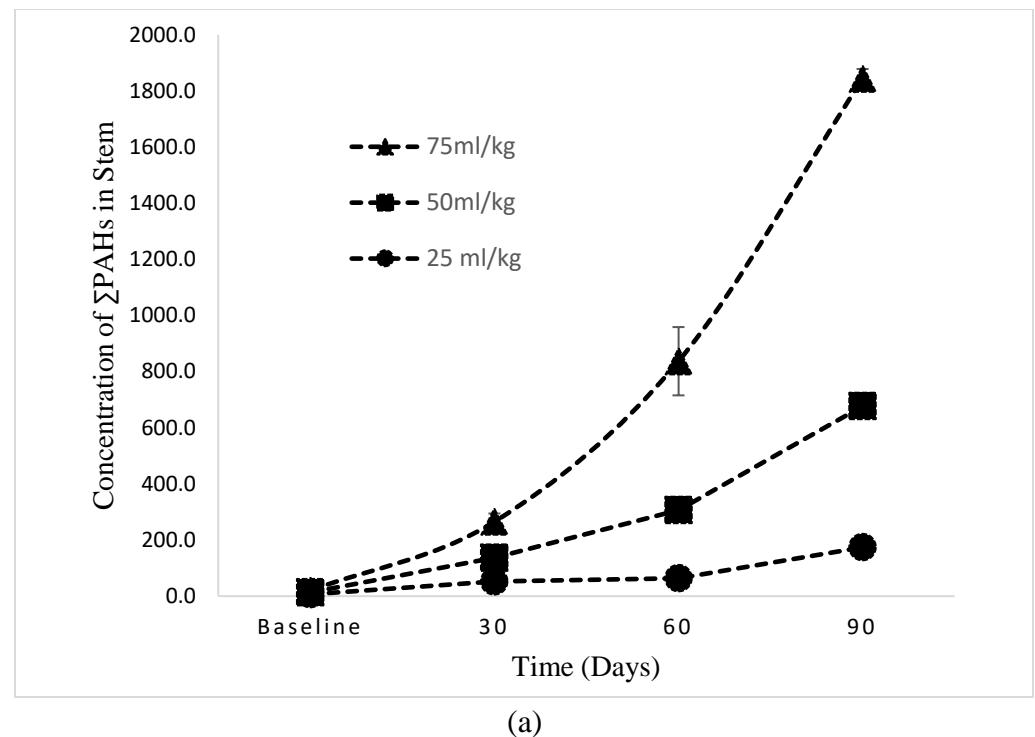


(a)

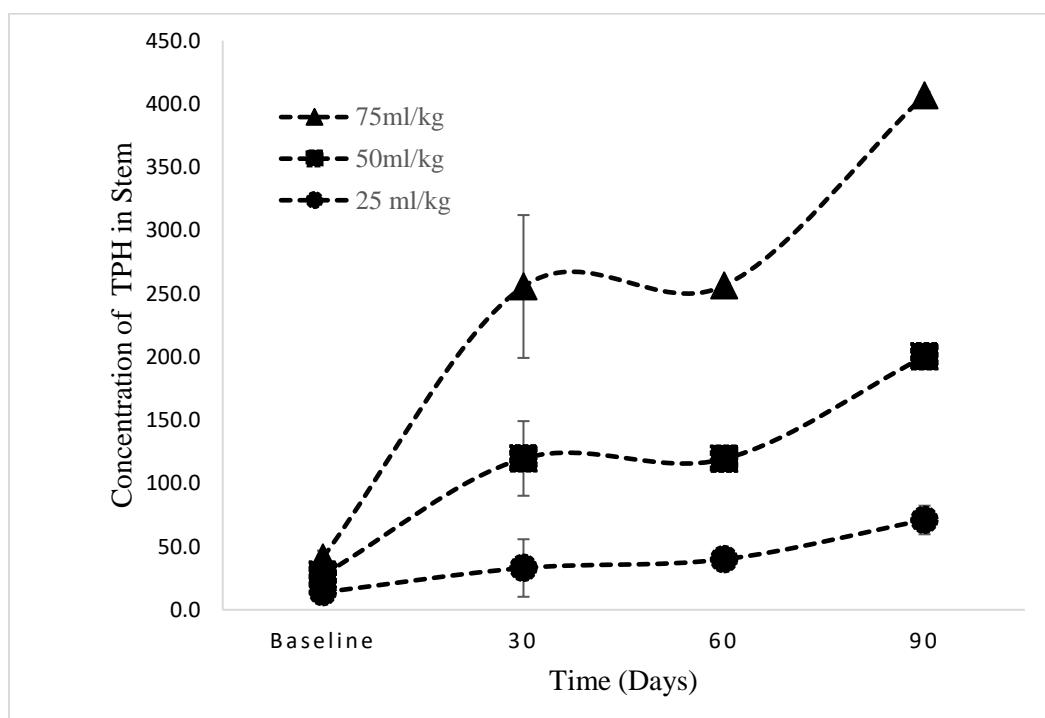


(b)

Fig 28: Trends of accumulation of hydrocarbon (a)  $\Sigma$ PAHs (b) TPH in leaf of *Avicennia marina* growing in diesel contaminated soil

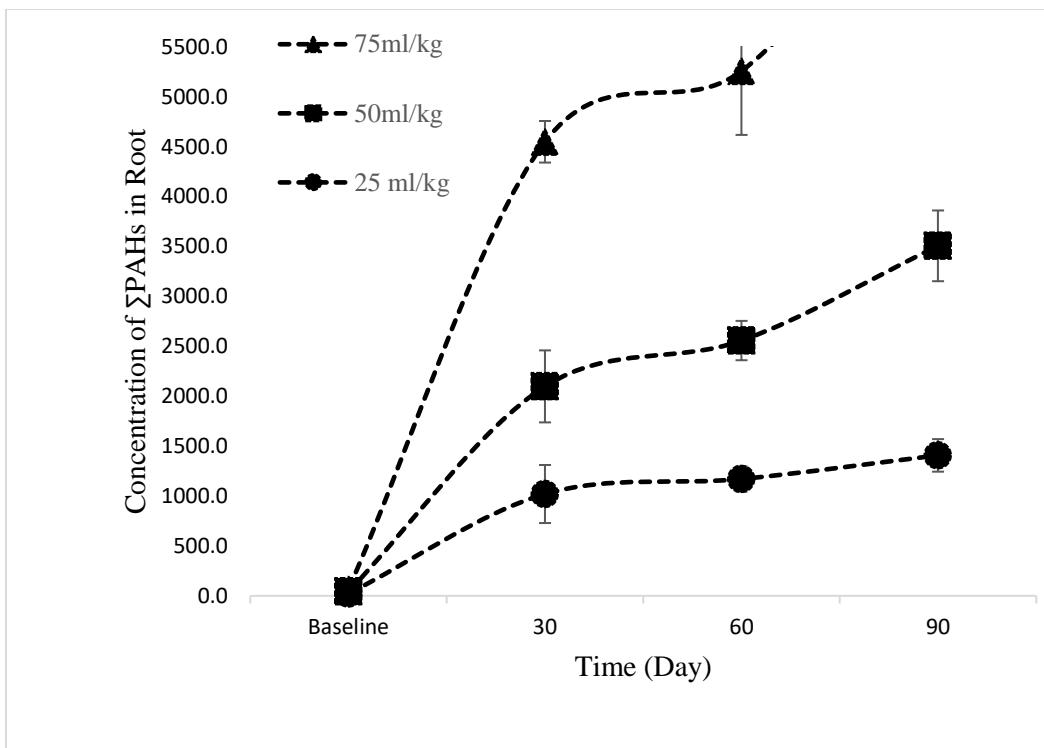


(a)

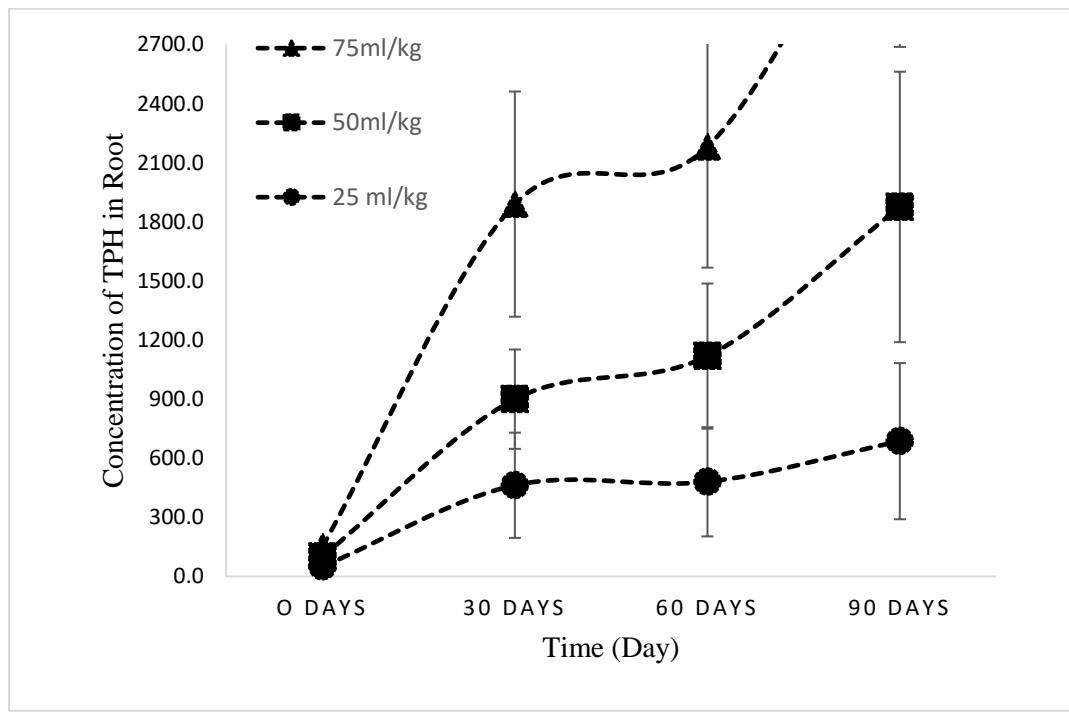


(b)

Fig 29: Trends of accumulation of (a)  $\Sigma$ PAHs (b) TPH in stem of *Avicennia marina* growing in diesel contaminated soil



(a)



(b)

Fig 30: Trends of accumulation of (a)  $\Sigma$ PAHs (b) TPH in root of *Avicennia marina* growing in diesel contaminated soil

#### **4.11.7 Bioaccumulation of hydrocarbon by plant tissue (leaf, bark and root)**

Plant concentration factors are estimated as the proportion of the hydrocarbon fixation in the vegetation to the concentration in soil on a dry weight basis [253]. Root concentration factors (RCFs), stem concentration factors, and leaf concentration factors for the accumulation hydrocarbon by plant as a function of contaminated soil concentrations are listed in Tables 9 and 10. The RCFs, SCFs, and LCFs increases with days for all cases but these do not exhibit a uniform upward trend with increasing PAHs and TPH concentration in sediment. The RCFs fall in the ranges of 1.02 – 3.17 (25 ml/kg), 0.22 – 1.86 (50 ml/kg), and 0.36 – 2.19 (75 ml/kg) for PAHs; and 0.36 – 3.62 (25 ml/kg), 0.21 – 1.68 (50 ml/kg), and 0.30 -1.7(75 ml/kg) for TPH during the 90 days experiment. The SCFs of PAH are found in the ranges of 0.02 – 0.76 (25 ml/kg), 0.02 – 0.44 (50 ml/kg), and 0.02 – 0.64 (75 ml/kg) while TPH are found in the ranges of 0.03 – 0.38 (25 ml/kg), 0.04 – 0.18 (50 ml/kg), and 0.04 – 0.18 (75 ml/kg). The results indicate that *Avicennia marina* is a potential plant species for accumulation of hydrocarbon and can be used for removing hydrocarbon from contaminated sediment. The translocation factor (TF) was used to estimate the translocation from plant roots to aboveground parts [254], which is expressed as  $TF = (SCFs + LCFs) / RCFs$ . Initially (within 30 days) the TF values for accumulation of both PAH and TPH by plant under all treatments (i.e., 25, 50, and 75ml/kg) are comparatively low and gradually increases at the end of experiment (tables 9 and 10). The highest value of TF for PAH accumulation is 0.94 under 25ml/kg treatment which is considered significant. Other cases suggest that the translocation of PAHs from root to aboveground body part of plant is not significant.

The scenario is almost same for the TF values of TPH excluding under 50 mg/kg treatment.

The TF values are 0.81, 0.91, and 0.86 for 30, 60, and 90 days, respectively.

