

Practical Approach to Reclamation of Post-Mining Sites

Von der Fakultät für Umwelt und Naturwissenschaften der Brandenburgischen Technischen Universität Cottbus-Senftenberg zur Erlangung des akademischen Grades eines Doktors der Naturwissenschaften (Dr. rer. nat)

genehmigte Dissertation

vorgelegt von

M.Sc. Environmental and Resource Management

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Tag der mündlichen Prüfung: 08.12.2021

Summary

The direct and indirect benefits of mining are known, but its induced ecosystem disturbances are enormous. Reclaiming the mine sites is important, however, there are no internationally recognized regulations guiding reclamation progress. The few countries with related national laws differ in their approaches with identifiable crucial omissions. While there are sites with false success claims, occurrences show that most reclaimed sites cannot cater for the downstream ecological hierarchy and productivity. The existing multiple panoply of ecological evaluation techniques fail to sufficiently integrate the interdisciplinary complexity and sustainability approach, define targets and endpoints necessary for reclamation progress. Most related restoration projects have been on agricultural degraded sites with low reflection of sustainable attributes and guidelines of the Society of Ecological Restoration (SER). However, the increasing global awareness and efforts towards sustainable land-use management and its influences in achieving the Sustainable Development Goals (SDGs) makes a comprehensive consideration of reclamation progress necessary and timely. Within this framework, the objective of this research is to advance knowledge in reclamation of post-mining sites on (i) international scale and (ii) national scale, taking Nigeria as an example. On the international scale (i), a systematic reclamation threshold scale for assessing, evaluating, documenting, and monitoring reclamation progress was developed. The threshold stages begin from the initial state I_0 down to degraded state D_0 (depending on the type of mining). Reclamation starts with soil reconstruction R_{-2} up to revegetation R_{-1} (red zones) to reach minimum threshold R_0 (amber zone). Beyond R_0 are the green zones R_1 , R_2 , and R_3 representing soil/abiotic condition, biological and improved threshold respectively. The reclamation thresholds also identified potential drivers, land-use options, targets and endpoints along the reclamation ladder. Adaptation of the threshold model in national and international laws is recommended. It is also applicable to all degraded ecosystems with representative picture of levels that have been crossed and to be crossed. On the national scale with Nigeria (ii), findings show that almost all mine sites in the country are below the minimum threshold scale R_0 . Nigeria is endowed with over thirty-four solid minerals and abundant crude oil. While the efforts and pace of reclamation is poor, the developmental reflection of these resources is as well low. Artisanal and Small Scale Mining (ASM) dominates the mining activities (>95 %), whereby, contamination and soil lithology disturbances are the state-of-the-art discussions on most mine sites. This is important because despite the ASM activities, farming, which is the main source of livelihood for most communities, kept ongoing. Therefore, for the crude

oil contaminated sites, this study highlights the status, impacts and challenges limiting remediation. The preferable remediation techniques, typical cogitation for large in-situ implementation, and potential species that can be employed were also identified. Bioremediation (phytoremediation) is the most feasible remediation technique in Nigeria. It is cheap, easy to maintain (even by the community), liable to gain public acceptance and restore livelihood to the communities. Gold mining was taken as a representative of the solid mineral resources. As a practical approach, experimental areas on an abandoned mining site (Site 1), an active mining site (Site 2) and an undisturbed vegetation site (Control) in the southwestern Nigeria were mapped out as representative of the mining and farming activities in the region. On the sites, (a) the impacts of the ASM activities on the floristic association were assessed. (b) the potential of 2D Electrical Resistivity Tomography (ERT) was explored to characterize the horizontal and vertical landscape homogeneity of the mine sites, and lastly, (c) the study identified native high-accumulating plants growing on the sites that can be employed for phytoremediation. Thus, the results show that (a) the floristic association of the mine sites have been stressed and disturbed. This is true with the identification of native species such as *Acanthus montanus* and *Icacina trichantha* on the control site while the presence of *Capsicum frutescens* and *Crassocephalum crepidioides* found on Site 2 shows human inference. The identification of *Adenia venenata* and *Grewia flavescens* on Site 1 show both original and disturbed floristic composition. (b) the resistivity structure of the sites shows that ASM has greatly impaired the lithological status of the sites. Dug pit that was covered with muds, buried foreign substance and unnoticeable uncovered pit were discovered. (c) out of the nine selected species (*Acanthus montanus*, *Crinum jagus*, *Chromolaena odorata*, *Melanthera scandens*, *Melochia corchorifolia*, *Palisota ambigua*, *Pteris togoensis*, *Musa sapientum*, and *Theobroma cacao*), *Crinum jagus* has the highest accumulation factor of 8.71, 37.47, 1.08 and 29.38 for Pb, Cd, Fe and Cu respectively. It is a novel plant recommendable for multiple heavy metals phytoextraction in the tropics. However, its hyperaccumulator potentials based on international threshold criteria needs further studies. Similarly, identification of more high accumulating plant species is important. Conclusively, further land-use of the post-mine sites in Nigeria is greatly discouraged, more so, effective approaches and policies to curb ASM activities and enhance remediation is urgently necessary.

Keywords: Threshold indicators, Artisanal and Small-Scale mining (ASM), Floristic association, Soil lithology, Electrical Resistivity Tomography (ERT), *Crinum jagus*, Hyperaccumulators.

Zusammenfassung

Zwar bringt der Bergbau sowohl direkten als auch indirekten Nutzen, jedoch sind die Störungen der betroffenen Ökosysteme enorm. Die Rekultivierung der Bergbauregionen ist demzufolge sehr wichtig, jedoch gibt es keine international anerkannten Vorschriften, die den Ablauf der Rekultivierung lenken. Die wenigen Länder mit entsprechenden nationalen Gesetzen unterscheiden sich in ihren Ansätzen mit erkennbaren kritischen Versäumnissen. Es gibt zwar Standorte mit falschen Erfolgsbehauptungen, aber es zeigt sich, dass die meisten zurückgewonnenen Standorte nicht auf die gegebene ökologische Hierarchie und Produktivität ausgerichtet sind. Darüber hinaus ist die Vielzahl an ökologischen Bewertungstechniken nicht in der Lage, die interdisziplinäre Komplexität, den Nachhaltigkeitsansatz sowie die Definition von Zielen und Endpunkten, die für den Fortschritt der Rekultivierung notwendig sind, ausreichend zu integrieren. Die meisten damit zusammenhängenden Rekultivierungsprojekte wurden an landwirtschaftlich degradierten Standorten durchgeführt, und spiegeln kaum die nachhaltigen Eigenschaften und Richtlinien der of Ecological Restoration (SER) wider. Nichtsdestotrotz macht das zunehmende globale Bewusstsein und die Bemühungen um ein nachhaltiges Landnutzungsmanagement und dessen Einfluss auf die Erreichung der Ziele der nachhaltigen Entwicklung (SDGs) eine umfassende Betrachtung der Fortschritte bei der Rekultivierung notwendig und aktuell. Innerhalb dieses Rahmens bestehen die Ziele dieser Arbeit darin, das Wissen über die Rekultivierung von Bergbaufolgelandschaften auf (i) internationaler und (ii) nationaler Ebene am Beispiel Nigerias zu erweitern. Auf internationaler Ebene (i) wurde eine systematische Skala von Rekultivierungsschwellenwerten für die Feststellung, Bewertung, Dokumentation und Überwachung des Rekultivierungsfortschritts entwickelt. Die Schwellenstufen beginnen vom Ausgangszustand P_0 bis hin zum degradierten Zustand D_0 (je nach Art des Abbaus). Die Rekultivierung beginnt mit der Bodenrekonstruktion R_{-2} bis zur Begrünung R_{-1} (rote Zonen), um den minimalen Schwellenwert R_0 (gelbe Zone) zu erreichen. Jenseits von R_0 befinden sich die grünen Zonen R_1 , R_2 und R_3 , die jeweils für Boden/abiotische Umwelt, Biologie und verbesserte Schwellenwerte stehen. Die Rekultivierungsschwellenwerte identifizierten auch potenzielle Triebkräfte, Landnutzungsoptionen, Ziele und Endpunkte entlang der Rekultivierungsleiter. Eine Anpassung des Schwellenwertmodells in nationalen und internationalen Gesetzen wird empfohlen. Es gilt auch für alle degradierten Ökosysteme mit einem repräsentativen Abbildung der Ebenen, die durchquert wurden und noch durchquert werden sollen. Auf der nationalen Skala mit Nigeria (ii) zeigen die Ergebnisse, dass fast alle Bergbaustandorte im Land

unter der Mindestschwellskala R_0 liegen. Nigeria ist mit über vierunddreißig festen Mineralien und reichlich Rohöl ausgestattet. Während die Anstrengungen und das Tempo der Rekultivierung gering sind, ist auch die entwicklungspolitische Bedeutung dieser Ressourcen gering. Der handwerkliche und kleinmaßstäbliche Bergbau (ASM) dominiert die Bergbauaktivitäten (>95 %), wobei Kontamination und Störungen der Bodendlithologie auf den meisten Bergbaustandorten Stand der Technik sind. Dies ist von Bedeutung, da trotz der ASM-Aktivitäten die Landwirtschaft, welche für die meisten Gemeinden die wichtigste Lebensgrundlage darstellt, weiterhin betrieben wird. Daher soll diese Studie für die durch Rohöl verunreinigten Standorte den Status, die Auswirkungen und die Herausforderungen aufzeigen, die den Erfolg der Sanierung limitieren. Es wurden auch die bevorzugten Sanierungstechniken, die typische Herangehensweise für die großflächige In-situ-Umsetzung und die möglichen Arten, die eingesetzt werden können, identifiziert. Im Allgemeinen ist die Phytoremediation die praktikabelste Sanierungstechnik in Nigeria. Sie ist kostengünstig, einfach zu unterhalten (sogar von der Gemeinde selbst), geeignet, die öffentliche Akzeptanz zu gewinnen und die Lebensgrundlage der Gemeinden wiederherzustellen. Der Goldbergbau wurde als ein Vertreter der festen Bodenschätze ausgewählt. Als praktischer Ansatz wurden Versuchsgebiete auf einer verlassenen Abbaustätte (Site 1), einer aktiven Abbaustätte (Site 2) und einer ungestörten Vegetation (Control) im Südwesten Nigerias als repräsentativ für die Bergbau- und landwirtschaftlichen Aktivitäten in der Region kartiert. An den Standorten wurden (i) die Auswirkungen der ASM-Aktivitäten auf die floristische Zusammensetzung untersucht (ii) das Potenzial der 2D-Widerstandstomographie (ERT) untersucht, um die horizontale und vertikale landschaftliche Homogenität der Bergwerksstandorte zu charakterisieren, und schließlich (iii) einheimische, hoch akkumulierende Pflanzen identifiziert, die auf den Standorten wachsen und für die Phytoremediation eingesetzt werden können. Die Ergebnisse zeigen, dass (i) die floristische Zusammensetzung der Bergwerksstandorte beansprucht und gestört wurde. Dies trifft auf die identifizierten einheimischer Arten wie *Acanthus montanus*. und *Icacina trichantha* auf der Kontrollfläche zu, während die Anwesenheit von *Capsicum frutescens* und *Crassocephalum crepidioides*, die auf Fläche 2 gefunden wurden, Rückschlüsse auf menschliche Eingriffe zulässt. Die Identifizierung von *Adenia venenata* und *Grewia flavescens* auf Fläche 1 zeigt sowohl die ursprüngliche als auch die gestörte floristische Zusammensetzung. (ii) die Struktur der elektrischen Widerstandsfähigkeit der Standorte zeigt, dass ASM die lithologischen Eigenschaften der Standorte stark beeinträchtigt hat. Es wurden eine mit Schlamm bedeckte Baugrube, vergrabene Fremdschubstanzen und eine unbemerkt freigelegte Grube entdeckt. (iii) von den neun ausgewählten

Arten (*Acanthus montanus*, *Crinum jagus*, *Chromolaena odorata*, *Melanthera scandens*, *Melochia corchorifolia*, *Palisota ambigua*, *Pteris togoensis*, *Musa sapientum*, und *Theobroma cacao*) hat *Crinum jagus* den höchsten Akkumulationsfaktor von 8,71, 37,47, 1,08 und 29,38 für Pb, Cd, Fe und Cu. Es handelt sich um eine neuartige Pflanze, die für die Phytoextraktion mehrerer Schwermetalle in den Tropen empfohlen wird. Ihr Hyperakkumulationspotential auf Grundlage internationaler Schwellenwerte muss jedoch noch weiter untersucht werden. Ebenso wichtig ist die Identifizierung von Pflanzenarten mit höheren Akkumulationspotentialen. Zusammenfassend lässt sich sagen, dass von einer weiteren Landnutzung der Tagebaurestlöcher in Nigeria stark abgeraten wird, mehr noch, dass wirksame Ansätze und Strategien zur Eindämmung der ASM-Aktivitäten erforderlich sind und dass eine Sanierung dringend notwendig ist.

Stichworte: Schwellenwertindikatoren, Handwerklicher und Kleinbergbau (ASM), Floristische Zusammensetzung, Bodolithologie, Elektrische Widerstandstomographie (ERT), *Crinum jagus*, Hyperakkumulatoren.

Table of contents

Summary	iii
Zusammenfassung	v
Table of contents	viii
List of tables	xiii
List of figures	xiv
Abbreviations	xv
Thesis at a glance	xvii
1. Introduction	1
1.1 Research questions	6
1.2 Objectives	7
2. An approach to thresholds for evaluating post-mining site reclamation	9
2.1 Abstract	9
2.2 Introduction	9
2.3 Reclamation success evaluation conceptual model	12
2.3.1 Initial/reference state (I_0)	14
2.3.2 Soil reconstruction (backfilling) (R_{-2})	14
2.3.3 Revegetation (R_{-1})	15
2.3.4 Minimum reclamation threshold (R_0)	15
2.3.5 Status assessment/decision making	17
2.3.6 Reclamation threshold 1 (R_1)	20
2.3.7 Reclamation threshold 2 (R_2)	21
2.3.8 Reclamation threshold 3 (R_3)	22
2.3.9 Anticipated targets and endpoints	23
2.4 Conclusion	23
3. Prospects of in-situ remediation of crude oil contaminated lands in Nigeria	25

3.1 Abstract.....	25
3.2 Introduction.....	25
3.3 Crude oil contamination in Nigeria.....	28
3.3.1 Level of crude oil contamination.....	29
3.3.2 Impacts of crude oil contamination.....	29
3.4 Remediation of contaminated soil	31
3.4.1 Targeted contaminants	31
3.4.2 Treatment techniques for contaminated soil	32
3.4.3 Challenges to remediation in Nigeria	34
3.4.4 Technique recommendable for Nigeria	37
3.5 Mechanisms of phytoremediation.....	38
3.6 Practical considerations for in-situ phytoremediation in Nigeria	39
3.6.1 Site condition	39
3.6.2 Plant characteristics	40
3.6.3 Agronomic measures	41
3.6.4 Cost estimation.....	42
3.6.5 Operation and maintenance.....	42
3.6.6 The fate of the harvested plants	43
3.6.7 Regulatory standards.....	44
3.7 Potential species for phytoremediation in Nigeria.....	44
3.7.1 Herbaceous species for remediation of petroleum hydrocarbons	44
3.7.2 Trees for phytoremediation of petroleum hydrocarbons	46
3.7.3 Combination of both trees and grasses for phytoremediation	46
3.7.4 Combination of techniques	47
3.8 Conclusion and recommendation.....	47
4. Impact of mining on the floristic association of gold mined sites in southwest Nigeria	49

4.1 Abstract.....	49
4.2 Introduction.....	50
4.3 Methods.....	52
4.3.1 Experimental area	52
4.3.2 Site selection and preparation	53
4.3.3 Plant sampling scheme and classification.....	54
4.3.4 Data analysis	55
4.4 Results.....	56
4.5 Discussion.....	62
4.5.1 All the sites	63
4.5.2 Both site 1 and the control site.....	64
4.5.3 Both site 2 and the control site.....	65
4.5.4 Both site 1 and site 2.....	65
4.5.5 Only the control site.....	65
4.5.6 Only on site 2.....	66
4.5.7 Only on site 1	66
4.6 Conclusions and recommendations.....	67
5. Characterizing landscape heterogeneity on gold post-mining sites.....	69
5.1 Abstract.....	69
5.2 Introduction.....	69
5.3 Methodology.....	71
5.3.1 Experimental areas.....	71
5.3.2 Experimental design.....	73
5.3.3 Electrical Resistivity Tomography (ERT)	74
5.3.4 Soil sampling and analysis.....	74
5.4 Results.....	75

5.4.1 Mine site 1 (Okutu-Omo).....	75
5.4.2 Mine site 2 (Itagunmodi)	76
5.4.3 Soil physicochemical properties	77
5.5 Discussion.....	78
5.6 Conclusion	80
6. Identification of tropical native high-accumulating plant species for phytoremediation	81
6.1 Abstract.....	81
6.2 Introduction.....	82
6.3 Method	83
6.3.1 Experimental areas and design.....	83
6.3.2 Soil sampling and analysis.....	84
6.3.3 Plants sampling and analysis	85
6.3.4 Data analysis	86
6.3.5 Bioconcentration, translocation, and accumulation factors	86
6.4 Results.....	87
6.4.1 Soil physicochemical properties	87
6.4.2 Concentration of heavy metals in soil.....	88
6.4.3 Analysis (soil physicochemical properties, heavy metals)	90
6.4.4 Plants heavy metal content and phytoremediation potentials	91
6.5 Discussion.....	92
6.5.1 Soil physicochemical properties	92
6.5.2 Soil heavy metal concentration.....	95
6.5.3 Analysis (heavy metals, soil physicochemical properties)	96
6.5.4 Plants heavy metal content and phytoremediation potentials	97
6.6 Conclusions and recommendations.....	99
7. Synthesis	100

7.1 Conclusions.....	100
7.2 Limitations	104
7.3 Outlooks.....	105
References.....	111
Appendix A.....	149
Dedication.....	151

List of tables

Table 1: Examples of sustainable target indicators.....	19
Table 2: Spectrum of earthworm species inhabiting Berzdorf mining region.....	23
Table 3: Potential herbaceous species for phytoremediation of oil contaminated lands	45
Table 4: Trees for potential phytoremediation of oil contaminated lands in Nigeria.....	46
Table 5: Biological diversity measurement (alpha and beta diversity).....	56
Table 6: Species and family compositions of Flora on Site 1.....	60
Table 7: Species and family compositions of Flora on Site 2.....	61
Table 8: Species and family compositions of Flora on Control site	62
Table 9: Description of the experimental areas	84
Table 10: Selected plants species from the three considered mine sites.....	85
Table 11: Mean values (n=3) for the physicochemical properties of the three sites.	87
Table 12: Mean values (n=3) for the total metal concentration (mg kg ⁻¹) at the three sites.	89
Table 13: Permissible limits standards for heavy metals.....	89
Table 14: Concentration of metals in <i>Theobroma cacao</i> and <i>Musa sapientum</i> in µg g ⁻¹	93
Table 15: Phytoremediation potential of the seven native plant species.	93

List of figures

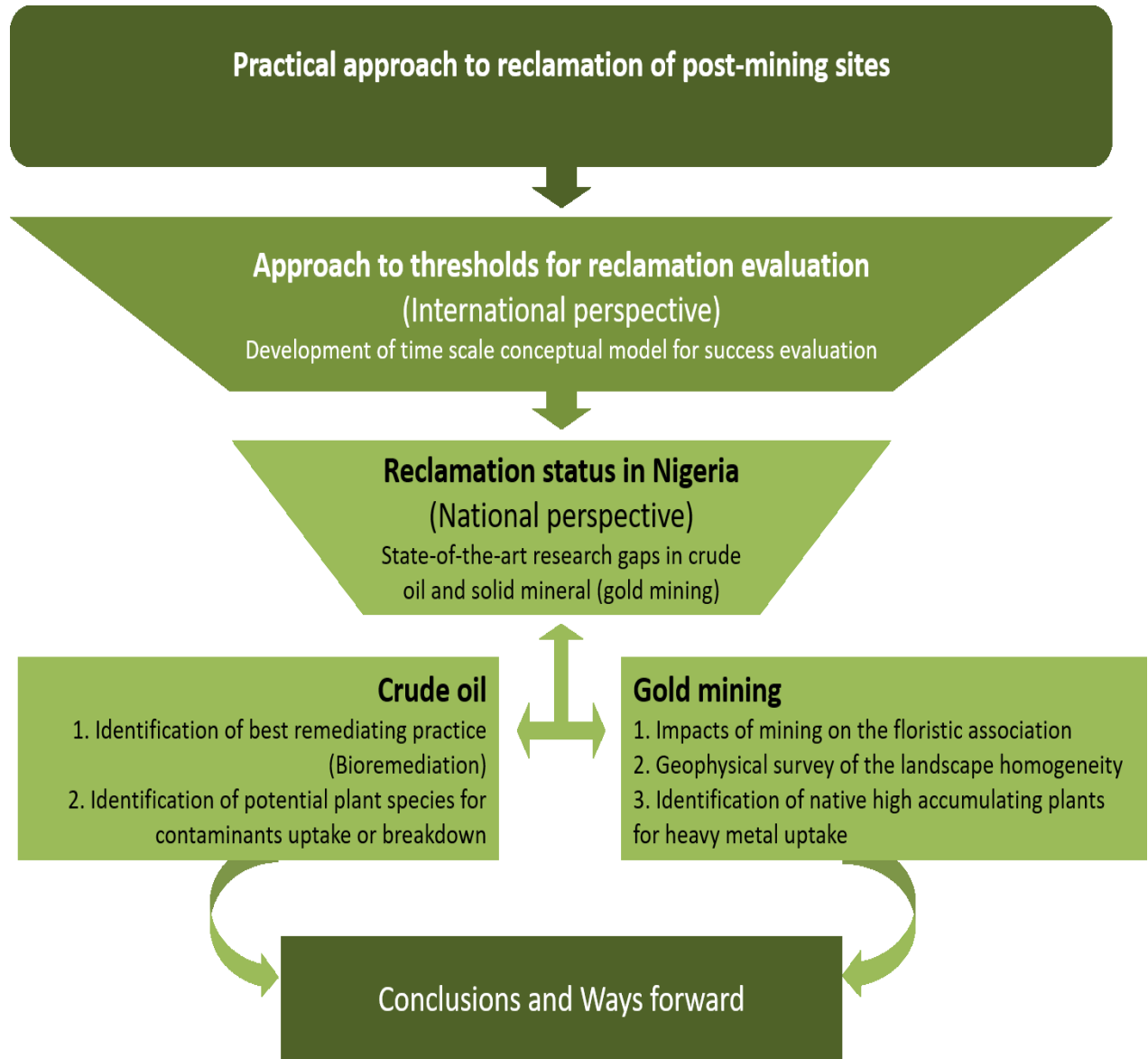
Figure 1: List of mineral resources in Nigeria and their locations	2
Figure 2: Common targets of most reclamation scheme	11
Figure 3: Time-Scale conceptual model for evaluating successful reclamation progress	13
Figure 4: considerations for sustainable reclamation development.....	18
Figure 5: Oil producing regions in Nigeria and their Natural gas infrastructure.....	28
Figure 6: Characterization factors in determining clean-up strategy.....	33
Figure 7: Conversion pathway for alkanes in plants.....	38
Figure 8: Scaled map of the study area.....	53
Figure 9: Personally taken pictorial view of the considered sites.....	54
Figure 10: Diagrammatic representation of the line transect sampling method	55
Figure 11: Species composition of the 3 sites by nDMS analysis.	57
Figure 12: Species dominance curve of the 3 studied sites..	58
Figure 13: Distinctive association of plant type to each of the 3 studied sites..	59
Figure 14: Interrelationship between the Flora species on the 3 sites	63
Figure 15: Geological map of the study areas.	72
Figure 16: Experimental areas, showing the geophysical data acquisition layouts and directions.	73
Figure 17: Data acquisition and orientation of the ERT survey.	74
Figure 18: 2D resistivity structure of Traverse line 1 (a) and 2 (b).	76
Figure 19: 2D Dipole-dipole pseudo-section of Traverse lines 3 (a) and 4 (b).	77
Figure 20: Box plot of the soil textural class.	78
Figure 21: Lithological differences along Traverse (TR) 2.	79
Figure 22: Box plot of the soil textural class.	88
Figure 23: Box plots of the soil heavy metal content.	90
Figure 24: Physicochemical composition of the 3 sites by nDMS analysis.	91
Figure 25: A comprehensive summary of the research objectives, outcomes and outlooks.	100

Abbreviations

AF	Accumulation Factor
ASM	Artisanal and Small-Scale Mine (ASM)
BCF	Bioaccumulation Factor
CEC	Cation Exchange Capacity
DPR	Department of Petroleum Resources
DRO	Diesel Range Organics
EC	Electrical Conductivity
ERT	Electrical Resistivity Tomography
EGASPIN	Environmental Guideline and Standard for Petroleum Industry in Nigeria
FAO	Food and Agriculture Organization of the United Nations
FME	Finland Ministry of Environment
GRO	Gasoline Range Organics
HM	Heavy Metals
IEES	Institute of Ecology and Environmental Studies, Nigeria
IUCN	International Union for Conservation of Nature
LGA	Local Government Area
LSM	Large Scale Mining
MPA	Maximum Permissible Addition
NAFDAC	National Agency for Food and Drug Administration and Control
ND	Not Detected
NIPHEN	National Institute for Public Health and the Environment, Netherlands

nMDS	non-metric Multi-Dimensional Scaling
NOSDRA	National Oil Spill Detection Agency
OM	Organic Matter
PA DER	Pennsylvania Department of Environmental Resources
PERMANOVA	Permutational Multivariate Analysis of Variance
PH	Petroleum Hydrocarbons
PRIMER-E	Plymouth Routines in Multivariate Ecological Research
RENA	Remediation by Enhanced Natural Attenuation
RSES	Reclamation Success Evaluation System
SER	Society of Ecological Restoration
SDGs	Sustainable Development Goals
SPDC	Shell Petroleum Development Company
TF	Translocation Factor
TN	Total Nitrogen
TR	Traverse
UNEP	United Nations Environment Programme
WHO	World Health Organization

Thesis at a glance



1. Introduction

The unending global demands for mineral resources make mining increasingly unavoidable. Though it is a crucial economic venture globally, but it subjects the ecosystem to severe and continuous disturbances (Ericsson 1991). Reclamation of these sites is important and has been extensively discussed (Chang et al. 2000; Kuter 2013), resulting in the development and improvement of diverse reclamation scheme. However, occurrences showed that approaches to reclamation differ around the world. Soil reconstruction (backfilling) and revegetation, which are the common reclamation targets of most mining companies (Maiti 2013), cannot cater for the downstream ecological hierarchy and productivity (Jorgensen & Nielsen 2013). While no existing internationally recognized regulations guiding reclamation progress, the few countries with related and monitored national laws have differences in their approaches with identifiable crucial omissions. The first scientific evaluation system for coal mine derelict sites was developed in a symposium at the annual meeting of the ‘American Society of Surface Mining and Reclamation’ in 1990 (April 23 – 26). It was entitled “Evaluating Reclamation Success; The Ecological Consideration” (Chambers & Wade 1992). Their listed ecosystem attributes for evaluating reclamation success is limited and not sustainable. More so, it has no clear evidence in most practical evaluation scheme. These omissions are same for other schemes established afterwards such as Reclamation Success Evaluation System (RSES) developed for field assessment of reclamation success by the Bureau of Abandoned Mine Reclamation, Pennsylvania Department of Environmental Resources (PA DER) (Hunsberger & Michaud 1994). This is same for indicator parameters highlighted by Maiti (2013) and related soil-quality evaluation systems (Paz-Kagan et al. 2014; Obade & Lai 2016; Mukhopadhyay et al. 2016).

Likewise, the existing multiple panoply of ecological and evaluation techniques fail to sufficiently integrate the interdisciplinary complexity, sustainability approach, define targets, and endpoints entailed in reclamation progress (Dudley et al. 2018). Majority of the practical restoration projects are on agricultural degraded sites (Wortley et al. 2013). They show low reflection of sustainable attributes and guidelines for assessing restoration projects as highlighted by the Society of Ecological Restoration (SER). More so, the use of only ecological indicators, which is common in most restoration projects, can create a form of bias or imperfect conclusions in the evaluation process. Variations in indicator species frequency and cover could be indecisive and limit certainty

of recovery (Dale & Beyeler 2001; Dale & Kline 2013; Erdos et al. 2017). While these limitations to evaluation of reclamation success remain, there are also sites with false success claims (Rooney et al. 2012). The increasing global awareness and efforts towards sustainable land-use, restoration, management, and its potential influences in achieving the Sustainable Development Goals (SDGs) make a comprehensive consideration of the reclamation process necessary and timely. Therefore, the first section of this study focus on development of a time scale model for evaluating post-mining sites reclamation.

Scaling down from the global approach to national cases, this research study took Nigeria as an example to assess its status of mining and reclamation. Nigeria is one of the most endowed West-African countries with over thirty-four (34) solid minerals (Figure 1) and abundant crude oil (13th largest producer according to Enerdata 2019 of the Global Energy Statistics). Despite these abundant resources, its expected developmental reflections are low with severe environmental, social and economic impacts. This low developmental reflection can be explained by the known ‘paradox of plenty’ or resource curses (Karl 1997).



Figure 1: List of mineral resources in Nigeria and their locations. **Source:** Nigeria Mining Week (2020)

Efforts and the pace of post-mining landscape reclamation in Africa are generally poor and sluggish (Festin et al. 2019). While the induced consequences persist, most of the miners and stakeholders are corrupt, illegal, inexperienced, erratic, unconcerned, poverty-driven, and unmindful of the attendant effects of their activities. Threshold scaling of most mine sites shows that they are below the minimum standard for any land-use option. Yet, farming is the increasing land-use options of most mine sites (Eludoyin et al. 2017). Though it is the main source of livelihood, but it is highly detrimental with incurred concerns ranging from soil lithology disturbances and increasing contamination. The contaminants (either from crude oil exploration or from solid minerals mining) expose the receptors to varying degrees of risk. It limits agricultural productivity, land-use, hampers public health, and in some cases leads to community death (Makinde et al. 2013; Lo et al. 2012; Plumlee et al. 2013; Bartrem et al. 2014). Therefore, contaminations of the pedosphere, biosphere, atmosphere and the hydrosphere as well as its induced lithological differences remain the state-of-the-art discussion in the country. These state-of-the-art research gaps regarding contamination from crude oil exploration and solid mineral mining (taking gold as an example) are therefore of interest and the considered study focus.

Crude oil

Environmental contamination (soil, water, air, and biota) from crude oil exploration and exploitation, as well as other activities such as processing, storage and transportation has been an age-long phenomenon in Nigeria (Linden & Palsson 2013; Fentiman & Zabbey 2015; Elum et al. 2016). Several agricultural soils have been rendered unproductive; the known mangrove ecosystems in the Niger-Delta region, which is the country's hub of crude oil is drastically degrading and several fauna and flora have reportedly gone extinct (Zabbey et al. 2017). Its impacts have gained both local and international attention, thereby scaling-up pressure for remediation. Although there have been some clean up attempts (Giadom & Tse 2015), but no significant success has been recorded. Failures of the attempts were attributed to erroneous operational wrong conclusions coupled with the adoption of unsustainable and ineffective approaches which are not specific to Nigeria (Zabbey et al. 2017). An example is the wrong assumptions that layers of clay soil covered the Niger-Delta soils, thereby supposing it might limit percolation of oil from the topsoil. Similar to that was the wrong adoption of Remediation by Enhanced Natural Attenuation (RENA) (Ebuehi et al. 2005; Steiner 2010), which was declared

unsuitable by the United Nations Environment Programme (UNEP) report in 2011. While several remediation attempts suffered setbacks, most related research studies have been ex-situ in pot experiments, greenhouses, or small-scale experiments. Therefore, identification of clean-up techniques liable of receiving public acceptance and on large scale, effective, cheap, efficient to render the soil agriculturally viable, capable of restoring livelihood, easy to maintain, overcome several remediation limitations, and stand out as a benchmark in Nigeria and other affected developing countries is paramount.

Solid minerals

Due to the oil boom phase since the last decades, national interest in Large Scale Mining (LSM) of solid minerals has greatly declined. The reduction in LSM has made Artisanal and small-scale mining (ASM) the most predominant for solid minerals. It accounts for over 95% of the entire mining activities (Akinbiola et al. 2016). This dominance of ASM over LSM can be attributed to the ores quantity, locations, technological demands, access to markets, formalization requirements, and poor performance of the LSM sector (Oramah et al. 2015). The ASM miners are mostly illegal, inexperienced, erratic, consistently increasing, and are less concerned of their induced environmental impacts. Their activities entail ecosystem destruction, drastic landscape degradation, diversion of watercourse/sources, digging of pits and trenches (sometimes without signage and barricades within farmlands), replacing the topsoil with excavated subsoil, which less supports plant growth and with low nutrient, as well as increasing pollution and contamination. One of the actively mined solid minerals in southwestern Nigeria is gold. Gold mining within this region can be dated back to 1942 (Salami et al. 2003), and several research studies have been done, analysing its environmental impacts (Aigbedion & Iyayi 2007; Adeoye 2016). However, there are several identified research gaps, which are of interest in this study.