**Table 9.** Concentrations (ng/g) and concentration factors (CFs) of  $\Sigma$ PAHs in plant during 90 days of experiment

Oil Conc	Days	Root	RCFs	Stem	SCFs	Leaf	LCFs	TFs
25 ml/kg	30	1020.13 $\pm$ 167.93	2.52	51.9 $\pm$ 21.32	0.02	289.73 $\pm$ 22.79	0.09	0.04
	60	1170.67 $\pm$ 73.28	1.02	64.2 $\pm$ 2.43	0.06	257.1 $\pm$ 85.14	0.22	0.27
	90	1407.2 $\pm$ 94.2	3.17	173.7 $\pm$ 1.0	0.76	558.6 $\pm$ 283.21	2.22	0.94
50 ml/kg	30	1078.33 $\pm$ 208.23	0.22	84.37 $\pm$ 1.08	0.02	434.77 $\pm$ 225.73	0.09	0.47
	60	1386.93 $\pm$ 113.80	0.47	242.57 $\pm$ 17.43	0.08	697.73 $\pm$ 93.75	0.23	0.66
	90	2099.4 $\pm$ 204.6	1.86	502.9 $\pm$ 3.5	0.44	517.9 $\pm$ 86.42	0.44	0.47
75 ml/kg	30	2450.73 $\pm$ 120.23	0.36	128.8 $\pm$ 16.95	0.02	537.93 $\pm$ 85.32	0.08	0.27
	60	2700.93 $\pm$ 369.77	0.71	530.2 $\pm$ 70.24	0.14	1046.33 $\pm$ 128.37	0.28	0.58
	90	4009.8 $\pm$ 59.4	2.19	1166.9 $\pm$ 20.1	0.64	1597.7 $\pm$ 405.70	0.87	0.69
Control		27.4 $\pm$ 7.03	-	13.9 $\pm$ 0.52	-	103.6 $\pm$ 8.97	-	-

In our study, the concentration of  $\Sigma$ PAHs in leaf and its BCF were more than that in root and there was significance difference root and sediment  $\Sigma$ PAHs. Therefore, The high values of BCF in leaf may support that hydrocarbons were taken up and accumulated in leaves either from contaminated sediment or atmospheric deposition [207][255]. Most hydrophobic organic chemicals are not easily absorbed by trees from contaminated soil

through transpiration [253] . In oiled roots of this species, the common portion of PAHs were low molecular weight, perhaps due to their larger water solubility, higher vapor pressure, and higher bioavailability [256]. In our finding, only a minor concentration of the hydrocarbon pool was translocated to stems from root, like to other study [251] .

Table 10. Concentrations (mg/kg) and concentration factors (CFs) of TPH in plant during 90 days of experiment

<b>Oil Conc</b>	<b>Days</b>	<b>Root</b>	<b>RCFs</b>	<b>Stem</b>	<b>SCFs</b>	<b>Leaf</b>	<b>LCFs</b>	<b>TFs</b>
<b>25 ml/kg</b>	30	462.63 ± 267.10	0.36	33.03 ± 13.13	0.03	50.07 ± 0.84	0.04	0.18
	60	480.1 ± 277.19	0.62	39.93 ± 3.05	0.05	152.73 ± 6.53	0.20	0.40
	90	686.3 ± 396.3	3.64	71 ± 6.5	0.38	355 ± 123.6	1.88	0.62
<b>50 ml/kg</b>	30	436.97 ± 252.28	0.21	86.63 ± 17.04	0.04	264.3 ± 22.77	0.13	0.81
	60	638.1 ± 368.41	0.47	79.33 ± 1.17	0.06	507.9 ± 123.37	0.37	0.91
	90	1189 ± 686.5	1.68	129.3 ± 4.0	0.18	894.9 ± 473.2	1.26	0.86
<b>75 ml/kg</b>	30	990.07 ± 571.62	0.30	135.97 ± 32.61	0.04	252.07 ± 46.07	0.07	0.39
	60	1062.17 ± 613.24	0.66	137.07 ± 0.72	0.09	600.53 ± 113.19	0.37	0.67
	90	1921.6 ± 1109.5	1.71	206.5 ± 1.6	0.18	670.7 ± 77.4	0.60	0.46
<b>Control</b>		66.07 ± 38.14	-	29.7 ± 1.65	-	43.17 ± 8.75	-	-

## **CHAPTER 5**

### **CONCLUSION AND RECOMMENDATIONS**

#### **5.1 Conclusions**

This research investigated the sequestration potential of *Avicennia marina* in removing selected metals and hydrocarbons and examined the distribution of the contaminants in different parts of the plant along the Saudi coast of the Arabian Gulf. The objective of this study is to assess the survival potential of *Avicennia marina* in harsh arid environment and the provided ecological services including bioremediation and contaminant accumulation. It will serve as a basis for the improvement of the natural ecosystem. Hence, this study provided important data on the existence, distribution and feasible source of trace metals and petroleum hydrocarbon in the mangrove ecosystem in the Saudi coast of Arabian gulf. The level of contaminants in both sediment and plant body of *Avicennia marina* varied significantly depending on sample locations. The metal concentrations in sediment were below the natural background levels and classified as less contaminated. Two and three ring PAHs were abundant in plant samples while high molecular PAHs were considerably high in sediment. According to the ecotoxicological valuation, the sediment in these areas are expected to cause limited adverse effects due to their low concentrations, although the accumulation of few specific PAHs compounds in some stations were above ERL and/or TEL. Therefore, the overall assessment showed that the sediment collected from the mangrove zone of the Western Arabian gulf has low ecological risk and a low possibility of toxic pollution.

Based on the experimental study, it is concluded that *Avicennia marina* seedlings absorbed and accumulated significantly higher concentration of petroleum hydrocarbon. The accumulation of total PAHs and TPH was high in roots with little translocation to stem. The exposure of *Avicennia marina* to oil is extensive due to its wider root system having larger surface area. The large root surface area permits more absorption and accretion of oil. As *Avicennia marina* performed well in biodegradation of diesel contaminated sediment, it can be considered as a potential species for bioremediation.

## 5.2 Recommendations

In order to build upon the findings in this study and to better understand the utilization of the mangrove plants for phytoremediation, the following recommendations are proposed:

1. The potential phytoremediation efficiencies of *Avicennia marina* should be investigated for different concentrations of heavy metals;
2. The effect of PAHs on the growth, germination, and reproduction should be monitored by raising seedling on the contaminated media;
3. The effect of microorganisms on the dissipation of PAHs should be evaluated; and
4. The performances of other types of aquatic plant like seagrass, micro-algae should be evaluated for similar studies.

## References

- [1] Y. Wang *et al.*, “Heavy metal contamination in a vulnerable mangrove swamp in South China,” *Environ. Monit. Assess.*, vol. 185, no. 7, pp. 5775–5787, Jul. 2013.
- [2] S. Y. Lee *et al.*, “Ecological role and services of tropical mangrove ecosystems: a reassessment,” *Glob. Ecol. Biogeogr.*, vol. 23, no. 7, pp. 726–743, 2014.
- [3] P. Chaudhuri, B. Nath, and G. Birch, “Accumulation of trace metals in grey mangrove *Avicennia marina* fine nutritive roots : The role of rhizosphere processes,” *Mar. Pollut. Bull.*, vol. 79, no. 1–2, pp. 284–292, 2014.
- [4] S. Sandilyan and K. Kandasamy, “Decline of mangroves – A threat of heavy metal poisoning in Asia,” *Ocean Coast. Manag.*, vol. 102, pp. 161–168, 2014.
- [5] W. Tang *et al.*, “Pollution, toxicity, and ecological risk of heavy metals in surface river sediments of a large basin undergoing rapid economic development,” *Mar. Pollut. Bull.*, vol. 119, no. 2, pp. 85–93, 2017.
- [6] I. Nagelkerken *et al.*, “The habitat function of mangroves for terrestrial and marine fauna: A review,” *Aquat. Bot.*, vol. 89, no. 2, pp. 155–185, 2008.
- [7] E. B. Barbier, “The protective service of mangrove ecosystems: A review of valuation methods,” *Mar. Pollut. Bull.*, vol. 109, no. 2, pp. 676–681, 2016.
- [8] D. C. Donato, J. B. Kauffman, D. Murdiyarso, S. Kurnianto, M. Stidham, and M. Kanninen, “Mangroves among the most carbon-rich forests in the tropics,” *Nat. Geosci.*, vol. 4, no. 5, pp. 293–297, 2011.
- [9] and J. K. Y. Ivan Valiela, Jennifer L. Bowen, “Mangrove forests: One of the world’s threatened major tropical environments,” *Biosci. · Sept. 2001*, no. 51(10), pp. 807–815, 2001.
- [10] N. C. Duke, J. Meynecke, S. Dittmann, and K. Anger, “A World Without Mangroves?,” *Sci. 2007*, p. 317:41–2., 2007.
- [11] C. Marchand, J.-M. Fernandez, B. Moreton, L. Landi, E. Lallier-Vergès, and F. Baltzer, “The partitioning of transitional metals (Fe, Mn, Ni, Cr) in mangrove sediments downstream of a ferralitized ultramafic watershed (New Caledonia),” *Chem. Geol.*, vol. 300–301, pp. 70–80, 2012.
- [12] C. Marchand, J. M. Fernandez, and B. Moreton, “Trace metal geochemistry in mangrove sediments and their transfer to mangrove plants (New Caledonia),” *Sci. Total Environ.*, vol. 562, pp. 216–227, 2016.

- [13] D. M. Alongi, "Present state and future of the world's mangrove forests," *Environ. Conserv.*, vol. 29, no. 03, pp. 331–349, 2002.
- [14] T. Youssef and P. Saenger, "Photosynthetic gas exchange and accumulation of phytotoxins in mangrove seedlings in response to soil physico-chemical characteristics associated with waterlogging," *Tree Physiol.*, vol. 18, no. 5, pp. 317–324, 1998.
- [15] G. R. MacFarlane and M. D. Burchett, "Toxicity, growth and accumulation relationships of copper, lead and zinc in the grey mangrove *Avicennia marina* (Forsk.) Vierh," *Mar. Environ. Res.*, vol. 54, no. 1, pp. 65–84, 2002.
- [16] M. W. Clark, D. McConchie, D. W. Lewis, and P. Saenger, "Redox stratification and heavy metal partitioning in Avicennia-dominated mangrove sediments: a geochemical model," *Chem. Geol.*, vol. 149, no. 3, pp. 147–171, 1998.
- [17] L. D. Lacerda *et al.*, "The fate of trace metals in suspended matter in a mangrove creek during a tidal cycle," *Sci. Total Environ.*, vol. 75, no. 2, pp. 169–180, 1988.
- [18] B. Miola, J. O. de Morais, and L. de Souza Pinheiro, "Trace metal concentrations in tropical mangrove sediments, NE Brazil," *Mar. Pollut. Bull.*, vol. 102, no. 1, pp. 206–209, 2016.
- [19] L. Jingchun, Y. Chongling, M. R. Macnair, H. Jun, and L. Yuhong, "Distribution and Speciation of Some Metals in Mangrove Sediments from Jiulong River Estuary, People's Republic of China," *Bull. Environ. Contam. Toxicol.*, vol. 76, no. 5, pp. 815–822, May 2006.
- [20] Y. Tian, Y. rong Luo, T. ling Zheng, L. z. Cai, X. xing Cao, and C. ling Yan, "Contamination and potential biodegradation of polycyclic aromatic hydrocarbons in mangrove sediments of Xiamen, China," *Mar. Pollut. Bull.*, vol. 56, no. 6, pp. 1184–1191, 2008.
- [21] Y. Wang, H. Zhu, N. Fung, and Y. Tam, "Effect of a polybrominated diphenyl ether congener (BDE-47) on growth and antioxidative enzymes of two mangrove plant species, *Kandelia obovata* and *Avicennia marina*, in South China," *Mar. Pollut. Bull.*, vol. 85, no. 2, pp. 376–384, 2014.
- [22] N. F. Y. Tam and Y. S. Wong, "Mangrove soils as sinks for wastewater-borne pollutants," *Hydrobiologia*, vol. 295, no. 1, pp. 231–241, Jan. 1995.
- [23] N. F. Y. Tam, L. Ke, X. H. Wang, and Y. S. Wong, "Contamination of polycyclic aromatic hydrocarbons in surface sediments of mangrove swamps," vol. 114, 2001.
- [24] N. F.Y. Tam, "Pollution Studies on Mangroves in Hong Kong and Mainland China," in *The Environment in Asia Pacific Harbours*, 2006, pp. 147–163.
- [25] S. Caeiro, M. H. Costa, T. B. Ramos, F. Fernandes, and N. Silveira, "Assessing heavy metal contamination in Sado Estuary sediment: An index analysis approach," vol. 5, pp. 151–169, 2005.

- [26] M. Cl, M. Jc, J. Otero, and C. L. Mejías-rivera, “Exploratory Evaluation of Retranslocation and Bioconcentration of Heavy Metals in Three Species of Mangrove at Las Cucharillas Marsh , Puerto Rico,” vol. 3, no. 1, pp. 14–22, 2013.
- [27] C. Marchand, E. Lallier-Vergès, F. Baltzer, P. Albéric, D. Cossa, and P. Baillif, “Heavy metals distribution in mangrove sediments along the mobile coastline of French Guiana,” *Mar. Chem.*, vol. 98, no. 1, pp. 1–17, 2006.
- [28] G. Agoramoorthy, F. A. Chen, and M. J. Hsu, “Threat of heavy metal pollution in halophytic and mangrove plants of Tamil Nadu, India,” *Environ. Pollut.*, vol. 155, no. 2, pp. 320–326, 2008.
- [29] R. K. Ranjan, J. Routh, A. L. Ramanathan, and J. V. Klump, “Polycyclic aromatic hydrocarbon fingerprints in the Pichavaram mangrove–estuarine sediments, southeastern India,” *Org. Geochem.*, vol. 53, pp. 88–94, 2012.
- [30] B. K. Patel and K. D. Vachrajani, “Pollution Status in Mangrove Ecosystem of Mahi and Dadhar River Estuaries,” *Present. Natl. Conf. Biodivers. Status Challenges Conserv. - “FAVEO,*” no. March, pp. 163–172, 2013.
- [31] A. Ismail, M. A. Badri, and M. N. Ramlan, “The background levels of heavy metal concentration in sediments of the west coast of Peninsular Malaysia,” *Sci. Total Environ.*, vol. 134, pp. 315–323, 1993.
- [32] K. Yunus, O. Chuan, M. S. Noor Azhar, S. Saad, and J. K.C.A, “Geochemistry of Sediment in the Major Estuarine Mangrove Forest of Terengganu Region, Malaysia,” *Am. J. Appl. Sci.*, vol. 5, 2008.
- [33] A. R. A. Usman, R. S. Alkredaa, and M. I. Al-Wabel, “Heavy metal contamination in sediments and mangroves from the coast of Red Sea: Avicennia marina as potential metal bioaccumulator,” *Ecotoxicol. Environ. Saf.*, vol. 97, pp. 263–270, 2013.
- [34] R. H. C. Emmerson, S. B. O'Reilly-Wiese, C. L. Macleod, and J. N. Lester, “A multivariate assessment of metal distribution in inter-tidal sediments of the Blackwater Estuary, UK,” *Mar. Pollut. Bull.*, vol. 34, no. 11, pp. 960–968, 1997.
- [35] K. Abou Seedo, M. S. Abido, A. A. Salih, and A. Abahussain, “Assessing Heavy Metals Accumulation in the Leaves and Sediments of Urban Mangroves (*Avicennia marina* (Forsk.) Vierh.) in Bahrain,” *Int. J. Ecol.*, vol. 2017, 2017.
- [36] R. A. Loughland and K. A. Al-Abdulkader, *Marine Atlas, Western Arabian Gulf*. Saudi Aramco, Environment Protection Department, 2011.
- [37] M. D. Spalding, F. Blasco, and C. D. Field, “World Mangrove Atlas,” *Int. Soc. Mangrove Ecosyst.*, p. 178, 1997.
- [38] B. Böer, “Anomalous pneumatophores and adventitious roots of *Avicennia marina* (Forssk.) Vierh. Mangroves two years after the 1991 Gulf War oil spill in Saudi Arabia,” *Mar. Pollut. Bull.*, vol. 27, no. C, pp. 207–211, 1993.

- [39] A. R. G. Price, C. R. C. Sheppard, and C. M. Roberts, “The Gulf: Its biological setting,” *Mar. Pollut. Bull.*, vol. 27, no. C, pp. 9–15, 1993.
- [40] KFUPM/RI, “Marine Environmental Studies. Volume: IV: Mangrove Investigations. Prepared for Saudi Aramco by the Water Resources and Environmental Division, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia, Report Project No.24,” 1994.
- [41] P. Saenger, “Chapter: Mangrove and Salt Marshes, Marine Atlas of the Western Arabian Gulf, Environmental Protection Department, Saudi Aramco, Saudi Arabia,” Environmental Protection Department, Saudi Aramco, Saudi Arabia, 2011, pp. 81–116.
- [42] M. A. Khan and A. Kumar, “Impact of urban development on mangrove forests along the west coast of the Arabian Gulf,” *J. Earth Sci. India*, vol. 2, no. Iii, pp. 159–173, 2009.
- [43] H. A. Naser, “Effects of Multi-Stage Flash and Reverse Osmosis Desalinations on Benthic Assemblages in Bahrain,Arabian Gulf,” *J. Environ. Prot. (Irvine,. Calif.)*, vol. 04, no. 02, pp. 180–187, 2013.
- [44] N. C. Duke, K. A. Burns, and O. Dalhaus, “Effects of Oils and Dispersed-Oils on Mangrove Seedlings in Planthouse Experiments: a Preliminary Assessment of Results Two Months After Oil Treatments,” *APPEA J.*, vol. 38, no. 1, p. 631, 1998.
- [45] C. G. Zhang, K. K. Leung, Y. S. Wong, and N. F. Y. Tam, “Germination, growth and physiological responses of mangrove plant (*Bruguiera gymnorhiza*) to lubricating oil pollution,” *Environ. Exp. Bot. - Env. EXP BOT*, vol. 60, pp. 127–136, 2007.
- [46] F. Emmanuel Olubunmi Corresponding Author and O. Edward Olorunsola, “Evaluation of the Status of Heavy Metal Pollution of Sediment of Agbabu Bitumen Deposit Area, Nigeria,” *Eur. J. Sci. Res.*, vol. 41, no. 3, pp. 1450–216, 2010.
- [47] S. Fdez-Ortiz de Vallejuelo, G. Arana, A. de Diego, and J. M. Madariaga, “Risk assessment of trace elements in sediments: The case of the estuary of the Nerbioi-Ibaizabal River (Basque Country),” *J. Hazard. Mater.*, vol. 181, no. 1–3, pp. 565–573, 2010.
- [48] B. R. Glick, “Phytoremediation: Synergistic use of plants and bacteria to clean up the environment,” *Biotechnol. Adv.*, vol. 21, no. 5, pp. 383–393, 2003.
- [49] J. S. Weis and P. Weis, “Metal uptake, transport and release by wetland plants: Implications for phytoremediation and restoration,” *Environ. Int.*, vol. 30, no. 5, pp. 685–700, 2004.
- [50] P. Tanhan and M. Kruatrachue, “Uptake and accumulation of cadmium , lead and zinc by Siam weed [ *Chromolaena odorata* ( L .) King & Robinson ],” vol. 68, pp. 323–329, 2007.

- [51] I. T. A. Moreira *et al.*, “Phytoremediation using Rizophora mangle L. in mangrove sediments contaminated by persistent total petroleum hydrocarbons (TPH’s),” *Microchem. J.*, vol. 99, no. 2, pp. 376–382, 2011.
- [52] D. Paquin, R. Ogoshi, S. Campbell, and Q. X. Li, “Bench-scale phytoremediation of polycyclic aromatic hydrocarbon-contaminated marine sediment with tropical plants,” *Int. J. Phytoremediation*, vol. 4, no. 4, pp. 297–313, 2002.
- [53] I. T. A. Moreira *et al.*, “Phytoremediation in mangrove sediments impacted by persistent total petroleum hydrocarbons (TPH’s) using Avicennia schaueriana,” *Mar. Pollut. Bull.*, vol. 67, no. 1–2, pp. 130–136, 2013.
- [54] M. K. Banks, P. Kulakow, A. P. Schwab, Z. Chen, and K. Rathbone, “Degradation of Crude Oil in the Rhizosphere of Sorghum bicolor,” *Int. J. Phytoremediation*, vol. 5, no. 3, pp. 225–234, 2003.
- [55] G. Naidoo, Y. Naidoo, and P. Achar, “Responses of the mangroves Avicennia marina and Bruguiera gymnorhiza to oil contamination,” *Flora*, vol. 205, no. 5, pp. 357–362, 2010.
- [56] K. Lindström *et al.*, “Potential of the Galega - Rhizobium galegae system for bioremediation of oil-contaminated soil,” *Food Technol. Biotechnol.*, vol. 41, no. 1, pp. 11–16, 2003.
- [57] T. Chekol, L. R. Vough, and R. L. Chaney, “Phytoremediation of polychlorinated biphenyl-contaminated soils: The rhizosphere effect,” *Environ. Int.*, vol. 30, no. 6, pp. 799–804, 2004.
- [58] P. Agamuthu and A. Dadrasnia, “Dynamics Phytoremediation of Zn and Diesel Fuel in Co-contaminated Soil using Biowastes,” *Biot remediation Biodegrad.*, 2014.
- [59] J. Schreel *et al.*, “Effect of crude oil on the development of mangrove (Rhizophora mangle L.) seedlings from Niger Delta, Nigeria,” *Mar. Pollut. Bull.*, vol. 119, no. 2, pp. 85–93, 2017.
- [60] N. J.I., P. Ravi SAJISH, R. N Kumar, G. BASIL, and V. SHAILENDRA, “An Assessment of the Accumulation Potential of Pb, Zn and Cd by Avicennia marina (Forssk.) Vierh. in Vamleshwar Mangroves, Gujarat, India,” *Not. Sci. Biol.*, vol. 3, 2011.
- [61] A. Kumar, “Temporal changes in mangrove cover between 1972 and 2001 along the south coast of the arabian gulf,” *34th Int. Symp. Remote Sens. Environ. - GEOSS Era Toward Oper. Environ. Monit.*, no. January, 2011.
- [62] G. R. MacFarlane, A. Pulkownik, and M. D. Burchett, “Accumulation and distribution of heavy metals in the grey mangrove, Avicennia marina (Forsk.)Vierh.: biological indication potential,” *Environ. Pollut.*, vol. 123, no. 1, pp. 139–151, 2003.
- [63] G. R. Macfarlane, C. E. Koller, and S. P. Blomberg, “Accumulation and partitioning of heavy metals in mangroves : A synthesis of field-based studies,” vol. 69, pp.

- 1454–1464, 2007.
- [64] C. Giri *et al.*, “Status and distribution of mangrove forests of the world using earth observation satellite data,” *Glob. Ecol. Biogeogr. (Global Ecol. Biogeogr.)*, pp. 154–159, 2011.
  - [65] S. Bayen, “Occurrence , bioavailability and toxic effects of trace metals and organic contaminants in mangrove ecosystems : A review,” *Environ. Int.*, vol. 48, pp. 84–101, 2012.
  - [66] Tomlinson P. B, “The Botany of Mangroves Second Edition,” 1986.
  - [67] P. Saenger, *Mangrove Ecology, Silviculture and Conservation*. Springer-Science+Business Media, B.V., 2002.
  - [68] M. Pittarello, J. Galba, P. Carletti, and L. Barros, “Chemosphere Possible developments for ex situ phytoremediation of contaminated sediments , in tropical and subtropical regions e Review,” *Chemosphere*, vol. 182, pp. 707–719, 2017.
  - [69] FAO, *The world's Mangroves 1980-2005*. FAO, Food and Agriculture Organization of the Rome, 2007.
  - [70] S. Sandilyan and K. Kandasamy, “Mangrove conservation: A global perspective,” *Biodivers. Conserv.*, vol. 21, pp. 3523–3542, 2012.
  - [71] G. Holguin, P. Vazquez, and Y. Bashan, “The role of sediment microorganisms in the productivity, conservation, and rehabilitation of mangrove ecosystems: an overview,” *Biol. Fertil. Soils*, vol. 33, no. 4, pp. 265–278, Apr. 2001.
  - [72] M. K. and L. C. Mark Spalding, “World Atlas of Mangroves,” *Hum. Ecol.*, vol. 39, 2010.
  - [73] P. Harbison, “Mangrove muds—A sink and a source for trace metals,” *Mar. Pollut. Bull.*, vol. 17, no. 6, pp. 246–250, 1986.
  - [74] C. Marchand, “Actualité scienti,” *fiche Actual. Sci.*, vol. 406, no. June, p. 406, 2012.
  - [75] N. Mukherjee, W. J. Sutherland, L. Dicks, J. Hugé, N. Koedam, and F. Dahdouh-Guebas, “Ecosystem Service Valuations of Mangrove Ecosystems to Inform Decision Making and Future Valuation Exercises,” *PLoS One*, vol. 9, no. 9, p. e107706, Sep. 2014.
  - [76] N. C. Duke, “Oil spill impacts on mangroves: Recommendations for operational planning and action based on a global review,” *Mar. Pollut. Bull.*, vol. 109, no. 2, pp. 700–715, 2016.
  - [77] K. Kathiresan and B. L. Bingham, “Biology of Mangroves and Mangrove Ecosystems,” vol. 40, pp. 1–145, 2001.
  - [78] A. K. Parida, V. Tiwari, and B. Jha, “Impacts of Climate Change on Asian Mangrove Forests,” in *Mangrove Ecosystems of Asia: Status, Challenges and Management*

*Strategies*, I. Faridah-Hanum, A. Latiff, K. R. Hakeem, and M. Ozturk, Eds. New York, NY: Springer New York, 2014, pp. 233–256.

- [79] U. Saint-Paul and H. Schneider, “The Need for a Holistic Approach in Mangrove Research and Management,” in *Ecological Studies* 211, 2010, pp. 3–8.
- [80] D. I. Al-Maslamani, M. Walton, H. Kennedy, M. Al-Mohannadi, and L. Le Vay, “Are mangroves in arid environments isolated systems? Life-history and evidence of dietary contribution from inwelling in a mangrove-resident shrimp species,” *Estuar. Coast. Shelf Sci.*, vol. 124, pp. 56–63, 2013.
- [81] E. Kristensen, S. Bouillon, T. Dittmar, and C. Marchand, “Organic carbon dynamics in mangrove ecosystems : A review,” vol. 89, pp. 201–219, 2008.
- [82] A. Catherine, “Carbon and nutrient exchange of mangrove forests with the coastal ocean,” no. March 2015, 2011.
- [83] K. Zhang *et al.*, “The role of mangroves in attenuating storm surges,” *Estuar. Coast. Shelf Sci.*, vol. 102–103, pp. 11–23, 2012.
- [84] R. Kulkarni, D. Deobagkar, and S. Zinjarde, “Metals in mangrove ecosystems and associated biota: A global perspective,” *Ecotoxicol. Environ. Saf.*, vol. 153, no. February, pp. 215–228, 2018.
- [85] H. Zhi, Z. Zhao, and L. Zhang, “Chemosphere The fate of polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs) in water from Poyang Lake , the largest freshwater lake in China,” *Chemosphere*, vol. 119, pp. 1134–1140, 2015.
- [86] H. Almahasheer, “Ecosystem Services of Avicennia marina in the Red Sea,” in *Dissertation*, KAUST, Ed. 2016.
- [87] L. M. Brander *et al.*, “Ecosystem service values for mangroves in Southeast Asia : A meta-analysis and value transfer application,” *Ecosyst. Serv.*, vol. 1, no. 1, pp. 62–69, 2012.
- [88] B. A. Polidoro *et al.*, “The loss of species: mangrove extinction risk and geographic areas of global concern,” *PLoS One*, vol. 5, no. 4, pp. e10095–e10095, Apr. 2010.
- [89] D. M. Alongi, “Present state and future of the world’s mangrove forests,” *Environ. Conserv.*, vol. 29, no. 3, pp. 331–349, 2002.
- [90] M. Lewis, R. Pryor, and L. Wilking, “Fate and effects of anthropogenic chemicals in mangrove ecosystems: A review,” *Environ. Pollut.*, vol. 159, no. 10, pp. 2328–2346, 2011.
- [91] J. C. Fernández-Cadena, S. Andrade, C. L. Silva-Coello, and R. De la Iglesia, “Heavy metal concentration in mangrove surface sediments from the north-west coast of South America,” *Mar. Pollut. Bull.*, vol. 82, no. 1, pp. 221–226, 2014.