A preliminary research gap is to understand the floristic association of the sites. Occurrences have shown that differences in the intensity of land use, human activities as well as climate change directly or indirectly influence the dynamics, quantitative and qualitative composition of the flora, fauna, biocoenoses and habitats within the ecosystem. Effects of these changes have been studied in varieties of ecosystems such as ecosystem functioning (Hötes et al. 2010), primates (Bicknell & Peres 2010), coral reefs (Graham et al. 2011), forest (Valois-Cuesta & Martinez-Ruiz 2016; Valois-Cuesta & Martinez-Ruiz 2017), etc. On the gold mining sites, it is hypothesized that the

knowledge about its floristic association is essential for many ecological studies such as succession and ecological balance. It is a representative of occurring changes on the sites such as the land-use, terrain and seasonal variations. The natural functions of native species in maintaining ecological balance within an ecosystem remains crucial (Walker 1992). The disappearance of these endemic species and introduction of exotic species alters ecological balance, composition, as well as functions and services such as pollination, seed dispersal, resilience, decomposition, etc. (Chornesky et al. 2005). These categories of plants are known as functional species and ecological indicators. Their loss poses replicable effects of their functions (Loreau et al. 2001; Scherer-Lorenzen et al. 2005). Although quantifying this ecological imbalance is difficult, but its meaningful characterization is a reflection of its responses to various impacts.

Since most of the ASM activities are on farmlands, and farming remains the main source of livelihood of the community, efforts to reinstate the farming potentials of these mining sites and guarantee safety is important and timely necessary. Reflections from previous studies on the sites (Salami et al. 2003; Oladipo et al. 2014), and in-situ observations suggest that lithological variations in the site's landscape homogeneity is one of the factors that debilitates the sites agricultural land-use potentials. Spots dominated with excavated subsoil muds, which are high in clay content less supports plants growth compare to spots with natural topsoil. A basic fundamental requirement to ascertain the agricultural land-use potentials is to characterize the sites landscape homogeneity and subsurface conditions. It is necessary for assurance of safety, detect hidden cavities, know the soil lithology variations, heterogeneity, detect foreign materials, and enhance decision-making process. This can be done preferably using geophysical techniques such as Electrical Resistivity Tomography (ERT). It is one of the extensively used non-intrusive methods for imaging soil physical characteristics (Romero-Ruiz et al. 2018). It is non-destructive, reliable, timely, cost-effective, in-situ and provides continuous streams of information (both horizontal and vertical) which are unattainable in discrete sampling or invasive procedures. It has been employed in mapping soil contamination (Nai et al. 2019), detect tillage effects (Rossi et al. 2013), landslides (Falae et al. 2019), boreholes (Adeoti et al. 2017), ion transportation (Wehrer et al. 2016), etc. However, there are difficulties in connecting resistivity and specific soil conditions (Hermans et al. 2015; Alamry et al. 2017). This was attributed to its insufficient studies (Nai et al. 2019). More so, its use on post-mining site is poorly considered.

Also, the increasing mining and processing of the gold ores enrich the surrounding areas with associated contaminants such as Pb, Cu, Cd, Fe, Hg, As, Zn, etc. (Fashola et al. 2016; Petelka et al. 2019). After the gold mining, spoil heaps (mixture of overburden soil and rock) with the contaminants are after some abandoned period used for cultivation by the local farmers. One of the major concerns is the transfer of the heavy metal contaminants into the trophic chain (either directly or indirectly). Its food chain entry and ingestion have been recorded in other parts of the country (Lo et al. 2012; Plumlee et al. 2013) leading to loss of life. Efforts to avert similar occurrence is necessary. Previous studies on the sites shows elevated heavy metals on the mine sites (Salami et al. 2003; Oladipo et al. 2014). Cd, Pb, and Fe, which were similarly analysed in 2003 and 2014, showed an increasing rate of 54 %, 1278 % and 116 % respectively. Thereby suggesting that the continuous mining activities is increasing the total content of its associated heavy metals. Phytoremediation remains the preferable remediation technique for the sites. However, despite recent research advancement in phytoremediation and identification of over 400 hyperaccumulator plant species for Cd, As, Ni, Zn, and Mn, elements such as Pb, Cu, Cr, Hg are largely limited. Moreover, less is known of tropical plant species.

The focus of this research is therefore framed by these identified research gaps and its characterized factors. To address the issues efficiently from the global approach down to the chosen national case, the research was divided into two sections; I. International approach to reclamation (Chapter 2), and II. National case (Nigeria). The national case section was further divided into two parts; (a) crude oil (Chapter 3), and (b) gold mining (Chapter 4 – 6). The defined research questions and objectives stated below are as well sectioned based on the international and national scale.

1.1 Research questions

The research gaps stated in the introduction generated some research questions, which this study looks into. These questions were highlighted below according to the above stated sections.

- **Section I:** International approach to reclamation

1. How and when can reclamation success be declared? What could be the targets and endpoints?

2. Are there internationally recognized regulations and defined thresholds guiding reclamation progress and success?

- **Section II:** National scale (Nigeria)

3. With the long existing crude oil exploration and several remediation efforts in Nigeria without any successful record, what are the limiting challenges and prospects towards success?
4. What are the impacts of ASM gold mining on the floristic association and soil landscape homogeneity of the mine sites in southwestern Nigeria?
5. Though bioremediation has been identified as the preferable remediation technique in Nigeria, are there indefinable potential hyperaccumulators, which are also applicable to other tropical countries?

1.2 Objectives

Considering the ‘atomic and molecular scale’ of this research framework, the general objective is to establish and advance knowledge in post-mining sites reclamation on (I) international scale and (II) National case (taking Nigeria as an example). Since there is no recognized international regulation monitoring reclamation progress, section I (i.e. international scale) focus on establishing an approach for evaluating post-mining sites reclamation progress and highlighting different thresholds that might have been crossed and/or to be crossed. While section II (i.e. the national scale) access the status of mining and reclamation in Nigeria, and practically access salient state-of-the-art research gaps to reclamation progress for both crude oil and gold mining (as an example of solid minerals). The specific objectives of these two sections are further highlighted below.

Section I: International scale

1. Develop a time-scale conceptual model that highlights essential considerations and thresholds for reclamation scheme and capable of assessing, evaluating, documenting and monitoring the overall long-term success of post-mine sites reclamation progress.
2. Highlight essential criteria for reclamation status assessments, decision making and land-use options at each threshold stage as well as anticipated targets and obtainable endpoints.

Section II: National scale (Nigeria)

- **Crude oil exploration**

3. Highlight crude oil contamination status, impacts and challenges limiting remediation measures in Nigeria.
4. Identify most preferable remediation technique, outline practical considerations for in-situ large scale remediation, and highlight potential species and other recommendations that can be employed.

- **Gold mining**

Observations that were deduced from the results obtained in objectives one and two above show that most of the mine sites in Nigeria are below minimum standard for any land use option. However, the increasing ASM activities and contamination along with farming activities have scaled up pressure for remediation. Bioremediation (phytoremediation) remains the preferable remediation technique for the sites. So, as a practical approach in this research, experimental sites on an abandoned mining site (Site 1), an active mining site (Site 2), and an undisturbed vegetation site (Control) in southwestern Nigeria were mapped out as representation of the ongoing mining and farming activities. Therefore, in respect to the experimental sites, other specific objectives of this research include;

5. Assessment of the impacts of mining on the floristic association of gold mine sites in southwestern Nigeria.
6. Explore the potentials of 2D Electrical Resistivity Tomography (ERT) for characterizing the heterogeneity variations of the gold mine sites.
7. Identify native high-accumulating plants with multiple and high heavy metals tolerance growing on the experimental sites.

2. An approach to thresholds for evaluating post-mining site reclamation ¹

2.1 Abstract

Here, a time-scale conceptual threshold model for assessing, evaluating, documenting, and monitoring post-mining sites reclamation progress was developed. It begins from initial state I_0 down to degraded state D_0 (which depends on the mining). Reclamation starts with soil reconstruction R_{-2} up to revegetation R_{-1} (red zones) to reach minimum threshold R_0 (amber zone). Beyond R_0 are green zones R_1 , R_2 , and R_3 representing soil/abiotic conditions, biological, and improved threshold, respectively. The model also identifies potential drivers, land-use options, targets and endpoints along the threshold reclamation ladder. It is applicable to all degraded ecosystems and adoptable in national and international laws. In this approach study, we identified threshold biotic/abiotic indicators for ascertaining success from R_0 , future work focuses on measurement and ascribing of threshold values to each of the threshold stage.

Keywords: Restoration, Sustainability, Ecological indicators, Land-use options, Drivers, Targets, Endpoints.

2.2 Introduction

Life survival and the development of human societies depend directly or indirectly on exploration of the abundant resources within the ecosystem (Nellemann & Corcoran 2010; Cherlet et al. 2018). Examples of typical parameters affected include topography, vegetation, air, soil and water quality, human health, habitation and aesthetics values. The subsequent impacts are not restricted only within the mined area boundaries (Maiti 2013), but may affect the landscape far beyond the mining areas. The impacts differ based on differences in the type and purpose of mining, law regulations, site conditions, surface area, level of disturbances, geology, depth, mining technologies, and the site and landscape hydrology. These differences determine the type of reclamation measure required and its progressive stages. While the various disciplines in science and practice view

¹ Published in Sustainability. MDPI

Adesipo, A. A., Freese, D., Zerbe, S., Wiegler, G. (2021). An approach to thresholds for evaluating post-mining site reclamation. *Sustainability, Reclamation and Environment*. **13**, 5618, 1-13. <https://doi.org/10.3390/su13105618>

reclamation with different perspectives. This ranges from improving the aesthetic values of degraded sites, to the ecological restoration of habitats, to reclamation or rehabilitation of post-mining sites, to rewilding extensive landscapes for restoring the structure, function or the ecological complexity of ecosystems and land-use systems (Dudley et al. 2018). Its terminologies (restoration, remediation, reclamation and rehabilitation) are sometimes used interchangeably, but these have been well defined by several authors (Bradshaw 2000; Cooke & Johnson 2002; Kuter 2013). Nevertheless, the increasing global awareness and efforts towards sustainable land management, restoration, and its potentials in achieving the Sustainable Development Goals (SDGs) makes a comprehensive consideration of reclamation process necessary and timely (Cherlet et al. 2018). Therefore, a broadly efficient evaluating and monitoring thresholds, with multidisciplinary approaches and multiple stakeholders, capable of defining the success of reclamation progress such as what level has been crossed and to be crossed, is necessary.

Approaches to reclamation differ around the world. In a number of countries, with well-structured and monitored regulations guiding reclamation, the mining companies are forced by law to reclaim the sites. Reclamation is not for profit making and takes time (several decades). Occurrences showed that soil reconstruction and revegetation are the main traditional targets (Box 1). While there are no international regulations guiding reclamation of post-mining sites, the few countries with functional national laws regarding post-mining reclamation have identifiable differences in their approaches with some crucial omissions. As a result, several reclamation schemes have been developed. The first scientific evaluation system for coal mine derelict sites was developed during the annual meeting of the ‘American Society of Surface Mining and Reclamation’ in 1990. Entitled “Evaluating Reclamation Success; The Ecological Consideration” (Chambers & Wade 1992). Other related schemes include Reclamation Success Evaluation System (RSES) developed for field assessment of reclamation success by the Bureau of Abandoned Mine Reclamation, Pennsylvania Department of Environmental Resources (PA DER) (Hunsberger & Michaud 1994); the indicator parameters highlighted by Maiti (2013) as well as related soil-quality evaluation systems (Paz-Kagan et al. 2014; Obade & Lai 2016; Mukhopadhyay et al. 2016). These schemes showed limited ecosystem attributes for evaluating reclamation success and not sustainability efficient. More so, it has no clear evidence in most practical evaluation scheme.

On the other hand, there have been extensive studies on restoration and use of ecological indicators in the last decades (Siddig et al. 2016; Gatica-Saavedra et al. 2017). However, the existing panoply of developed ecological evaluation techniques does not sufficiently integrate the complexity and/or multidimensional nature of a characterized post-mine site ecosystem. Majority of the practical restoration projects are on sites degraded by agricultural activities or similar anthropogenic disturbances (Wortley et al. 2013; Zerbe 2019).

Box 1 | Traditional reclamation scheme

Landscape reclamation schemes are in several cases trial-by-error and sometimes entail rebuilding the ecosystem from bedrock. The traditional targets are (1) backfilling and soil reconstruction using machines, energy, and geological materials followed by (2) biological materials for revegetation (Maiti 2013) (Figure 2). Summary of its key objectives is to reduce potential damage, prevent negative impacts to the environment within and near the mined areas, restore the viability and vegetation potentials of the soil, compensates, and maintain or improve the landscape aesthetic values coupled with few functional qualities (Nilsson et al. 2016; Dudley et al. 2018). These efforts have resulted in the development and improvement of several evaluation schemes (Chambers & Wade 1992; Hunsberger & Michaud 1994; Tischew et al. 2010; Maiti 2013), which are mostly limited to the analysis of the reclaimed sites' revegetation cover or plant community, soil erosion protection, landscape hydrologic functions, and aesthetic values (Maiti 2013). Several ecosystem components and processes are not considered which are crucial for ecosystem functions, services and sustainability (Stahl et al. 2009). The soil properties are mostly below standard. Also are the air and water quality, climatic conditions and other essential ecosystem components (Hobbs & Harris 2001; Anderson & Ostler 2002; MEA 2005; Kolodziej et al. 2016). Therefore, due to its characterized challenges, most post land-use options cannot cater for the downstream ecological hierarchy and productivity demands.



Figure 2: Common targets of most reclamation scheme

The assessments are region-specific without relation to the degree of degradation (Gatica-Saavedra et al. 2017). More so, the use of ecological indicators only can create a form of bias or imperfect conclusions in the evaluation process. Variations in the indicator species frequency and cover could be indecisive, and this might limit certainty of recovery (Erdos et al. 2017). While a modified model for incorporating imperfect detection was proposed (Urban et al. 2012), integration of a

multi-variant threshold, especially when species representing both failure and success co-occur within the same site is necessary. In addition to that is the low reflection of sustainable attributes and guidelines for assessing restoration projects, established by the international Society for Ecological Restoration (SER) (Wortley et al. 2013). Moreover, monitoring post-mine site reclamation success ought to be scientifically defensible and sustainable. Although it has been argued that mining cannot be done sustainably rather responsibly, nevertheless, reclamation can be sustainable. The establishment of an evaluation system that unequivocally identifies success, in consideration of its entire ecosystem and sustainability suggests enhancing efficient prediction of restoration success rather than false success claims e.g. Rooney et al. (2012).

Adequate incorporation of these gaps demands active involvement of multidisciplinary stakeholders characterizing attributes of the new ecosystem and integrating both the ecological integrity and human well-being in a single framework (Dufrene & Legendre 1997; Sengl et al. 2017). It is interdisciplinary, cutting across traditional subject boundaries, and predicated on the hypothesis that ought to create enabling avenue for diverse ecosystems and land-use systems with its sustainable and cultural values (Sweeny et al. 2010; Wortley et al. 2013; Gatica-Saavedra et al. 2017; Dudley et al. 2018). In that light, this study presents a time-scale conceptual model that highlight essential considerations and thresholds for reclamation scheme and capable of assessing, evaluating, documenting and monitoring the overall long-term success of post-mine sites reclamation progress. With respect to the model, each highlighted thresholds were briefly discussed with essential considerations at each stage. Also discussed are the status assessments, land-use options and decision-making, which are to be considered at each threshold level as well as the targets and endpoints at the end of each threshold level.

2.3 Reclamation success evaluation conceptual model

The conceptual model for assessing, evaluating, monitoring and documenting the long-term post-mining sites reclamation success is presented in Figure 3. The model has been adapted from the ecosystem degradation and restoration concept model by Whisenant (1999); Parks Canada & The Canadian Parks Council (2008). It is a time-scale model with different threshold levels ranging from the initial state I_0 down to the low degraded and/or non-functional stage D_0 . The condition of D_0 depends on the type of mining and its involved attributes, and since degradation cannot be measured directly (Anas et al. 2013), experiences on each site vary. However, reclamation efforts

start with soil reconstruction R_{-2} up to revegetation R_{-1} (the red zones) which serves as the basis in attaining the minimum threshold stage R_0 (amber zone). Above the amber zone are the green zones (R_1 , R_2 , and R_3), representing soil/abiotic condition, biological and improved threshold respectively. R_{-2} and R_{-1} are basic reclamation measures, which have been well studied, but from R_0 , we identified threshold indicators for ascertaining and monitoring reclamation success. Land-use options strongly depend on the threshold level reached, as well as adequate considerations and decision by the multidisciplinary stakeholders involved. Considerations of positive and negative drivers which exerts up/down pressures along the reclamation progress is necessary. Examples of such drivers include climate, potential biota changes (e.g. invasive species), uncontrollable anthropogenic disturbances and encroachment, natural occurrences such as draught, temperature variance within the seasons (winter and summer), precipitation, etc. These drivers can influence some ecosystem properties attain targets quickly, dawdle, or follow either linear or threshold response (Bradshaw 2000; Urban et al. 2012; Gonzalez et al. 2013; Gonzalez et al. 2014; Sherrouse et al. 2014). However, beyond R_3 the endpoints can be (1) improved, (2) maintained or later (3) degraded, especially due to the unending demand for its resources. These three endpoints are also applicable at the end of each threshold level. Further elucidations of each stage are highlighted in the following subchapters.

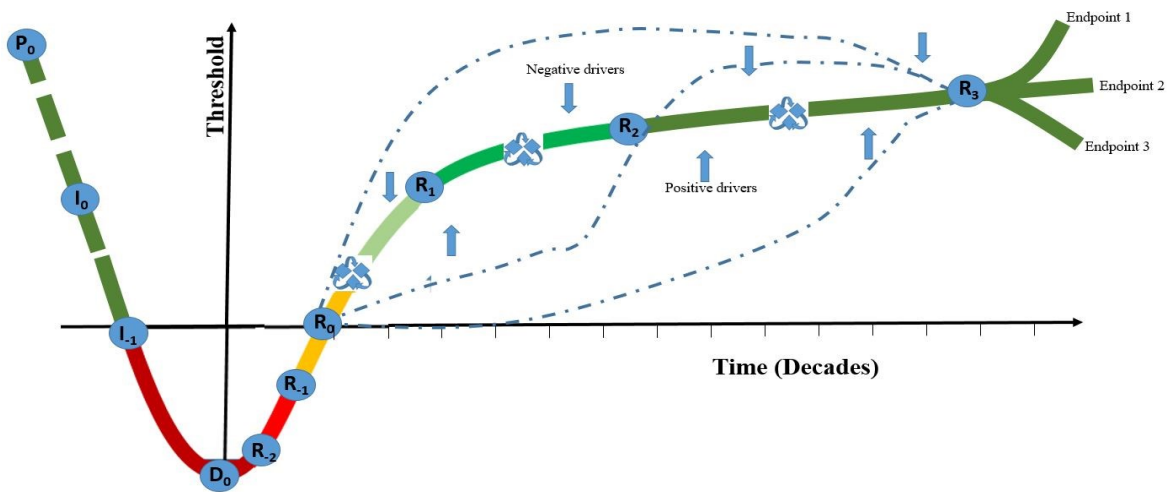


Figure 3: Time-Scale conceptual model for evaluating successful reclamation progress. It starts from the Initial state I_0 down to the very low, non-functional, Degraded state D_0 (depending on the type of mining) and rising up to Soil Reconstruction R_{-2} and Revegetation R_{-1} (Red zones) to reach Minimum reclamation threshold R_0 (amber zone). Above R_0 are the increasing green zones R_1 , R_2 , R_3 representing Soil/Abiotic condition, Biological, and Improve threshold stage respectively. Beyond R_0 , assessments and decisions (i.e. the blue boxes along the threshold ladder) are made considering the drivers along the reclamation ladder. Endpoints 1, 2 and 3 represents improve, maintain and deteriorating endpoints respectively.

2.3.1 Initial/reference state (I₀)

The pristine state (P₀) is a critical issue, as it no longer exists in many countries. Several occurrences causing degradation are in most circumstances not recorded, these reduce the ecosystem to the initial state (I₀), then further to I₋₁, which begins the intentional degradation condition. Most countries have not record of the pristine state, and only few developed countries keep this record before degradation, especially countries with functioning reclamation laws such as Germany, where the mining companies are to present an efficient reclamation plan prior to mining. Alongside this, an adequate record of the site's initial state is also necessary. Nevertheless, identification of a sustainable cultural landscape (reference or baseline plots) as representative of post-reclamation conditions, for comparisons and other correspondence during the reclamation period, is necessary. Ruiz-Jaen & Aide (2005) recommend a minimum of two reference sites for capturing potential ecosystem variations and inclusion of crucial ecosystem attributes (diversity, vegetation structure, and ecological processes) in relation to ecosystem functioning. Additionally, influencing factors such as the distance to the mined sites, vegetation zone, geology, weather, encroachment, and disturbances should be considered. However, the traditional comparison to reference sites for similar composition and/or condition (Higgs et al. 2014; Martin 2017) is not enough; reclaimed sites rarely have similar biotic and abiotic condition (Sengl et al. 2017), and it may lack or degrade due to unavoidable disturbances (natural/anthropogenic), or fluctuate over time.

2.3.2 Soil reconstruction (backfilling) (R₋₂)

The landscape condition and soil physicochemical properties are basis of ecosystem structure (Naeth et al. 1991; Chambers & Wade 1992; Anderson et al. 2008; Liu et al. 2017). Approaches towards soil reconstruction depends on the type of mining, e.g. opencast mining using conveyor belt technology (Krümmelbein et al. 2012) or others (Sahu et al. 2015; Zhang et al. 2019). At this stage, the essential considerations, which were to be ensured include the landscape, reclaiming waterways, handling soils, removal of potential threats and contaminants, capacity to sustain biological populations, integration with the landscape, resilience of natural disturbances, aesthetic values (the affected community), and influencing drivers such as landscape, weather, erosion, etc. These considerations and procedures have been extensively discussed (Häge 1996; Ghose 2004; Morenode las Heras et al. 2011). Damage from underground mining primarily occurs due to subsidence over-extracted areas and pollution/contamination (e.g. spillage). It is influenced by

factors such as the minerals horizon, its thickness, depth, the employed mining method, etc. Also of concern is its created cavity if not well managed. Prominent areas with soft soil e.g. in Singapore (Leung 2016) requires ground improvement works. Against compaction (Krümmelbein & Raab 2012; Kolodziej et al. 2016), soils should be handled neither in a too dry nor too wet state (10–15 % moisture content). Techniques such as deep gouging, ripping, extreme roughening, pocking, and surface scarification can be employed or use of manual tools for small-scale mine (Miao & Marrs 2000). It is a pedogenetically young soil, with traceable developments from mixtures of fragmented and pulverized rock materials (anthropogenic soil and Technosols), and can be enhanced by topsoiling, amendments, afforestation, and plantation (Larney & Angers 2012; Mukhopadhyay & Maiti 2018). The later interest at this stage are essential soil properties that support plant growth such as soil nutrients, soil organic carbon, pH, N-pools, etc. The soil condition at this stage does not give a direct assessment of ecological functioning; it provides information and/or indication of the soil potential long-term vegetation productivity and successional trajectories.

2.3.3 Revegetation (R₋₁)

Revegetation remains the most common well-known strategy to improve the soil and environmental conditions of degraded sites (RCC State 1999; DSE 2006; Skousen & Zipper 2014; Mensah 2015). Prior to revegetation, goals and objectives need to be established coupled with plans towards utmost success. It involves planning, implementation, evaluation and adequate monitoring. Essential considerations include site assessment, goals and standards, site preparation, topsoiling, species selection and source, plantation and revegetation techniques, conservation and water treatments, the cost, timing and climatic conditions (temperature, rainfall), proneness to anthropogenic disturbance, soil development, and natural recruitment (Shu et al. 2005; Courtney et al. 2009). Adequate and continual topsoil management is necessary and has been extensively discussed (FAO 1998; Ghose 2001; Ghose 2004; Bowen et al. 2005; Sheoran et al. 2010), also are its strategies and recorded success within the arid region (Anderson & Ostler 2002). For an adequate monitoring, the selection of an efficient manager is essential.

2.3.4 Minimum reclamation threshold (R₀)

R₋₂ and R₋₁ are basic reclamation measures common on post-mining sites to reach the minimum reclamation threshold (R₀). R₀ partially corresponds to the status of most marginal or degraded

sites. Occurrences show that the soil properties and environmental conditions are usually below standard range of values (Naeth et al. 1991; Miao & Marrs 2000; Sheoran et al. 2010; Shrestha & Lai 2011; Krümmelbein & Raab 2012). The effective practices in R₋₂ and R₋₁ make the appearance and characteristics (especially at the early period) of mine soils seldom resemble native soils or normal agricultural soils, thereby making it difficult to ascertain its quality, and other ecosystem functions and services. However, further reclamation efforts are needed. From R₀, the use of efficient indicators to ascertain success is recommendable. The use of ecological indicators has evolved efficiently (Jorgensen et al. 2013; Gonzalez et al. 2013; Nielsen & Jorgensen 2013; Rapport & Hilden 2013; Gonzalez et al. 2014). Selective indicators should be sensitive to variations in agro-ecological regions, representative of the physical, chemical and biological properties of the environment, easy to assess, time and cost-effective, accessible, assessable by both quantitative and qualitative approaches and reflect relevant existing data. Other considerations include the cost (budget), adequate equipment, expertise, stakeholder's interest, the reclamation goals and land-use potentials.

The identified R₀ abiotic indicators include accessibility, sustainability, erodibility, safety, contaminants-free, waterways network, hydrology (water quality and quantity), aesthetic value, and the soil physicochemical properties necessary for plant growth such as soil nutrients, salinity, pH, infiltration/penetration resistance, bulk density, aggregation, etc. These parameters are essential as a proxy for soil fertility, nutrient availability, plant-available nutrients and potential nutrient loss, indicatives of productivity and environmental quality, water and nutrient availability, understanding the proneness to erosion, variability, as well as the general landscape and geography. The habitability and productivity at this stage is as well important.

R₀ biotic indicators include dispersal, rate of decomposition, pollination, recruitment, symbionts (e.g. the popular mycorrhizae), exotic species, diversity (genetic, taxonomic and functional), nitrogen fixation, soil microbial biomass C and N, potentially mineralize-able N and soil respiration as well as the pattern (which involves the patch size, vegetation type, etc.). All these factors are important for understanding the microbial catalytic potential, repository for carbon and nitrogen, productivity, estimates of biomass, microbial activity, prior warning towards organic matter, etc. and they are vital indicator parameters. Worthy of note is that attainment of these biotic

components comprehensively at this minimum threshold stage is very difficult with several limitations. However, significance of its evidence is necessary.

2.3.5 Status assessment/decision making

The importance of restoring the ecological value of mine soils cannot be overemphasized (Zerbe et al. 2019). But considering the ecological hierarchy, cost, and other requirements, it is not all mined sites that can be efficiently reclaimed ecologically. Agriculture and forestry are the most land-use options globally. They remain the basic natural wealth of the earth and are of irreplaceable importance to fight against food shortage, poverty, and other principal environmental components. More so, they significantly contribute to achieving the SDGs and its equity internationally. For example, within the European Union, about 50 % of reclaimed mine lands are used for forest and grassland, while in China due to shortage of land; over 70 % is used for agriculture (Miao & Marrs 2000; Bian et al. 2010). Beyond R_0 , progressive status assessments in line with precise decisions making are important along the thresholds ladder. An adequate monitoring is imperative to success. Further reclamation effort will likely fail if the causes (e.g. positive and negative drivers) are not well addressed (Hobbs & Harris 2001; Hosonuma et al. 2012). These drivers can influence decision-making and effective response to policy (Rapport & Hilden 2013). Some may be direct or relatively straightforward while others may be indirect and complex. Nevertheless, decisions should be made without partiality, interdisciplinary, involving multiple stakeholders, cut across boundaries “thinking outside the box”, and sustainable (Box 2). Examples of sustainable target indicators, recommendable for considerations are presented in Table 1. The well-known pressure-state-response model is recommendable for continuous monitoring. Also applicable for evaluation and decision-making is the back-and-front conceptual framework developed by Nilsson et al. (2016) for evaluating the ecological restoration process. Furthermore, the inclusion of social values (Sherrouse et al. 2014) and alternatives that are sustainably balanced (Suding et al. 2004) is important.

Box 2 | Status assessment and decision-making

Prior to extraction of natural resources and its characterized disturbances, adequate planning towards reclamation is essential. This is important for impact assessment and establishment of targets and goals, which serve as a benchmark to define, identify, and measure success with potential unambiguous occurrences. Considerations for reclamation should be sustainably balanced (Figure 4). An example is the post-coal mining policies and practices in the Eastern USA as highlighted by Skousen & Zipper (2014) which follows the 1977 Federal Surface Mining Control and Reclamation Act (SMCRA) in the USA (Barry & Hamlet 1980), as well as the Federal Mining Law in Germany (Chang et al. 2000). Consideration of the guiding principles and major pillars of sustainable development is significant (ACPMSC 2011; Nayak 2015; Vrablikova et al. 2016; Yurnita et al. 2017). Inadequacy of its social values is non-marketable (Egan & Estrada-Bustillo 2011), are also the cultural values (aesthetic, spiritual, etc.).

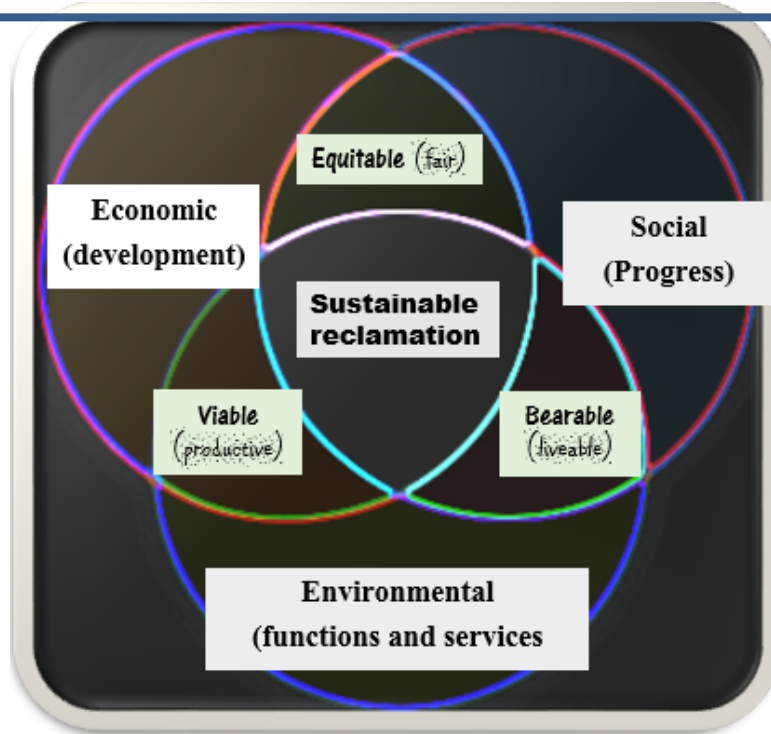


Figure 4: considerations for sustainable reclamation development

Table 1: Examples of sustainable target indicators

<i>Environment</i>		<i>Economy</i>		<i>Social</i>	
Class	Recommendable Considerations	Class	Recommendable Considerations	Class	Recommendable Considerations
Soil	The soil physicochemical and biological conditions, land use options and other supporting functions and services.	Costs	Pros and Cons of direct costs (e.g. capital, operational cost), indirect cost (e.g. legal actions) and alternatives	Health and safety	Human health risks, on/off-site workers risks, public and neighbors, hazardous emissions, etc.
Water	Portability based on regulatory standards (e.g. contaminants), ecological (e.g. ecosystem functions), chemical, water abstraction effects, groundwater tables, acidification, etc.	Benefits	Internal investment, multiple stakeholders, collaboration, international funding, etc.	Ethical and equity	Social justice, equity, ethical values, aesthetic, culture, spiritual and vitality (e.g. 'polluter pays principle').
Biota	Both direct and indirect influence on flora, fauna, and food chain, invasive/alien/native species, alterations in ecological community, structure, services and functions, etc.	Risk and life span	Unpredictable project life span, unforeseen project risks (e.g. community, contractual, environment, procurement, technology, etc.)	Community	Compensations, services (residential, transportation, occupation, education, etc.), public participation, transparency, compliance/satisfaction assessment, national/local authority policies, etc.
Air	Emissions influencing climate change/ozone/air quality e.g. CO ₂ , CH ₄ , N ₂ O, NO _x , SO _x , O ₃ , VOCs, etc.	Socio-economical influence	Employment opportunities short/long term education, innovations, training, seminars, workshops, skilled laborers, etc.	External Impacts	Off-site impacts on neighborhoods and region (dust, GHG emissions, odor, vibrations, traffic, etc.), operational inconveniences (e.g. weekend and night shift), loss (e.g. environmental, archaeological)
Natural resources depletion/Waste	Ratio of exploited resources, left overs and substitutions, renewable energy and alternatives, etc. / Measures of waste disposal, short and long term management, etc.	Flexibility	Project flexibility to time-scales, additional contamination, etc., and economic beneficial robust plan.	Laws and regulations	Policies compliance, regulatory standards, evidences showing quality assessments and accuracy, and plans for uncertainties.

2.3.6 Reclamation threshold 1 (R₁)

R₁ focusses on the landscape, soil and abiotic conditions of the site. Occurrences have shown that mine soils are characteristically different from normal agricultural soil; they have poor soil-use properties (e.g. soil texture, void ratio, and pH) and behavioural qualities (e.g. infiltration, hydraulic conductivity, and soil strength). Also is the temperature (Böhm et al. 2011) and presence of leftover contaminants/foreign materials, which may influence the soil pH and nutrients. However, an interacting and functioning balance is necessary within the soil components (physical, chemical and biological) as well as its constituents (solid, liquid and gas). Similar to experiences from Rosebud mine and Dave Johnson mine (Dey & Schweitzer 2014), this stage might take over three or four decades. Healthy soil function promotes robust productivity, functions and services. It requires collective efforts of multidisciplinary experts in both field and laboratory. In addition is the identification of influencing drivers and trends such as socio-economic, biophysical and technological (Techen & Helming 2017), which brings about both quantitative and qualitative changes (pressures) and influence soil processes and functions (state).

The abiotic threshold indicators involve the landscape, micro-topography, contour and landforms, geology, soil profile and aggregates' formation, decomposition rates, basic net primary productivity, soil water (quality, quantity, and network), air quality (especially with crude oil exploration and gas flaring) and the soil sustainable properties. The key soil sustainable management indicators include the soil productivity (e.g. yield), soil organic carbon, physical properties (e.g. bulk density), and biological activities (e.g. soil enzymes, respiratory rate). Also of importance are nutrients (e.g. Phosphorus being a stable and less mobile element), salinity, pH, exchangeable ions, and soil biodiversity such as microorganisms (bacteria, fungi, protozoa), meso-fauna (acari, springtails), and macro-fauna (earthworms, termites). Though R₁ focuses on the abiotic components, some biotic components are involved. This is due to the interlink between soil physicochemical properties and biological components, it is strong and cannot be overlooked (Stahl et al. 2003). These indicator thresholds can be categorized into different classes such as structure, composition, functions, etc. Ascribing values for the indicators is complex as it depends on the spatial and temporal scale, data availability, as well as regional differences in climate, soil characteristics, and sophistication in measurements (Riley 2001; Stein et al. 2001; Dale & Kline 2013). Moreover, an open and flexible approach is important (Higgs et al. 2018). Soil quality framework is an example of suggested tools for assessing site-specific soil conditions and

developing adaptive management strategies. Also is the use of indicators (Uuemaa et al. 2013; Skalos et al. 2014; Walz 2015), soil quality index (Mukhopadhyay et al. 2016) as well as Status of the World's Soil Resources (SWSR) and Voluntary Guidelines for Sustainable Soil Management (VGSSM). Recommendable land-use options at R_1 are limited to less bio-demanding land use such as recreational, industrial, airports, schools, shopping centres, solid waste or rubble storage area, etc. This is due to its low biological integrity, resilience and low self-improving capacity.

2.3.7 Reclamation threshold 2 (R_2)

R_2 focusses on the biological properties of the ecosystem. It considers the community stands such as flora and fauna, functional aspects, which are enhanced by plantation, immigration and colonization. Attainment of this threshold stage strongly depends on the level of achievement or success in R_1 , time (decades), goals/targets of the reclamation projects and land-use, and active involvement of expertise and stakeholders. A good example of immigration of species was reported in the Rhenanian brown coal post-mine district in Berzdorf region (Dworschak 1997; Dunger & Voigtländer 2009). Though colonization depends on the immigration potential of the ecological species, other potential constraints exist such as

- Activation of sulphuric acids by oxidation (e.g. lignite mine sites), it affects species (e.g. integument of earthworms), even if lime is used to increase the pH. Colonization of species with better acid tolerance is recommendable.
- Potential dry condition of most mine sites that influence substrate water repellent ability, vegetation, etc. and are detrimental to ecological species (e.g. mucous cover of epidermis).
- Limited availability of food especially at the beginning stage (e.g. litter falls) and microorganism biomass.

The biotic components at R_2 include nutrient cycling, energy flows, decomposition, recruitment (through reproduction and/or migration/colonization), available pollinators and dispersers, efficient symbionts (i.e. epiphytes, mycorrhiza), soil micro-biocenoses, animal biomass, survival of early successional native species that can develop into a structurally complex and diverse ecosystem. Additionally, population size of flagship species and key species might increase. These indicators can potentially measure complex interactions and significant ecosystem services return. Soil organisms are also good indicators (Pankhurst et al. 1997; Doran & Zeiss 2000; Hartley et al. 2008). This is due to their high sensitivity to anthropogenic perturbations, changes in land

management practices, ecosystem functions, and climate. They also can be used to explain ecosystem processes simply and cost-effective (Doran & Zeiss 2000). The few species of soil taxa that remarkably and historically met this criterion include earthworms, insects such as mites, molds, bacteria, fungi, and Collembola. Although, representation of the key attributes and functional groups (more or less than taxa) in a way gives a picture of the threshold attainment and what to be identified, monitored and improved, only the use of indicators does not explicitly adapt probability of detection into its abundance or occupancy estimates. The recommendable land-use options at this stage include bioenergy croplands, forest, developed water resources, recreation (parks, hunting, bird watching, etc.), residential use/settlement, site improving, special reserve, etc. These land-use options are in response to its revamped biological integrity.

2.3.8 Reclamation threshold 3 (R₃)

The arguments that mined site cannot be restored back to its pre-mining state, it can only be rehabilitated suggests true. However, a more improved condition can be reached. R₃ involves improving and refitting the sites to a defined endpoint. Similar to other threshold stages, it takes a long time. Take for instance, spectrum of earthworm species inhabiting Berzdorf mine sites as presented in Table 2 (Dunger & Voigtländer 2009). It focuses on the ecosystem functioning, which depends on the integration of structural and functional components such as energy flow, nutrients/biogeological cycles, food web, diversity patterns, etc. It entails several considerations (e.g. new species introduction), practices (e.g. rotation/mixed cropping), and monitoring. The indicator threshold employable at R₃ focusses on improving the quantity and quality of R₁ and R₂ in relation to their structure (such as age, size, habitat quality and quantity as well as connectivity). It includes composition (such as genetic diversity, sex ratio, etc.) as well as functions and services (such as reproduction, breeding rate and success, population viability, gene flow, adaptation, productivity/mortality, etc.). All land-use options are recommendable at this stage, especially croplands, and other agroecosystems including pasture, rangelands, which require high quality for its economic demands and adequate for human health.

Table 2: Spectrum of earthworm species inhabiting Berzdorf mining region.

Species	Brief description	Years
<i>Lumbricus rubellus rubellus</i>	Epigeic species, saprophage, exhibit preference for high organic substrate	After 7 years
<i>Lumbricus terrestris</i>	Potentially used in stabilizing organic materials	After 14 years
<i>Dendrobaena octaedra</i>	Small (2-4 cm), litter dwelling species, native to Europe	After 6 years
<i>Dendrodrilus rubidus rubidus</i>	Native to Europe, small (<10 cm), pigmented epigeic species	After 33 years
<i>Aporrectodea caliginosa caliginosa</i>	Endogeic species, found in first 15 cm temperate zones, used in ecotoxicological tests.	After 3 years
<i>Aporrectodea rosea rosea</i>	Has distinct seasonal clone structure, which proves ecological differentiation of clones.	After 10 years
<i>Octolasion tyrraetum</i>	Cosmopolite species with two genetic forms small (4-8 cm) and large (10-14 cm).	After 10 years

2.3.9 Anticipated targets and endpoints

Setting endpoints and targets is a complicated task (Dey & Schweitzer 2014). This is necessary at each threshold scale end. It is best achieved by active involvement of multidisciplinary stakeholders targeting a set of feasible ecosystem structures, compositions, functions and services, which then have to be discussed in a round table. Example of an applicable methodological approach is LDA (Linear Discriminant Analysis) (Gonzalez et al. 2014). Representation of success does not necessarily have to be static. It could be a successional trajectory towards a self-regulating functional ecosystem. Here, we identified three endpoints; (1) improved stage, (2) maintained state, and (3) deteriorating status (Figure 3). These endpoints are not only applicable at the end of R₃, it applies to each threshold level and depends on the land-use options and sustainable decision made by the multidisciplinary stakeholder's consortium. Deterioration might occur due to global increasing demand for the site's potential ecological resources, or insufficient/non-continuous monitoring, and this might cut across its sustainable values (i.e. social, economic and environment).

2.4 Conclusion

This study gives a comprehensive approach applicable to national and international regulations guiding reclamation of post-mining sites. Although it is a step-by-step process with identifiable threshold describing the reclamation stages, however, it should be kept flexible as there could be

possibilities of overlap from one threshold indicator to the other. This is true considering the differences in the causes and state of degradation. The identification of each threshold indicators does not explicitly adapt probability of a perfect condition, however, representation of the key attributes and functional groups can give a picture of the threshold attainment, what to be identified, monitored and improved while climbing the reclamation success ladder. With this approach, ascribing values for each threshold stage is complex with several limiting constraints; however, access to related dataset can be of help. In addition, future study focus on being detailed on the threshold values, measurements, assessments and its harmonization. This time-scale conceptual model is not limited to post-mining sites; it is also applicable to other degraded ecosystem. It has representative pictures of levels that has been crossed and to be crossed, and can be widely employed in restoration related studies globally.

3. Prospects of in-situ remediation of crude oil contaminated lands in Nigeria²

3.1 Abstract

The effects of crude oil exploration in Nigeria have gained both local and international attention, thereby scaling up pressure for remediation. However, there have been no significant successes recorded from previous remediation attempts. Moreover, most related research studies have been ex-situ in pot experiments, greenhouses, or small-scale experimental sites. In lieu of that, this paper discussed the prospects of in-situ remediation of the crude oil contaminated sites on a large scale in Nigeria. In consideration of current Nigeria's status of crude oil contamination and associated limiting factors to remediation, phytoremediation is the most preferable treatment technique recommendable. It is cheap, easy to manage (even by the community), liable to gain public acceptance, and restore livelihood (agriculture and fishing) to the inhabitants. Practical factors such as site conditions, plant characteristics, agronomic measures, cost estimation, operation and maintenance, the fate of the harvested plants, and regulatory standards were also outlined. Herbaceous species and trees (i.e. for dendroremediation) which are climatically and environmentally adapted to Nigeria (and other tropical climates) were listed. However, on heavily contaminated soils, phytoremediation can be employed as a final "polishing step" after conventional clean-up and can be combined with other techniques such as vermiremediation so as to enhance efficiency.

Keywords: Phytoremediation, Dendroremediation, Petroleum Hydrocarbons, In-situ remediation, Tropical regions.

3.2 Introduction

Despite the recent advancements in harnessing renewable energies, the exploration of crude oil remains a necessity for several countries. The impacts of crude oil activities such as exploration, exploitation, processing, storage, and transportation are of great concern. It requires adequate

² Published in Scientific Africa Journal. Elsevier

Adesipo, A. A., Freese, D., Nwadinigwe, A. O. (2020). Prospects of in-situ remediation of crude oil contaminated lands in Nigeria. *Scientific Africa*, **8**, e00403, 1-15. DOI: <https://doi.org/10.1016/j.sciaf.2020.e00403>

monitoring and prompt remediation measures to avert its consequences both on the present and future generations. In response, several approaches and policies have been established in most developed countries, and implementations of the policies are ensured. However, this does not occur in most developing countries like Nigeria. Effective approaches and policies with appropriate implementation strategies that can meet up with international standards on issues dealing with soil contamination are yet to be developed (Sam 2016; Sam et al. 2017). Moreover, responses from the different stakeholders in Nigeria when compared with stakeholders in other countries (e.g. the Gulf of Mexico) are not impressive and have been referred to as ‘double standards’ (Steiner 2010). Nevertheless, successful responses to the upscaling pressure for efficient remediation are essential (Adesipo et al. 2020b).

Environmental contamination from Petroleum Hydrocarbons (PH) has been an age-long phenomenon in Nigeria. This was previously considered a relatively rare event with a poor understanding of its associated impacts (Döberl et al. 2013). However, experiences in the last decades have been so alarming. There have been recent records of large-scale contamination, destruction, and/or disturbance of the environment (i.e. soil, water, air, and biota). Its challenges on livelihood and the environment have been highlighted by several authors (Linden & Palsson 2013; Ite et al. 2013; Anaejionu et al. 2015; Tinsley & Farewell 2015; Fentiman & Zabbey 2015; Elum et al. 2016). According to Enerdata 2019 of the Global Energy Statistics, Nigeria was globally ranked as the 13th largest oil producer. Though there are still ongoing recent new discoveries in the country’s crude oil deposits, the Niger-Delta remains the major oil and gas region. This region is rated as one of the most severe petroleum impacted ecosystems in the world (Steiner 2010). It has been subjected to heavy exploration and the activities involved in oil extraction, processing and transportation have resulted in massive destruction, and land contamination (Sam 2016). Several agricultural soils have been rendered unproductive, the known mangrove ecosystems located in the Niger-Delta region is drastically degrading and both aquatic fauna and flora have reportedly gone extinct (Zabbey et al. 2017). These have resulted in an age long public protest and outrage from communities, demanding urgent remediation measures that will reduce its human health effects, as well as restore the environmental ecosystem and livelihood, especially agriculture and fishing; which are the major occupation of the most affected populace.

Thus, several attempts for clean-up have been made in some regions (Giadom & Tse 2015), but no significant success has been recorded. Some of the employed techniques were inappropriate; they pose negative impacts on the environment (e.g. pollution due to open burning). Zabbey et al. (2017) highlighted that failures of previous remediation attempts were subjected to erroneous operational wrong conclusions coupled with the adoption of unsuitable and ineffective approaches that ought to be site specific. An example is a wrong assumption by the oil industry operators that it was a layer of clay soil that covers the Niger-Delta soil, and was assumed to limit the percolation of oil within the topsoil. In addition, it was wrongly assumed that Remediation by Enhanced Natural Attenuation (RENA) technique was suitable (Ebuehi et al. 2005; Steiner 2010). The United Nations Environment Programme (UNEP) in 2011 released a report on Environmental Assessment of Ogoniland which gave a deeper insight and draws much international attention. It shows that continuous use of RENA is inappropriate for this region; percolation of the spilled oil has gone few meters down the soil in some areas thereby potentially causing groundwater contamination (Orji et al. 2012). This has therefore called for urgent actions (both locally and internationally) towards effective clean-up of this region. The government's inability to carry out remediation of the contaminated sites has made this area volatile, generating several related conflicts (Koos & Pierskalla 2016). Examples of such conflicts are the murder of 7 industrial workers and military personnel, in Delta State in April 2004 and several occurrences of kidnapping and hostage-taking. In response to the UNEP report, the Federal Government of Nigeria (FGN) on June 02, 2016, at Port Harcourt flagged off a project targeting the clean-up and restoration of Ogoniland on the shores of Creek (Sam 2016; UNEP 2016; Zabbey et al. 2017). The project; Hydrocarbon Pollution Restoration Project (HYPREP) was ensured under the Ministry of Environment for implementation. Though previous efforts have suffered setbacks, however, the present one is optimistically positive, and the success of any viable efforts can stand out as a benchmark in Nigeria. Therefore, clean-up technique liable to receive public acceptance against any unpredictable communal challenges; cheap; easy to be employed; environmentally friendly; and potentially efficient to render the agricultural soil productive and restore livelihood within the affected regions is highly recommended.

The general aim of this review is to discuss the prospects of large scale in-situ remediation of crude oil contaminated sites in Nigeria. To understand the current status; the extent of contamination and its impacts on the environment are discussed. Also, applicable treatment techniques and the

characterized challenges limiting effective remediation in Nigeria over the years are identified. In consideration of these factors, the paper further aims to suggest a preferable technique to be employed with explicit details on implementation and specific examples typical for Nigeria and other tropical countries with similar climatic conditions.

3.3 Crude oil contamination in Nigeria

The Niger Delta remains the major oil-producing region in Nigeria (Figure 5), though efforts to discover new oil wells are ongoing in the country. According to Irhivben & Omonona (2013), oil and its exploratory activities have not been much of a blessing to this region, it has rather brought agony and anguish with disastrous impacts on the environment (air, water, soil, and biota). As far back as in 1558, history showed that the major source of foreign exchange for the country was the oil palms from this region. However, crude oil contamination has regrettably deprived them of this fortune by destroying the ecosystem (Emuedo & Abam 2015), including the oil palms.

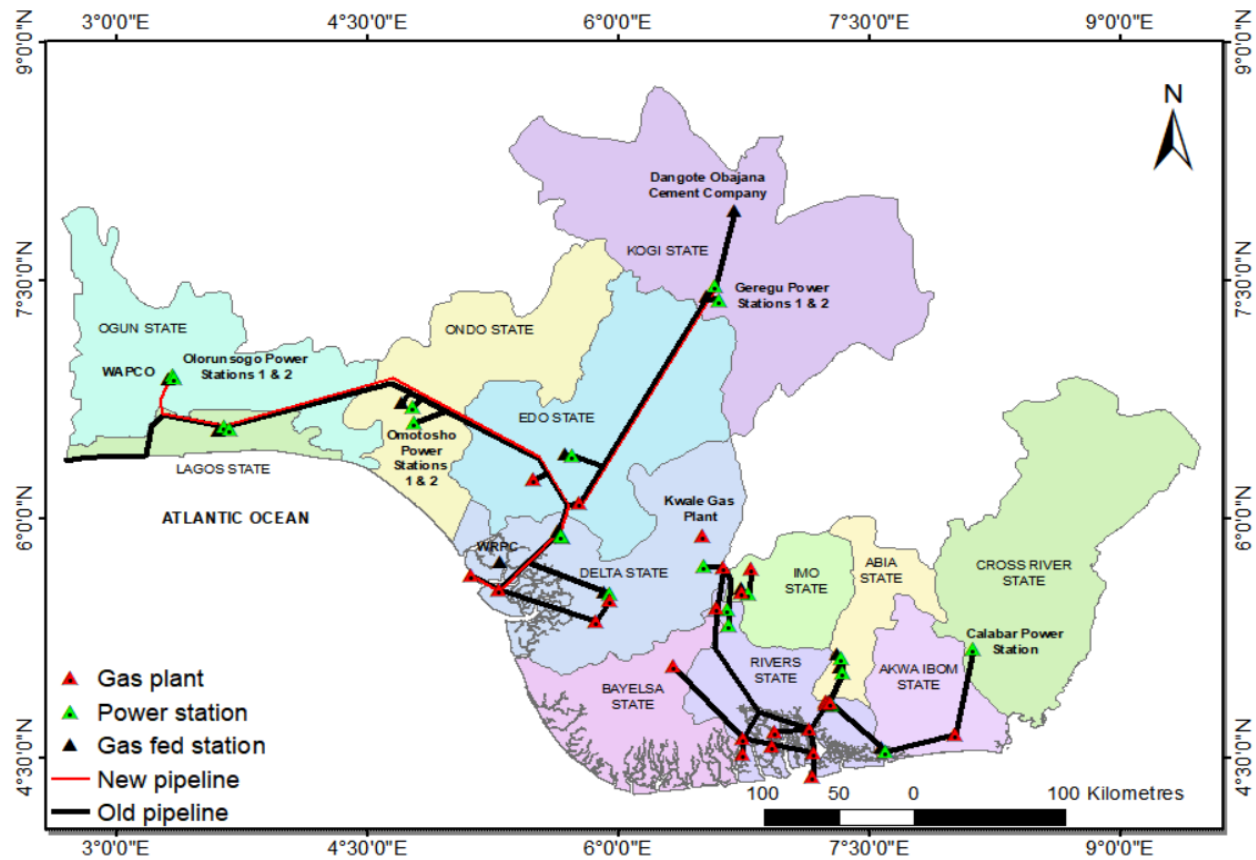


Figure 5: Oil producing regions in Nigeria and their Natural gas infrastructure

3.3.1 Level of crude oil contamination

Several studies have been conducted and others still ongoing to unravel the levels of crude oil contaminations. It depends on the quantity, chemical composition, grade or type, size of the contaminants, and properties of the polluting media. Records obtained from the Department of Petroleum Resources (DPR) between 1976 and 2005 showed that about 31,121,909.80 barrels of oil were spilled into the environment in about 9107 incidents, though this volume was alleged to be under-reported by the Green peace. Similar records were highlighted by Anejionu et al. (2015) who also outlined the geography of pollution, its magnitude, and spatial coverage. Linden & Palsson (2013) discussed the level of contamination in Ogoniland, which according to UNEP 2011 report, was regarded as the worst hit in Nigeria. Their findings revealed its contamination level on rivers, creeks, and groundwater. Extractable Petroleum Hydrocarbons in surface water was about $7420 \mu\text{gL}^{-1}$; in drinking water wells about $42\ 200 \mu\text{gL}^{-1}$; while benzene was about $9000 \mu\text{gL}^{-1}$ which was 900 times greater than the World Health Organization (WHO) guidelines. In sediments, it was about 17900 mg kg^{-1} , while Polycyclic aromatic hydrocarbons concentration in most of these contaminated sites was about 8.0 mg kg^{-1} . Apart from Ogoniland, Ordinioha & Brisibe (2013) observed the presence of contaminants in Ughoton stream in the Niger Delta region, two months after the oil spill. Also, the vandalization of the Shell Petroleum Development Company (SPDC) oil pipeline at Ekakpramre in Ughelli South Local Government Area (LGA) led to a spilling of about 100,000 barrels of oil in that area (Akpofure 2015). Aghalino & Eyinla (2009) reported the FUNIWA 5 (Texaco) oil-well blown out in Koluama village, releasing about 400,000 barrels of crude oil into the ecosystem and resulting in the drying up of vegetation. According to the authors, the blow-out was so disastrous that the effects spread to neighbouring villages like Kuluma-1, Kuluma-2, and Otua Island. These same authors reported that on Jan 12, 1998, MOBIL/QUA IBOE oil spillage occurred because of a leakage from the pipeline, and this covered a distance of two hundred kilometres, reaching areas such as the fish town, and Pennington beach in Bayelsa State.

3.3.2 Impacts of crude oil contamination

The complexity of the constituents in crude oil makes it difficult to identify the effects of each constituent within the context of the hydrocarbon mixture. Variance in their properties such as solubility, low molecular weight, volatility, susceptibility to biodegradation, influence their fate and impacts on the environment (Yavari et al. 2015). In the aquatic environment, crude oil

contaminants are exposed to a series of reactions that affect their physical and chemical properties. Toxic and volatile components evaporate while some are oxidized by UV radiation from sunlight. Few low molecular weight toxic compounds dissolve in water and degrade while others react with fine particles and settle at the bottom. In soil, crude oil contamination renders the soil unproductive (though it may not permanently destroy the soil). Once crude oil is exposed to the soil, it alters the soil's physicochemical and biological properties, thereby influencing soil fertility and agricultural crops, especially crops that are less tolerant of oil (Moses & Uwah 2015).

Mangroves make up the main vegetation in the Niger Delta (Anaejionu et al. 2015); they are known to occupy extensive freshwater swamp and tropical rain forest. They are endowed with unique biological diversity and are the most sensitive of all coastal vegetation. Mangrove sediments retain oil, therefore, act as sinks and this leads to the persistence of oil on or inside the sediments (Maia Santos et al. 2012). Emuedo et al. (2014) added that mangrove destruction due to crude oil contamination has led to the death of plants, poor water quality, and eventual loss of aquatic organisms. Anyadiegwu & Uwaezuoke (2015) in their environmental assessment of benthic organisms in the Niger Delta revealed that much harm has been done to these organisms and they have either been lost or destabilized as a result of crude oil contamination. Similar to that is fish production by Osuagwu & Olaifa (2018). Osumgborogwu et al. (2017) affirm the negative impacts on the environment, agriculture, and economic sectors.

Ordinioha & Brisibe (2013) revealed the presence of trace metals, which was attributed to oil spills in the Ughotom stream in Edo State area of Niger Delta. Also, Amangabara & Njoku (2012), analysed groundwater at the site of an artisanal refining site in Bolo, Rivers State, and showed that this water contained up to 986.07 ppm THC (Tetrahydrocannabinol). Studies by Emuedo et al. (2014), in three (3) Local Government Areas (LGAs) of three (3) States (Nembe in Nembe LGA of Bayelsa State, Okpare in Ughelli North LGA of Delta State and Okrika in Okrika LGA of Rivers State) showed that some waters bodies are acidic due to crude oil contamination, thereby negatively impacting on the survival of the plants and animals. It was observed that emitted hydrocarbons caused by unburnt and partially burnt hydrocarbons were sources of pollution in the Okitipupa area of Ondo State of the Niger Delta (Bayode et al. 2011). The level of contamination is so massive that villagers have to travel a distance on canoes to fetch their drinking water. The biodiversity is also negatively impacted. The ecosystem of this area consists of different species

of plants and animals as well as humans, such that this zone had been recognized as an area of extraordinary biodiversity within the western coast of Africa (Emuedo & Emuedo 2018), but these views are fast changing due to extensive oil contamination in this region. The loss of the mangroves to oil spill has grave consequences. It is the main breeding ground for aquatic species, but oil contamination has led to a steady decline in the flora and fauna. Catfish, Iguana, edible frog, and red crayfish are almost becoming extinct (Omoweh 1998). These occurrences distort the natural balance, affect the food chain, and could lead to an ecosystem catastrophe.

3.4 Remediation of contaminated soil

3.4.1 Targeted contaminants

Understanding the physicochemical characteristics, prediction of the fate, and behaviour (short- and long-term) of the contaminants prior to remediation design is important. This is because of the complexity of the contaminant constituents. Oti (2005) described it as a combination of Aliphatic (Alkanes, Alkenes, Alkynes, and Cycloalkanes) and Aromatics (Polycyclic Aromatic Hydrocarbons (PAHs) and Mono-aromatics) hydrocarbons as well as non-hydrocarbons such as Sulphur, Nitrogen, Oxygen, and metals. Total Petroleum Hydrocarbons (TPH) is a persistent hazardous pollutant containing compounds that can bio-concentrate or bio-accumulate in food chains. They possess varying physicochemical properties, are highly toxic and some compounds (e.g. benzene) are regarded as mutagens and carcinogens (Gao et al. 2014). It can be further subdivided into Gasoline Range Organics (GRO) and Diesel Range Organics (DRO) (Kamath et al. 2004). The former consists of small chain alkanes ($C_6 - C_{10}$) with a low boiling point of $60 - 170^\circ\text{C}$ such as iso-pentane, n-pentane, butane, 2,3-dimethyl butane, as well as some volatile aromatic compounds such as Benzene, Ethylbenzene, Xylenes (BTEX), etc. The latter consists of longer chain Alkanes ($C_{10} - C_{40}$) made up of middle-end distillates with a boiling point between $200 - 300^\circ\text{C}$, and can be cracked to produce smaller molecules. The higher molecular weight fractions with carbon number >20 such as PAHs, Naphthalene, Anthracene, Pyrene, and their alkylated derivatives tend to be more resistant (Yavari et al. 2015).

For effective remediation, the properties of the mixture and the extent of spillage should be known. Volatility increases with molecular weight; compounds with lower boiling points i.e. low end and middle-end distillates (generally the aliphatic) are more volatile than aromatic compounds (Yavari et al. 2015). Also, the polarity of the compounds in an aqueous medium is important. Highly

soluble and less hydrophobic compounds are most susceptible to leaching. Generally, solubility and volatility decrease with increasing molecular weight. Therefore, due to the delocalization of electrons within the aromatic ring structure, aromatic hydrocarbons are more polar and soluble than aliphatic hydrocarbons (Kamath et al. 2004). The biodegradation rate is also important. It largely depends on the environmental conditions (oxygen, microbial population, etc.) and susceptibility of the hydrocarbon. Straight chain alkanes degrade more easily than the branched alkanes or cycloalkanes. BTEX compounds are more amenable to biodegradation and more mobile than the less immobile PAHs. The higher the benzene rings the lower the biodegradation potential (Kamath et al. 2004). Nevertheless, it is important to note that TPHs are not the only contaminants present on most contaminated sites in Nigeria since the presence of heavy metals has also been recorded. Therefore, employing remediation technology capable of cleaning up all potential contaminants is necessary.

3.4.2 Treatment techniques for contaminated soil

The differences within the oil exploitation regions in Nigeria (soil types, habitats, interlinked water bodies, contaminants, etc.) influence its successful remediation attempts. An appropriate understanding of suitable remediation technology to employ is necessary. There are four basic recommendable steps described by Ezeji et al. (2007) which should be considered. These include (1) site preliminary assessment, (2) selection and implementation of the adequate temporal remedial measure, (3) investigation of the site and conduction of feasibility studies and (4) selection of the final remedial measure to be employed. The ITRC developed a conceptual model stating essential factors for characterization and decision making (Figure 6). Below are 3 common methods for remediation of contaminated sites.

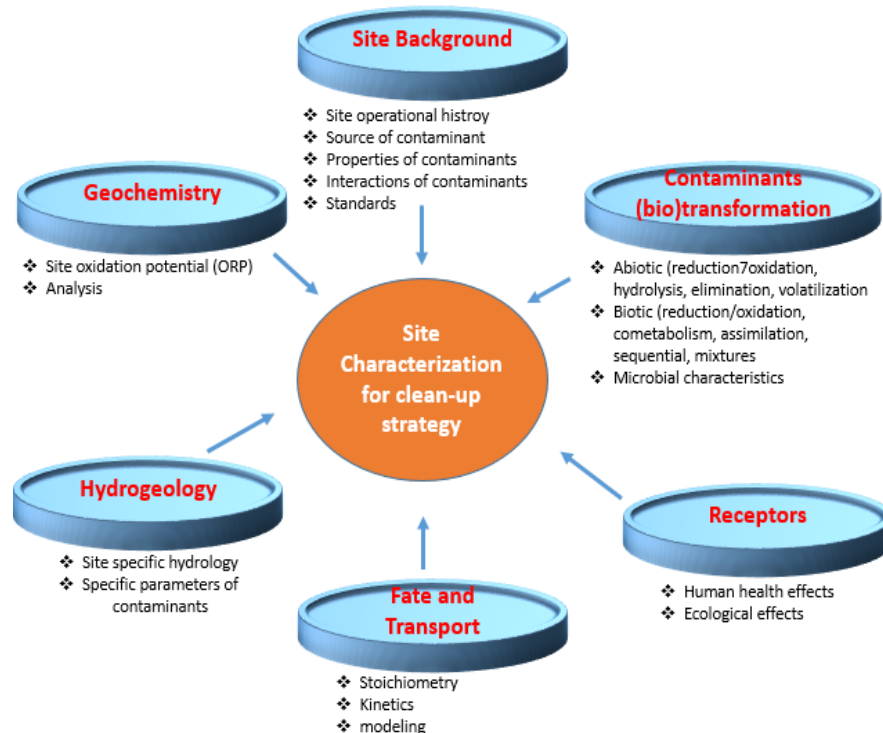


Figure 6: Characterization factors in determining clean-up strategy (Modified from ITRC 2002).

3.4.2.1 Physicochemical methods

Examples of physicochemical methods are soil excavation, soil vapour extraction, soil washing (with water, reagents, and solvents such as dispersants, demulsifiers, bio-surfactants), achievable through methods such as chemical immobilization, oxidation, vitrifying technology, chemical fixation, chemical leaching and electro-kinetic remediation (Zabbey et al. 2017). These methods are very fast and can be effectively employed on heavily contaminated soils. However, they are intensive, generally cost demanding with the potential to re-contaminate other media. Also, this technique is technologically demanding and practically applicable to a small-scale (Khan et al. 2004), thereby limiting its applicability for large-scale remediation in Nigeria.

3.4.2.2 Thermal methods

This includes thermal desorption and incineration. Thermal desorption requires subjecting the soil to high temperatures (200 – 1000°F) to vaporize and desorb (physically separate) low boiling point contaminants (Ezeji et al. 2007). The higher boiling point contaminants remaining in the soil can then be treated with other conventional methods. As regards incineration, at high temperatures (1600 – 2500°F), the contaminants are burnt off the soil with fire (Ezeji et al. 2007). The efficiency

of this method is high, however, it can cause environmental re-pollution, total or partial destruction of necessary soil organic matters, and disruption of soil physicochemical properties for plant growth. These methods may be unsuitable due to Nigeria's limited energy source, cost demanding, time-consuming and hazardous.

3.4.2.3 Biological methods

These methods involve biostimulation, bioventilation, bioremediation, phytoremediation, bioaugmentation, etc. They involve the use of plants especially fast-growing plants, microorganisms such as fungi and bacteria, soil animals such as earthworms (vermiremediation), and other biological systems for clean-up. The techniques are environmentally friendly and can be combined to enhance the remediation process. Biological treatment has been identified as the most preferable method for moderately contaminated soils. It is cheap, of low-technology demand, low re-contamination potential and is applicable on a large scale. It also renders agricultural soil productive and aesthetically appealing. It has been receiving considerable attention over the last decades in Nigeria (Ekperusi & Aigbodion 2015; Ofoegbu et al. 2015; Benyahia & Embaby 2016; Ikuesan et al. 2016).