- [92] FAO, *Mangrove forest management guidelines*. 1994.
- [93] B. Nath, P. Chaudhuri, and G. Birch, “Assessment of biotic response to heavy metal contamination in Avicennia marina mangrove ecosystems in Sydney Estuary, Australia,” *Ecotoxicol. Environ. Saf.*, vol. 107, pp. 284–290, 2014.
- [94] S. H. Yu, L. Ke, Y. S. Wong, and N. F. Y. Tam, “Degradation of polycyclic aromatic hydrocarbons by a bacterial consortium enriched from mangrove sediments,” *Environ. Int.*, vol. 31, no. 2, pp. 149–154, 2005.
- [95] A. Binelli *et al.*, “Concentration of polybrominated diphenyl ethers (PBDEs) in sediment cores of Sundarban mangrove wetland, northeastern part of Bay of Bengal (India),” *Mar. Pollut. Bull.*, vol. 54, no. 8, pp. 1220–1229, 2007.
- [96] C. Vane, I. Harrison, A. W. Kim, V. Moss-Hayes, B. P Vickers, and K. Hong, “Organic and metal contamination in surface mangrove sediments of South China,” *Mar. Pollut. Bull.*, vol. 58, pp. 134–144, 2008.
- [97] Barbier, E.B.,Hacker,S.D.,Kennedy,C.,Koch,E.W.,Stier,A.C.,Silliman,B.R., “The value of estuarine and coastal ecosystem services,” *Ecol. Monogr.*, vol. 81, no. 2, pp. 169–193, 2011.
- [98] S. L. Coles and J. C. McCain, “Environmental factors affecting benthic infaunal communities of the Western Arabian gulf,” *Mar. Environ. Res.*, vol. 29, no. 4, pp. 289–315, 1990.
- [99] C. Sheppard *et al.*, “The Gulf: A young sea in decline,” *Mar. Pollut. Bull.*, vol. 60, no. 1, pp. 13–38, 2010.
- [100] A. S. El-Sorogy and M. Youssef, “Assessment of heavy metal contamination in intertidal gastropod and bivalve shells from central Arabian Gulf coastline, Saudi Arabia,” *J. African Earth Sci.*, vol. 111, pp. 41–53, 2015.
- [101] R. C. Randolph, J. T. Hardy, S. W. Fowler, A. R. G. Price, and W. H. Pearson, “Toxicity and persistence of nearshore sediment contamination following the 1991 Gulf War,” *Environ. Int.*, vol. 24, no. 1–2, pp. 33–42, 1998.
- [102] A. R. G. Basson, P.W., Burchard, Jr., J. E., Hardy, J. T., and Price, *Biotoxies of the Western Arabian Gulf: marine life and environments of Saudi Arabia*. Dhahran, Saudi Arabia : Aramco Dept. of Loss Prevention and Environmental Affairs, 1977.
- [103] KFUPM/RI, “Progress Report. Saudi Aramco/KFUPM-RI Sustaining Research Project- Marine Environmental Studies- Phase V- Prepared for Saudi Aramco by the Center for Environment and Water, Research Institute, King Fahd University of Petroleum and Minerals, Project No.22,” Dhahran, Saudi Arabia, 2010.
- [104] C. Sheppard and R. Loughland, “Coral mortality and recovery in response to increasing temperature in the southern Arabian Gulf,” *Aquat. Ecosyst. Health Manag.*, vol. 5, no. 4, pp. 395–402, 2002.

- [105] A. Price, “Simultaneous ‘hotspots’ and ‘coldspots’ of marine biodiversity and implications for global conservation,” *Mar. Ecol. Ser. - MAR ECOL-PROGR SER*, vol. 241, pp. 23–27, 2002.
- [106] H. Naser, J. Bythell, and J. Thomason, “Ecological assessment: an initial evaluation of the ecological input in environmental impact assessment reports in Bahrain,” *Impact Assess. Proj. Apprais.*, vol. 26, no. 3, pp. 201–208, 2008.
- [107] N. Y. Khan, “Multiple stressors and ecosystem-based management in the Gulf,” *Aquat. Ecosyst. Heal. Manag.*, vol. 10, no. 3, pp. 259–267, 2007.
- [108] J. Allan, S. Ramirez, C. & Vasquez, “Effects of dredging on subtidal macrobenthic community structure in Mejillones Bay, Chile,” *Int. J. Environ. Heal.*, vol. 2, no. 1, pp. 64–81, 2008.
- [109] W. Hamza and M. Munawar, “Protecting and managing the Arabian Gulf: Past, present and future,” *Aquat. Ecosyst. Health Manag.*, vol. 12, pp. 429–439, 2009.
- [110] F. Al-Jamali, J. M. Bishop, D. A. Jones, J. Osment, and L. Le Vay, “A review of the impacts of aquaculture and artificial waterways upon coastal ecosystems in the Gulf (Arabian/Persian) including a case study demonstrating how future management may resolve these impacts,” *Aquat. Ecosyst. Health Manag.*, vol. 8, pp. 81–94, 2005.
- [111] H. Al-Sayed, H. Naser, and K. Al-Wedaei, “Observations on macrobenthic invertebrates and wader bird assemblages in a protected marine mudflat in Bahrain,” *Aquat. Ecosyst. Health Manag.*, vol. 11, pp. 450–456, 2008.
- [112] J. A. Shatti and T. H. A. Abdullah, “Marine pollution due to wastewater discharge in Kuwait,” *Water Sci. Technol.*, vol. 40, no. 7, pp. 33–39, 1999.
- [113] M. Sadiq and T. H. Zaidi, “Sediment composition and metal concentrations in mangrove leaves from the Saudi coast of the Arabian Gulf,” *Sci. Total Environ.*, vol. 155, no. 1, pp. 1–8, 1994.
- [114] K. AlKahtany, M. Youssef, and A. El-Sorogy, “Geochemical and foraminiferal analyses of the bottom sediments of Dammam coast, Arabian Gulf, Saudi Arabia,” *Arab. J. Geosci.*, vol. 8, no. 12, pp. 11121–11133, 2015.
- [115] R. Dodd, F. Blasco, Z. A Rafii, and E. Torquebiau, “Mangroves of the United Arab Emirates: Ecotypic diversity in cuticular waxes at the bioclimatic extreme,” *Aquat. Bot.*, vol. 63, pp. 291–304, 1999.
- [116] Hery Purnobasuki and Mitsuo Suzuki, “Functional Anatomy of Air Conducting Network on the Pneumatophores of a Mangrove Plant, Avicennia marina (Forsk.) Vierh,” *Asian J. Plant Sci.*, vol. 4, no. 4334–347, 2005.
- [117] B. Spalding, “World mangrove atlas. International Society for Mangrove Ecosystems, Okinawa 903-01, Japan. 178 pp.,” *J. Trop. Ecol.*, vol. 14, pp. 723–724, 1997.

- [118] R. YU, X. YUAN, Y. ZHAO, G. HU, and X. TU, “Heavy metal pollution in intertidal sediments from Quanzhou Bay, China,” *J. Environ. Sci.*, vol. 20, no. 6, pp. 664–669, 2008.
- [119] A. Zahra, M. Zaffar, and R. Naseem, “Science of the Total Environment Enrichment and geo-accumulation of heavy metals and risk assessment of sediments of the Kurang Nallah — Feeding tributary of the Rawal Lake,” vol. 471, pp. 925–933, 2014.
- [120] T. Alharbi and A. El-Sorogy, “Assessment of metal contamination in coastal sediments of Al-Khobar area, Arabian Gulf, Saudi Arabia,” *J. African Earth Sci.*, vol. 129, pp. 458–468, 2017.
- [121] M. P. Karuppasamy, M. A. Qurban, P. K. Krishnakumar, S. A. Mushir, and N. Abuzaid, “Evaluation of toxic elements As, Cd, Cr, Cu, Ni, Pb and Zn in the surficial sediments of the Red Sea (Saudi Arabia),” *Mar. Pollut. Bull.*, vol. 119, no. 2, pp. 181–190, 2017.
- [122] P. Ruiz-Compean *et al.*, “Baseline evaluation of sediment contamination in the shallow coastal areas of Saudi Arabian Red Sea,” *Mar. Pollut. Bull.*, vol. 123, no. 1–2, pp. 205–218, 2017.
- [123] V. Subhashini, A. V. V. S. Swamy, E. Sciences, and G. Ap, “Open Access Phytoremediation of Pb and Ni Contaminated Soils Using Catharanthus roseus ( L .) Abstract :,” vol. 3, no. 4, pp. 465–472, 2013.
- [124] M. Abdus, E. Kaipiainen, M. Mohsin, and A. Villa, “Effects of contaminated soil on the growth performance of young Salix ( Salix schwerinii E . L . Wolf ) and the potential for phytoremediation of heavy metals,” vol. 183, 2016.
- [125] S. A. El-Sayed, E. M. M. Moussa, and M. E. I. El-Sabagh, “Evaluation of heavy metal content in Qaroun Lake, El-Fayoum, Egypt. Part I: Bottom sediments,” *J. Radiat. Res. Appl. Sci.*, vol. 8, no. 3, pp. 276–285, 2015.
- [126] A. Gómez-Álvarez, J. L. Valenzuela-García, S. Aguayo-Salinas, D. Meza-Figueroa, J. Ramírez-Hernández, and G. Ochoa-Ortega, “Chemical partitioning of sediment contamination by heavy metals in the San Pedro River, Sonora, Mexico,” *Chem. Speciat. Bioavailab.*, vol. 19, no. 1, pp. 25–35, 2007.
- [127] F. Fu and Q. Wang, “Removal of heavy metal ions from wastewaters: A review,” *J. Environ. Manage.*, vol. 92, no. 3, pp. 407–418, 2011.
- [128] S. Noegrohati, “bioaccumulation dynamic of heavy metals in ( Predicted Through A Bioaccumulation Modelcontructed Based On Biotic Ligand,” pp. 29–40, 2005.
- [129] B. Amin, A. Ismail, A. Arshad, C. K. Yap, and M. S. Kamarudin, “Anthropogenic impacts on heavy metal concentrations in the coastal sediments of Dumai, Indonesia,” *Environ. Monit. Assess.*, vol. 148, no. 1–4, pp. 291–305, 2009.
- [130] N. F. Y. Tam and Y.-S. Wong, “Accumulation and distribution of heavy metals in a

- simulated mangrove system treated with sewage,” *Hydrobiologia*, vol. 352, no. 1, pp. 67–75, Sep. 1997.
- [131] P. E. Peters EC, Gassman NJ, Firman JC, Richmond RH, “Ecotoxicology of Tropical Marine Ecosystems,” *Env. Toxicol. Chem.*, vol. 16, no. 1, pp. 12–40, 1997.
- [132] P. Saenger and D. McConchie, “Heavy metals in mangroves: methodology, monitoring and management,” *Envis For. Bull.*, vol. 4, no. December, pp. 52–62, 2004.
- [133] N. Pumijumnong and S. Danpradit, “Heavy metal accumulation in sediments and mangrove forest stems from Surat Thani Province, Thailand,” *Malaysian For.*, vol. 79, no. 1–2, pp. 212–228, 2016.
- [134] P. Sruthi, A. M. Shackira, and J. T. Puthur, “Heavy metal detoxification mechanisms in halophytes: an overview,” *Wetl. Ecol. Manag.*, vol. 25, no. 2, pp. 129–148, Apr. 2017.
- [135] E. Ruiz, “Heavy metal distribution and chemical speciation in tailings and soils around a Pb – Zn mine in Spain,” vol. 90, pp. 1106–1116, 2009.
- [136] Y. Tian, H. J. Liu, T. L. Zheng, K. K. Kwon, S. J. Kim, and C. L. Yan, “PAHs contamination and bacterial communities in mangrove surface sediments of the Jiulong River Estuary, China,” *Mar. Pollut. Bull.*, vol. 57, no. 6–12, pp. 707–715, 2008.
- [137] N. F. Y. Tam and Y. S. Wong, “Spatial and temporal variations of heavy metal contamination in sediments of a mangrove swamp in Hong Kong,” *Mar. Pollut. Bull.*, vol. 31, no. 4, pp. 254–261, 1995.
- [138] N. F. Y. Tam and Y. S. Wong, “Spatial variation of heavy metals in surface sediments of Hong Kong mangrove swamps,” *Environ. Pollut.*, vol. 110, no. 2, pp. 195–205, 2000.
- [139] F. I. Almasoud, A. R. Usman, and A. S. Al-Farraj, “Heavy metals in the soils of the Arabian Gulf coast affected by industrial activities: analysis and assessment using enrichment factor and multivariate analysis,” *Arab. J. Geosci.*, vol. 8, no. 3, pp. 1691–1703, 2015.
- [140] A. S. Basaham and S. S. Ai-Lihabi, “Trace Elements in Sediments of the Western Gulf,” *Mar. Pollut. Bull.*, vol. 27, pp. 103–107, 1993.
- [141] M. S. Akhter and O. Al-Jowder, “Heavy metal concentrations in sediments from the coast of Bahrain,” *Int. J. Environ. Health Res.*, vol. 7, no. 1, pp. 85–93, 1997.
- [142] F. S. Al Ketbi, E. Z. Isnasious, and A. M. Al Mahyas, “Practical observations on reverse osmosis plants including raw water contamination problems, different intake stations and permeator performance,” *Desalination*, vol. 93, no. 1–3, pp. 259–272, 1993.

- [143] M. Sadiq, "Metal contamination in sediments from a desalination plant effluent outfall area," *Sci. Total Environ.*, vol. 287, pp. 37–44, 2002.
- [144] P. Saenger, "The Gulf of Guinea Project: Managing mangroves to protect biodiversity in West Africa," no. June 2014, 1997.
- [145] R. Chowdhury, Y. Lyubun, and P. J. C. Favas, "Phytoremediation Potential of Selected Mangrove Plants for Trace Metal Contamination in Indian Sundarban Wetland," pp. 283–310, 2016.
- [146] P. L. Baker, A. J. M. ; Walker, "Ecophysiology of metal uptake by tolerant plants," *Heavy Met. Toler. plants; Evol. Asp.*, pp. 155–178, 1990.
- [147] W. Machado, M. Moscatelli, L. G. Rezende, and L. D. Lacerda, "Mercury, zinc, and copper accumulation in mangrove sediments surrounding a large landfill in southeast Brazil," *Environ. Pollut.*, vol. 120, no. 2, pp. 455–461, 2002.
- [148] L. F. F. Silva, W. Machado, S. D. Lisboa Filho, and L. D. Lacerda, "Mercury Accumulation in Sediments of a Mangrove Ecosystem in SE Brazil," *Water. Air. Soil Pollut.*, vol. 145, no. 1, pp. 67–77, May 2003.
- [149] W. Machado, B. B. Gueiros, S. D. Lisboa-Filho, and L. D. Lacerda, "Trace metals in mangrove seedlings: role of iron plaque formation," *Wetl. Ecol. Manag.*, vol. 13, no. 2, pp. 199–206, Apr. 2005.
- [150] C. Silva, L. Lacerda, and C. Rezende, "Metals Reservoir in a Red Mangrove Forest," *Biotropica*, vol. 22, p. 339, 1990.
- [151] L. H. Defew, J. M. Mair, and H. M. Guzman, "An assessment of metal contamination in mangrove sediments and leaves from Punta Mala Bay , Pacific Panama," vol. 50, pp. 547–552, 2005.
- [152] R. G. O. Che, "Concentration of 7 Heavy Metals in Sediments and Mangrove Root Samples from Mai Po, Hong Kong," *Mar. Pollut. Bull.*, vol. 39, no. 1, pp. 269–279, 1999.
- [153] G. Thomas and T. V Fernandez, "Incidence of heavy metals in the mangrove flora and sediments in Kerala, India," *Hydrobiologia*, vol. 352, no. 1, pp. 77–87, Sep. 1997.
- [154] S. Saifullah, S. H. Khan, and S. Ismail, "Distribution of nickel in a polluted mangrove habitat of the Indus Delta," *Mar. Pollut. Bull.*, vol. 44, pp. 570–576, 2002.
- [155] M. Preda and M. E. Cox, "Trace metal occurrence and distribution in sediments and mangroves, Pumicestone region, southeast Queensland, Australia," *Environ. Int.*, vol. 28, no. 5, pp. 433–449, 2002.
- [156] N. F. Y. Tam and Y. S. Wong, "Retention of nutrients and heavy metals in mangrove sediment receiving wastewater of different strengths," *Environ. Technol.*, vol. 14, no. 8, pp. 719–729, 1993.

- [157] H. A. Naser, “Assessment and management of heavy metal pollution in the marine environment of the Arabian Gulf: A review,” *Mar. Pollut. Bull.*, vol. 72, no. 1, pp. 6–13, 2013.
- [158] A. M. Freije, “Heavy metal, trace element and petroleum hydrocarbon pollution in the Arabian Gulf: Review,” *J. Assoc. Arab Univ. Basic Appl. Sci.*, vol. 17, pp. 90–100, 2015.
- [159] M. F. Nazli and N. R. Hashim, “Heavy Metal Concentrations in an Important Mangrove Species, *Sonneratia caseolaris*, in Peninsular Malaysia,” *Environ. Asia*, vol. 3, pp. 50–55, 2010.
- [160] K. Pan and W.-X. Wang, “Trace metal contamination in estuarine and coastal environments in China,” *Sci. Total Environ.*, vol. 421–422, pp. 3–16, 2012.
- [161] KFUPM/RI, “Aramco Sustaining Research Project -- Environmental Studies. Volume IV, Tarut Bay Biotopes Investigation, Mangrove Communities. Final Report Project No PN24079 sponsored by Saudi Aramco Oil Company, The Research Institute, King Fahd University of Petroleum,” 1990.
- [162] S. De Mora, S. W. Fowler, E. Wyse, and S. Azemard, “Distribution of heavy metals in marine bivalves, fish and coastal sediments in the Gulf and Gulf of Oman,” *Mar. Pollut. Bull.*, vol. 49, no. 5–6, pp. 410–424, 2004.
- [163] A. C. Bejarano and J. Michel, “Large-scale risk assessment of polycyclic aromatic hydrocarbons in shoreline sediments from Saudi Arabia: Environmental legacy after twelve years of the Gulf war oil spill,” *Environ. Pollut.*, vol. 158, no. 5, pp. 1561–1569, 2010.
- [164] S. Uno *et al.*, “Monitoring of PAHs and alkylated PAHs in aquatic organisms after 1 month from the Solar I oil spill off the coast of Guimaras Island, Philippines,” *Environ. Monit. Assess.*, vol. 165, no. 1, pp. 501–515, Jun. 2010.
- [165] S. Miki, S. Uno, K. Ito, J. Koyama, and H. Tanaka, “Distributions of polycyclic aromatic hydrocarbons and alkylated polycyclic aromatic hydrocarbons in Osaka Bay, Japan,” *Mar. Pollut. Bull.*, vol. 85, no. 2, pp. 558–565, 2014.
- [166] F. Wania and D. MacKay, “Peer Reviewed: Tracking the Distribution of Persistent Organic Pollutants,” *Environ. Sci. Technol.*, vol. 30, no. 9, p. 390A–396A, Aug. 1996.
- [167] T. Günther, U. Dornberger, and W. Fritzsche, “Effects of ryegrass on biodegradation of hydrocarbons in soil,” *Chemosphere*, vol. 33, no. 2, pp. 203–215, 1996.
- [168] D. Bernard, H. Pascaline, and J.-J. Jeremie, “Distribution and origin of hydrocarbons in sediments from lagoons with fringing mangrove communities,” *Mar. Pollut. Bull.*, vol. 32, pp. 734–739, 1996.
- [169] N. F. Y. Tam, T. W. Y. Wong, and Y. S. Wong, “A case study on fuel oil contamination in a mangrove swamp in Hong Kong,” *Mar. Pollut. Bull.*, vol. 51, no.

8–12, pp. 1092–1100, 2005.

- [170] M. Raza, M. Zakaria, N. Rasidah Hashim, U. H. Yim, N. Kannan, and S. Y. Ha, “Composition and source identification of polycyclic aromatic hydrocarbons in mangrove sediments of Peninsular Malaysia: Indication of anthropogenic input,” *Environ. Earth Sci.*, vol. 70, 2013.
- [171] U. V Okere and K. T. Semple, “Biodegradation of PAHs in ‘Pristine’ Soils from Different Climatic Regions Bioremediation & Biodegradation,” pp. 1–11, 2012.
- [172] M. M. Hoque, A. H. M. Kamal, M. H. Idris, O. H. Ahmed, A. T. M. R. Hoque, and M. M. Billah, “Litterfall production in a tropical mangrove of Sarawak, Malaysia,” *Zool. Ecol.*, vol. 25, no. 2, pp. 157–165, 2015.
- [173] Z.-W. Zhang, X.-R. Xu, Y.-X. Sun, S. Yu, Y.-S. Chen, and J.-X. Peng, “Heavy metal and organic contaminants in mangrove ecosystems of China: a review,” *Environ. Sci. Pollut. Res.*, vol. 21, no. 20, pp. 11938–11950, Oct. 2014.
- [174] C. O. Farias, C. Hamacher, A. D. L. R. Wagener, and A. D. L. Scofield, “Origin and degradation of hydrocarbons in mangrove sediments (Rio de Janeiro, Brazil) contaminated by an oil spill,” vol. 39, pp. 289–307, 2008.
- [175] L. G. Luz, R. S. Carreira, C. O. Farias, A. D. L. Scofield, A. H. Nudi, and A. D. L. R. Wagener, “Trends in PAH and black carbon source and abundance in a tropical mangrove system and possible association with bioavailability,” *Org. Geochem.*, 2010.
- [176] A. Binelli *et al.*, “A comparison of sediment quality guidelines for toxicity assessment in the Sunderban wetlands (Bay of Bengal, India),” *Chemosphere*, vol. 73, no. 7, pp. 1129–1137, 2008.
- [177] O. Zuloaga *et al.*, “Polycyclic Aromatic Hydrocarbons in Intertidal Marine Bivalves of Sunderban Mangrove Wetland, India: An Approach to Bioindicator Species,” *Water. Air. Soil Pollut.*, vol. 201, no. 1, p. 305, Jan. 2009.
- [178] O. Zuloaga *et al.*, “Distribution of polycyclic aromatic hydrocarbons in recent sediments of Sundarban mangrove wetland of India and Bangladesh: A comparative approach,” *Environ. earth Sci.*, vol. 68, pp. 355–367, 2013.
- [179] L. Dsikowitzky *et al.*, “Anthropogenic organic contaminants in water, sediments and benthic organisms of the mangrove-fringed Segara Anakan Lagoon, Java, Indonesia,” *Mar. Pollut. Bull.*, vol. 62, no. 4, pp. 851–862, 2011.
- [180] O. S. Sojinu, O. O. Sonibare, and E. Y. Zeng, “Concentrations of polycyclic aromatic hydrocarbons in soils of a mangrove forest affected by forest fire,” *Toxicol. Environ. Chem.*, vol. 93, no. 3, pp. 450–461, 2011.
- [181] N. Mohd Tahir, M. F. Fadzil, J. Ariffin, H. Maarop, and A. K. H. Wood, “Sources of polycyclic aromatic hydrocarbons in mangrove sediments of Pulau Cik Wan Dagang, Kemaman,” *J. Sustain. Sci. Manag.*, vol. 6, pp. 98–106, 2011.

- [182] Y. Liang, M. F. Tse, L. Young, and M. H. Wong, "Distribution patterns of polycyclic aromatic hydrocarbons (PAHs) in the sediments and fish at Mai Po Marshes Nature Reserve, Hong Kong," *Water Res.*, vol. 41, no. 6, p. 1303—1311, Mar. 2007.
- [183] J. P. Essien, S. I. Eduok, and A. A. Olajire, "Distribution and ecotoxicological significance of polycyclic aromatic hydrocarbons in sediments from Iko River estuary mangrove ecosystem," *Environ. Monit. Assess.*, vol. 176, no. 1, pp. 99–107, May 2011.
- [184] S. L. Mohebbi-Nozar, M. P. Zakaria, M. S. Mortazavi, W. R. Ismail, and K. K. Jokar, "Concentrations and Source Identification of Polycyclic Aromatic Hydrocarbons (PAHs) in Mangrove Sediments from North of Persian Gulf," *Polycycl. Aromat. Compd.*, vol. 36, no. 5, pp. 601–612, 2016.
- [185] J. Zhang, L. Cai, D. Yuan, and M. Chen, "Distribution and sources of polynuclear aromatic hydrocarbons in Mangrove surficial sediments of Deep Bay, China," *Mar. Pollut. Bull.*, vol. 49, no. 5, pp. 479–486, 2004.
- [186] G. Ramdine, D. Fichet, M. Louis, and S. Lemoine, "Polycyclic aromatic hydrocarbons (PAHs) in surface sediment and oysters (*Crassostrea rhizophorae*) from mangrove of Guadeloupe: Levels, bioavailability, and effects," *Ecotoxicol. Environ. Saf.*, vol. 79, pp. 80–89, 2012.
- [187] R. Boonyatumanond, G. Wattayakorn, A. Amano, Y. Inouchi, and H. Takada, "Reconstruction of pollution history of organic contaminants in the upper Gulf of Thailand by using sediment cores: First report from Tropical Asia Core (TACO) project," *Mar. Pollut. Bull.*, vol. 54, no. 5, pp. 554–565, 2007.
- [188] K. K. Domínguez\*, Carmen; Sarkar, S. K.; Bhattacharya, A.; Chatterjee, M.; Bhattacharya, B. D.; Jover Comas, Eric; Albaigés Riera, Joan; Bayona Termens, Josep María; Alam, Md. A.; Satpathy, "Quantification and Source Identification of Polycyclic Aromatic Hydrocarbons in Core Sediments from Sundarban Mangrove Wetland, India," *Environ. Contam. Toxicol.*, 2010.
- [189] P. Baumard and P. Garrigues, "POLYCYCLIC AROMATIC HYDROCARBONS IN SEDIMENTS AND MUSSELS OF THE WESTERN MEDITERRANEAN SEA," *Environ. Chem.*, vol. 17, no. 5, pp. 765–776, 1998.
- [190] L. Ke, K. S. H. Yu, Y. S. Wong, and N. F. Y. Tam, "Spatial and vertical distribution of polycyclic aromatic hydrocarbons in mangrove sediments," *Sci. Total Environ.*, vol. 340, no. 1, pp. 177–187, 2005.
- [191] C. Li, H. Zhou, Y. Wong, and N. F. Tam, "Science of the Total Environment Vertical distribution and anaerobic biodegradation of polycyclic aromatic hydrocarbons in mangrove sediments in Hong Kong , South China," *Sci. Total Environ.*, vol. 407, no. 21, pp. 5772–5779, 2009.
- [192] R. M. Cavalcante, F. W. Sousa, R. F. Nascimento, E. R. Silveira, and G. S. S. Freire,

“The impact of urbanization on tropical mangroves (Fortaleza, Brazil): Evidence from PAH distribution in sediments,” *J. Environ. Manage.*, vol. 91, no. 2, pp. 328–335, 2009.