3.4.3 Challenges to remediation in Nigeria

Success stories of some remediated oil-contaminated soils have been recorded around the world. Similar stories are yet to be told in Nigeria due to some highlighted potential challenges briefly elucidated below.

3.4.3.1 Heterogeneity and lack of initial data status

There are differences in both the physical and chemical properties of the spilled contaminants; also, the time and length of contamination vary. Some contaminants occur during extraction, processing and/or transportation, while some are recent or over decades. Also, there are differences in soil properties for each region such as pH, organic matter, texture, and environmental factors like temperature. Therefore, initial site analysis is necessary to characterize all dynamics involved and complexities related to contamination on each site. In addition, this helps in making concrete decisions as regards the necessity for clean-up, where and how to clean up, what extent should the clean-up be carried out, and sustainable approaches that should be employed. However, similar to most oil-producing developing countries, there are very little or no existing related data describing the pre-contamination status of most oil-contaminated sites in Nigeria. These data are necessary

for pre- and post-impact assessment. Lack of these baseline data could limit the efficient evaluation process (Yavari et al. 2015). Recent studies by Luiselli et al. (2015) and Eniang et al. (2016) highlighted certain species of fauna and flora existing prior to disturbance. Other related studies including the soil properties and geomorphology status are necessary.

3.4.3.2 Frequent spills and re-contamination

The contextual nature and quality of infrastructural facilities within the contaminated site highly contribute to the unpredictable contamination and/or re-contamination experienced on most of the sites contaminated. Oil pipelines are easily accessible for vandalization by the youths for artisanal refining especially those close to settlements and farmlands. Complementing this is the engineering failures coupled with pipeline rupture and fatigue, lack of maintenance and surveillance model, as well as sabotage bombing activities by the community (most especially the Niger-Delta militants). The use of quality infrastructure and effective devices for automatic leakage detection is necessary for appropriate monitoring against frequent spills and re-contamination.

3.4.3.3 Governance and stakeholders structure

Another major but underground challenge to remediation of contaminated sites in Nigeria is the observed lapses in the administrative bodies towards remediation. Responsibilities of established regulations within the Niger Delta contaminated region is being shared between agencies. This has created multiple standards that compromise synergy between the involved agencies. A good example is a constant conflict between the National Oil Spill Detection Agency (NOSDRA) and the Department of Petroleum Resources (DPR) (UNEP 2011; Ambituuni et al. 2014; Rim-rukeh 2015). The differences in administration and standards have created several overlapping loopholes, which the exploration operators (the polluters) are capitalizing on to escape appropriate regulations. Therefore, there is a need for definite delineation of responsibility for each agency, and a unified standard governing them should be established similar to what is obtainable in other developed countries. Moreover, the nature of the policy framework existing in Nigeria is a tenure-based agenda (Sam 2016). Each succeeding administrative tenure develops different policies and agendas; neglecting previous ones in pursuit of their own political fame. The restoration of contaminated sites requires continuous and sustainable commitments that are scientific and well financed. Also, apart from the double standard exhibited by all the stakeholders (Adeyemo 2002;

Steiner 2010), there is a high level of wrong perceptions, disposition, and misappropriation which has been generating several unresolved conflicts within the region. To the local population, they observed that the government is not interested and weak in implementing strict policies with appropriate actions towards the remediation of the contaminated sites. Therefore, the affected inhabitants take the law into their hands by engaging in several detrimental activities like kidnapping and pipeline vandalization. Consequently, the oil companies accuse the communities of negative activities and therefore withdraw from the necessary clean-up. Hence, they also lack trust and confidence among themselves, especially with bribery. So it becomes difficult for the stakeholders to engage in necessary dialogues, which could initiate an appropriate step towards remediation (Zabbey et al. 2017). It is recommended that Nigeria should establish a transparent and robust stakeholder engagement process, capable of admitting its complex dynamics, as well as help in decision-making.

3.4.3.4 Lack of expertise and technical know-how

Before effective remediation can be done, efficient characterization of the contamination effects and implementation of appropriate technical demand is required. In areas with complex nature of the contamination, professional personnel are required. Such technical expertise is currently missing in Nigeria. To worsen the situation, Eneh (2011), noted that even the regulators often depend on the operators' expertise for their investigation activities. Besides that, Nigeria in most cases adopts standards from other counties with less focus on creating its own standards. A very good example is the adopted Environmental Guideline and Standard for Petroleum Industry in Nigeria (EGASPIN), which has generated several contradictions (DPR 2002; UNEP 2011). Therefore, it is necessary to establish standards within the country's context (Sam 2016).

3.4.3.5 Funds

Inadequate supply of funds remains one of the major factors limiting remediation in Nigeria; it is highly detrimental to several efforts towards remediation. Fund limitation can be considered in two ways; (1) lack of funds for remediation from the relevant authorities and (2) siphoning of the very little available fund by the involved administrative bodies. An example of this was the 2011 UNEP report which optimistically would have established an initial USD 1 billion Trust Fund for Ogoniland, but there was no tangible outcome (Konnet 2014). However, there are suggested approaches towards this; developing sustainable funding mechanisms from the operators and from

the sales of petroleum. The first approach is similar to the USA Superfund programme, where a certain level of tax can be placed on each operator towards remediation and this can be used regularly. As regards the second approach, a percentage of each petroleum sale can be kept for remediation when there is a significant threat to the people or lack of funds from other sources.

3.4.4 Technique recommendable for Nigeria

Considering the different highlighted techniques and the above-stated challenges occurring in the country, it appears that phytoremediation is the most recommended technique that can be employed. This is in consideration of the contaminants' heterogeneous mixtures, ecosystem services, social, environmental, and economic values. Phytoremediation is described as a plant-based biological technique that employs the intrinsic physiological abilities of plants to reduce the mobility, volume or toxicity of contaminants in soil, water, or other contaminated media. It is a cost-effective and environmentally friendly technology that enhances the plants' natural and/or artificial occurrence in the soil processes to degrade and detoxify organic contaminants. It employs the plant and its root-associated soil microorganisms, soil amendments, and other possible agronomic measures to remove, contain (immobilize), degrade and/or render the soil contaminants harmless (Pilon-Smiths 2005). Both the plant and its associated microorganisms are involved in the phytoremediation process (Agnello 2014). The favourable climatic conditions in the tropics, which enhance plant growth and stimulate microbial activities, affirm the efficient potential of this technology (Ogbo et al. 2009). The uniqueness and selective uptake abilities of the plant, its bioaccumulation, its translocation, and degradation abilities are part of the basic criteria in making decisions on plants to be employed. Apart from the above listed beneficial characteristics of phytoremediation, it is aesthetically pleasing; the plants can be easily monitored, and its biomass can be converted. Moreover, it enhances climatic conditions (e.g. carbon sequestration especially with trees) and it is of high benefit to the environment (e.g. biodiversity). Though this technique is not profitable on heavily contaminated soils and it has some gamut challenges, however, it can be employed after conventional clean-up where necessary and combination of some biological techniques together with the application of appropriate agronomic measure can potentially enhance its efficiency (Ighovie & Ikechukwu 2014; Gouda et al. 2016). Moreover, it requires a minimal level of skilfulness for implementation and monitoring, thereby encouraging community acceptance, self-implementation, and monitoring. Also is its beneficial independent nature as supported by the tenure-based policy framework in Nigeria.

3.5 Mechanisms of phytoremediation

The general phytoremediation mechanisms include phytoextraction, rhizofiltration, phytodegradation, phytostabilization, phytovolatilization, hydraulic control, and rhizodegradation (Angulu et al. 2018). Some overlaps or similarities exist in some of the mechanisms and it is contaminant specific; especially on sites with other contaminants such as heavy metals. For Petroleum Hydrocarbons (PH), plants and its associated micro-organisms employ three primary mechanisms; these include degradation, containment, and phytovolatilization of the hydrocarbons from the soil to the atmosphere (Eskander & Saleh 2015). Degradation of organic pollutants can be direct or indirect. There is still a scarcity of information on the direct degradation of PH in plants but some studies reported that corn seedlings, tea, and poplar shoots were able to metabolize methane into various acids (Ndimele 2010). The plants have the ability to assimilate n-alkanes and liberate $^{14}\text{CO}_2$ in both their leaves and roots, with the conversion pathway in Figure 7.



Figure 7: Conversion pathway for alkanes in plants (Adapted from Ndimele 2010)

Indirect degradation of PHs involves the following processes: (1) root exudates supply, thereby influencing cometabolic degradation, (2) release of root-associated enzymes that can transform organic pollutants, and (3) influence on soil physicochemical properties thereby affecting plants and roots. Root exudates are the link between the plants and microbes that lead to the rhizosphere effect. The type and quantity of root exudates are dependent on the plant species and the stage of development. Organic contaminants are transformed by catalytic chemical reactions by the enzymes in the soil. Isolated enzymes include dehalogenase, nitro-reductase, peroxidase, laccase, and nitrilase (Schnoor et al. 1995). Micro-organisms also use organic pollutants as a source of carbon and electrons for energy purposes. This process is achieved by degrading the organic contaminants in the absence of higher plants, which is called Bioremediation or in the presence of

higher plants which is referred to as phyto-assisted Bioremediation or phytoremediation. This synergistic co-operation of plant roots and soil micro-organisms promotes the degradation of persistent organic contaminants in the soil. The Poaceae family or true grass family has been shown to be more effective in the degradation of PAHs than many other herbaceous plants (Olson et al. 2007; Cooks & Hesterberg 2013). Environmental factors like carbon/energy sources, oxygen sources, water sources, and nutrient sources also affect the degradation of PHs (Cooks & Hesterberg 2013). Containment of contaminants involves its bioavailability reduction, though this does not necessarily mean they are degraded. The process could be direct or indirect. Direct containment could be in the form of accumulation of contaminants within the plants or through adsorption of the contaminants within the rhizosphere by some enzymatic activities. For indirect containment, plants supply enzymes that bind the contaminants with soil organic matter through humification. Phytovolatilization describes the plants' ability to volatilize the already taken up contaminants. It is suitable for those under conventional air-stripping techniques such as BTEX, with Henry's constant higher than $10 \text{ atm m}^3 \text{ water} / (\text{m}^3 \text{ air})$ (Eskander & Saleh 2015). Phytoremediation is applicable both in the soils and in aquatic ecosystems. In contaminated aquatic ecosystems, different macrophytic plants thriving in or within the water body that are emergent, submerged or floating exist (Angulu et al. 2018). Likewise, there are numerous species with high tolerant ability used for remediating contaminated soils.

3.6 Practical considerations for in-situ phytoremediation in Nigeria

The successive design of phytoremediation technique is influenced by factors such as the type of contaminant(s), the site condition, extent and/or level of contamination (i.e. the level of clean-up required), as well as the required clean-up time, type of plants to be employed and the failure mode analysis. Therefore, it is necessary to highlight some specific design considerations.

3.6.1 Site condition

The first essential consideration is the condition of the site (site treatability). This is explained in 5 summarized categories; (1) Assurance of terminal contamination from the source i.e. areas with no possibility of future pollution. This is a very important pre-requisite in Nigeria because continuous contamination is detrimental to the plants, and it can limit the effectiveness of the technique indefinitely. (2) Types and mixtures of contaminants: Apart from the knowledge of the type of contaminants (as discussed in 3.1 above), many sites within the country potentially have

other contaminants that also require remediation. This may pose a challenge in identifying plant species to use (Palmroth 2006). Therefore, this may require mixed cropping of appropriate species.

(3) Depth of contamination: Phytoremediation is most effective on sites with shallow depth of contamination. This is because the efficiency of this technique is found within the plant root depth (irrespective of the mechanism involved). This is necessary because some areas have deeper oil spilled percolation (beyond 5 m) as reported by Zabbey et al. (2017). However, relevant agronomic measures such as optimization of irrigation patterns that facilitate biodegradation can be employed.

(4) The soil characteristics; soil quality influences the plant's germination, growth, and health. High levels of contamination can potentially influence the soil physicochemical conditions thereby limiting plant growth and rhizosphere bacteria. Prior knowledge followed by appropriate amendments to improve the soil quality against common limitations such as poor aeration, poor soil physical properties, and nutrients is necessary.

(5) The climatic condition: Occurrences suggest that this technology is preferable in the tropics due to its possibility of all year round growing opportunity (especially the Niger Delta mangrove region). This is unlike the temperate climates, which might be limited only to the growing seasons.

3.6.2 Plant characteristics

The basic criteria for selection include the targeted contaminants, mechanism, and the plant's attributes such as growth rate, phytotoxicity/tolerance, climate, soil, and the root system. Phytoremediation is a complex technique. It is employed with respect to the plant's specific physiological responses (i.e. morpho-anatomical, biochemical, and molecular responses) to differences in the concentration and type of the contaminants (Kamath et al. 2004). The plant should be able to bio-accumulate pollutants and either transform or translocate them to its above-ground harvestable biomass. Studies have shown that the efficiency of the plant's uptake, accumulation, degradation, and/or volatilization of the contaminants varies from plant to plant (Oh et al. 2014). It also varies according to the plant's rate of growth and biomass, depth of the plant's root zone, level of tolerance, optimized plant density, and ability to transpire groundwater (Oh et al. 2013). However, prior consideration of native plants is preferable in order to avert the possibility of introducing invasive species and other related ecosystem effects. Adesipo et al. (2020b) did a similar study on a gold mine site. Several researchers prefer the use of trees. This is due to their long roots with deeper penetration, high biomass as well as its climatic benefit such as carbon sequestration (Gonzalez-Oreja et al. 2008; Pajevic et al. 2016) which are important for the

characterized oil-contaminated regions in Nigeria. Grasses can be planted in tandem with trees. This enhances the root structure development, which helps bind and transform hydrophobic contaminants such as BTEX, TPH, and PAHs (Kamath et al. 2004). Similar to that is the potential use of legume species. Atangana et al. (2014) highlighted that in tropical agroforestry, legumes have soil decontamination ability since there is a symbiotic association between the plant and symbionts (*Mycorrhiza* and *Rhizobium spp.*) and actinomyorrhizal plants (*Mycorrhiza* and *Frankia spp.*) which enhance their phytobial remediation. The plant's tolerance ability and responses to a wide range of environmental conditions (e.g. weather, different contaminants, etc.) are important especially in Nigeria with heterogeneous conditions. Studies show that phytotoxicity of contaminants is a function of its specific composition, concentration, and characteristics of the employed plants (Ogbo et al. 2009). Differences in the level of concentration and the period between contamination and remediation (i.e. old spills and fresh spills) can influence the plant's germination, growth, and efficiency (Wiltse et al. 1996). Low bioavailability of toxic compounds in aged contaminants showed minimal phytotoxicity in comparison to fresh spills. However, speciation of the contaminants should be determined for better understanding. After the selection of the plants, plant density and other design requirements' considering the timescale of clean-up are recommendable. For the heavily contaminated soils, phytoremediation may be employed as a final "polishing step" after the use of the previous conventional clean-up technique.

3.6.3 Agronomic measures

Different agronomic measures can be employed to enhance phytoremediation. One of these is irrigation, which is necessary at the initial stage. Water is essential for plant and microbial activities. It enhances the bioremediation of contaminants. Drip type of irrigation is preferable to spray irrigation. This is to avert the possibility of encouraging weed growth with high competition. However, hydrologic modelling is necessary to monitor groundwater percolation and other potential occurrences especially for the Niger Delta region (Giadom & Tse 2015). Another measure is the fertilizer application. Contaminated soils are usually deficient in basic nutrients that are needed to attain vigorous plant growth and stimulate microbial activity. Although there have been differences in results obtained from previous studies, it could be summarized that both organic and inorganic fertilization enhance plant's phytoremediation efficiency such as germination, growth, and biomass (Hutchinson et al. 2001; Joner et al. 2002). Similar to that is the study by Palmroth et al. (2006) which showed that fertilized plots (NPK fertilizer) have a 60 %

reduction in TPH than unfertilized plots. The use of organic fertilizers is preferable to the use of inorganic fertilizer. This is due to its slow release of Nitrogen as well as soil structure improvement. However, as a result of the differences in some previous studies, its use should be site-specific with utmost consideration in balancing biodegradation and plant growth. Balanced amendments exclusively towards plant growth will result in optimum clean-up for the Niger Delta region. In addition, in order to attain optimal aerobic microbial degradation, there is a need to amend soil oxygen. Lee et al. (2000) showed that plants may serve as a net positive or negative source of oxygen, and the basis of this has been well described (Lijuan 2012). In addition, the use of native plants is highly recommended depending on the nature and age of the site.

3.6.4 Cost estimation

In comparison to other soil treatment techniques, phytoremediation is the most cost-effective. Although it requires longer time, it is practicable, either on a large scale or on a small scale with minimal cost requirement and minimal skill/technic, thereby encouraging active involvement of the local communities. Schnoor (1997) reported that the incurred cost of 5-year phytoremediation experiment period was low compare to other treatments like fixation and landfilling. In addition, the identified safety issue was mainly its residue disposal. Agunwamba & Mbogu (2013) also compared the cost requirement of different bioremediation techniques obtainable in Nigeria and reported that apart from the cost incurred in the analysis of the necessary phytoremediation parameters and its continual effective monitoring, other costs were similar to the normal establishment of vegetation for agricultural purposes. However, it would be sagacious to apply an ex-situ preliminary experiment in a greenhouse to widen knowledge and understanding. In addition, modelling could be employed to simulate the effectiveness of the technique in line with necessary regulatory standards. The logistics to be estimated in the list of cost analysis include design, site preparation (with its associated machinery), planting (including the cost of seed and necessary machinery), maintenance, revegetation and/or replacement (if need be), regular monitoring, traveling and involved logistics, data collection and experimental analysis on regular time steps.

3.6.5 Operation and maintenance

This consideration is very vital for the in-situ application of the phytoremediation technique in Nigeria. Possible limiting factors to in-situ implementation include soil quality (especially soil

nutrient), weeds, pest and disease attacks, external invaders (both humans and animals), weather conditions (especially drought), and the country's recent climate change issues. All these may necessitate replanting over 30 % of the plants. However, continuous monitoring and maintenance are necessary to ensure success, and agricultural measures such as weeding, monitoring, pruning, harvesting, irrigation, fertilization, etc. are all recommended. Examples of application on a field scale were highlighted by Jordahl et al. (2003); Amanda (2006); Vangronsveld et al. (2009); and Caliman et al. (2011), and these may be recommended for the Niger Delta region. In addition, ecosystem service potential; most especially carbon sequestration should be considered for most of the polluted regions in Nigeria due to gas flaring. For example, at the industrial facility in Wisconsin, 300 willow trees were planted, and following the total plant biomass calculation (Nowak & Crane 2002; Jenkins et al. 2003), 8000 pounds of carbon was estimated to have been stored by the project (approximately 1.3 tons of carbon per acre per year) and this is a commendable high value (Carman et al. 2000).

3.6.6 The fate of the harvested plants

After the plants might have been used to achieve its target, the question that usually arises, and that remains one of the limitations for phytoremediation is the fate of the plant biomass. This means that high consideration should be given to the use of energy plants that are capable of both phytoremediation and efficient energy generation. The transformation of each kind of biomass to energy (conversion) is based on different conversion technologies. Energy plants (e.g. wood) can be directly converted (combustion in heat), while plants such as silage can be converted by a multistage process into fuel (e.g. biogas). According to Jank et al. (2013), guinea grass is a good source of ethanol production because of their higher cellulose concentration in leaves (29.5 %) and stems (35.6 %). Otherwise, the plant biomass can be used for direct burning to produce charcoal (though it may be soft and powdery). It has a combustion power of 16.7 – 17.3 %. Pre-treated biomass of nut-grass was inoculated with *Aspergillus niger* for enzymatic hydrolysis. This produced cellulose enzymes that hydrolysed polysaccharides into simple sugar. Also, Vetiver grass has a biogas yield of 140,434 m³/m³/t; and biogas utilization of 58.46 % Yuying et al. (2014). A pre-treated sample of *Pennisetum purpureum* (elephant grass) yielded 42 % of ethanol; while the untreated sample yielded 83 % of ethanol (Aiyejagbara et al. 2016).

3.6.7 Regulatory standards

Compliance with both national and international appropriate regulatory bodies is critical in consideration of this in-situ phytoremediation technology. Provision for this in Nigeria is highly necessary for related national environmental law (Sam 2016). These regulatory standards are needed to ensure appropriate monitoring and also address concerns related to its state and community acceptance (Caliman et al. 2011). Although this technique is aesthetically preferable, cost-effective, easy to implement and maintain, capable of restoring ecosystem function, and render the soil agriculturally productive, however, attitudinal responses of the community towards acceptance is necessary. This will help to avert every potential social background challenges that are already in existence or may arise later in the future in almost all the oil-contaminated regions in Nigeria.

3.7 Potential species for phytoremediation in Nigeria

3.7.1 Herbaceous species for remediation of petroleum hydrocarbons

Section 4.2.2 describes essential plant characteristics necessary for consideration. Several previous studies have highlighted the attributes of plants employed for phytoremediation in relation to the plant's efficiency. Considering the involved environmental and climatic factors in Nigeria, Table 3 below presents a list of some potential herbaceous species capable of phytoremediation.

Table 3: Potential herbaceous species for phytoremediation of oil contaminated lands in Nigeria

Species	Country	Research scale	Summary of Outcome	References
<i>Axonopus compressus</i>	Nigeria	Field experimental plots	66 % loss of hydrocarbons, increased soil pH, enhanced accumulation of organic matter and moisture content.	(Ighovie & Ikechukwu 2014)
<i>Ipomoea batatas</i>	Nigeria	Both field work and Lab experiment	<i>Ipomoea batatas</i> can grow, sustain growth, reduce TPH content from 75.46 mg/g–19.876 mg/g in 16 weeks, predicted to take 27 weeks to reach zero.	(Izinyon & Seghosime 2013a)
<i>Melampodium paludosum</i>	Nigeria	Both field work and Lab experiment	At 75.46 mg/g contaminated soil, the plant can steadily grow, stabilize and enhance degradation. Reduce initial TPH content from 75.46 mg/g–49.822 mg/g in 2 wks after plant stabilization and 30.07 mg/g after 16 wks of plant stabilization. Predicted to take 28 wks to reduce TPH content to zero.	(Izinyon & Seghosime 2013b)
<i>Vigna unguiculata</i>	Nigeria	Field experiment	Recommenable for phytoremediation of crude oil contaminated soil, Total hydrocarbon significantly reduced to 600 mg/kg from 1300 mg/kg.	(Tanee & Akonye 2009)
<i>Sida rhombifolia</i>	Nigeria	Pot experiment	The plants cause reduction of over 60 % saturated hydrocarbons, greater than <i>Phyllanthus amarus</i> (35.30 %) and <i>Hyptis spicigera</i> (39.04 %).	(Ogbo et al. 2009)
<i>Mariscus alternifolius</i> <i>Amaranthus viridis</i> and <i>Talinum triangulare</i>	Nigeria	Pot experiment	<i>Amaranthus viridis</i> is an efficient hyperaccumulator, the two plants can survive on contaminated soils, and can as well uptake heavy metals on oil polluted soils.	(Oti 2015)
<i>Paspalum. vaginatum, Cynodon.dactylon, Pueraria. phaseoloides, Centrosema. pubescens, Panicum. maximum, Schrankia. leptocarpa, Eclipta. alba (Linn.), Cyperus. haspen (Linn.), Melastromastrum. capitatum, Acreceras. zizanioides Dandy, Pteridium aquilinum (Linn), Ludwigia. decurrens Walt, Setaria longiseta P.Beauv., Physalis angulata (Linn.), and Desmodium scorpiurus Desv</i>	Nigeria / Ghana	Field	Native plants existing on previously polluted crude oil sites within Niger-Delta of Nigeria. <i>Paspalum vaginatum</i> and <i>Cynodon dactylon</i> were highly tolerant and recommendable for phytoremediation.	(Oyibo 2013)
<i>Sorghum bicolor</i> and <i>Linum usitatissimum</i>	Iran	Outdoor pot experiment	Contaminants reduced the plants growth, but both plants reduced TPH concentration by 9500 and 18500 mg/kg respectively compared to control.	(Shirdam et al. 2008)
<i>Glycine max</i>	Nigeria	Biological Garden Pot experiment	Within 110 days, the plant can cause clean-up of crude oil contaminated soil and crude oil toxicity in soil.	(Njoku et al. 2009)
<i>Glycine max, Vigna unguiculata, Arachis hypogaea, Sphenostylis stenocarpa, Chrysopogon zizanioides, Zea mays, Axonopus fissifolius, and Heteropogon contortus</i>	Nigeria	Field experiment	Petroleum significantly affected soil properties, <i>Glycine max</i> reduced the bulk density, increased available K, exchangeable Ca, and exchangeable Mg of the soil, which is important for optimum soil fertility replenishment for planting.	(Anikwe et al. 2017)
<i>Brachiaria brizantha, Centrosema brasilianum and Calopogonium mucunoides</i>	Venezuela	Pot experiment	The plant species are promising for phytoremediation, they combined high seedling emergence with least affected biomass production.	(Merkl et al. 2004)
<i>Pennisetum glaucum (L.) R. Br</i>	Nigeria	Outdoor pot experiment	Reduced more than 90 % TPH content of the contaminated soil after 2 months of pollution.	(Nwadinigwe & Obi-Amadi 2014)

3.7.2 Trees for phytoremediation of petroleum hydrocarbons

Dendroremediation (use of trees for remediation) is a known efficient remediating technique over the years. In addition to its remediating effects, it also has several environmental values, which include large biomass, deep root system, carbon sequestration, etc. (Pajevic et al. 2016). All these are of great importance within the oil exploration sites, which are characterized by heavy air-pollution and deep percolation of oil contaminants. So trees with deep root systems can prevent offsite migration of contaminants to groundwater. Due to its symbiotic association with nitrogen-fixing bacteria and arbuscular mycorrhizal fungi (AMF), the use of leguminous trees is recommended (Bento et al. 2012). A list of tree species from previous studies for potential phytoremediation of contaminated sites is presented in Table 4 below.

Table 4: Trees for potential phytoremediation of oil contaminated lands in Nigeria

Species	Country	Outcome / Suggestions	Reference
<i>Treculia africana</i>	Nigeria	<i>Treculia africana</i> can potentially remediate low contaminated soils. Number of leaves, leaf area, plant height, collar girth and dry biomass of the plant were insignificant up to 4.56 %, but significant at higher level.	(Agbogidi et al. 2011)
<i>Irvingia gabonensis</i>	Nigeria	Efficient for remediating low concentration of crude oil impacted soil and influence its growth significantly.	(Agbogidi & Dolor 2007)
<i>Thespesia populnea</i> , <i>Cordia subcordata</i> , <i>Prosopis pallida</i>	Hawaii USA	The three species show phytoremediation potential in coastal tropics, however, the first two appeared more promising	(Sun et al. 2004)
<i>Jatropha curcas</i>	Nigeria	Effect of spent engine oil contamination on <i>J. curcas</i> growth, development and yield (biomass accumulation) is significantly negative and increases in its trace elements	(Agbogidi 2011; Agbogidi & Eruotor 2012)
<i>Acacia angustissima</i> , <i>Acacia auriculiformis</i> , <i>Acacia holosericea</i> , <i>Acacia mangium</i> , <i>Mimosa artemisiana</i> , <i>Mimosa caesalpinifolia</i> , and <i>Samanea saman</i>	Brazil	Decreasing potential of <i>Samanea saman</i> is high due to its symbiotic micro-organisms. <i>A. angustissima</i> and <i>M. caesalpinifolia</i> have high tolerant ability but did not decrease TPH. <i>M. artemisiana</i> significantly decreased soil TPH but its growth was severely affected, suggesting that plant growth and adaptation were not directly related to its TPH reduction but to the plants association with symbionts.	(Bento et al. 2012)
<i>Tectona grandis</i> (Linn.), <i>Gmelina arborea</i>	Nigeria	At 10 and 15 % respectively, plant height, number of leaves, leaf area, plant girth and dry biomass were significantly affected but effect was not significant in comparison with uncontaminated site.	(Agbogidi et al. 2007)

3.7.3 Combination of both trees and grasses for phytoremediation

Several studies have identified the benefits of combining both trees and grasses for phytoremediation (Pajevic et al. 2016). An effective combination of trees and grasses depends on several factors, which are interdependent. In addition to the above-stated factors in selecting the plant species (Section 3.6.2), additional essential factors to be considered in agroforestry system

is the competitive functional efficiency of the mixed planting compared to single planting (e.g. competition for space, nutrient, light, water) as well as planting factors such as spacing and arrangement. The agroforestry ecosystem can be extremely dynamic, with available resources and environmental conditions changing over time. A basic, yet useful approach to address this variability is to observe the resource pools (light, water, nutrients) as well as how the plants can utilize them in the horizontal, vertical, and time dimensions.

3.7.4 Combination of techniques

In addition to the possibility of combining both grasses and trees together, bioremediation techniques using earthworm and bacteria are recommended. Vermiremediation potential studies by Ekperusi & Aigbodion (2015) with earthworm (*Hyperiodrilus africanus* Beddard) on some crude oil contaminated soil showed that it significantly enhanced soil physicochemical properties. It decreases TPH by 84.99 %, benzene by 91.66 %, and toluene, xylene, and ethylbenzene by 100 %. Also, the bioaccumulated/biodegraded percentage ratios by the earthworm for the considered contaminants were high. Similarly, Nwadinigwe & Onyeidu (2012) reported that bioaugmentation with bacteria and biostimulation with poultry manure showed positive results in remediating crude oil polluted soil to biostimulation. Enhanced phytoremediation by inoculation of plant roots with hydrocarbon-degrading bacteria and/or plant growth-promoting bacteria has been well discussed (Yavari et al. 2015). These techniques can be combined with the highlighted agronomic measures discussed in Section 3.6.3 above. However, on heavily contaminated soils where these techniques cannot efficiently clean-up, it is recommended that they are employed after using conventional techniques. The right choice of technique depends on the contaminants, level of spillage, and the media as described in Section 3.2.

3.8 Conclusion and recommendation

This paper outlined the prospects of in-situ remediation in the clean-up of oil-contaminated soils in Nigeria. Among the three categorized treatment techniques highlighted; physicochemical methods, thermal methods, and biological methods, phytoremediation is the most recommended technique for Nigeria. This is in consideration of existing challenges to remediation of the oil-contaminated sites in the country (such as lack of initial environmental-related data, its characterized dynamic nature and environmental heterogeneity, frequent spills and re-contamination, governance, stakeholders structure, and funds), the vital need of restoring the

source of livelihood (agriculture and fishing), the cost, management, and skill demands. Moreover, it is environmentally friendly with zero greenhouse gas emissions. The highlighted essential practical considerations necessary for its in-situ application such as site condition, plant characteristics, agronomic measures, cost estimation, operation maintenance, the aftermath of harvested plants, and regulatory standards are very important at the planning phase, its implementation should be followed up with efficient maintenance and monitoring. In line with the use of plants, the use of trees (dendroremediation) is recommended due to the deep level of percolation and its effective environmental values such as carbon sequestration which is necessary due to heavy air pollution occurrences (gas flaring) on some sites. Although dendroremediation is still in its infancy with limited understanding, yet, it possesses tremendous prospects for the future. It is strongly recommended that different treatment techniques should be combined; for example, vermiremediation (use of earthworms) which had been successfully employed with significant influence. However, the choice of further applicable options should be guided by the necessary sustainable factors (social, environmental, and economic factors) along with climatic factors and its long-term applicability. For sites with very heavy pollution, phytoremediation can be employed as a “polishing step” after the conventional clean-up. In order to maximize its obtainable results, community acceptance and active participation are necessary. Since it requires little skill/management technique, it can be further employed and managed in each community by the citizens with less continuous demand from the government. However, provision needs to be made for it in the national environmental law in order to enact necessary standards and monitoring regulations. Capacity strengthening, adequate attention, and funding, as well as the active involvement of the stakeholders and the affected community should accompany this. These prospects are not limited to Nigeria; it is applicable to neighbouring countries as well to other tropical countries with similar climate conditions around the globe.