- [193] S. K. Sarkar *et al.*, “Distribution and Ecosystem Risk Assessment of Polycyclic Aromatic Hydrocarbons (PAHs) in Core Sediments of Sundarban Mangrove Wetland, India,” *Polycycl. Aromat. Compd.*, vol. 32, no. 1, pp. 1–26, 2012.
- [194] M. Tobiszewski and J. Namieśnik, “PAH diagnostic ratios for the identification of pollution emission sources,” *Environ. Pollut.*, vol. 162, pp. 110–119, 2012.
- [195] L.-Y. Liu, J.-Z. Wang, G.-L. Wei, Y.-F. Guan, and E. Y. Zeng, “Polycyclic aromatic hydrocarbons (PAHs) in continental shelf sediment of China: Implications for anthropogenic influences on coastal marine environment,” *Environ. Pollut.*, vol. 167, pp. 155–162, 2012.
- [196] P. Bigus, M. Tobiszewski, and J. Namieśnik, “Historical records of organic pollutants in sediment cores,” *Mar. Pollut. Bull.*, vol. 78, no. 1, pp. 26–42, 2014.
- [197] Z. Zhao, Y.-X. Zhuang, and J.-D. Gu, “Abundance, composition and vertical distribution of polycyclic aromatic hydrocarbons in sediments of the Mai Po Inner Deep Bay of Hong Kong,” *Ecotoxicology*, vol. 21, no. 6, pp. 1734–1742, Aug. 2012.
- [198] C. O. Farias, C. Hamacher, A. Wagener, and A. Scofield, “Origin and degradation of hydrocarbons in mangrove sediments (Rio de Janeiro, Brazil) contaminated by an oil spill,” *Org. Geochemistry - ORG GEOCHEM*, vol. 39, pp. 289–307, 2008.
- [199] L. Ke, T. W. Y. Wong, Y. S. Wong, and N. F. Y. Tam, “Fate of polycyclic aromatic hydrocarbon (PAH) contamination in a mangrove swamp in Hong Kong following an oil spill,” vol. 45, pp. 339–347, 2002.
- [200] E. Manoli, A. Kouras, and C. Samara, “Profile analysis of ambient and source emitted particle-bound polycyclic aromatic hydrocarbons from three sites in northern Greece,” *Chemosphere*, vol. 56, no. 9, pp. 867–878, 2004.
- [201] R. C. Brändli, T. D. Bucheli, T. Kupper, J. Mayer, F. X. Stadelmann, and J. Tarradellas, “Fate of PCBs, PAHs and their source characteristic ratios during composting and digestion of source-separated organic waste in full-scale plants,” *Environ. Pollut.*, vol. 148, no. 2, pp. 520–528, 2007.
- [202] K. S. Sukhdhane, P. K. Pandey, A. Vennila, C. S. Purushothaman, and M. N. O. Ajima, “Sources, distribution and risk assessment of polycyclic aromatic hydrocarbons in the mangrove sediments of Thane Creek, Maharashtra, India,” *Environ. Monit. Assess.*, vol. 187, no. 5, p. 274, Apr. 2015.
- [203] H. Chen, Y. Teng, and J. Wang, “Source apportionment of polycyclic aromatic hydrocarbons (PAHs) in surface sediments of the Rizhao coastal area (China) using diagnostic ratios and factor analysis with nonnegative constraints,” *Sci. Total Environ.*, vol. 414, pp. 293–300, 2012.

- [204] Z. Ebrahimi-Sirizi and A. Riyahi-Bakhtiyari, "Petroleum pollution in mangrove forests sediments from Qeshm Island and Khamir Port---Persian Gulf, Iran," *Environ. Monit. Assess.*, vol. 185, no. 5, pp. 4019–4032, May 2013.
- [205] M. Chen, L. Ma, W. G. Harris, and A. G. Hornesby, "Background concentrations of trace metals in Florida surface soils: taxonomic and geographic distributions of total-total and total-recoverable concentrations of selected trace metals," *Florida Cent. Solid Hazard. Waste Manag.*, pp. 99–7, 1999.
- [206] W. E. Pereira, F. D. Hostettler, S. N. Luoma, A. van Geen, C. C. Fuller, and R. J. Anima, "Sedimentary record of anthropogenic and biogenic polycyclic aromatic hydrocarbons in San Francisco Bay, California," *Mar. Chem.*, vol. 64, no. 1, pp. 99–113, 1999.
- [207] A. M. Kipopoulou, E. Manoli, and C. Samara, "Bioconcentration of polycyclic aromatic hydrocarbons in vegetables grown in an industrial area," *Environ. Pollut.*, vol. 106, no. 3, pp. 369–380, 1999.
- [208] Z. Lu, W. Zheng, and L. Ma, "Bioconcentration of polycyclic aromatic hydrocarbons in roots of three mangrove species in Jiulong River Estuary," *J. Environ. Sci. (China)*, vol. 17, pp. 285–289, 2005.
- [209] F. Li *et al.*, "Contamination of polycyclic aromatic hydrocarbons (PAHs) in surface sediments and plants of mangrove swamps in Shenzhen, China," *Mar. Pollut. Bull.*, vol. 85, no. 2, pp. 590–596, 2014.
- [210] Z. Wang, Z. Liu, Y. Yang, T. Li, and M. Liu, "Distribution of PAHs in tissues of wetland plants and the surrounding sediments in the Chongming wetland, Shanghai, China," *Chemosphere*, vol. 89, no. 3, pp. 221–227, 2012.
- [211] R. E. Carver, *Procedures in Sedimentary Petrology*. Wiley-Interscience, 1971.
- [212] F. . Sheppard, "Nomenclature based on sand-silt-clay ratios," *J. Sediment Petrol.*, vol. 24, no. 3, pp. 151–158, 1954.
- [213] W. . Folk, R.L., Ward, "Brazos River bar: a study in the significance of grain size parameters," *J. Sediment. Petrol.*, no. 27, pp. 3–26, 1957.
- [214] and W. C. W. Folk, R. L., "Brazos River bar: a study in the significance of grain size parameters," *J. Sediment. Petrol.*, vol. 27, pp. 3–26, 1957.
- [215] L. E. Nelson, D.W. and Sommers, "Total carbon, organic carbon and organic matter. In: Page, A.L., Ed., Methods of Soil Analysis. Part 2. Chemical and microbiological properties.," *2nd Ed. Agron. Ser. No. 9, ASA SSSA, Madison.*, 1982.
- [216] C. S. Bremner, J.M. and Mulvaney, "Nitrogen-Total. In: Methods of soil analysis. Part 2. Chemical and microbiological properties, Page, A.L., Miller, R.H. and Keeney, D.R. Eds., American Society of Agronomy, Soil Science Society of America, Madison, Wisconsin," pp. 595–624, 1982.

- [217] S. Baran, P. Oleszczuk, A. Lesiuk, and E. Baranowska, "Trace Metals and Polycyclic Aromatic Hydrocarbons in Surface Sediment Samples from the Narew River (Poland)," *Polish J. Environ. Stud.*, vol. 11, no. 4, pp. 299–305, 2002.
- [218] S. Steed and J. Reed, "Measuring pH of Soils," *Dep. Agric. Coop. Ext. Serv. Univ. Florida, IFAS, Florida*, vol. 33584, no. 813, 2005.
- [219] S. R. Taylor and S. M. McLennan, "The geochemical evolution of the continental crust," *Rev. Geophys.*, vol. 33, no. 2, pp. 241–265, 1995.
- [220] S. M. McLennan, "Relationships between the trace element composition of sedimentary rocks and upper continental crust," *Geochemistry, Geophys. Geosystems*, no. 2(4), 2001.
- [221] S. Lotfinasabasl and V. R. G. N. S. Rajurkar, "Petroleum Hydrocarbons Pollution in Soil and its Bioaccumulation in mangrove species , Avicennia marina from Alibaug Mangrove Ecosystem , Maharashtra , India \*," vol. 2, pp. 1–7, 2013.
- [222] G. Muller, "Index of Geo-Accumulation in Sediments of the Rhine River," *GeoJournal*, no. 2, pp. 108–118, 1969.
- [223] M. Varol, "Assessment of heavy metal contamination in sediments of the Tigris River ( Turkey ) using pollution indices and multivariate statistical techniques," *J. Hazard. Mater.*, vol. 195, pp. 355–364, 2011.
- [224] Tomlinson and C. R. Harris, "Problems in the assessment of heavy metal levels in estuaries and the formation of pollution index," vol. 575, pp. 566–575, 1980.
- [225] L. Hakanson, "An ecological risk index for aquatic pollution control. a sedimentological approach," vol. 14, 1980.
- [226] E. R. Long, C. Bin, S. L. Smith, and F. D. Calder, "Incidence of Adverse Biological Effects Within Ranges of Chemical Concentrations in Marine and Estuarine Sediments," vol. 19, no. 1, pp. 81–97, 1995.
- [227] M. W. Yim and N. F. Y. Tam, "Effects of Wastewater-borne Heavy Metals on Mangrove Plants and Soil Microbial Activities," *Mar. Pollut. Bull.*, vol. 39, no. 1, pp. 179–186, 1999.
- [228] N. Koleli, A. Demir, C. Kantar, G. A. Atag, K. Kusvuran, and R. Binzet, "Chapter 22 - Heavy Metal Accumulation in Serpentine Flora of Mersin-Findikpinari (Turkey) – Role of Ethylenediamine Tetraacetic Acid in Facilitating Extraction of Nickel," in *Soil Remediation and Plants*, K. R. Hakeem, M. Sabir, M. Öztürk, and A. R. Mermut, Eds. San Diego: Academic Press, 2015, pp. 629–659.
- [229] J. Yoon, X. Cao, Q. Zhou, and L. Q. Ma, "Accumulation of Pb , Cu , and Zn in native plants growing on a contaminated Florida site," *Sci. Total Environ.*, vol. 368, pp. 456–464, 2006.
- [230] M. Musterman and P. Placeholder, "Bio-concentration of Polycyclic Aromatic

Hydrocarbons in the grey Mangrove ( *Avicennia marina* ) along eastern coast of the Red Sea,” pp. 344–351, 2017.

- [231] M. Orif, A. El-maradny, M. Musterman, and P. Placeholder, “Bio-accumulation of Polycyclic Aromatic Hydrocarbons in the Grey Mangrove ( *Avicennia marina* ) along Arabian Gulf , Saudi Coast,” no. April, 2018.
- [232] M. S. Massoud, F. Al-Abdali, and A. N. Al-Ghadban, “The status hof oil pollution in the Arabian Gulf by the end of 1993,” *Environ. Int.*, vol. 24, no. 1–2, pp. 11–22, 1998.
- [233] M. Sadiq and T. H. Zaidi, “Sediment composition and metal concentrations inmangrove leaves from the {Saudi} coast of the {Arabian} {Gulf},” vol. 155, pp. 1–8, 1994.
- [234] D. A. Alzahrani, E. M. Selim, M. M. El-sherbiny, and R. Sea, “Ecological assessment of heavy metals in the grey mangrove ( *Avicennia marina* ) and associated sediments along the Red Sea coast of Saudi Arabia,” *Oceanologia*, vol. 60, no. 4, pp. 513–526, 2018.
- [235] H. Almahasheer, “Remobilization of Heavy Metals by Mangrove Leaves Frontiers in Marine Science Remobilization of Heavy Metals by Mangrove Leaves,” 2018.
- [236] R. A. Abohassan, “Heavy Metal Pollution in *Avicennia marina* Mangrove Systems on the Red Sea Coast of Saudi Arabia,” vol. 24, no. 1, pp. 35–53, 2013.
- [237] A. Louvado, N. Gomes, M. Simoes, A. Almeida, D. Cleary, and A. Cunha, “Polycyclic aromatic hydrocarbons in deep sea sediments: Microbe–pollutant interactions in a remote environment,” *Sci. Total Environ.*, vol. 526, Apr. 2015.
- [238] H. Jia *et al.*, “Rhizodegradation potential and tolerance of *Avicennia marina* ( Forsk .) Vierh in phenanthrene and pyrene contaminated sediments,” *Mar. Pollut. Bull.*, vol. 110, no. 1, pp. 112–118, 2016.
- [239] Z. Zhang, Q. Zhou, S. Peng, and Z. Cai, “Remediation of petroleum contaminated soils by joint action of *Pharbitis nil* L. and its microbial community,” *Sci. Total Environ.*, vol. 408, no. 22, pp. 5600–5605, 2010.
- [240] J. Pichtel and P. Liskanen, “Degradation of Diesel Fuel in Rhizosphere Soil,” *Environ. Eng. Sci.*, vol. 18, no. 3, pp. 145–157, 2001.
- [241] K. Euliss, C. Ho, A. P. Schwab, S. Rock, and M. K. Banks, “Greenhouse and field assessment of phytoremediation for petroleum contaminants in a riparian zone,” vol. 99, pp. 1961–1971, 2008.
- [242] S. Sadashiv, S. Min, T. Kim, S. Sudha, D. Kim, and J. Lee, “Phytoremediation of diesel-contaminated soil and saccharification of the resulting biomass,” *Fuel*, vol. 116, pp. 292–298, 2014.
- [243] M. Ali *et al.*, “Kinetic modeling and half life study on bioremediation of crude oil

- dispersed by Corexit 9500," *J. Hazard. Mater.*, vol. 185, no. 2–3, pp. 1027–1031, 2011.
- [244] T. Xu, L. Lou, L. Luo, R. Cao, D. Duan, and Y. Chen, "Science of the Total Environment Effect of bamboo biochar on pentachlorophenol leachability and bioavailability in agricultural soil," *Sci. Total Environ.*, vol. 414, pp. 727–731, 2012.
- [245] A. D. P. Agamuthu, "Dynamics of diesel fuel degradation in contaminated soil using organic wastes," pp. 769–778, 2013.
- [246] A. S. Nwankwegu *et al.*, "Kinetic modelling of total petroleum hydrocarbon in spent lubricating petroleum oil impacted soil under different treatments," *Environ. Technol.*, vol. 0, no. 0, pp. 1–10, 2018.
- [247] S. Dimitrov *et al.*, "A kinetic model for predicting biodegradation," *SAR QSAR Environ. Res.* 18, pp. 443–457, 2010.
- [248] L. Mohajeri, H. A. Aziz, M. H. Isa, M. A. Zahed, and S. Mohajeri, "Effect of remediation strategy on crude oil biodegradation kinetics and half life times in shoreline sediment samples," *Int. J. Mar. Sci. Eng.*, vol. 3, no. 2, pp. 99–104, 2013.
- [249] P. Wang, K. Z. Du, Y. X. Zhu, and Y. Zhang, "A novel analytical approach for investigation of anthracene adsorption onto mangrove leaves," *Talanta*, vol. 76, no. 5, pp. 1177–1182, 2008.
- [250] S. and Hites, "Organic Pollutant Accumulation in Vegetation," *Environ. Sci. Technol.*, vol. 29, no. 12, pp. 2905–2914, 1995.
- [251] F. Kang, D. Chen, Y. Gao, and Y. Zhang, "Distribution of polycyclic aromatic hydrocarbons in subcellular root tissues of ryegrass ( *Lolium multiflorum* Lam .)," vol. 1, pp. 1–7, 2010.
- [252] and O. G. A. Ryan J.A, Bell R.M., Davidson J.M., "Plant uptake of non-ionic organic chemicals from soils," *Chemosphere*, vol. 17, no. 12, pp. 2299–2323, 1989.
- [253] H. Jia *et al.*, "Rhizodegradation potential and tolerance of *Avicennia marina* ( Forsk .) Vierh in phenanthrene and pyrene contaminated sediments," *MPB*, vol. 110, no. 1, pp. 112–118, 2016.
- [254] Y. Gao, Y. Wang, Y. Zeng, and X. Zhu, "Phytoavailability and Rhizospheric Gradient Distribution of Bound-Polycyclic Aromatic Hydrocarbon Residues in Soils," *Soil Sci. Soc. Am. J.*, vol. 77, pp. 1572–1583, 2013.
- [255] R. Lohmann, M. Dapsis, E. J. Morgan, V. Dekany, and P. J. Luey, "Determining Air - Water Exchange , Spatial and Temporal Trends of Freely Dissolved PAHs in an Urban Estuary Using Passive Polyethylene Samplers," pp. 2655–2662, 2011.
- [256] G. Naidoo, "Uptake and accumulation of polycyclic aromatic hydrocarbons in the mangroves *Avicennia marina* and *Rhizophora mucronata*," 2018.

# Appendix

## Appendix 1. Data analysis result of $\Sigma$ PAHs in sediment during experimental study

Tukey test			
	k	4	
	n obv	15	
	df	32	
	ms	125369.1767	
	combination	6	
	Q	3.85	
<b>comparison</b>	<b>absolute difference</b>	<b>critical value</b>	<b>result</b>
25 ml/kg to 50 ml/kg	1920.2625	351.9739216	significantly different
25 ml/kg to 75 ml/kg	3473.371667	351.9739216	significantly different
25 ml/kg to control	1852.968333	351.9739216	significantly different
50 ml/kg to 75 ml/kg	1553.109167	351.9739216	significantly different
50 ml/kg to control	3773.230833	351.9739216	significantly different
75 ml/kg to control	5326.34	351.9739216	significantly different

### Anova: Two-Factor with Replication

SUMMARY	0 days	30 days	60 days	90 days	Total
<b>Diesel @25 ml/kg</b>					
Count	3	3	3	3	12
Sum	9558.26	8485.91	3463.49	727.96	22235.62
Average	3186.086667	2828.6367	1154.49667	242.6533333	<b>1852.968333</b>
Variance	75992.61373	70741.062	12257.7221	4452.904933	1614292.67
<b>Diesel @50 ml/kg</b>					
Count	3	3	3	3	12
Sum	17343.3	14879.94	9557.52	3498.01	45278.77
Average	5781.1	4959.98	3185.84	1166.003333	<b>3773.230833</b>
Variance	163528.7439	262174.22	977506.597	47450.89603	3695367.92
<b>Diesel @75 ml/kg</b>					
Count	3	3	3	3	12
Sum	26603.04	20250.31	11560.9	5501.83	63916.08
Average	8867.68	6750.1033	3853.63333	1833.943333	<b>5326.34</b>
Variance	72897.1777	188114.6	125310.262	5480.028233	7962297.766
<b>control</b>					
Count	3	3	3	3	12
Sum	0	0	0	0	0
Average	0	0	0	0	<b>0</b>
Variance	0	0	0	0	0
<b>Total</b>					
Count	12	12	12	12	
Sum	53504.6	43616.16	24581.91	9727.8	
Average	4458.716667	3634.68	2048.4925	810.65	
Variance	11698820.68	7000974.7	2806643.42	597664.0253	
<b>ANOVA</b>					
S. of Variation	SS	df	MS	F	P-value
Sample	192613581.7	3	64204527.2	512.1237047	4.12567E-27
Columns	95459992.94	3	31819997.6	253.8103741	2.21991E-22
Interaction	46519735.32	9	5168859.48	41.22910921	4.21772E-15
Within	4011813.656	32	<b>125369.177</b>		2.188765768
Total	338605123.7	47			

## Appendix 2. Data analysis result of TPH in sediment during experimental study

Tukey test					
	k	n obv	df	ms	4
				combination	15
					32
					<b>103982.8796</b>
				Q	6
					<b>3.85</b>
comparison	absolute difference	critical value	result		
25 ml/kg to 50 ml/kg	840.1792274	320.5501763	significantly different		
25 ml/kg to 75 ml/kg	1639.441046	320.5501763	significantly different		
25 ml/kg to control	1086.898482	320.5501763	significantly different		
50 ml/kg to 75 ml/kg	799.2618184	320.5501763	significantly different		
50 ml/kg to control	1927.077709	320.5501763	significantly different		
75 ml/kg to control	2726.339528	320.5501763	significantly different		

### Anova: Two-Factor With Replication

SUMMARY	0 days	30 days	60 days	90 days	Total
<b>Diesel @25 ml/kg</b>					
Count	3	3	3	3	12
Sum	6253.656492	3902.21803	2334.5216	566.818565	13057.21472
Average	2084.552164	1300.73934	778.17388	188.939522	<b>1088.101227</b>
Variance	387747.3623	2405.12239	820.60857	1.50351407	600907.0652
<b>Diesel @50 ml/kg</b>					
Count	3	3	3	3	12
Sum	10860.03133	6056.41493	4099.67	2123.24919	23139.36545
Average	3620.010442	2018.80498	1366.5567	707.749731	<b>1928.280454</b>
Variance	1170344.706	2946.37114	869.67102	9.24559736	1488587.426
<b>Diesel @75 ml/kg</b>					
Count	3	3	3	3	12
Sum	14349.83	10187.3358	4817.8811	3375.46033	32730.50727
Average	4783.276667	3395.7786	1605.9604	1125.15344	<b>2727.542272</b>
Variance	46270.80163	50984.8061	1072.2461	253.222158	2335609.172
<b>control</b>					
Count	3	3	3	3	12
Sum	0	3.5725131	5.4047898	5.45563335	14.4329362
Average	0	1.1908377	1.8015966	1.81854445	<b>1.202744683</b>
Variance	0	0.00444992	0.048187	0.35434169	0.669787797
<b>Total</b>					
Count	12	12	12	12	
Sum	31463.51782	20149.5413	11257.478	6070.98372	
Average	2621.959818	1679.12844	938.12313	505.91531	
Variance	3791032.115	1652312.28	418277.83	212442.659	
<b>ANOVA</b>					
Source of Variation	SS	df	MS	F	P-value
Sample	49081174.68	3	16360392	157.337358	3.12213E-19
Columns	30942608.62	3	10314203	99.1913564	2.74679E-16
Interaction	14406086.9	9	1600676.3	15.3936526	2.65853E-09
Within	3327452.147	32	<b>103982.88</b>		2.18876577
Total	97757322.35		47		

### Appendix 3. Data analysis result of $\Sigma$ PAHs in leaf during experimental study

Tukey test		k	4
comparison	absolute difference	n obv	15
		df	32
		ms	74052.6825
		combination	6
		Q	3.85
25 ml/kg to 50 ml/kg	136.225	270.5113536	not significantly different
25 ml/kg to 75 ml/kg	519.125	270.5113536	significantly different
25 ml/kg to control	206.0833333	270.5113536	not significantly different
50 ml/kg to 75 ml/kg	382.9	270.5113536	significantly different
50 ml/kg to control	342.3083333	270.5113536	significantly different
75 ml/kg to control	725.2083333	270.5113536	significantly different

#### Anova: Two-Factor with Replication

SUMMARY	0 days	30 days	60 days	90 days	Total
<b>Diesel @25 ml/kg</b>					
Count	3	3	3	3	12
Sum	128.4	869.2	771.3	1675.9	3444.8
Average	42.8	289.7333333	257.1	558.63333	<b>287.0666667</b>
Variance	573.57	148910.9633	21748.53	240617.52	111514.5897
<b>Diesel @50 ml/kg</b>					
Count	3	3	3	3	12
Sum	128.4	1304.3	2093.2	1553.6	5079.5
Average	42.8	434.7666667	697.73333	517.86667	<b>423.2916667</b>
Variance	573.57	152865.1633	26367.123	22402.773	99265.63538
<b>Diesel @75 ml/kg</b>					
Count	3	3	3	3	12
Sum	128.4	1613.8	3139	4793.1	9674.3
Average	42.8	537.9333333	1046.3333	1597.7	<b>806.1916667</b>
Variance	573.57	21837.70333	49439.863	493774.33	467990.8572
<b>control</b>					
Count	3	3	3	3	12
Sum	128.4	265.1	310.8	267.5	971.8
Average	42.8	88.36666667	103.6	89.166667	<b>80.98333333</b>
Variance	573.57	2769.333333	241.33	1574.0033	1508.123333
<b>Total</b>					
Count	12	12	12	12	
Sum	513.6	4052.4	6314.3	8290.1	
Average	42.8	337.7	526.19167	690.84167	
Variance	417.141818	90428.73091	168045.23	473831.82	
<b>ANOVA</b>					
Source of Variation	SS	df	MS	F	P-value
Sample	3360698.67	3	1120232.9	15.127513	2.6392E-06
Columns	2783817.85	3	927939.28	12.530799	1.3889E-05
Interaction	2329567.57	9	258840.84	3.4953608	0.004135371
Within	2369685.84	32	<b>74052.683</b>		2.188765768
Total	10843769.9	47			

#### Appendix 4. Data analysis result of $\Sigma$ PAHs in stem during experimental study

Tukey test		k	4
		n obv	15
		df	32
		ms	1202.470208
		combination	6
		Q	3.85
<b>comparison</b>	<b>absolute difference</b>	<b>critical value</b>	<b>result</b>
25 ml/kg to 50 ml/kg	135.0166667	34.47087144	significantly different
25 ml/kg to 75 ml/kg	384.025	34.47087144	significantly different
25 ml/kg to control	62.86666667	34.47087144	significantly different
50 ml/kg to 75 ml/kg	249.0083333	34.47087144	significantly different
50 ml/kg to control	197.8833333	34.47087144	significantly different
75 ml/kg to control	446.8916667	34.47087144	significantly different

#### Anova: Two-Factor with Replication

SUMMARY	0 days	30 days	60 days	90 days	Total
<b>Diesel @25 ml/kg</b>					
Count	3	3	3	3	12
Sum	20.1	155.7	192.6	521.1	889.5
Average	6.7	51.9	64.2	173.7	<b>74.125</b>
Variance	6.28	1363.63	17.77	3.01	4358.425682
<b>Diesel @50 ml/kg</b>					
Count	3	3	3	3	12
Sum	20.1	253.1	727.7	1508.8	2509.7
Average	6.7	84.366666	242.566666	502.9333333	<b>209.1416667</b>
Variance	6.28	3.5233333	911.853333	36.65333333	39442.11174
<b>Diesel @75 ml/kg</b>					
Count	3	3	3	3	12
Sum	20.1	386.4	1590.6	3500.7	5497.8
Average	6.7	128.8	530.2	1166.9	<b>458.15</b>
Variance	6.28	862.33	14800.89	1206.43	226649.1573
<b>control</b>					
Count	3	3	3	3	12
Sum	20.1	29.5	41.7	43.8	135.1
Average	6.7	9.8333333	13.9	14.6	<b>11.25833333</b>
Variance	6.28	2.3433333	0.81	5.16	13.82265152
<b>Total</b>					
Count	12	12	12	12	
Sum	80.4	824.7	2552.6	5574.4	
Average	6.7	68.725	212.716666	464.5333333	
Variance	4.567272727	2479.8711	47388.9560	213450.4624	
<b>ANOVA</b>					
Source of Variation	SS	df	MS	F	P-value
Sample	1411596.132	3	470532.044	391.3045336	2.75635E-25
Columns	1490132.397	3	496710.799	413.0753474	1.18608E-25
Interaction	1446487.24	9	160720.805	133.658866	8.41839E-23
Within	38479.0466	32	<b>1202.47020</b>		2.1887657
Total	4386694.82	47			