4. Impact of mining on the floristic association of gold mined sites in southwest Nigeria³

4.1 Abstract

Occurrences in land use, human activities and climate change have both direct and indirect influences on the environment. Of interest for this study is mining; a common activity in developing countries such as Nigeria which is endowed with over 34 solid minerals. The gold mining sites in the Southwest region of the country is predominantly by Artisanal and Small-Scale Mining (ASM). Though the benefits are known, its induced consequences are enormous. To understand its extent of floristic diversity, identification of functional plants and plant species surviving on the mined sites (despite its characterized mining and alteration level); this study compared the floristic composition of an abandoned mining site (Site 1), an active mining site (Site 2) and an undisturbed vegetation sites (Control) of similar vegetation zone. A total of 54, 28 and 37 species belonging to 31, 20 and 23 families were found on Site 1, Site 2 and the control site, respectively. It shows that the floristic composition of all the sites has been altered due to its past intense agricultural colonization and human activities, but severe on Site 1 and 2 due to mining. Lots of the identified species are functional species and stand as ecological indicators. Species such as *Acanthus montanus* and *Ipomoea trichantha* found on the Control sites are native and significance but species such as *Capsicum frutescens* and *Crassocephalum crepidioides* on Site 2 are due to human inference while most species on Site 1 shows both original and altered floristic composition (e.g. *Adenia venenata* and *Grewia flavescens*). Apart from the on-going farming activities, ASM activities such as pollution, deforestation and exposure of the forest soils to direct sunlight has greatly stressed and disturbed the floristic composition, species richness, life form patterns, of the mined sites as well as introduction of non-native plant species. It is therefore necessary to develop effective approaches and policies to curb these illegal ASM activities,

³ Published in BMC Ecology. Springer Nature

Adesipo, A. A., Akinbiola, S., Awotoye, O. O., Salami, A. T., Freese, D. (2020) Impact of mining on the floristic association of gold mined sites in southwest Nigeria. *BMC Ecology*, **20**(9), 1-13. DOI: <https://doi.org/10.1186/s12898-020-00276-9>

empower the community (especially youths), stabilize the economy and establish sustainable development strategies with adequate reclamation measures.

Keywords: Biodiversity loss, Artisanal and Small-Scale Mining (ASM), Tropics, Functional plants, Ecological indicators, Invasive species.

4.2 Introduction

Biodiversity loss is not just region specific; it is a global challenge and can be attributed to different occurrences in land use, human activities as well as climate changes (Giam et al. 2010). Depending on the type and intensity of these occurrences, there are identifiable direct and indirect effects it poses to the environment; they play a crucial role in its dynamics thereby inducing notable quantitative and qualitative changes in the composition of the flora, fauna, biocoenoses, and habitats (Kim et al. 2002). Thus, the status of biological diversity in many settlements is a reflection of its environmental conditions, and the susceptibility of each community to the nature and magnitude of these external forces differs (UNESCO/UNEP/FAO 1978). Effects of these external forces on biological diversity have been studied in varieties of ecosystem such as ecosystem functioning (Hötes et al. 2010), primates (Bicknell & Peres 2010), coral reefs (Graham et al. 2011), forest (Valois-Cuesta & Martinez-Ruiz 2016; Valois-Cuesta & Martinez-Ruiz 2017) tundra communities (Jorgenson et al. 2010), and multiple levels such as molecular pathways (Spagnuolo et al. 2009). The floristic composition is of interest for this study, it is a representative of occurring changes such as the terrain and seasonal variations (e.g. temperature and precipitation). Knowledge about it is essential for many ecological studies such as succession, ecological balance, etc. The natural functions of native species in maintaining ecological balance within an ecosystem remains crucial (Walker 1992; Diaz et al. 2003). The disappearance of these endemic species and the introduction of exotic species alter the ecological balance and composition as well as ecosystem functions and services such as pollination, seed dispersal, decomposition, resilience, disease control, etc. (Chornesky et al. 2005). These categories of plants are known as functional species, their functions cannot be replaced by alien species, and their existences remain crucial.

In Nigeria, there are several identified factors that are responsible for modifying the original composition (both floristic and structural) of the rainforest. This includes human activities such as agriculture, increase in rural settlements, mining, rural road networks evolution, government

policies, etc. (Osunade 1991; Salami 1995; Salami 2001; Orimoogunje 2010). But of importance for this study is mining. Although the benefits of mining are known, its environmental consequences have been of great concern (Aigbedion & Iyayi 2007; Lameed & Ayodele 2010; Musa & Jiya 2011). Examples of its effects include deforestation, exposure of forest soil to direct sunlight, removal of top soil and subsoil, pollution, contamination, and other characterized activities which change the soil physical, chemical and biological properties. However, the level or extent of the impacts in most cases differs, and it depends on the type of mining.

Artisanal and Small-scale Mining (ASM) is the most predominant in the southwest region of Nigeria. It accounts for over 95 % of the entire mining activities and has been in existence since 1902 which connotes the advent of the colonial mining (Salami et al. 2003; Aigbedion & Iyayi 2007; Mallo 2012). The artisanal miners' activities are uncoordinated and illegal, majorly practiced by poverty-driven people seeking means of livelihood. Examples of mined minerals within the southwest region include gold, tin, zinc, etc. For the gold mining regions under consideration in this study, spoil heaps (a mixture of overburden soil and rock) with its associated gold waste are deposited on the ground surface after the gold mining, and it is thereafter used for cultivation by the farmers after some abandoned period (Salami et al. 2003). These activities, therefore, lead to increase in the gold waste contaminants, especially heavy metals such as Pb, Cu, Cd, Fe, Hg, As, Zn, etc. (Oladipo et al. 2014). In addition to that is the increased solubility of the contaminants; becoming more available for plants uptake and posing great potential of entry into the food chain coupled with its associated effects. The significant impacts of ASM in increasing the environmental problems within this part of the country have been well discussed. The nature of its activities is characterized informal, uncontrollable with great influence on the floristic composition of this area.

Being in the lush tropical rainforest forest estate, this area is known as a biodiversity sanctuary with the complex terrestrial ecosystem (Ojo 2004). Due to its complex diversity; it is sometimes assumed that there still remains some species yet to be identified. It is part of the agrarian communities typical for growing cash crops such as cocoa and cola-nut, but it has drastically reduced. Most of the cash crop farmlands are gradually becoming normal subsistence farms with the incorporation of food crops such as banana plantation, tuber crops, etc. (Salami et al. 2003; Akinbiola et al. 2016). Its less productivity can as well be attributed to the presence of

contaminants from the gold mining and changes in the soil properties. The typical native species are being endangered; these endemic species are being replaced by exotic/invasive species, and their relics are found existing in patches across the landscape especially in ecologically sensitive environments. Moreover, there are no adequate regulations guiding the conservation of these endangered species within the region. An example is *Milicia excelsa*; listed as an IUCN near threatened species and ought to be worked with based on appropriate permission. Such regulation is necessary, it helps to conserve, regulate and monitor any ecological imbalance. Altering of ecological balance influences the economic, social, environmental and even cultural values of the community. In addition is the level of importance usually attached to some species in providing necessary goods and services; the importance of some of these species to Nigeria was highlighted by Nigeria Fifth National Biodiversity Report. National Reports (Nigeria Fifth National Biodiversity Report 2015). These species are also known as functional species as well as ecological indicators. Their loss poses replicable effects of their functions (Loreau et al. 2001; Scherer-Lorenzen et al. 2005). However, quantifying this ecological imbalance is difficult, but its meaningful characterization is a reflection of its responses to various impacts (Salami 2001; Shameem et al. 2010).

This study was therefore conducted in order to understand the impact of mining on the floristic association of the gold mined sites within the southwest region of Nigeria. It aims to know the current status of its floristic diversity, identification of functional plants and ecological indicators as well as characterized plant species surviving on the mined sites (despite its high level of disturbance from the mining activities and contamination). This may also serve as fundamental and applied reasons especially towards reclamation of the mined sites.

4.3 Methods

4.3.1 Experimental area

The study areas consisted of an abandoned mining site (Site 1) an active mining site (Site 2) and an undisturbed vegetation site for control. Site 1 is situated at Okutu-Omo ($7^{\circ} 30' 30''$ N, $4^{\circ} 38' 15''$ E), Site 2 at Itagunmodi village ($7^{\circ} 31' 30''$ N, $4^{\circ} 39' 03''$ E) and the Control site (or reference site) at Igila ($7^{\circ} 34' 56''$ N, $4^{\circ} 39' 50''$ E) in Atakunmosa west Local Government Area (LGA) of Osun state, within the southwest region of Nigeria (Figure 8). This area belongs to the Ife-Ilesha schist belts, it remains the main source of both alluvial and primary gold field deposits and the

gold mining in this region can be dated back to 1942. The mean annual rainfall is approximately 1400 mm, and the average temperature ranges between 23 and 31 °C. The textural class of the soil series is classified loamy (58 % sand, 10 % clay and 32 % silt), with pH of 4.5 (Olabiya et al. 2009), and it is in the lowland rainforest vegetation zone (Salami et al. 2003). Despite the characterized mining activities and high level of disturbances, farming remains on-going; since it is the major occupation of the local communities.

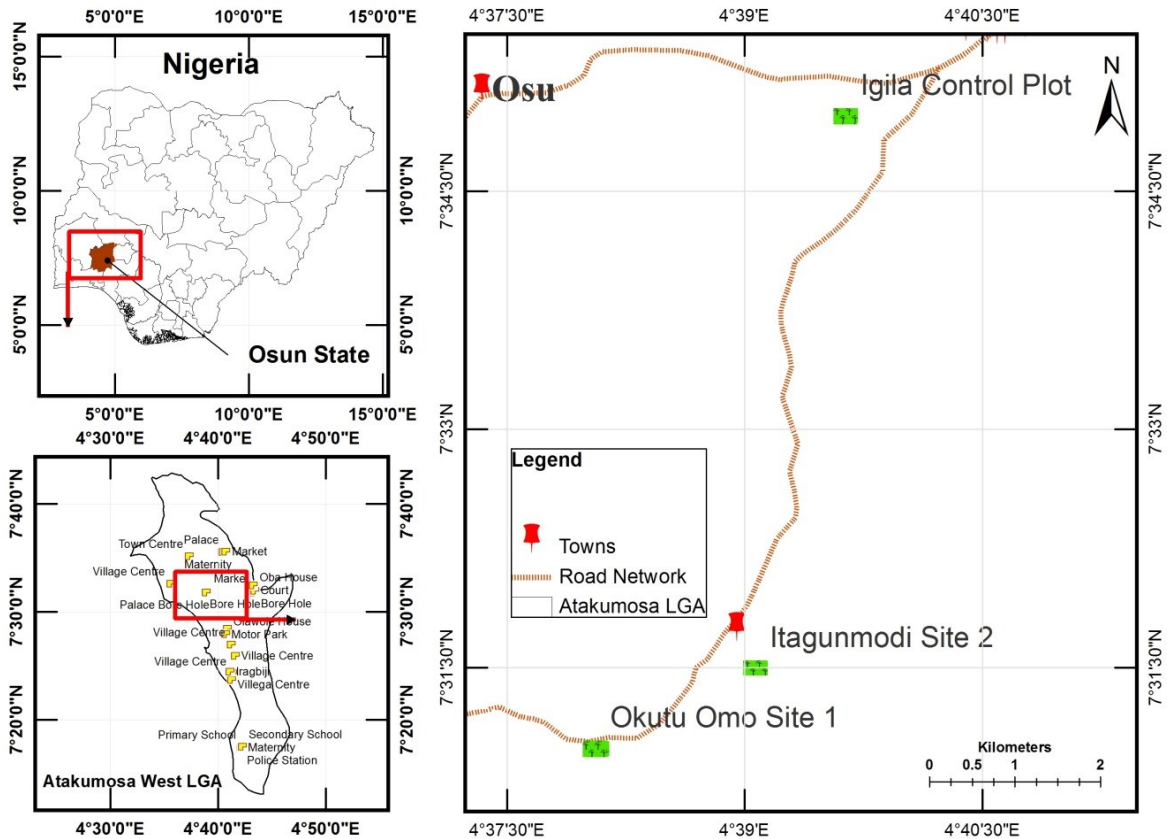


Figure 8: Scaled map of the study area

4.3.2 Site selection and preparation

Based on reconnaissance surveys, the three sites were purposefully selected to represent the mining and farming activities within this region. As presented in Figure 9; Site 1 is an old abandoned mined site; occupied by degraded secondary lowland rainforest under regrowth. It had some relics of original forest that were still present. Site 2 is a recent mine site depicted by the presence of pits and spoil heap. It has been subjected to large scale mining and covered with secondary succession plants. Some of the existing pits (about 1.5 × 1 m each) on the site remain uncovered, surrounded

by excavated subsoil, which are less productive and suggests having influence on plant growth. On the other hand, the control site was an undisturbed vegetation site (also confirmed by the local farmers and inhabitants); it was majorly covered with secondary regrowth forest, located at about 7 km away from the mined sites. Although there were other areas where mining was ongoing, they were not considered due to the suspicious and dangerous disposition of the artisanal miners. Moreover, these 3 considered sites were within the same vegetation zone with similar geology, land use and land cover. On each of the 3 different selected sites, experimental sample plots of 10×10 m were mapped out in 2 replicates, and there GPS coordinates were recorded accordingly. Due to the uncontrollable easy access of the ASM miners as well as the local farmers to the sites (especially on Site 2), each of the mapped out sample plots were demarcated from potential invaders throughout the sampling period.



Figure 9: Personally taken pictorial view of the considered sites. (a) Control site (b) Mined site 1 and (c) Mining site 2

4.3.3 Plant sampling scheme and classification

Considering the aim of the study, the plant sampling scheme involves complete enumeration and identification of both lower and higher plants species on each of the mapped out experimental plots. Line transect sampling method was employed; placed on each diagonal edge of the sample plots (Figure 10) and each line representing a replicates (i.e. total of 4 replicates per site). The line transect was diagonally placed to have a longer sampling length than simple straight line from one edge to the other. All the plant species found at about 1 m on both right and left sides of the lines were recorded. The sampling was done both to and from along the transect line for reaffirmation. Compare to other sampling methods, line transect was employed due to the nature of the landscape and the plant species growing on the sites (Buckland et al. 2007). This also helps to identify the potential occurrence of changes along the line especially on areas with patchy nature of some plant species. The Herbarium of the Obafemi Awolowo University of Ile-Ife was consulted for unidentified plants coupled with the online portal of The Plant List as well as African Plant

Database for confirmation. On each of the sites, all the identified plant species were grouped into their various families and habitat preference. Based on the frequency of the plant species occurrence, they were classified into the different status of abundance ranging from very abundant, abundant, to sparse and rare.

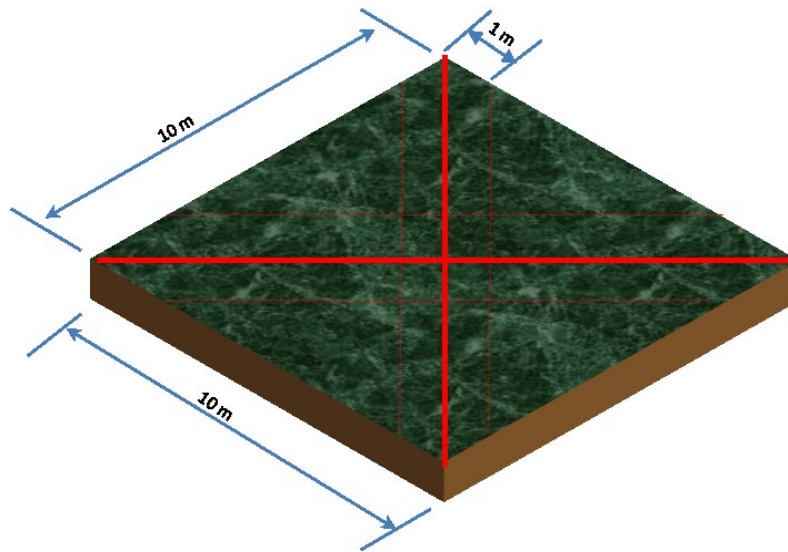


Figure 10: Diagrammatic representation of the line transect sampling method

4.3.4 Data analysis

Plymouth Routines in Multivariate Ecological Research (PRIMER-E) was used for analyzing the data. The significance of difference among the study sites were analysed using PERMANOVA (Permutational multivariate analysis of variance) and pairwise comparison between the sites. Vegetation data were log transformed ($\text{Log}(X+1)$) to improve homogeneity of variances. Species richness, number of individuals, Pielous evenness, Shannon and Simpson indices were estimated from the log transformed data with the “DIVERSE” function in PRIMER 7 (Anderson et al. 2008b). A one-factorial Permanova design using Bray–Curtis distance measure and 9999 permutations with site as fixed factor for each site at 0.05 significant level was used to test for the significant differences of plant species composition of each site. Also, a Non-Metric Multi-Dimensional scaling (nMDS) based on Bray–Curtis distance measure (Oksanen 2015) was created to produce a 2D representation of species composition. Plant types were then overlaid on the nMDS ordination to show linkages between sites and plant types. The goodness of fit of the nMDS results was evaluated with a stress value. The data set employed for the analysis is available in (Adesipo et al. 2020a).

4.4 Results

The biological diversity of the 3 studied sites are presented in Table 5. It shows a species richness of 41, 22 and 33 species with recorded total individual ranging from 424, 225 and 336 on Site 1, Site 2 and the reference site, respectively. Permutational multivariate analysis of variance (PERMANOVA) results showed significant differences in species composition between the three sites (Sites— $F_{2,9}=28.953$, $p < 0.001$). A pair-wise test further shows significant differences between Site 1 and Site 2 ($p=0.03$), between Site 1 and the reference ($p=0.03$) and between Site 2 and the reference ($p=0.03$). Simple results for species contributions at 50 % cut off for low contribution revealed average similarity of 73 % for Site 1, 78 % for Site 2 and 80 % for the reference site.

Table 5: Biological diversity measurement (alpha and beta diversity), N per site = 4

1. Community composition	Site1	Site2	Reference
1A. Species richness (S) \pm SE	41.00 \pm 1.0	22.00 \pm 0.4	33.00 \pm 1.2
1B. No. of individuals (N) mean \pm SE	106.00 \pm 6.7	56.25 \pm 1.1	91.50 \pm 2.6
2. Diversity			
2A. Pielous evenness (J) \pm SE	0.95 \pm 0.01	0.95 \pm 0.01	0.95 \pm 0.01
2B. Shannon (H'loge) \pm SE	3.53 \pm 0.02	2.93 \pm 0.01	3.34 \pm 0.3
2C. Simpson (1-Lambda) \pm SE	0.97 \pm 0.01	0.96 \pm 0.01	0.97 \pm 0.01

The most contributing species for Site 1 include *Melanthera scandens*, *Melochia corchorifolia*, *Paullinia pinnata*, *Sida pilosa*, *Desmodium adscendens*, all contributing about 23 % out of the total 73 %. Site 2 were characterised by *Palisota ambigua*, *Justicia insularis*, *Drynaria laurentii*, *Pentodon pentandrus*, *Chromolaena odorata*, *Cissus quadrangularis* and *Sida pilosa* all contributing about 53 % of the average similarities within Site 2. The reference site was characterised by *Theobroma cacao*, *Pteris togoensis*, *Crinum jagus*, *Drynaria laurentii*, *Justicia insularis* all contributing cumulative 23 % of the average similarities within the reference site. Site 1 and Site 2 shared about 70 % average dissimilarity, while Site 1 and the reference site shared 64 % average dissimilarity, and also 64 % average dissimilarity exist between Site 2 and the reference

site. The Non-Metric Multi-Dimensional scaling (nDMS) analysis using bootstrap averages revealed a clear separation of the sites in terms of species composition (Figure 11) as supported by the stress value (0.08).

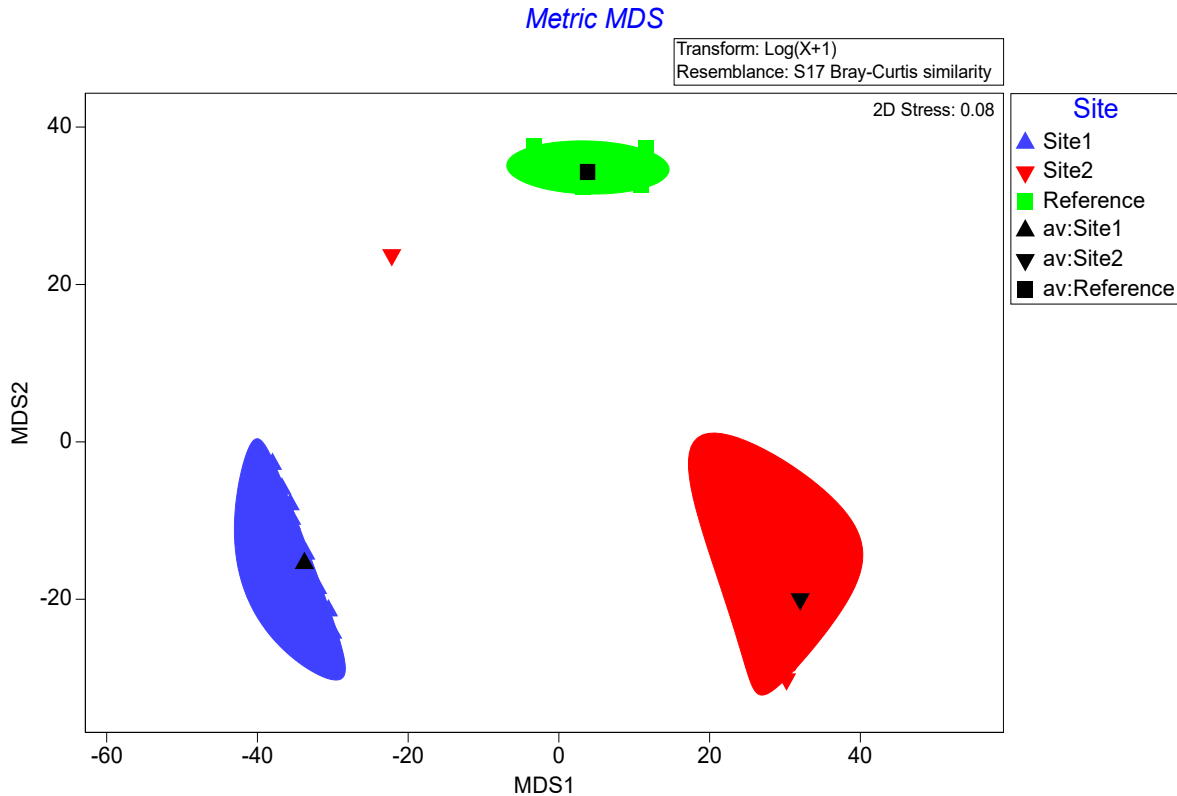


Figure 11: Species composition of the 3 sites by nDMS analysis (with stress value of 0.08). It shows a distinctive separation from the 3 sites: Site 1 (blue); Site 2 (red) and the reference site (green).

The three sites are distinctively different with no significant similarity between them. This goes on to confirm the PERMANOVA results that all the three sites in this study are different from each other. Species dominance curve revealed the dominance of most species for all the sites with few rare species (Figure 12). The species were ranked on the horizontal axis in terms of abundance and on the vertical axis in terms of percentage dominance. And it shows the different slope of the 3 sites. A distinction between the plant types revealed an association of fern, tree and shrub to the reference site (Figure 13).

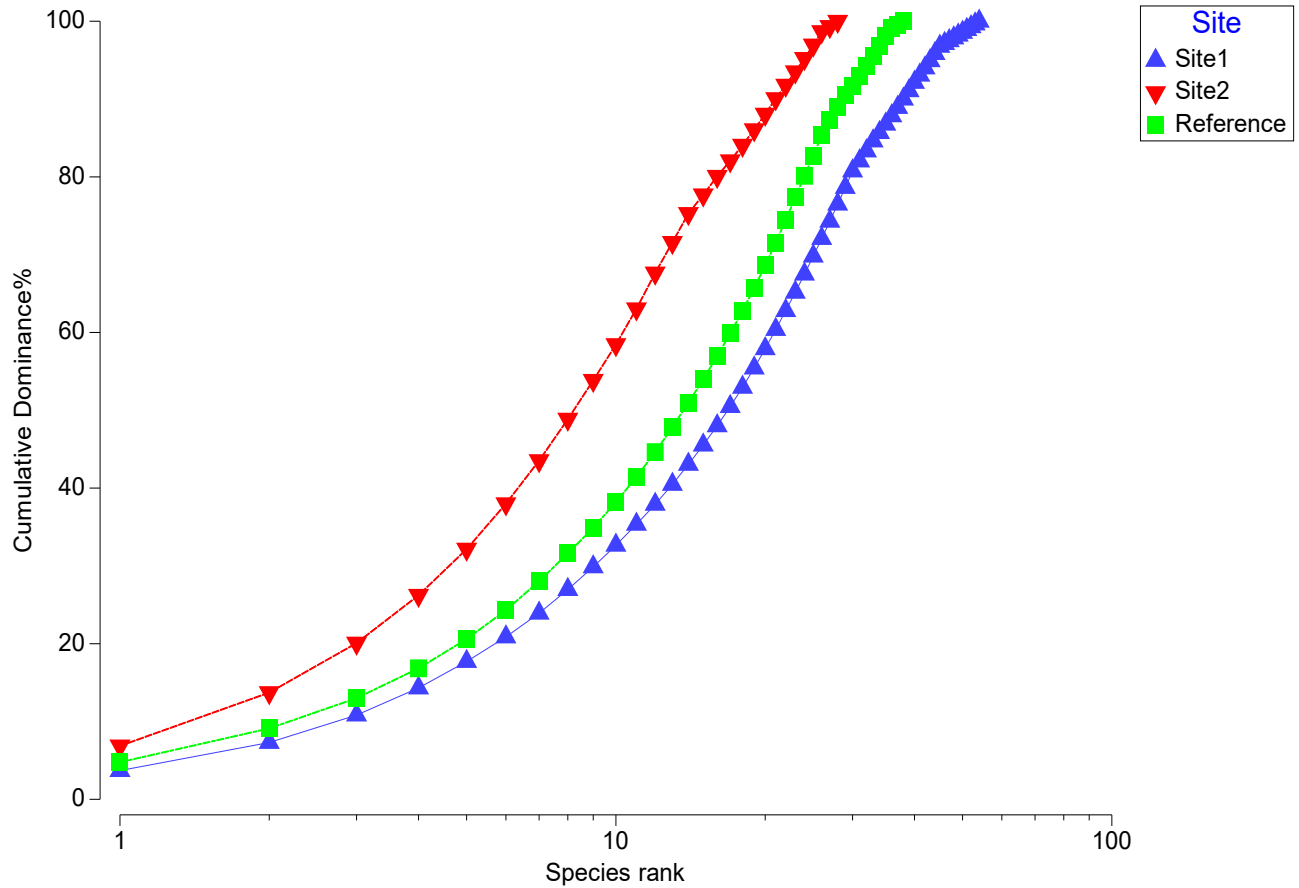


Figure 12: Species dominance curve of the 3 studied sites. The species were ranked on the horizontal axis in terms of abundance and on the vertical axis in terms of percentage dominance with each of the site having different slope.

As presented in Figure 13, Site 1 was more associated with plant types like herbs, tuber plants, climbers and creepers. No association was however, established for any of the plant types on Site 2. Details of the identified plant species on Site 1, Site 2 and the control site are presented in Tables 6, 7, and 8 respectively. Despite the mentioned (in the methodology) consultations efforts in identifying the plants, 3 plant species were not identifiable on Site 1, while 5 plant species on Site 2 were not identifiable, but all the plant species on the control site were identifiable. The high number of unidentifiable species on the mined sites may be due to its high level of disturbance by the ASM whereby new invasive species might have been introduced to the sites.

Non-metric MDS

Transform: Log(X+1)
Resemblance: S17 Bray-Curtis similarity

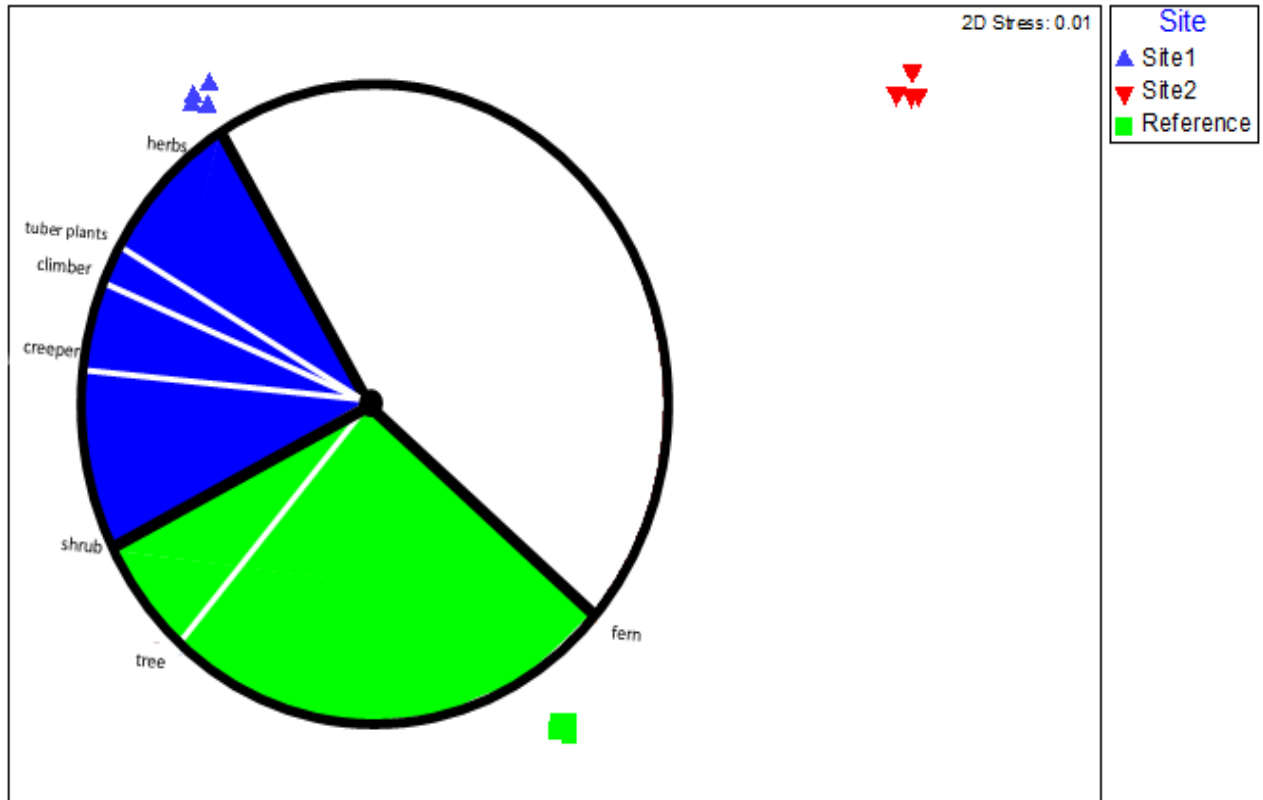


Figure 13: Distinctive association of plant type to each of the 3 studied sites. The reference site (green) is associated with fern, tree and shrub, Site 1 (blue) with herb, tuber plants, climber and creeper while the Site 2 (red) has no distinctive association.