## Appendix 5. Data analysis result of $\Sigma$ PAHs in root during experimental study

**Tukey test**

k	4
n obv	15
df	32
ms	<b>55417.09875</b>
combination	6
Q	<b>3.85</b>

comparison	absolute difference	critical value	result
25 ml/kg to 50 ml/kg	241.6666667	234.0113881	significantly different
25 ml/kg to 75 ml/kg	1390.875	234.0113881	significantly different
25 ml/kg to control	876.025	234.0113881	significantly different
50 ml/kg to 75 ml/kg	1149.208333	234.0113881	significantly different
50 ml/kg to control	1117.691667	234.0113881	significantly different
75 ml/kg to control	2266.9	234.0113881	significantly different

Anova: Two-Factor with Replication

SUMMARY	0 days	30 days	60 days	90 days	Total
<b>Diesel @25 ml/kg</b>					
Count	3	3	3	3	12
Sum	66	3060.4	3512	4221.5	10859.9
Average	22	1020.13333	1170.66666	1407.16667	<b>904.9916667</b>
Variance	42.37	84602.2233	16107.8233	26620.2633	327439.0754
<b>Diesel @50 ml/kg</b>					
Count	3	3	3	3	12
Sum	66	3235	4160.8	6298.1	13759.9
Average	22	1078.33333	1386.93333	2099.36666	<b>1146.658333</b>
Variance	42.37	130084.303	38850.5433	125606.523	663081.5663
<b>Diesel @75 ml/kg</b>					
Count	3	3	3	3	12
Sum	66	7352.2	8102.8	12029.4	27550.4
Average	22	2450.73333	2700.93333	4009.8	<b>2295.866667</b>
Variance	42.37	43364.4033	410187.423	10569.25	2346966.021
<b>control</b>					
Count	3	3	3	3	12
Sum	66	81.6	82.2	117.8	347.6
Average	22	27.2	27.4	39.2666666	<b>28.96666667</b>
Variance	42.37	257.16	148.32	105.863333	144.3660606
<b>Total</b>					
Count	12	12	12	12	
Sum	264	13729.2	15857.8	22666.8	
Average	22	1144.1	1321.48333	1888.9	
Variance	30.8145454	858178.543	1067661.66	2264815.84	
<b>ANOVA</b>					
Source of Variatio	SS	df	MS	F	P-value
Sample	31407317.7	3	10469105.9	188.914723	1.99443E-20
Columns	22023703.5	3	7341234.51	132.472371	4.02741E-18
Interaction	12916890.6	9	1435210.06	25.8983256	2.9625E-12
Within	1773347.16	32	<b>55417.0987</b>		2.18876576
Total	68121259.04	47			

## Appendix 6. Data analysis result of TPH in leaf during experimental study

Tukey test						
		k	4			
		n obv	15			
		df	32			
		ms	52015.85542			
		combination	6			
		Q	3.85			
comparison	absolute difference	critical value	result			
25 ml/kg to 50 ml/kg	277.3083333	226.7164186	significantly different			
25 ml/kg to 75 ml/kg	241.375	226.7164186	significantly different			
25 ml/kg to control	87.575	226.7164186	not significantly different			
50 ml/kg to 75 ml/kg	35.93333333	226.7164186	not significantly different			
50 ml/kg to control	364.8833333	226.7164186	significantly different			
75 ml/kg to control	328.95	226.7164186	significantly different			
Anova: Two-Factor with Replication						
<b>SUMMARY</b>	0 days	30 days	60 days	90 days	Total	
<b>Diesel @25 ml/kg</b>						
Count	3	3	3	3	12	
Sum	163	150.2	458.2	1065.1	1836.5	
Average	54.33333333	50.06666667	152.7333333	355.0333333	<b>153.0416667</b>	
Variance	276.6233333	2.123333333	127.9633333	45822.70333	25082.05174	
<b>Diesel @50 ml/kg</b>						
Count	3	3	3	3	12	
Sum	163	792.9	1523.7	2684.6	5164.2	
Average	54.33333333	264.3	507.9	894.8666667	<b>430.35</b>	
Variance	276.6233333	1555.77	48667.39	671850.2033	237904.7809	
<b>Diesel @75 ml/kg</b>						
Count	3	3	3	3	12	
Sum	163	756.2	1801.6	2012.2	4733	
Average	54.33333333	252.0666667	600.5333333	670.7333333	<b>394.4166667</b>	
Variance	276.6233333	6366.923333	38436.00333	17960.12333	80940.44333	
<b>control</b>						
Count	3	3	3	3	12	
Sum	163	129.5	244.3	248.8	785.6	
Average	54.33333333	43.16666667	81.43333333	82.93333333	<b>65.46666667</b>	
Variance	276.6233333	229.7733333	8.163333333	120.0533333	437.5460606	
<b>Total</b>						
Count	12	12	12	12	12	
Sum	652	1828.8	4027.8	6010.7		
Average	54.33333333	152.4	335.65	500.8916667		
Variance	201.1806061	13716.94909	69839.33	237416.8281		
<b>ANOVA</b>						
Source of Variation	SS	df	MS	F	P-value	F crit
Sample	1156411.011	3	385470.3369	7.410631504	0.00066457	2.901119584
Columns	1411506.887	3	470502.2958	9.045363034	0.000174768	2.901119584
Interaction	711998.7819	9	79110.97576	1.520901178	0.182926593	2.188765768
Within	1664507.373	32	<b>52015.85542</b>			
Total	4944424.053	47				

## Appendix 7. Data analysis result of TPH in stem during experimental study

Tukey test					
	k	n obv	4		
	df		15		
	ms		32		
	combination		362.4175		
	Q		6		
			3.85		
<b>comparison</b>	<b>absolute difference</b>	<b>critical value</b>	<b>result</b>		
25 ml/kg to 50 ml/kg	37.816667	18.924294	significantly different		
25 ml/kg to 75 ml/kg	83.891667	18.924294	significantly different		
25 ml/kg to control	14.808333	18.924294	not significantly different		
50 ml/kg to 75 ml/kg	46.075000	18.924294	significantly different		
50 ml/kg to control	52.625000	18.924294	significantly different		
75 ml/kg to control	98.700000	18.924294	significantly different		

### Anova: Two-Factor with Replication

SUMMARY	0 days	30 days	60 days	90 days	Total
<b>Diesel @25 ml/kg</b>					
Count	3	3	3	3	12
Sum	41.4	99.1	119.8	213	473.3
Average	13.8	33.03333333	39.93333333	71	<b>39.44166667</b>
Variance	28.99	517.4933333	27.85333333	303.21	621.7535606
<b>Diesel @50 ml/kg</b>					
Count	3	3	3	3	12
Sum	41.4	259.9	238	387.8	927.1
Average	13.8	86.63333333	79.33333333	129.2666667	<b>77.25833333</b>
Variance	28.99	870.6533333	4.12333333	72.81333333	2038.657197
<b>Diesel @75 ml/kg</b>					
Count	3	3	3	3	12
Sum	41.4	407.9	411.2	619.5	1480
Average	13.8	135.9666667	137.0666667	206.5	<b>123.3333333</b>
Variance	28.99	3189.623333	1.56333333	511.63	5931.906061
<b>control</b>					
Count	3	3	3	3	12
Sum	41.4	83.6	81.5	89.1	295.6
Average	13.8	27.86666667	27.16666667	29.7	<b>24.63333333</b>
Variance	28.99	128.0633333	47.56333333	8.13	82.29151515
<b>Total</b>					
Count	12	12	12	12	
Sum	165.6	850.5	850.5	1309.4	
Average	13.8	70.875	70.875	109.1166667	
Variance	21.08363636	2973.8675	2011.296591	4976.348788	
<b>ANOVA</b>					
Source of Variation	SS	df	MS	F	P-value F crit
Sample	69963.555	3	23321.185	64.34894838	1.20038E-13 2.901119584
Columns	55575.685	3	18525.22833	51.11571139	2.6339E-12 2.901119584
Interaction	28247.64667	9	3138.627407	8.660253457	1.92643E-06 2.188765768
Within	11597.36	32	<b>362.4175</b>		
Total	165384.2467	47			

## Appendix 8. Data analysis result of TPH in root during experimental study

Tukey test						
		k	4			
		n obv	15			
		df	32			
		ms	45495.35021			
		combination		6		
		Q	3.85			
comparison	absolute difference	critical value	result			
25 ml/kg to 50 ml/kg	158.758333	212.030631	not significantly different			
25 ml/kg to 75 ml/kg	586.200000	212.030631	significantly different			
25 ml/kg to control	353.200000	212.030631	significantly different			
50 ml/kg to 75 ml/kg	427.441667	212.030631	significantly different			
50 ml/kg to control	511.958333	212.030631	significantly different			
75 ml/kg to control	939.400000	212.030631	significantly different			

Anova: Two-Factor with Replication						
SUMMARY	0 days	30 days	60 days	90 days	Total	
<b>Diesel @25 ml/kg</b>						
Count	3	3	3	3	12	
Sum	150.6	1387.9	1440.3	2059	5037.8	
Average	50.2	462.6333333	480.1	686.3333333	<b>419.8166667</b>	
Variance	649.24	17231.04333	16260.43	17228.01333	67462.03061	
<b>Diesel @50 ml/kg</b>						
Count	3	3	3	3	12	
Sum	150.6	1310.9	1914.3	3567.1	6942.9	
Average	50.2	436.9666667	638.1	1189.033333	<b>578.575</b>	
Variance	649.24	94813.86333	15086.01	253494.0633	250399.3948	
<b>Diesel @75 ml/kg</b>						
Count	3	3	3	3	12	
Sum	150.6	2970.2	3186.5	5764.9	12072.2	
Average	50.2	990.0666667	1062.1666667	1921.633333	<b>1006.0166667</b>	
Variance	649.24	91023.62333	54016.86333	165895.0033	535382.6615	
<b>control</b>						
Count	3	3	3	3	12	
Sum	150.6	213.7	198.2	236.9	799.4	
Average	50.2	71.23333333	66.06666667	78.96666667	<b>66.61666667</b>	
Variance	649.24	71.44333333	133.6633333	74.62333333	289.8978788	
<b>Total</b>						
Count	12	12	12	12	12	
Sum	602.4	5882.7	6739.3	11627.9		
Average	50.2	490.225	561.6083333	968.9916667		
Variance	472.1745455	153932.7566	154258.0227	577939.7772		
<b>ANOVA</b>						
Source of Variation	SS	df	MS	F	P-value	F crit
Sample	5462594.886	3	1820864.962	40.02310024	6.11341E-11	2.901119584
Columns	5098838.677	3	1699612.892	37.35794723	1.44075E-10	2.901119584
Interaction	2834183.949	9	314909.3276	6.921791484	1.7937E-05	2.188765768
Within	1455851.207	32	<b>45495.35021</b>			
Total	14851468.72	47				

## **Vitae**

**Full Name** : Md Iqram Uddin Al Amran

**Nationality** : Bangladeshi

**Email** : md.iqramuddinalamran@gmail.com

**Address** : Abdus Samad Dofador House, South Halishahar (Newmooring),  
Bandar, Chittagong, Bangladesh 4218.

### **Academic Background:**

2016 – 2019: MS in Environmental Science, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia

2010-2012: MS in Forestry, Institute of Forestry and Environmental Science, University of Chittagong, Chittagong, Bangladesh

2005-2009: B.Sc. in Forestry, Institute of Forestry and Environmental Science, University of Chittagong, Chittagong, Bangladesh

### **Professional Experience:**

10/2014 – 01/2016: Site Manager, IUCN (International Union for Conservation of Nature) Bangladesh Country Office, World Bank Funded SRCWP project

02/2014 – 09/2014: NRM Facilitator, CODEC (Community Development Centre), USAID'S Funded Climate Resilient Ecosystems and Livelihood Project

06/2011- 05/2013: Program Officer, Songshoptaque, European Union Funded Climate Change and Food Security Program

**Conferences Attended:**

8<sup>th</sup> Petro Environment Conference and Exhibition on 22-24<sup>th</sup> February 2016, Al Khobar, Saudi Arabia

20<sup>th</sup> Middle East Oil and Gas Show and Conference on 6-9<sup>th</sup> March 2017, Bahrain

9<sup>th</sup> Petro Environment Conference and symposium on environmental progress in the petroleum and petrochemical industry on 19-21th February 2019, Al Khobar, Saudi Arabia

**Publications:**

Al Amran, M.I.U., Manikandan, K.P., Tawabini, B.S., Qurban, M.A., Loughland, R., Abdulghani, W. Phytoremediation in mangrove sediment impacted by diesel contamination using *Avicennia marina* (manuscript ready for submission on Marine Pollution Bulletin - Elsevier)

Al Amran, M.I.U., Manikandan, K.P., Tawabini, B.S., Qurban, M.A., Loughland, R., Abdulghani, W. An overview of the distribution, occurrence and sources of heavy metals and poly aromatic hydrocarbons in the mangrove systems of Arabian Gulf (manuscript ready for submission on Marine Pollution Bulletin -Elsevier)

|