Table 6: Species and family compositions of Flora on Site 1

S/N	Name	Family	Habit	Status
1	<i>Adenia cissampeloides</i>	Passifloraceae	Climber	Sparse
2	<i>Adenia venenata</i>	Passifloraceae	Climber	Abundant
3	<i>Albizia leebek</i>	Mimosaceae	Tree	Abundant
4	<i>Albizia zygia</i>	Mimosaceae	Tree	Abundant
5	<i>Alchornea cordifolia</i>	Euphorbiaceae	Shrub	Rare
6	<i>Alchornea laxiflora</i>	Euphorbiaceae	Shrub	Abundant
7	<i>Aneilema aequinoctiale</i>	Commelinaceae	Climber	Abundant
8	<i>Aneilema beniniense</i>	Commelinaceae	Climber	Abundant
9	<i>Aspilia africana</i>	Asteraceae	Herb	Abundant
10	<i>Asystasia gangetica</i>	Acanthaceae	Herb	Very abundant
11	<i>Chasmanthera dependens</i>	Menispermaceae	Climber	Sparse
12	<i>Chromolaena odorata</i>	Asteraceae	Herb	Very abundant
13	<i>Cissampelos owarensis</i>	Menispermaceae	Climber	Abundant
14	<i>Cissus quadrangularis</i>	Vitaceae	Climber	Sparse
15	<i>Clerodendrum splendens</i>	Verbenaceae	Climber	Rare
16	<i>Clerodendrum volubile</i>	Verbenaceae	Climber	Abundant
17	<i>Cola nitida</i>	Sterculiaceae	Tree	Sparse
18	<i>Colocasia esculentum</i>	Araceae	Herb	Abundant
19	<i>Commelina erecta</i>	Commelinaceae	Herb	Abundant
20	<i>Desmodium adscendens</i>	Leguminosae	Creeper	Very abundant
21	<i>Dissotis rotundifolia</i>	Melastomataceae	Herb	Abundant
22	<i>Ficus asperifolia</i>	Moraceae	Shrub	Sparse
23	<i>Ficus exasperata</i>	Moraceae	Tree	Sparse
24	<i>Ficus mucoso</i>	Moraceae	Tree	Sparse
25	<i>Gliricidia sepium</i>	Leguminosae	Shrub	Rare
26	<i>Grewia flavescens</i>	Tiliaceae	Shrub	Sparse
27	<i>Hippocratea indica</i>	Celastraceae	Climber	Sparse
28	<i>Holarrhena floribunda</i>	Apocynaceae	Tree	Sparse
29	<i>Laportea aestuans</i>	Utricaceae	Herb	Abundant
30	<i>Lonchocarpus cyanescens</i>	Papilionaceae	Tree	Sparse
31	<i>Manihot esculenta</i>	Euphorbiaceae	Tuber plant	Abundant
32	<i>Melanthera scandens</i>	Asteraceae	Herb	Very abundant
33	<i>Melochia corchorifolia</i>	Malvaceae	Herb	Very abundant
34	<i>Milicia excelsa</i>	Meliaceae	Tree	Rare
35	<i>Mondia whitei</i>	Asclepiadaceae	Climber	Abundant
36	<i>Morinda lucida</i>	Rubiaceae	Tree	Sparse
37	<i>Momordica charantia</i>	Cucurbitaceae	Climber	Abundant
38	<i>Mucuna pruriens</i>	Papilionaceae	Climber	Abundant
39	<i>Musa paradisiaca</i>	Musaceae	Shrub	Sparse
40	<i>Musa sapientum</i>	Musaceae	Shrub	Abundant
41	<i>Newbouldia laevis</i>	Bignoniaceae	Tree	Rare
42	<i>Paullinia pinnata</i>	Sapindaceae	Climber	Very abundant
43	<i>Pouzolzia guineensis</i>	Utricaceae	Herb	Abundant
44	<i>Pteris togoensis</i>	Pteridaceae	Fern	Rare
45	<i>Senecio biafrae</i>	Asteraceae	Herb	Sparse
46	<i>Senna occidentalis</i>	Caesalpiniaceae	Herb	Rare
47	<i>Sida acuta</i>	Malvaceae	Herb	Abundant
48	<i>Sida pilosa</i>	Malvaceae	Creeper	Abundant
49	<i>Spondias mombin</i>	Anacardiaceae	Tree	Rare
50	<i>Talinum triangulare</i>	Portulacaceae	Herb	Abundant
51	<i>Theobroma cacao</i>	Sterculiaceae	Tree	Sparse
52	<i>Triumfetta cordifolia</i>	Tiliaceae	Herb	Abundant
53	<i>Vigna unguiculata (Wild)</i>	Papilionaceae	Climber	Rare
54	<i>Voacanga africana</i>	Apocynaceae	Tree	Abundant

Table 7: Species and family compositions of Flora on Site 2

S/N	Name	Family	Habit	Status
1	<i>Alchornea cordifolia</i>	Euphorbiaceae	Tree	Sparse
2	<i>Acmella oleracea</i>	Asteraceae	Herb	Sparse
3	<i>Asystasia gangetica</i>	Acanthaceae	Herb	Very abundant
4	<i>Capsicum frutescens</i>	Solanaceae	Herb	Sparse
5	<i>Chromolaena odorata</i>	Asteraceae	Herb	Very abundant
6	<i>Cissus quadrangularis</i>	Vitaceae	Climber	Abundant
7	<i>Clerodendrum volubile</i>	Verbenaceae	Climber	Sparse
8	<i>Commelina erecta</i>	Commelinaceae	Creeper	Abundant
9	<i>Crassocephalum crepidioides</i>	Asteraceae	Herb	Sparse
10	<i>Drynaria laurentii</i>	Polypodiaceae	Fern	Very abundant
11	<i>Ficus asperifolia</i>	Moraceae	Shrub	Sparse
12	<i>Ficus exasperata</i>	Moraceae	Tree	Sparse
13	<i>Justicia insularis</i>	Acanthaceae	Herb	Very abundant
14	<i>Laggera pterodonta</i>	Asteraceae	Herb	Sparse
15	<i>Melanthera scandens</i>	Asteraceae	Herb	Abundant
16	<i>Momordica foetida</i>	Cucurbitaceae	Climber	Abundant
17	<i>Musa sapientum</i>	Musaceae	Herb	Sparse
18	<i>Palisota ambigua</i>	Commelinaceae	Herb	Very abundant
19	<i>Paullinia pinnata</i>	Sapindaceae	Climber	Abundant
20	<i>Pentodon pentandrus</i>	Rubiaceae	Herb	Abundant
21	<i>Pouzolzia guineensis</i>	Urticaceae	Herb	Abundant
22	<i>Pteris togoensis</i>	Pteridaceae	Fern	Sparse
23	<i>Rauvolfia vomitoria</i>	Apocynaceae	Tree	Rare
24	<i>Sida pilosa</i>	Malvaceae	Creeper	Abundant
25	<i>Spilanthes filicaulis</i>	Asteraceae	Herb	Abundant
26	<i>Spondias mombin</i>	Anacardiaceae	Tree	Sparse
27	<i>Theobroma cacao</i>	Sterculiaceae	Tree	Sparse
28	<i>Trema orientalis</i>	Ulmaceae	Tree	Sparse

Table 8: Species and family compositions of Flora on Control site

S/N	Name	Family	Habit	Status
1	<i>Acanthus montanus</i>	Acanthaceae	Herb	Very abundant
2	<i>Adenia cissampeloides</i>	Passifloraceae	Climber	Abundant
3	<i>Adenia lobata</i>	Passifloraceae	Climber	Abundant
4	<i>Albizia leebeck</i>	Mimosaceae	Tree	Abundant
5	<i>Albizia zygia</i>	Mimosaceae	Tree	Abundant
6	<i>Alchornea laxiflora</i>	Euphorbiaceae	Shrub	Very abundant
7	<i>Aneilema aequinoctiale</i>	Commelinaceae	Creeper	Very abundant
8	<i>Asystasia gangetica</i>	Acanthaceae	Herb	Abundant
9	<i>Blepharis maderaspatensis</i>	Acanthaceae	Creeper	Abundant
10	<i>Brachiaria deflexa</i>	Poaceae	Grass	Abundant
11	<i>Chromolaena odorata</i>	Asteraceae	Herb	Sparse
12	<i>Cissampelos owariensis</i>	Menispermaceae	Climber	Abundant
13	<i>Cola nitida</i>	Sterculiaceae	Tree	Abundant
14	<i>Combretum hispidum</i>	Combretaceae	Shrub	Sparse
15	<i>Commelina erecta</i>	Commelinaceae	Herb	Abundant
16	<i>Crinum jagus</i>	Amaryllidaceae	Herb	Very abundant
17	<i>Drynaria laurentii</i>	Polypodiaceae	Fern	Very abundant
18	<i>Elaeis guineensis</i>	Arecaceae	Tree	Abundant
19	<i>Ficus exasperata</i>	Moraceae	Tree	Sparse
20	<i>Ficus mucoso</i>	Moraceae	Tree	Sparse
21	<i>Hewittia sublobata</i>	Convolvulaceae	Climber	Sparse
22	<i>Icacina trichantha</i>	Icacinaceae	Shrub	Sparse
23	<i>Justicia insularis</i>	Acanthaceae	Herb	Very abundant
24	<i>Melanthera scandens</i>	Asteraceae	Herb	Abundant
25	<i>Milicia excelsa</i>	Meliaceae	Tree	Rare
26	<i>Mondia whitei</i>	Asclepiadaceae	Climber	Sparse
27	<i>Musa sapientum</i>	Musaceae	Herb	Abundant
28	<i>Paullinia pinnata</i>	Sapindaceae	Climber	Sparse
29	<i>Pentodon pentandrus</i>	Rubiaceae	Herb	Abundant
30	<i>Phyllanthus amarus</i>	Euphorbiaceae	Herb	Abundant
31	<i>Pteris togoensis</i>	Pteridaceae	Fern	Very abundant
32	<i>Senecio biafrae</i>	Asteraceae	Herb	Sparse
33	<i>Sida acuta</i>	Malvaceae	Herb	Abundant
34	<i>Sida pilosa</i>	Malvaceae	Creeper	Abundant
35	<i>Sterculia tragacantha</i>	Malvaceae	Tree	Sparse
36	<i>Theobroma cacao</i>	Sterculiaceae	Tree	Very abundant
37	<i>Voacanga africana</i>	Apocynaceae	Tree	Abundant

4.5 Discussion

For detailed understanding of the interrelationship and species significance of the investigated flora composition for the 3 considered sites; this section discusses the ecological significance of the floristic composition of the plants species identified on the 3 studied sites. Just for clear view, a simple subset diagram was used to present the interrelationships between the sites (Figure 14).

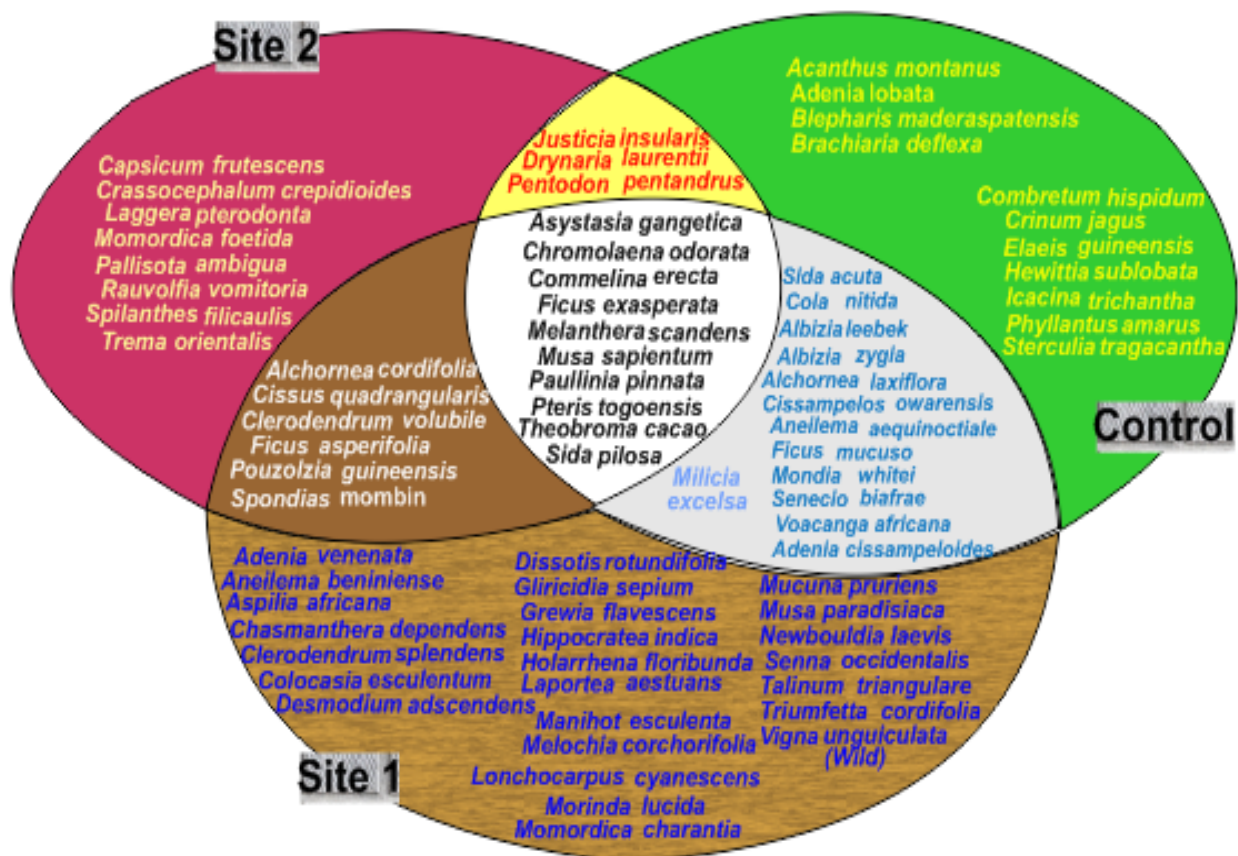


Figure 14: Interrelationship between the Flora species on the 3 sites

4.5.1 All the sites

A total of 10 plant species were common to all the 3 considered sites; they include *Asystasia gangetica*, *Chromolaena odorata*, *Commelina erecta*, *Ficus exasperata*, *Melanthera scandens*, *Musa sapientum*, *Paullinia pinnata*, *Pteris togoensis*, *Sida pilosa* and *Theobroma cacao*. *Musa sapientum* and *Theobroma cacao* are typical plantation crops commonly cultivated in these areas; they are evidence of human activities and intense agricultural colonization that these areas have been subjected to (Salami 2001). *Asystasia gangetica* is a plantation weed, with wide distribution within this area (Hamid et al. 2011); they are very abundant on the two mined sites, but just abundant on the control site. Similar to that is *Chromolaena odorata*, it is known as a fast growing perennial shrub, and invasive weeds. It is an aggressive competitor with allelopathy effects. Its sparse status on the control site compared to the two mined sites suggests low level of disturbance (Uyi et al. 2014). Also widespread in the tropics include *Melanthera scandens*, *Sida pilosa* and *Paullinia pinnata* which is usually in regrowth vegetation, and *Commelina erecta*; particularly in the forest woodland areas. *Ficus exasperata* is a deciduous tree, which belongs to the classified

forest communities as noted by Salami (Salami 2001). It is found in drier types of forest and also widely distributed (Hutchinson & Dalziel 1972). Most of the plant species characterizing the three sites are evidences suggesting that the original forest has been subjected to intense agricultural activities which influence the type of floristic association found on the sites.

4.5.2 Both site 1 and the control site

For both Site 1 and the control site; 13 plant species were similar most of which are significant indicators. The species include *Adenia Cissampeloides*, *Albizia leebeck*, *Albizia zygia*, *Alchornea laxiflora*, *Aneilema aequinoctiale*, *Cola nitida*, *Cissampelos owarensis*, *Ficus mucuso*, *Milicia excelsa*, *Mondia whitei*, *Senecio biafrae*, *Sida acuta* and *Voacanga africana*. According to Orwa et al. (2009), *Albizia zygia* is a light demanding pioneer species, indigenous to tropical Africa with wide distribution ranging from Senegal to east Africa. It is found in areas of mature secondary regrowth and identified as forest tree capable of ameliorating degraded cocoa farms (Anim-Kwapong & Teklehaimanot 2001). Similar to that is *Albizia leebeck*; also naturalized in many tropical countries, found in deciduous and semi-deciduous monsoon forest and rainforest in its native habitat. It is cultivated and often naturalized on old farms. Although these two *Albizia* species are common and abundant on both Site 1 and the control site, however, the species on the control site are fully grown and matured indicating no disturbances unlike Site 1 with young and tender species, which are just re-growing due to the mining activities. Likewise, is *Milicia excelsa* (popularly known as Iroko), it grows in deciduous, semi-deciduous or evergreen, primary or secondary forest. It is a considered pioneer species, categorized as Lower Risk/near threatened by the IUCN Red List of Threatened species, with low characterized potential of competition with climbers and shrubs in young secondary forest (World Conservation Monitoring Centre 1998). Also, typical of this rainforest trees are *Ficus mucuso* and *Cola nitida* (Salami 2001). Their absence on Site 2 is suggestive of high level of disturbance. The existence of *Alchornea laxiflora* (an understory shrub) indicates disturbance within the last 100 years (Akinbiola et al. 2016), while *Voacanga africana* is known to be original occupant of the forest, and species such as *Adenia cissampeloides*, *Sida acuta*, *Cissampelos owarensis*, *Aneilema aequinoctiale* are common and wide spread in the forest regions. *Mondia whitei* is characterized to be rare in rainforest (African Plant Database 2016; Hutchinson & Dalziel 1972; PROTA4U 2016).

4.5.3 Both site 2 and the control site

Common to both Site 2 and the control site are only 3 plant species which include *Justicia insularis*, *Drynaria laurentii* and *Pentodon pentandrus*. All the 3 species are typical for this region with wide distribution. *Justicia insularis* is known as weed of plantation and it is usually characterized with competing potentials (Adeyemi & Babatunde 2014; Global Plants 2016). Also is *Drynaria laurentii*; found in the wet tropical environments with native range extending from equatorial Africa to tropical south and East Asia, and *Pentodon pentandrus* found in wet environments, and considered of least concern by IUCN Red List (Lansdown 2013).

4.5.4 Both site 1 and site 2

A total of 6 plant species characterized both Sites 1 and 2 where mining activities has been done. They include *Alchornea cordifolia*, *Cissus quadrangularis*, *Clerodendrum volubile*, *Ficus asperifolia*, *Pouzolzia guineensis* and *Spondias mombin*. According to Hutchinson & Dalziel (1972), *Spondias mombin* is a deciduous tree, though known as an ancient introduction from America; but also possibly a native of West Africa. It is widespread and common in farmlands, regrowth and villages especially in the forest regions, as well as in the savanna. In fact, it was classified as a savanna species by Salami (2001) and areas with its presence were referred to as ecotone community. *Pouzolzia guineensis* is found mainly in the tropics and it is an evidence of succession, while *Ficus asperifolia* is usually found in river areas; its presence on the two mined site is probably because of the availability of water used in washing the mined gold unlike on the control site (Hutchinson & Dalziel 1972). *Alchornea cordifolia* is a forest disturbance indicator, largely due to anthropogenic activities, the plant extracts from leaf and bark exudates has medicinal properties, hence used locally by villagers. *Clerodendrum volubile* is a climber found in forest or thicket; it is also medicinal and ornamental in nature.

4.5.5 Only the control site

On the control site, 11 plant species were observed which include *Acanthus montanus*, *Adenia lobata*, *Blepharis maderaspatensis*, *Brachiaria deflexa*, *Combretum hispidum*, *Crinum jagus*, *Elaeis guineensis*, *Hewittia sublobata*, *Icacina trichantha*, *Pentodon pentandrus*, *Phyllanthus amarus* and *Sterculia tragacantha*. *Acanthus montanus* is majorly found in high forest, with wide distribution within Central and West Africa, it is classified under plant with less concern according to the IUCN, but is easily threatened by land and water pollution (Ghogue 2010). This suggests

the reason of its inexistence on the two mined sites due to contamination from the gold wastes. Also is *Icacina trichantha*, a small tropical family, in forest and forest regrowth vegetation, found mainly within few countries in West Africa; Nigeria, Ivory Coast, and Benin (Hutchinson & Dalziel 1972). *Sterculia tragacantha* is a deciduous tree, remnant of original forest with distributed undergrowth while *Elaeis guineensis* (palm tree), is a cultivated crop (indicating human interference), but its survival on contaminated soils is very low. Also, *Adenia lobata* occurs in the secondary rainforest, while *Combretum hispidum*; a scandent shrub is found majorly in the west part of Nigeria. *Brachiaria deflexa* originated from Africa, and has reached tropics of the new and old world like Middle East, India and south East Asian countries. *Crinum jagus* is a native range of tropical Africa found in the secondary/primary forest, swamp forest, and riverine vegetation while *Phyllanthus amarus*, and *Hewittia sublobata* are widespread in the tropics,

4.5.6 Only on site 2

8 different plant species were observed on Site 2 compared to the other two sites. These include *Capsicum frutescens*, *Crassocephalum crepidioides*, *Laggera pterodonta*, *Momordica foetida*, *Pallisota ambigua*, *Rauvolfia vomitoria*, *Spilanthes filicaulis* and *Trema orientalis*. *Capsicum frutescens* is widely dispersed throughout the tropics, cultivated but sometimes naturalized and it is an evidence of human activities (Hutchinson & Dalziel 1972). Similar to that is *Crassocephalum crepidioides*, which also indicates very prominent human disturbance. But *Trema orientalis* is an indicator of forest regrowth while *Laggera pterodonta*, *Momordica foetida* are species widespread in tropical Africa and *Pallisota ambigua* in lowland rainforest. *Rauvolfia vomitoria* is also locally called “Asofeyeje” in Yoruba, a shrub common in secondary forest and used medicinally by the locals as medicinal, making of dye, and planted as a shade tree for cocoa.

4.5.7 Only on site 1

On Site 1, 25 different species were identified compared to other two sites. These include *Adenia venenata*, *Aneilema beniniense*, *Aspilia africana*, *Chasmanthera dependens*, *Clerodendrum splendens*, *Colocasia esculentum*, *Desmodium adscendens*, *Dissotis rotundifolia*, *Gliricidia sepium*, *Grewia flavescens*, *Hippocratea indica*, *Holarrhena floribunda*, *Laportea aestuans*, *Lonchocarpus cyanescens*, *Manihot esculenta*, *Melochia corchorifolia*, *Morinda lucida*, *Momordica charantia*, *Mucuna pruriens*, *Musa paradisiaca*, *Newbouldia laevis*, *Senna occidentalis*, *Talinum triangulare*, *Triumfetta cordifolia* and *Vigna unguiculata*. Typical plantation

crops common in this region which might not have been identified on other sites include *Manihot esculenta* and *Musa paradisiaca*. *Talinum triangulare* (Water leave) is a cosmopolitan/naturalized weed, sometimes cultivated, edible and useful as ethnomedicine (Aja et al. 2010). Its presence suggests that this area has been disturbed. But widespread species in the tropics include *Mucuna pruriens*, *Vigna unguiculata* (Wild), *Hippocratea indica*. *Lonchocarpus cyanescens* (the Yoruba Indigo), *Newbouldia laevis*, and *Clerodendrum splendens*, as well as *Holarrhena floribunda*, *Morinda lucida*, *Clerodendrum splendens*, *Aneilema beniniense* in the rainforest, with *Colocasia esculentum* which is native to tropical Asia and South-West Pacific, listed as least concern according to IUCN with no major threats (Nguyen 2011). However, its existence on this site suggests invasive. *Dissotis rotundifolia* are often in damp places as well as *Triumfetta cordifolia*. *Melochia corchorifolia* is common in wet places and widespread in the tropics of the old world, *Cissampelos owariensis* is a twiner mainly in secondary growth in forest regions, while *Adenia venenata* is majorly found in Nigeria; suggesting that this area still maintains some original vegetation significance. But there are some identified savannah plant species which indicate the high intense of disturbance this site has been subjected to. These include *Grewia flavescens*, and *Chasmanthera dependens*, and similar to that are *Momordica charantia*, but *Aspilia africana* is common and widespread in the warmer part of the world.

4.6 Conclusions and recommendations

It could be deduced from the study that the floristic composition of all the three sites has been altered with significant differences from one site to the other. This can be attributed to the intense agricultural colonization and human activities on the sites in time past. However, the ASM activities have as well significantly influenced the floristic composition of the mined sites, its species richness, life form patterns, with occurrence of non-native plant species on the mined sites. Many of the differently identified species found on the control sites are native and significance (e.g. *Acanthus montanus* and *Icacina trichantha*), species found on Site 2 (e.g. *Capsicum frutescens* and *Crassocephalum crepidioides*) are due to human inference while the species on Site 1 shows both original and disturbed floristic composition (e.g. *Adenia venenata* and *Grewia flavescens*). In addition is the presence of *Ficus asperifolia* usually associated with gold found on the two mined sites but not on the control site. Though all the studied sites have been stressed; resulting in less number of species characterized for these sites compared to previous studies.

However, the mined sites had not only been stressed but had also been greatly disturbed. This can be traced to the on-going farming activities and ASM activities such as pollution, deforestation and exposure of the forest soils to direct sunlight. The stress decreases the biodiversity of the species while the disturbance increases its productivity. The washing and processing of the mined gold might have also influenced the substrate conditions of the mine sites, which act as an 'environmental sieve' especially for the groundwater. It is therefore necessary to develop effective approaches and policies that will curb illegal ASM activities within the south-west region of Nigeria. In doing this, it is also of importance to investigate its supply chains; this is because several nationalities are sometimes noticed illegally on the sites. The community (especially the youths that are used in the mining activities) need to be empowered to discourage this illegal source of income. Coupled with that is conservation and management measures that can enhance the sustainable development and stabilize the economy of this area, thereby discouraging the continuation of ASM mining and encourage adequate reclamation.

5. Characterizing landscape heterogeneity on gold post-mining sites⁴

5.1 Abstract

Gold mining in southwestern Nigeria is dominated by artisanal and small-scale mining (ASM). Despite the ASM induced landscape impacts and heavy contaminations, farming kept ongoing. To ascertain the sites' agricultural land-use potentials and safety, characterizing the landscape heterogeneity of the sites remains a fundamental requirement and timely important. However, this is poorly considered in several post-mining land-use studies. Here, we explore the efficiency of Electrical Resistivity Tomography (ERT) for characterizing the horizontal and vertical variations in the subsurface properties of two gold mining sites. Resistivity structure of the sites shows that ASM has greatly impaired the lithological properties of the site. We identified dug pit backfilled with muds, buried foreign substance and an unnoticeable inappropriate pit left uncovered. The results correspond with the soil textural analysis of the site. In case that allowing the sites for self-recovery is not feasible, we recommend organic manuring, deep-ploughing and top-soiling (if possible) along other necessary post-mining studies before agricultural use. Also, we advocate further use of other geophysical techniques on post-mining sites for studies such as identification of foreign substances, cavity, pits, hazardous materials, and determination of contaminants prior to its post land-use decisions.

Keywords: Artisanal small-scale mining (ASM), Post-mining land-use, 2D Electrical Resistivity Tomography (ERT), Soil lithology

5.2 Introduction

The unending global demands for mineral resources make mining increasingly unavoidable. Its activities subject the mining sites to immense disturbances, which differ based on differencing factors such as the type of mining, type of mineral, site conditions, technology, etc. Nigeria is endowed with over 34 solid minerals (Adesipo et al 2020c), mined in over 450 locations. One of

⁴ Submitted to Reclamation Science

Adesipo, A., Akande, B., Freese, D. Characterizing subsurface heterogeneity on gold post-mining sites. *Reclamation Science*, (Submitted manuscript).

these is gold, characterize by Artisanal and Small-scale Mining (ASM) in Southwestern Nigeria (Adeoye 2016; Adesipo et al. 2020b). The dominance of ASM over Large-Scale Mining (LSM) can be attributed to the ores quantity, locations, technological demands, access to markets, formalization requirements, and poor performance of the large-scale mining sector (Oramah et al. 2015). The ASM miners are illegal, inexperienced, erratic, unconcerned, poverty-driven, seasonal, and consistently increasing in numbers. The impacts of the ASM activities are enormous and are mostly on farmlands (Eludoyin et al. 2017; Adesipo et al. 2020c).

ASM entails diversion of water courses/sources, digging of pits and trenches (sometimes without signage and barricades within farmlands), drastic landscape disturbances, generates pollutants and contaminants. Also, to trap alluvial deposits, make the mining smooth and accumulate water for gold panning and mineral ore processing, miners use local digging tools such as shovels and hoe to build berms along stream channels. After the gold mining, the excavated waste spoil, piled up as heaps are left without adequate backfilling. These are later on levelled and used for cultivation after a while by the local farmers (Salami et al. 2003). It causes mixing and/or replacing the excavated sub-soils with the top-soils. Although the soils are agriculturally viable and typical for growing cash and food crops such as cocoa, kola, oil-palm, and plantain, its productivity is drastically declining, and this has been attributed to the ASM activities (Adesipo et al. 2020b). Reflections from previous studies on the sites (Salami et al. 2003; Oladipo et al. 2014; Adesipo et al. 2020c), and in-situ observations suggest that lithological variations in the subsurface properties of the sites is one of the identified factors that debilitates the sites agricultural land-use potentials. Spots dominated with excavated subsoil muds, which are high in clay content less supports plants growth compare to spots with natural topsoil. However, since farming remains the main source of livelihood of the community (Adesipo et al. 2020b), efforts to reinstate the farming potentials of these mining sites and guarantee safety is paramount and timely necessary, restore livelihood and contribute to the economy. A basic fundamental requirement to ascertain its agricultural land-use potentials is to characterize the sites landscape heterogeneity status. This can be preferably done using geophysical techniques. It is necessary for assurance of safety, detect hidden cavities, know the soil lithology variations, heterogeneity, detect foreign materials, and enhance decision-making process towards successful reclamation of the sites, e.g. top-soiling or organic manuring.

Electrical Resistivity Tomography (ERT) is one of the extensively used non-intrusive methods for imaging soil physical characteristics (Romero-Ruiz et al. 2018). It is non-destructive, reliable, timing, cost-effective, in-situ and provides continuous streams of information (both horizontal and vertical) which are unattainable in discrete sampling or invasive procedures. It has been employed in mapping soil contamination (Nai et al. 2019), detect tillage effects (Rossi et al. 2013), landslides (Falae et al. 2019), boreholes (Adeoti et al. 2017), ion transportation (Wehrer et al. 2016), etc. However, there are difficulties in connecting resistivity and specific soil conditions (Hermans et al. 2015; Alamry et al. 2017), this was attributed to its insufficient studies (Nai et al. 2019). Moreover, its use on post-mining site is poorly considered. In this study, we aim to explore the efficiency of 2D (ERT) for characterizing the horizontal and vertical variations in the subsurface properties of two gold mining sites in southwestern Nigeria.

5.3 Methodology

5.3.1 Experimental areas

The study areas are the gold mine sites in the known gold state of Osun states Nigeria. The state has lots of gold mine sites such as Igun-Ijesha (24 carats alluvial gold), Ijana Wasare (24 carats alluvial gold), Iperindo (18 carats alluvial gold), Isanlu (18 carats alluvial gold), Itagunmodi (18 carats alluvial gold), okutu-omo (18 carats alluvial gold), etc. Varied geomorphic units, drainage pattern and floristic composition (Adesipo et al. 2020b) also characterize these sites. The sites belong to the six classes of the Basement Complex rock, which are from slightly migmatized to nonmigmatized, metasedimentary, metasedimentary and metaigneous rock known as the Schist belt (Taiwo & Awomeso 2017). There are 11 identified Schist belt (Figure 15); the study sites belong to the Ife-Schist belt. Most of the gold mining sites are situated in the eastern region of the east Ifewara fault zone, which has quartzite, quartz schist and amphibole schist. Pyrite, galena, sphalerite, ilmenite, magnetite, pyrrhotite and minor chalcopyrite are list of ores the gold exists (Onyedim 2007).

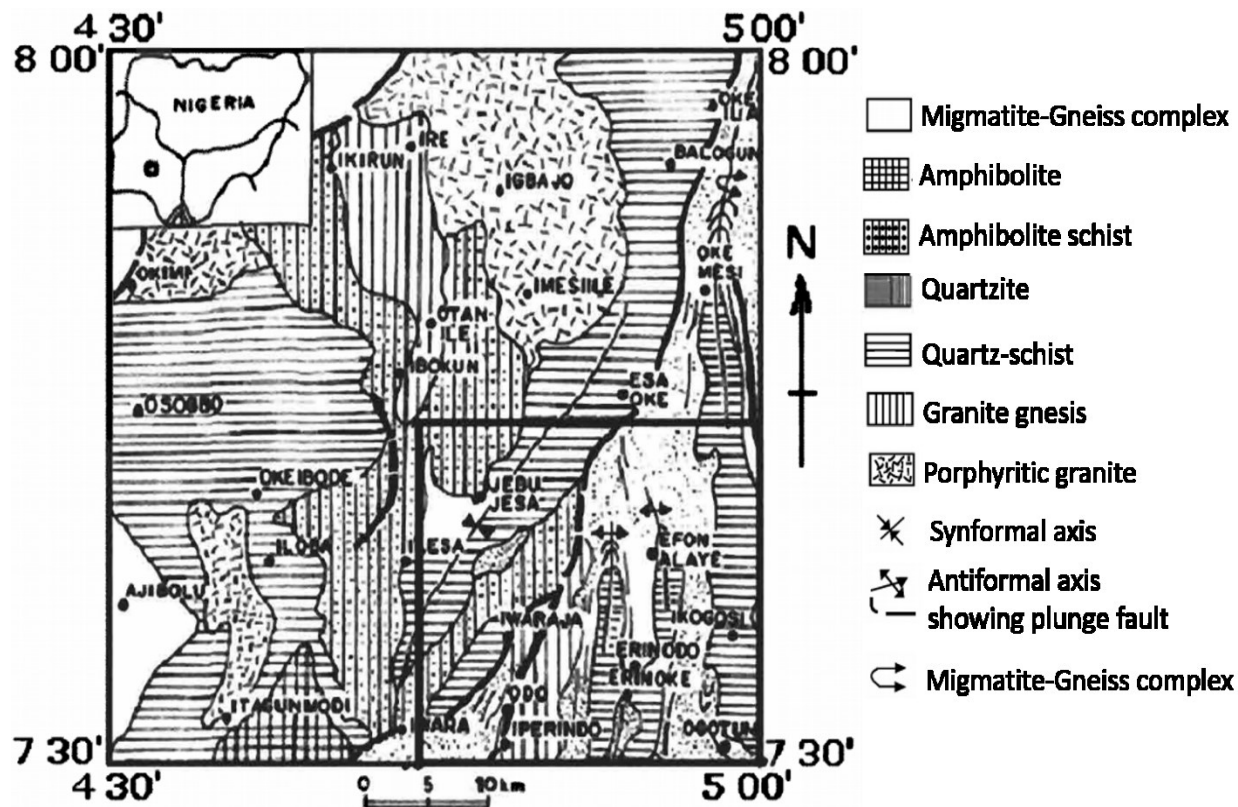


Figure 15: Geological map of the study areas (Source: Onyedim 2007).

Within the Ife-Schist belt, an abandoned mining site (Site 1 in Okutu-omo) and an active mining site (Site 2 in Itagunmodi) were considered for this study (Figure 16). Itagunmodi is occupied by degraded secondary lowland rainforest under regrowth with some relics of the original forest. While Okutu-Omo is depicted by several uncovered pits (about 1.5×1 m) with spoil heaps all around the site. They were purposefully selected as representative of the ongoing mining and farming activities in this region. Please, see previous studies (Salami et al. 2003; Oladipo et al. 2014; Adesipo et al. 2020b; Adesipo et al. 2020c) for further details. The sites landscapes are punctuated with projecting hills of 366 – 394 m above sea level. The soils are tropical ferruginous red soils, generally deep, and ranges from deep clayed soil formed from low smooth hill crest and upper slopes, as well as sandier hill wash soils on lower slopes (Adeoye 2016). Most significance for this region is the well-drained clayed soils of the hill crest and slopes which are characterized for growing cash crops such as Cocoa (*Theobroma cacao*) typical of these regions. The textural class is loamy; 58 % sand, 10 % clay and 32 % silt, but has been impaired due to ASM (Adesipo et al. 2020c).

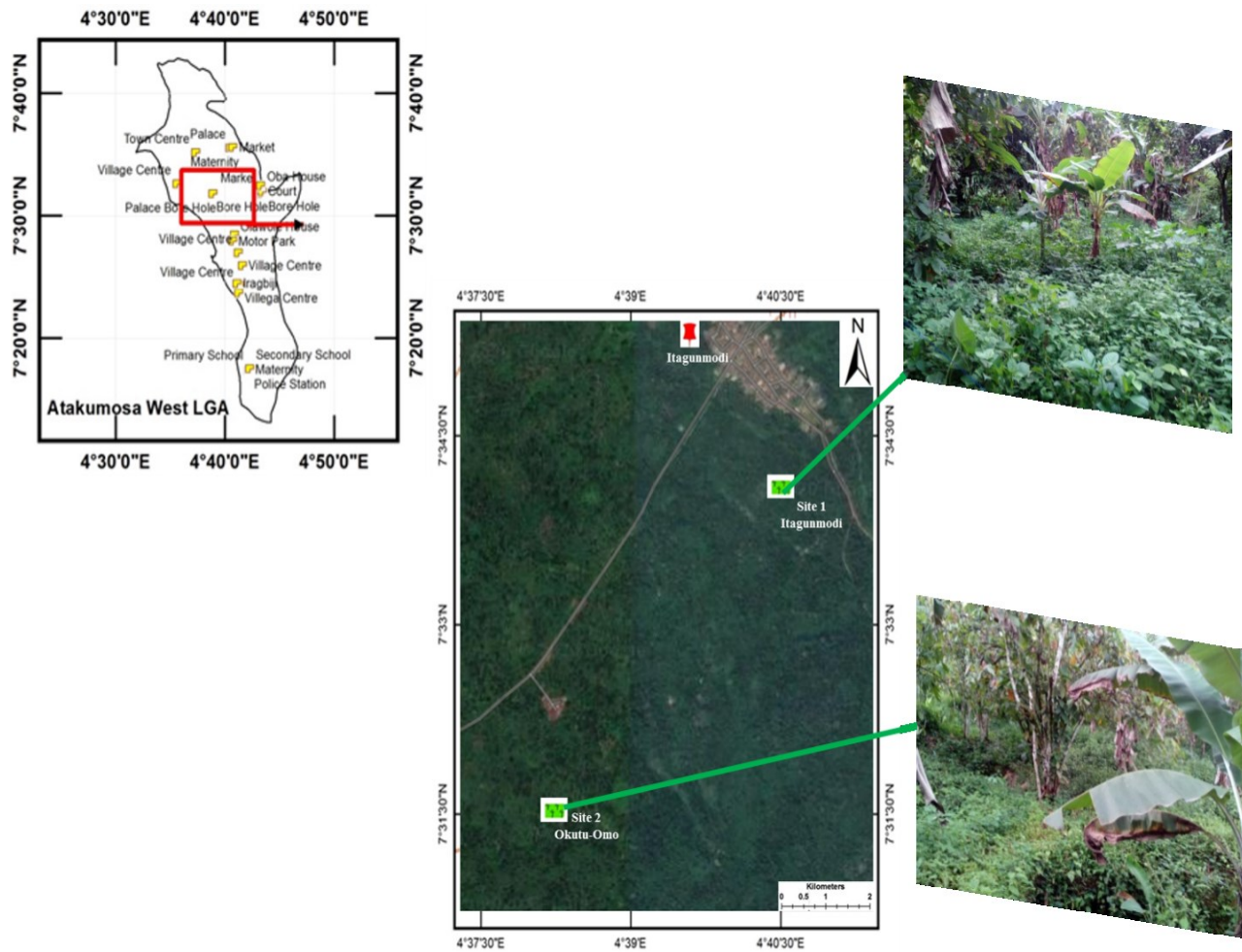


Figure 16: Experimental areas, showing the geophysical data acquisition layouts and directions.

5.3.2 Experimental design

Following the site preparation (Adesipo et al. 2020b), the layout for ERT data acquisition and path directions for the geophysical survey are presented in Figure 17. On Site 1, a wider experimental plot 20×20 m was mapped out, while 10×10 m was investigated on Site 2. The differences in size was because of several uncovered pits and excavated subsoil piled-up as spoil heaps in several locations of Site 2, whereby it was not possible to have a consistent 20 m straight line. Two traverses were established on each site with orientations from the ends (i.e. NS-EW).

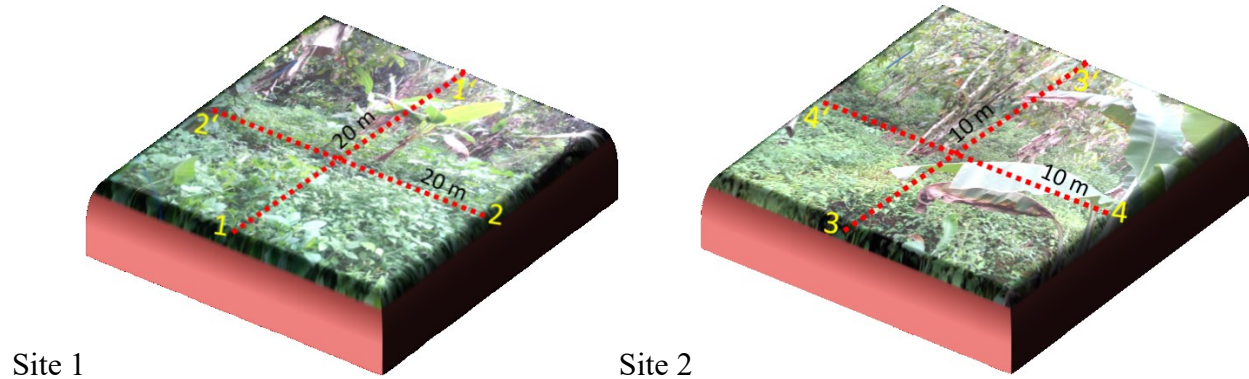


Figure 17: Data acquisition and orientation of the ERT survey.

5.3.3 Electrical Resistivity Tomography (ERT)

Two dimensional (2D) ERT was employed for the electrical resistivity survey with the dipole-dipole profiling array. The array was adopted at an electrode spacing of 1 m and the apparent resistivity measurements were ensured using ABEM SAS 300 C Terrameter Unit. Dipole-dipole profiling array was preferably chosen as a practical, economic compromise between accuracy, (especially its high horizontal resolution), time consumption, and the cost of survey (Samouelian et al. 2005; Loke et al. 2013). Moreover, there was minimal background noise, since it was on a farmland and the maximum ‘n’ value was below 6 ($n = 1 - 5$). As a rule of thumb, resistivity data was plotted using pseudosection contouring method and profile plot. This enables the elimination of error data, however, observable error data was very few, moreover, avoidable noise and interferences (e.g. from external materials such as phones, metallic objects, etc.), which might make important data difficult to see were also averted while surveying. The resistivity dataset was inverted using DIPPRO™ Software, and the RMS errors for the four traverses were below 2 %.

5.3.4 Soil sampling and analysis

In line with the ERT survey and visual observations on the sites, laboratory textural analysis of the sites soil samples was performed to support affirmations by the ERT survey. At two sampling depths (0–20 and 20–40 cm) and in replicates, soil samples were randomly collected at different locations on each site. The soil samples were mixed and homogenized. In the laboratory, the samples were air-dried to a constant weight, thoroughly mixed and sieved for homogeneity and removal of roots, stones and other foreign materials. The soil particle size was determined using the hydrometer method (Bouyoucos 1962) after dispersion with Calgon™.

5.4 Results

The 2D pseudosection subsurface image obtained from the inversion of the dipole-dipole resistivity dataset for four traverse orientations are presented in Figure 18 and 19. The resistivity structures show the lateral and lithological variations with different colours for easy characterization as delineated by the 2D images. The investigating depth was approximately two m, since it is of interest and falls within the plant root depth.

5.4.1 Mine site 1 (Okutu-Omo)

Traverse 1 (TR 1) and Traverse 2 (TR 2) has resistivity range of 78 – 306 Ωm and 88 – 180 Ωm respectively (Figure 18). From the resistivity structure, lateral variation within the first 3 m along TR 1 shows higher resistivity range than from 3 – 5 m, with similar resistivity down the profile. From 5 – 8.3 m, lower range of resistivity was obtained; 78.3 – 96.9 Ωm , which goes deeper into the subsoil. However, from 8.5 – 11 m, a parabolic high range of resistivity values were obtained within the subsoil 166 – 306 Ωm while the topsoil was 98 – 123 Ωm . Beyond 11 m, similar range of resistivity was observed till 14.5 m, but between 14.5 – 16.8 m, lower range of resistivity was obtained and towards the end of the traverse, higher resistivity could be observed. With the resistivity structure for TR 2 (Figure 18b), the resistivity in the subsoil is mostly higher than the topsoil. High range of resistivity was observed within the first 3 m, afterwards were lower resistivity. But between 4 – 9.8 m, significant high resistivity (141 – 180 Ωm) was observed in the subsoil than the top soil 99.8 – 129 Ωm . This is same for 11 – 13.7 m and 15 – 20 m. However, a very low resistivity of 88 Ωm was obtained within 14 – 15 m, which is significantly low compare to other parts of the traverse. And beyond 17 m, the high resistivity was observed from the topsoil down the subsoil unlike other part of the traverse.

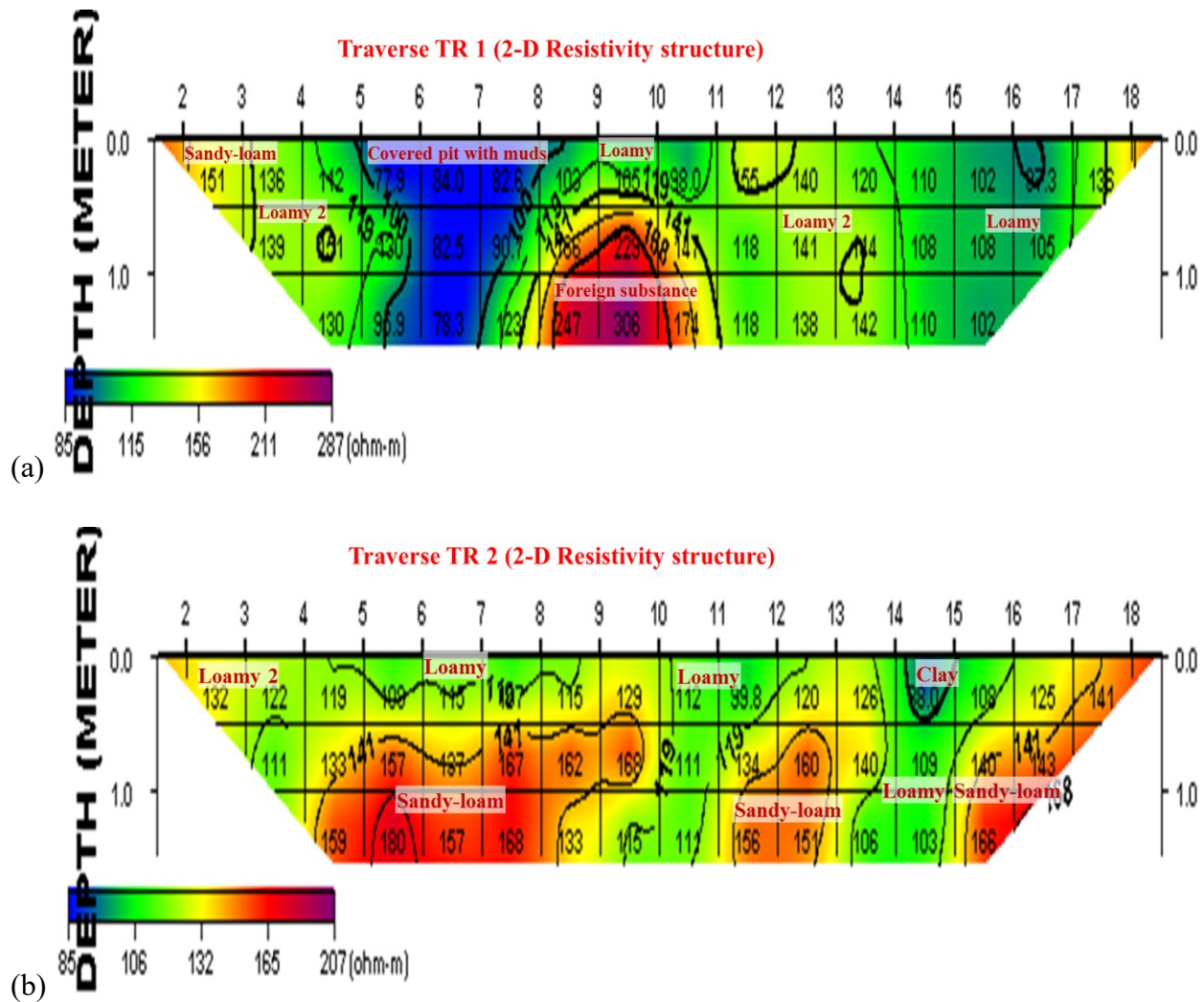


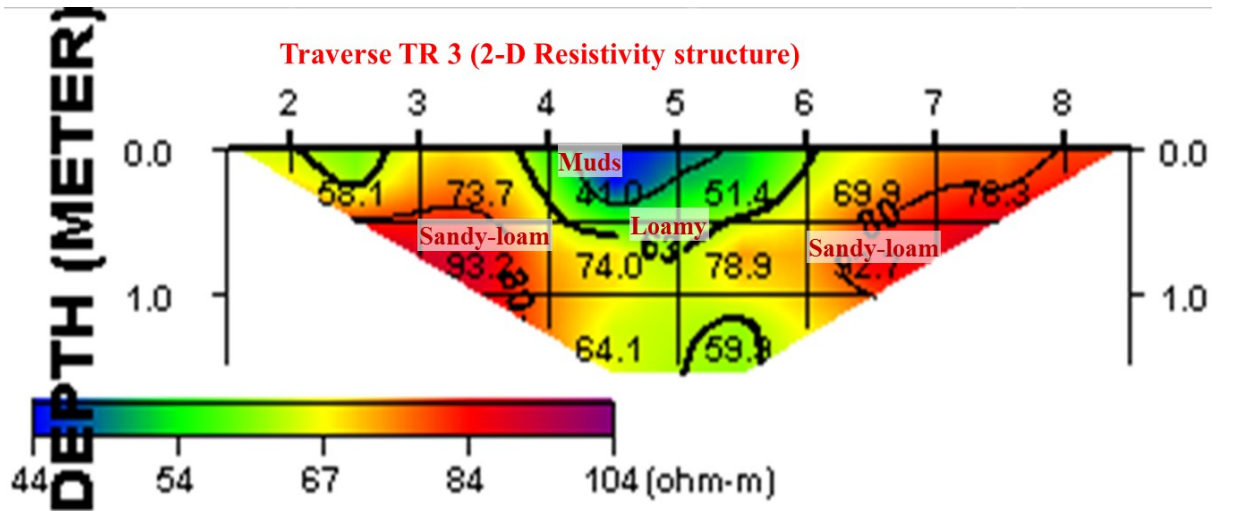
Figure 18: 2D resistivity structure of Traverse line 1 (a) and 2 (b).

5.4.2 Mine site 2 (Itagunmodi)

In Itagunmodi, Traverse 3 (TR 3) and Traverse 4 (TR 4) show resistivity range of 41 – 94 Ω m and 36 – 131 Ω m, respectively (Figure 19). TR 3 (Figure 19a) comparatively shows lower resistivity in the topsoil than the subsoil. However, there is a significantly low resistivity (41 Ω m) observed between 4.4 – 5.5 m at the topsoil. Within the subsoil (same 4.4 – 5.5 m), average resistivity values (51 – 78 Ω m) could be observed, which extend down the profile. The subsoil generally shows high resistivity (78 – 94 Ω m) except 6.7 – 10 m where higher resistivity values were observed from the topsoil extending down the profile. On the other hand, TR 4 shows different resistivity variations (Figure 19b), there is no observable variation between the topsoil and subsoil unlike other traverse. Between 2 – 4 m, resistivity range of 65 – 70 Ω m was observed, whereas from 4 – 6 m, high resistivity values; 92 – 131 Ω m was obtained down the soil profile. However, from 6.4 – 10 m, the

resistivity decreases along the traverse, with a noticeable difference from 7.2 – 10 m, having a resistivity range as low as 36 Ω m.

(a)



(b)

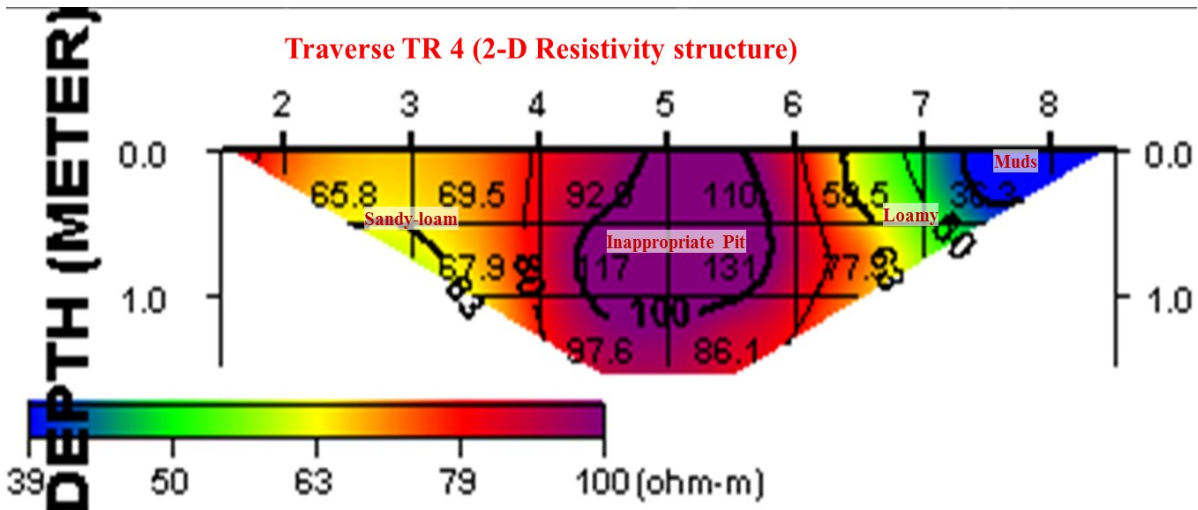


Figure 19: 2D Dipole-dipole pseudo-section of Traverse lines 3 (a) and 4 (b).

5.4.3 Soil physicochemical properties

The obtained soil textural analysis for the two sampling depth on site 1 and 2 are presented in Figure 20 below. Percentage sand and silt decreases down the soil profile on both sites unlike clay. Although a greater percentage of clay was observed in the subsoil of the two mine sites, however, mine Site 2 has higher clay content than mine Site 1. The percentage of silt on Site 1 is greater than Site 2, similarly is the percentage content of sand. This shows that Site 2 is characterized by higher clay content than the textural class obtained in Site 1.

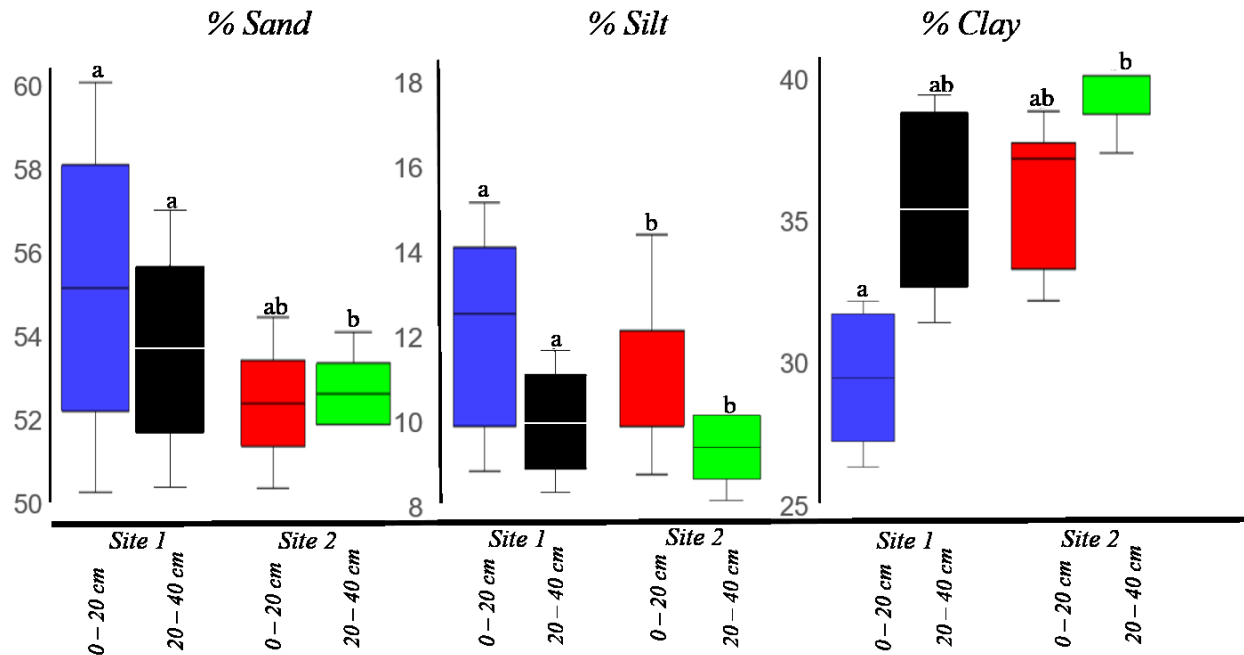


Figure 20: Box plot of the soil textural class (sand, silt, and clay) on Site 1 (Blue and Black) and Site 2 (Red and Green); representing 0 – 20 cm and 20 – 40 cm respectively.

5.5 Discussion

The high range of resistivity values on mine site 1 with both TR 1 and 2 shows a high sand content than clay, which dominates Site 2. This correlates with the obtained laboratory textural analysis. In comparison to the sites textural class in 2009 (Olabiya et al. 2009), an average 58 % sand, 10 % clay and 32 % silt was recorded for the region. There has been drastic loss of silt from the sites, with increasing clay content. This is more evident on Site 2 and can be attributed to its ongoing intense ASM activities. Apart from the ASM activities, the textural variations can also be attributed to the landscape orientation. This was more evident on Site 1 with TR 1 and 2. TR 2 was surveyed along the slope, suggesting that large sand content might have been lost on the sites due to the heavy rainfall (1400 mm) typical for this region. However, on Site 2, the survey was at a low elevation, expecting to have high sand content, which might have been washed down the slope with erosion, but its clay content is rather high. This shows that the ASM activities have greater influence on the textural class. Many of the subsoils have been excavated, which have now replaced the topsoil. On the other hand, the level of contamination (Olhoeft 1985; Yoon & Park 2001; Berube et al. 2017) could also influence differences in resistivity range. Related studies on the soil contaminants (Adesipo et al 2020) shows that Site 2 is heavily contaminated. Although the applied current in

this study and its multiple pollutants (Adesipo et al. 2020c) makes this assumption difficult, however, application of complex resistivity (Grimm et al. 2005; Nai et al. 2019) could explain better.

On mine Site 1, higher lateral variations could be observed along TR 1, which extend from the topsoil down to the subsoil. The blue colour between 5 – 8.5 m showed that a backfilled pit with muds by the ASM miners after mining. While the high resistivity within the subsoil from 8 – 11 m shows the presence of a foreign substance. Along TR 2, the lithological differences could be better observed (Figure 21). The topsoil has lower resistivity than the subsoil and this is typical of most soil (Adeoti et al. 2016; Aigbedion et al. 2019) with distinctive lithological layers. Areas where extended similar resistivity were obtained down the soil profile are areas affected by the ASM activities. Since Site 1 is an abandoned mining site, it shows a better recovery potential with significant lithological level. Nevertheless, the entire sites might need further examination to ascertain safety, especially with the identification of foreign substances.

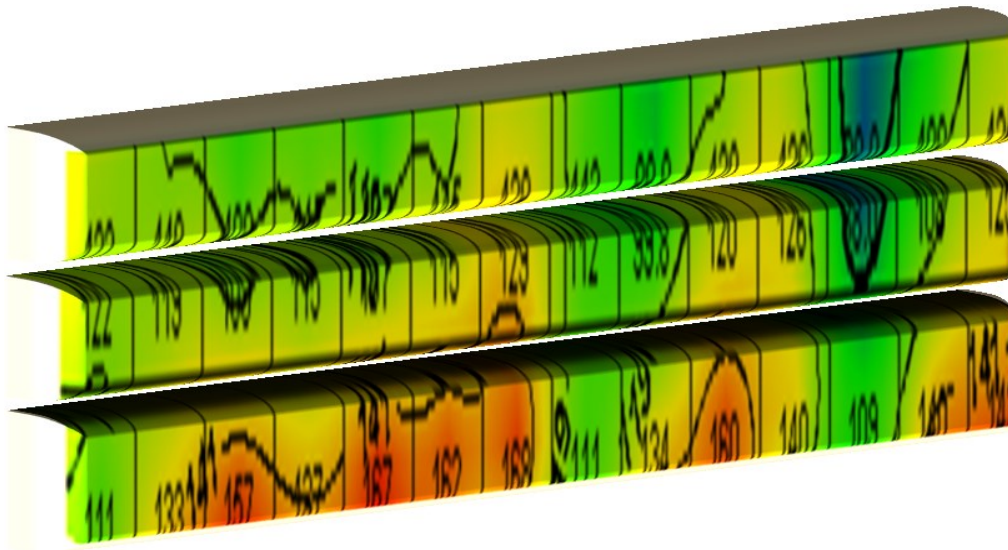


Figure 21:Lithological differences along Traverse (TR) 2.

On mine site 2, the differences in the obtained resistivity show that the site has been greatly disturbed. Most parts of the resistivity structure show lateral difference with limited lithological layer variations. This confirms its high level of ASM disturbances. Within 0.4 m of the soil profile from 4 – 5.5 m along TR 3, the obtained low resistivity shows high clay content from muds overlaying the spot. This suggests that the spot might have been dug, backfilled with muds and

abandoned. This is common on areas where the miners wrongly assume the presence of gold, since the technological knowhow is very poor. TR 4 also showed high state of ASM disturbance. It shows lateral changes in resistivity almost throughout the traverse. This suggests the site might have been heavily dug, backfilled and disturbed. Prior identification of the observed inappropriate pit between 4 – 6 m with significantly high resistivity was difficult. This limits the safety assurance of the sites and it requires further investigation.

Related studies by Oramah et al. (2015) highlighted that the miners are incognizant of the impacts their activities cause, with wrong perception that their actions are merely temporal, and could be remedied by backfilling which is mostly left undone. Similar occurrence could be inferred on the sites, backfilling by the ASM miners might be inefficient, also, is the possibility of backfilling the pits with some foreign materials such as observed with TR 1. Self-recovery of mining site is very crucial in reclamation efforts (Higgs et al. 2018). Observations from Site 1, which was formerly subjected to heavy mining and abandoned show self-rehabilitation process due to its improved subsurface properties compare to Site 2. This is similar to previous studies (Adesipo et al. 2020b) with the floristic association on the site.

5.6 Conclusion

ERT is an efficient geophysical technique, applicable in characterising subsurface properties of post-mining sites. This study showed that the mining sites show high lithological variations, presence of foreign substance and inappropriate uncovered pit. This limits the sites agricultural land-use potentials. However, ploughing and top-soiling is recommended, else, the sites can be left for some decades for self-recovery. On the other hand, application of organic manure rather suggests effective than topsoiling, this is due to its large-scale demand and limited resources. In addition, use of other geophysics techniques such as ground penetrating radar (GPR), complex resistivity (CR), also with deeper penetrating depth is necessary. The investigating depth in this study was about 2 m, which is within the plant root depth; higher depth might give more information where necessary. Aside ascertaining its potential agricultural land-use potentials, this is also important to ensure safety. However, formalizing ASM in Nigeria is necessary. Similar consideration was discussed in the 2020 DRC Mining Week of the Mining Review Africa. In a haze, we recommend the use of geophysics on post-mining site prior to consideration and decision of its post land-use.

6. Identification of tropical native high-accumulating plant species for phytoremediation⁵

6.1 Abstract

Heavy metal contaminants from gold mine sites in southwest Nigeria are posing a high tendency of entry to the food chain. To avert the risk, phytoremediation of the sites is paramount. However, despite recent research advancements in phytoremediation and identification of over 400 hyperaccumulators plant species for Cd, As, Ni, Zn, and Mn, elements such as Pb, Cu, Cr, Hg are largely limited, moreover, less is known of tropical species. This study aims to identify native high-accumulating plants with a high level of heavy metals tolerance growing on three sites an abandoned gold mining site (Site 1); an active gold mining site (Site 2), and an undisturbed vegetation site (Control site) in southwestern Nigeria. Soil properties; pH, textural class, electrical conductivity, available P, percentage Total Nitrogen (TN), Organic Carbon (OC) and Organic Matter (OM), as well as total Pb, Cd, Fe, and Cu concentration, were analyzed at two sampling depths (0-20 and 20-40 cm). The accumulation and enrichment potential of Pb, Cd, Fe, and Cu in *Acanthus montanus*, *Chromolaena odorata*, *Crinum jagus*, *Melanthera scandens*, *Melochia corchorifolia*, *Palisota ambigua*, *Pteris togoensis*, *Musa sapientum*, and *Theobroma cacao*, were determined. High clay content, low nutrients and elevated metal contamination characterized the mine sites soils, with significant differences indicated by PERMANOVA results and confirmed by nDMS analysis. All plants showed elevated metal content and high accumulating potential of Pb with high Fe. None of the plants meets the threshold criteria for hyperaccumulators, but they show high-accumulating potential for phytoremediation. *Crinum jagus* has the highest accumulation factor of 8.71, 37.47, 1.08, and 29.38 for Pb, Cd, Fe, and Cu, respectively. It is a novel recommendable plant species for phytoremediation and can be employed both in the tropical regions and in other climatic adaptable regions around the globe.

⁵ Published in Journal of American Society of Mining and Reclamation.
Adesipo, A. A., Freese, D., Awotoye, O.O., Salami, A. T., Oyedele, D. J. (2020). Identification of tropical native high-accumulating plant species for phytoremediation. *Journal of American Society of Mining and Reclamation*, 9(1), 1-28. DOI: <http://dx.doi.org/10.21000/JASMR20010001>

Keywords: Hyperaccumulators, Phytoremediation, *Crinum jagus*, Tropical regions, Gold mining, Artisanal miners.

6.2 Introduction

Although the benefits of mining are known, it induces several impacts on the environment (Ericsson 1991; Kuter 2013). Examples of such impacts include contamination and huge loss of viable agricultural lands to mining. Contrary to most developed countries, both the national and international stakeholders involved in mining in several developing countries usually show little or no concern towards appropriate remediation and sustainable management of the mine sites (Festin et al. 2019). However, the increasing demand for agriculture in highly populated countries, like Nigeria, calls for restoration of the agricultural sites that are lost to mining. According to the Nigeria Mining Journal 2006, Nigeria mines over thirty-four solid minerals at more than 450 locations. In southwest Nigeria, gold mining dates back to 1942. However, due to the ongoing oil boom phase in the country, national interest in the mining has greatly declined. Recently, local artisanal miners (ASM) have invaded these mine areas (Makinde et al. 2013). Generally, mining and processing of the gold ores enrich the surrounding areas with its associated contaminants such as Pb, Cu, Cd, Fe, Hg, As, Zn, etc. (LaPerriere et al. 1985; Fashola et al. 2016; Wasiu et al. 2016; Petelka et al. 2019). After the gold mining, spoil heaps (mixture of overburden soil and rock) with its associated gold waste contaminants are after some abandoned period used for cultivation by the local farmers. This is because most of the mine sites are around farmlands (Eludoyin et al. 2017). This region is agriculture viable, typical for growing both cash and food crops, such as cocoa and plantain (Adesipo et al. 2020b), and it's the main source of living of the local communities. The severe impacts characterizing these ASM activities have been highlighted (Oramah et al. 2015; Adeoye 2016), but a major concern is connected with the transfer of the heavy metal contaminants (either directly or indirectly) into the trophic chain. Its entry into the food chain and direct ingestion has been recorded in the northern region of Nigeria (Lo et al. 2012; Plumlee et al. 2013; Bartrem et al. 2014), and efforts to avert similar occurrence are therefore necessary.

Previous studies within the study areas highlighted environmental impacts of the mining activities on the vegetation and soil (Salami et al. 2003; Adeoye 2016), ecology (Oladipo et al. 2014), human health (Olujimi et al. 2015; Awomeso et al. 2017), and its floristic association (Adesipo et al. 2020). Results showed elevated heavy metals such as Pb, Cu, Cd, Fe, Hg, As, and Zn on the mine

sites compared to control sites. Some of the contaminant concentrations are higher than the average limits for agricultural soils and are present in the soil and in the surrounding water bodies (Makinde et al. 2013; Wasiu et al. 2016) as well as in both leaves and fruits of plant tissues growing on the sites (Salami et al. 2003). For Cd, Pb, and Fe, which two authors similarly analysed in 2003 (Salami et al. 2003) and 2014 (Oladipo et al. 2014) on Itaganmodi, there has been an increase of 54 %, 1278 %, and 116 %, respectively. This reveals that continuous exploitation is further degrading the sites, increasing their acidity, and hence the solubility of the heavy metals. Therefore, immediate attention to alleviate the associated risks is paramount, in addition, enhancing food security and serving as a basis for other contaminated sites, both nationally and internationally. For practical efforts towards amelioration, phytoremediation has been suggested as the preferable remediation technique. It was hypothesized that understanding the floristic association of the sites is necessary, the characterization and classification of the contaminants based on the chemical profile, age of contamination, and efficient high-accumulating native plants growing on the sites. This is important because despite the increasing knowledge in phytoremediation around the world (Mao et al. 2015), with over 400 experimentally confirmed hyperaccumulator species for elements such as Cd, As, Ni, Zn, and Mn, other elements such as Pb, Cu, Cr, Hg are largely limited (van der Ent et al. 2013). In addition, research on efficient hyperaccumulating species within the tropical region is largely limited. Moreover, the threshold criteria for defining hyperaccumulators need critical review, some of which were highlighted by (van der Ent et al. 2013). In lieu of that, the aim of the present study is to identify native high-accumulating plant species with a high level of tolerance that are growing on the sites that can be employed for phytoremediation of multi-metal(loid) contaminated soils. This is hypothesized to help obtain appropriate native plant seed mixes for future remediation purposes.

6.3 Method

6.3.1 Experimental areas and design

The experimental areas are constituted of three main sites; an abandoned mining site (Site 1), an active mining site (Site 2), and the control site (or reference site), which is an undisturbed vegetation site (Table 9). The areas belong to the Ife-Ilesha schist belts; it is a known source of both alluvial and primary gold-field deposits, with a historical gold mining traceable back to 1942. It is situated in the lowland rainforest vegetation zone (Salami et al. 2003); mean annual rainfall

of 1400 mm and temperature range of 23°C – 31°C. A previous study within the sites shows that the soil textural class is classified loamy (58 % sand, 10 % clay, and 32 % silt), with an average pH of 4.5 (Olabiyi et al. 2009).

Table 9: Description of the experimental areas

No	Site	Description	Situated	Location
1	Site 1	Abandoned mining site	Okutu-Omo	7° 30' 30"N, 4° 38'15"E
2	Site 2	An active mining site	Itangunmodi	7°31'30"N, 4°39'03"E
3	Control	Undisturbed vegetation site	Igila	7°34'56"N, 4°39'50"E

Based on reconnaissance surveys, the three experimental sites were purposefully selected as representatives of the ongoing mining and farming activities within the region. Site 1 is occupied by degraded secondary lowland rainforest under regrowth with some relics of the original forest. Several uncovered pits (about 1.5 × 1 m) depict Site 2, with spoil heaps all around the site. However, the control site is an undisturbed vegetation site with a cocoa plantation; located about 7 kilometres from the mined sites, but within the same vegetation zone. On each of the three sites, experimental sample plots of 10 × 10 m were mapped out in duplicates; their GPS coordinates were recorded accordingly and the sites were barricaded from potential invaders.

6.3.2 Soil sampling and analysis

Soil samples were randomly collected at two sampling depths (0–20 and 20–40 cm) from each site to obtain a representative sample. The samples were mixed and homogenized, and transported to the laboratory in labelled polythene plastic bags. In the laboratory, soil samples were air-dried at ambient temperature to a constant weight, then thoroughly mixed and sieved for homogeneity in order to remove foreign materials such as stones and roots. To determine the soil particle size, the hydrometer method (Bouyoucos 1962) was used for the soil particle size analysis after dispersion with Calgon™. Soil pH was determined in water and 0.01 M CaCl₂ extracts using glass electrode. Standard tests were employed to measure the electrical conductivity (EC) of extracts from the soil paste using conductivity meter, total nitrogen (TN), organic carbon (OC), and organic matter (Walkley and Black 1934; Bremner and Keeney 1966). Available P was extracted using the Bray I method (Bray and Kurtz 1945). For heavy metal analysis, soil samples were first extracted using

0.1 M HCl and the total concentration of Pb, Cd, Fe, and Cu were determined using Atomic Adsorption Spectrometer (AAAnalyst 400).

6.3.3 Plants sampling and analysis

Nine plant species were selected for assessment of their total metal accumulation (mg/kg) of Pb, Cd, Fe, and Cu (Table 10). However, seven species were considered for the identification of their phytoremediation and accumulating efficiency. The plants were chosen based on previous related studies (Salami et al. 2003), floristic association (Adesipo et al. 2020b), ecological and economic significance, interest in phytoremediation, and adaptability to the environment.

Table 10: Selected plants species from the three considered mine sites

Plant	Local name	Family	Habit	Sites		
				Site 1	Site 2	Control
<i>Theobroma cacao</i> *	Cocoa	Sterculiaceae	Tree	✓	✓	✓
<i>Musa sapientum</i> *	Banana	Musaceae	Herb	✓	✓	✓
<i>Chromolaena odorata</i>	Siam weed	Asteraceae	Herb	✓	✓	✓
<i>Melanthera scandens</i>	Black anther	Asteraceae	Herb	✓	✓	✓
<i>Melochia corchorifolia</i>	Chocolate weed	Malvaceae	Herb	✓	✗	✗
<i>Palisota ambigua</i>	Flowering plant	Commelinaceae	Herb	✗	✓	✗
<i>Pteris togoensis</i>	Ferns	Pteridaceae	Fern	✗	✓	✗
<i>Acanthus montanus</i>	Mountain thistle	Acanthaceae	Herb	✗	✗	✓
<i>Crinum jagus</i>	Giant lilly	Amaryllidaceae	Herb	✗	✗	✓

*These are economic plants; only parts of the plants were investigated for heavy metal content.

The plant sampling was carefully done just after sunrise to ensure the activeness and freshness of the plants for accurate measurements. The shoot (both the leaves and stem) and root of each plant were collected, except *Musa sapientum* and *Theobroma cacao*. These two species are economic plants, purposefully grown, and are of interest to the local farmers. Moreover, they have complex root systems. Therefore, only parts of the shoot i.e. the beans (both pods and beans inside) and leaves were collected to know the level of contamination. The plant samples were thoroughly washed, placed in bags, and oven-dried (60°C) to constant weight. Dried plant tissues were pulverized to powder for metal concentration analysis. Samples were digested (acid digestion using concentrated H₂SO₄), and the total concentrations of Pb, Cd, Fe, and Cu were determined using Atomic Adsorption Spectrometer (AAAnalyst 400).

6.3.4 Data analysis

To analyse the obtained data, a statistical package of Plymouth Routines in Multivariate Ecological Research (PRIMER-E) was employed. The significance of difference among the study sites was analyzed using PERMANOVA (Permutational multivariate analysis of variance) and pairwise comparison between sites (Anderson et al. 2008b). The soil physico-chemical properties data were log-transformed ($\text{Log}(X+1)$) to improve the homogeneity of variances. A one-factorial Permanova design using Bray-Curtis distance measure and 9999 permutations with the site as a fixed factor for each site at 0.05 significant level was used to test for the significant differences of the composition of each site. In addition, a Non-Metric Multi-Dimensional scaling (nMDS) based on Bray-Curtis distance measure (Oksanen 2015) was created to produce a 2D representation of the composition. The goodness of fit of the nDMS results was evaluated with a stress value.

6.3.5 Bioconcentration, translocation, and accumulation factors

For the determination of the phytoremediation potentials, only the total metal concentrations in the soil samples from the rooting zone (0–20 cm) were employed for the calculations. Bioaccumulation factor (BCF) (Equation 1) was expressed as the ratio of the obtained total metal concentration in the roots to the soil (Yoon et al. 2006). It shows the plant's potential to take up, transport, and accumulate the metals in the shoots (McGrath & Zhao 2003; Wang et al. 2009). Translocation factor (TF) of each considered metal in each plant was estimated as the ratio of the metal concentration in the shoots to that in the roots (Zu et al. 2005), as shown in Equation 2. Plants with BCF and TF values greater than one (i.e., BCF and TF > 1) show the potential to be used for phytoextraction. Plants with BCF values greater than one and TF less than one (i.e., BCF > 1 and TF < 1) show the potential to be used for phytostabilization (Yoon et al. 2006). Since the main interest is the accumulating efficiency of the plants, the accumulation factor (AF) (Equation 3) expressed as the ratio of metals in the plant shoots (i.e., harvestable part) to the concentration in the soil was also considered (Marrugo-Negrete et al. 2016). In this paper, high accumulators are defined as plants with AF and TF values greater than one (i.e., AF and TF > 1).

$$\text{BioaccumulationFactor } BCF = \frac{\text{Totalmetalcontent}\in\text{root}}{\text{Totalmetalcontent}\in\text{soil}} \quad \text{Equation 1}$$

$$\text{TranslocationFactor } TF = \frac{\text{Totalmetalcontent}\in\text{shoot}}{\text{Totalmetalcontent}\in\text{root}} \quad \text{Equation 2}$$

$$\text{AccumulationFactor } AF = \frac{\text{Totalmetalcontent}\in\text{shoot}}{\text{Totalmetalcontent}\in\text{soil}} \quad \text{Equation 3}$$

6.4 Results

6.4.1 Soil physicochemical properties

The physical and chemical properties for the three sites are presented in Table 11. At each site, pH (both H₂O and CaCl₂) decreases with depth in the soil profile, ranging from slightly acidic (6.30) to acidic (4.30). The control site is more acidic followed by mine Site 1, while mine Site 2 showed the greatest pH values. Similarly, the percentage organic matter (OM) decreases down the soil profile, with the greatest values (2.21 %) on the control site and the least value (1.20 %) obtained on the mined sites. The electrical conductivity (EC) also decreases down the profile on the mined sites but vice versa on the control site. However, the topsoil of mine Site 2 showed an extraordinarily high EC of over 65 % higher than other sites. While the TN percent was greater on mine Site 1 (1.015 %) but TN was the same on both the control Site and mine Site 2 (0.945 %). On the other hand, available P was higher in the subsoil on both the control Site and mine Site 2, but vice versa on mine Site 1. The least available P (3.34 ppm) was obtained on the control site and the greatest (5.54 ppm) on Site 2. Percentage clay on the three considered sites increases down the soil profile (Figure 22). Nevertheless, a greater percentage of clay was observed in the subsoil of the mine sites (i.e., Site 1 and Site 2) compare to the control Site. Site 2 has the greatest clay content on the topsoil while the control site has the greatest percentage silt.

Table 11: Mean values (n=3) for the physicochemical properties of the three sites.

Sites	pH (H ₂ O)	pH (CaCl ₂)	EC (mSm ⁻¹)	% TN	% OC	% OM	P (ppm)
Site 1; 0-20 cm	5.50	5.03	23.70	1.015	1.25	2.15	5.03
Site 1; 20-40 cm	5.37	4.80	17.12	1.015	0.70	1.20	5.26
Site 2; 0-20 cm	6.30	5.83	71.50	0.945	1.05	1.81	5.54
Site 2; 20-40 cm	6.00	5.70	24.70	0.945	0.70	1.20	4.35
Control; 0-20 cm	4.60	4.60	18.46	0.945	1.29	2.21	3.34
Control; 20-40 cm	4.30	4.30	27.00	0.945	0.86	1.48	4.64

EC, TN, OC, OM and P represent electrical conductivity, total nitrogen, organic carbon, organic matter, and available P, respectively.

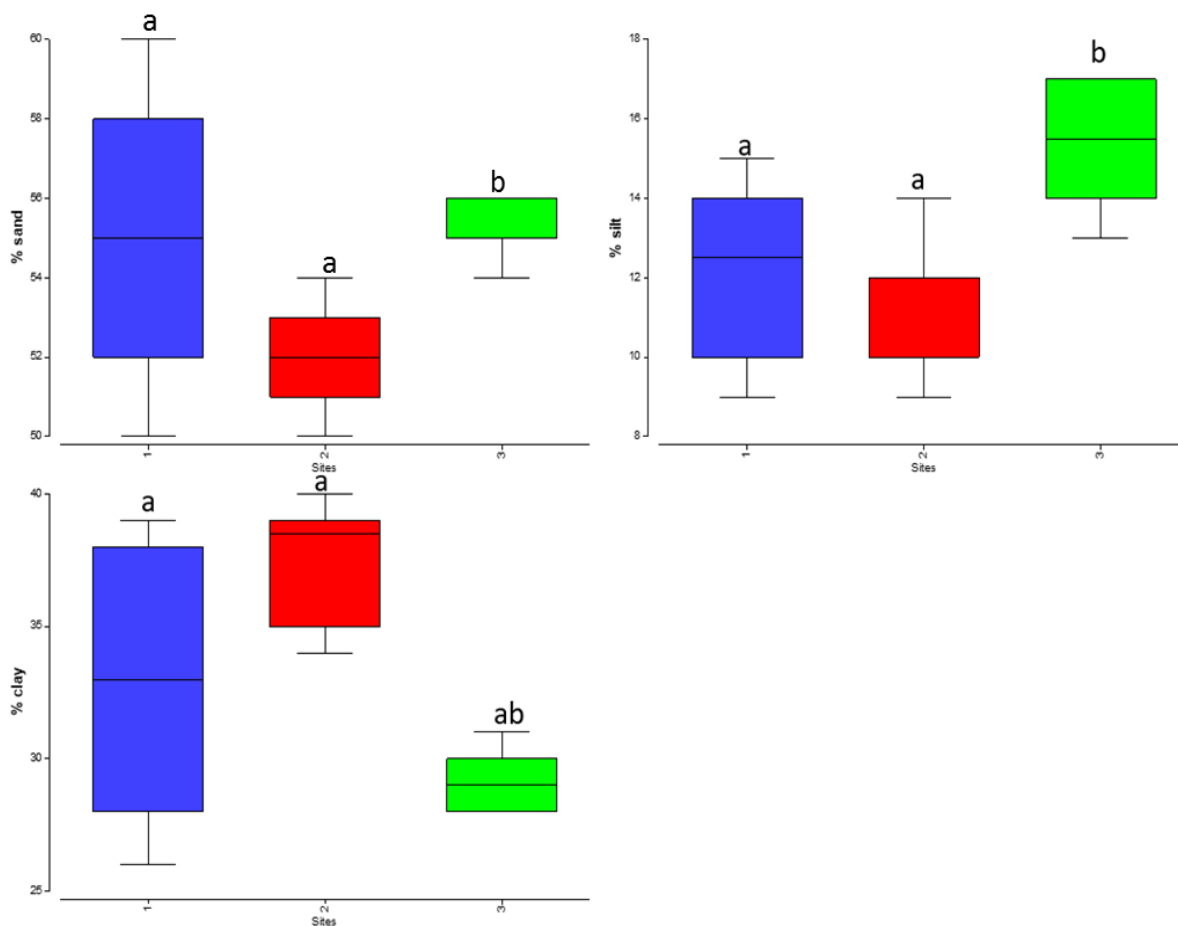


Figure 22: Box plot of the soil textural class (sand, silt, and clay) on Site 1 (Blue), Site 2 (Red), and the control site (green). Different letters indicate significant differences between the sites.

6.4.2 Concentration of heavy metals in soil

The total content of Pb, Cd, Fe, and Cu (mg kg^{-1}) in the soils measured on the three investigated sites is presented in Table 12. Table 13 presents the heavy metal permissible limit by Finland Ministry of Environment (FME) (Ministry of Environment 2007), National Institute for Public Health and the Environment, Netherlands (NIPHEN) (Crommentuijn et al. 1997), World Health Organization/Food and Agriculture Organization of the United Nations (WHO/FAO), and the National Agency for Food and Drug Administration and Control (NAFDAC) of Nigeria (Lawal and Audu 2011; Opaluwa et al. 2012). All investigated metals (except Cu on the control site and in the subsoil of Site 1) exceed the natural concentration on uncontaminated soil by FME, but are all below the threshold values except Cd which shows elevated concentrations above the threshold values (from 23 – 153 %) on the mine sites. This is same in comparison to the Maximum Permissible Addition (MPA) of NIPHEN, except for Cu with MPA of 3.5 mg kg^{-1} .

Table 12: Mean values (n=3) for the total metal concentration (mg kg⁻¹) at the three sites.

Sites	Pb (mg kg ⁻¹)	Cd (mg kg ⁻¹)	Fe (mg kg ⁻¹)	Cu (mg kg ⁻¹)
Site 1; 0-20 cm	36.90	1.23	637.20	36.12
Site 1; 20-40 cm	29.64	1.30	684.60	13.40
Site 2; 0-20 cm	38.28	2.33	537.00	34.50
Site 2; 20-40 cm	12.96	2.53	663.00	29.10
Control; 0-20 cm	8.34	0.83	584.60	3.24
Control; 20-40 cm	16.86	0.80	483.60	3.72

Table 13: Permissible limits standards for heavy metals.

Standards	Pb (mg kg ⁻¹)	Cd (mg kg ⁻¹)	Fe (mg kg ⁻¹)	Cu (mg kg ⁻¹)
Finland Ministry of environment*	60 (5)	1 (0.03)	-	100 (22)
Maximum Permissible Addition; NIPHEN	55	0.76	3.5	
FAO/WHO limits for food and vegetables	2	1	48	30
NAFDAC limit for fresh vegetables	2	-	-	20

* Threshold values (natural concentration)

The highest Pb concentration of 38.28 mg kg⁻¹ was found on mine Site 2, while the lowest recorded concentration of 8.34 mg kg⁻¹ was on the control site. On the mine sites, Pb concentration decreases down the soil profile, but vice versa on the control site; the Pb concentration in the subsoil was higher than the topsoil. The mean Cd concentration ranged from 0.80 mg kg⁻¹ on the control site to 2.53 mg kg⁻¹ on mine Site 2. Unlike Pb, Cd concentration increases down the soil profile on the mine sites, but not on the control site. Similar to the Pb reduction down the soil profile is the Cu concentration, which ranges from 3.24 mg kg⁻¹ on the control site to 36.12 mg kg⁻¹ on mine Site 1. The obtained concentration of Fe on the sites followed a different trend compared to other considered metals. Although the lowest concentration of Fe was observed in subsoil of the control site (483.60 mg kg⁻¹), the topsoil of mine Site 2 also has low Fe concentration compared to other sites. Box plots were used to present the relations between the heavy metal contents on the three sites (Figure 23).

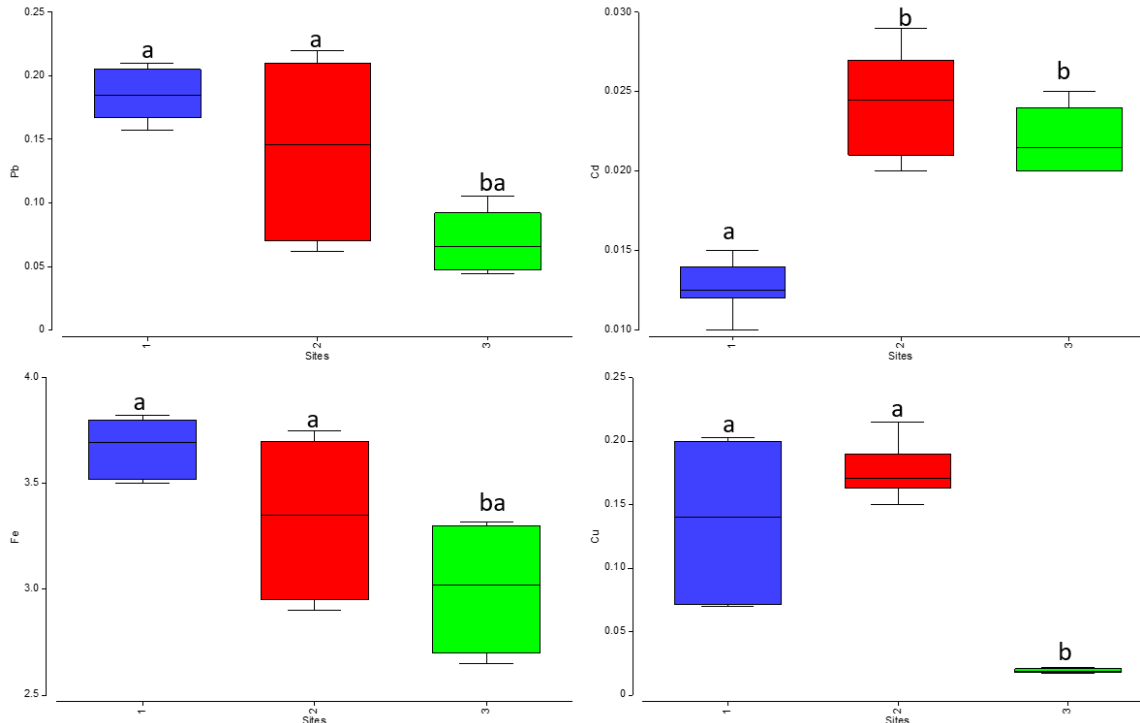


Figure 23: Box plots of the soil heavy metal content (Pb, Cd, Fe and Cu) on Site 1 (Blue), Site 2 (red) and the control site (green). Different letters indicate significant difference between the sites.

6.4.3 Analysis (soil physicochemical properties, heavy metals)

PERMANOVA results for TN showed significant differences in activity density among the three sites (Sites - $F_{2,15} = 35.549$, $P < 0.001$). Pairwise comparison revealed significant differences between Site 1 and Site 2, between Site 1 and the control site, but not between Site 2 and the control site. In terms of EC, significant differences were observed among the sites (Sites - $F_{2,15} = 7.002$, $P < 0.001$). Pairwise comparison revealed significant differences between Site 1 and Site 2, between Site 2 and the control site, but not between Site 1 and the control site. Similarly, pairwise comparison for the % OM indicates significant differences between Site 1 and the control site, between Site 2 and the control site, but not between Site 1 and 2. The nDMS analysis shows a distinct separation of the sites (Figure 24) as supported by the stress value of 0.03. However, Site 2 and Site 1 share some similarities with both the blue and red triangles within the same sides. Likewise, Site 1 and Site 3 (the control site) show some similarities with the blue triangles and green squares on the same sides. Results of the nDMS analysis confirm the PERMANOVA results with a significant difference in some of the soil properties and similarities in others.

Non-metric MDS

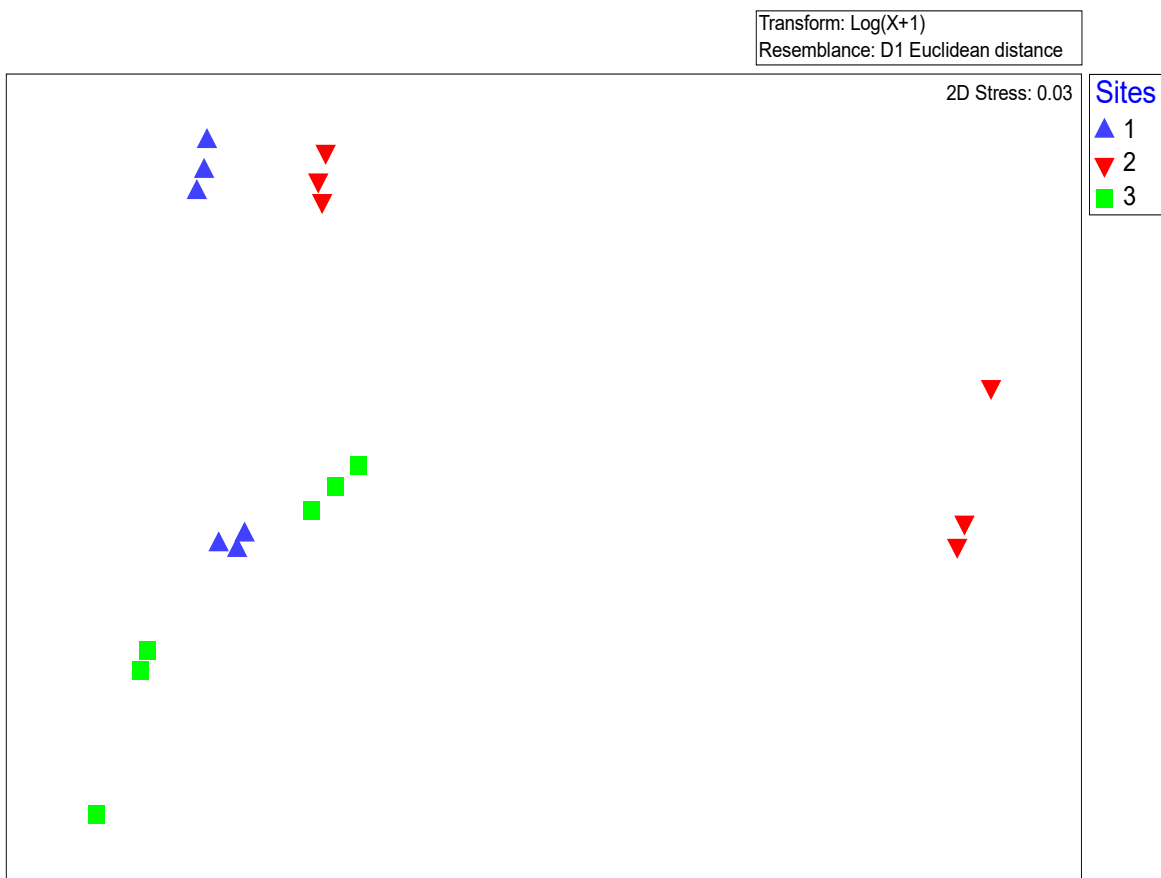


Figure 24: Physicochemical composition of the 3 sites by nDMS analysis (with stress value of 0.03). It shows distinctive separation from the 3 sites, but Site 1 shares some similarities with the control site (the blue and green points) while Site 1 and Site 2 also shares some similarities (the blue and red points).

6.4.4 Plants heavy metal content and phytoremediation potentials

As previously explained, the total heavy metal content from the obtained parts of *Theobroma cacao* and *Musa sapientum* are presented in Table 14. In *Theobroma cacao*, the mean concentration of Pb for both the beans and leaves range from 24.2 $\mu\text{g g}^{-1}$ (on control site) to 50.8 $\mu\text{g g}^{-1}$ (on Site 2); Cd, from 0.1 $\mu\text{g g}^{-1}$ (on control site) to 5.1 $\mu\text{g g}^{-1}$ (on Site 2). While for Fe, from 47.2 $\mu\text{g g}^{-1}$ (on Site 2 beans) to 232.0 $\mu\text{g g}^{-1}$ (on Site 2 beans), and Cu, from 6.6 $\mu\text{g g}^{-1}$ (on control site) to 19.59 $\mu\text{g g}^{-1}$ (on Site 1). In *Musa sapientum*, Pb was in concentration range of 12.1 $\mu\text{g g}^{-1}$ (on control site) to 42.3 $\mu\text{g g}^{-1}$ (on Site 1). Cadmium ranges from 0.1 $\mu\text{g g}^{-1}$ (on Site 1) to 3.6 $\mu\text{g g}^{-1}$ (on Site 2). Fe ranged from 27.9 $\mu\text{g g}^{-1}$ (on control site) to 186.9 $\mu\text{g g}^{-1}$ (on Site 2), and Cu is contained from 0.4 $\mu\text{g g}^{-1}$ (on Site 2) to 7.9 $\mu\text{g g}^{-1}$ (on Site 1). In comparison to the permissible limit by WHO/FAO and NAFDAC (Table 13), all the plants showed elevated Pb, Cd, and Fe in both *Theobroma cacao* and *Musa sapientum* on all the sites. However, concentration of Cu was low

except in the leaves of *Theobroma cacao* on mine Site 1. Rather than presenting the total concentration of the other seven investigated plant species, their mean values ($n = 3$) were used to calculate its respective phytoremediation potentials; Bioaccumulation (BCF), Translocation (TF), and Accumulation (AF) factors. They were classified appropriately as phytoextraction (PE), phytostabilization (PS), and high-accumulators (HP) species. Results for each plant are presented in Table 15 accordingly. The Fe concentrations in several of the investigated plants were greater than that of the highest standard and were represented as (ND; not detected).

For Pb, all the plants showed hyperaccumulating potential for Pb (Table 15). The species *C. jagus* has the greatest BCF (5.44) and AF (8.71) while *A. monthanus* has the highest TF (3.74). Four plants showed high-accumulating potential for Cd; *C. odorata*, *C. jagus*, *M. scanetenes* and *P. ambigua*. *A. monthanus* showed potential for phytostabilization of Cu with BCF >1 but TF <1. The species *A. monthanus* has the highest BCF (2.01), and *C. jagus* the highest TF (34.56) and AF (37.47). Most of the plants showed high Fe content above the highest standard and were therefore not detected. However, *C. odorata*, *A. monthanus* and *C. jagus* showed high-accumulating potential for Cu. *A. monthanus* has the highest BCF (14.54), *C. odorata*; the highest TF (6.00) while *C. jagus* has the highest AF (29.38).

6.5 Discussion

6.5.1 Soil physicochemical properties

Soil textural class is a permanent physical property (Hartati & Sundarmadji 2016), its distribution on the sites is not influenced by the crops, rather by the ASM activities. ASM involved activities such as excavation of the subsoil that is higher in clay content, piling them up as spoil heaps, which are later, used for farming in place of the original nutrient-rich topsoil. This influenced the textural class distribution of the sites. As a result, high percentage loss of silt and sand soil particles to erosion is unavoidable on mine sites, enhanced by heavy rainfall and the landscape characterizing the region. This is more evident on Site 2, which contains a high percentage of clay and less sand and silt compared to the other sites. Also, since high clay content supports lower plant growth, it might contribute to the noticeable lower vegetation on Site 2 (Adesipo et al. 2020b). Moreover, the ability of clay minerals to regulate the mobility and bioavailability of heavy metals (Rieuwerts et al. 1998) might enhance retaining of metal ions on Site 2.

Table 14: Concentration of metals in *Theobroma cacao* and *Musa sapientum* in $\mu\text{g g}^{-1}$.

Species	Sites	Pb		Cd		Fe		Cu	
		Beans	Leaves	Beans	Leaves	Beans	Leaves	Beans	Leaves
<i>T. Cacao</i>	Site 1	29.1	45.7	0.7	0.3	48.7	90.3	12.3	195.9
	Site 2	31.9	50.8	5.1	2.4	232.0	47.2	8.0	9.1
	Control	-	24.2	-	0.1	-	113.4	-	6.6
<i>M. Sapientum</i>	Site 1	42.3	27.5	0.1	0.2	163.3	157.8	0.8	7.9
	Site 2	35.3	34.0	3.4	3.6	61.4	186.9	0.4	4.5
	Control	12.1	28.9	1.3	0.7	27.9	64.9	1.1	0.6

Table 15: Phytoremediation potential of the seven native plant species.

Species	Pb				Cd				Fe				Cu			
	BCF	TF	AF	Class	BCF	TF	AF	Class	BCF	TF	AF	Class	BCF	TF	AF	Class
<i>C. odorata</i> ¹	0.60	2.68	1.61	–	1.46	1.61	2.36	HP	0.37	2.54	0.94	–	0.07	3.00	0.21	–
<i>C. odorata</i> ²	1.09	1.70	1.84	HP	0.94	2.09	1.97	–	ND	ND	ND	–	0.18	4.61	0.83	–
<i>C. odorata</i> ^C	4.29	1.22	5.22	HP	0.72	3.33	2.41	–	0.02	45.53	0.69	–	1.02	6.00	6.11	HP
<i>A. Monthanus</i> ^C	1.95	3.74	7.30	HP	2.01	0.53	1.08	PS	ND	ND	0.56	–	14.54	1.20	17.38	HP
<i>C. Jagus</i> ^C	5.44	1.60	8.71	HP	1.08	34.56	37.47	HP	ND	ND	1.08	–	12.19	2.41	29.38	HP
<i>M. corchorifolia</i> ¹	1.33	1.60	2.13	HP	0.24	4.67	1.14	–	ND	ND	0.37	–	0.20	0.19	0.04	–
<i>M. Scanetenes</i> ¹	1.71	1.46	2.49	HP	1.30	3.13	4.07	HP	ND	ND	0.90	–	0.11	0.88	0.10	–
<i>P. ambigua</i> ²	1.67	1.01	1.68	HP	1.29	1.97	2.53	HP	ND	ND	ND	–	0.49	1.74	0.86	–
<i>P. togoensis</i> ²	1.07	1.58	1.70	HP	0.94	2.68	2.53	–	ND	ND	0.84	–	0.22	0.43	0.09	–

BCF, TF and AF represent Bioaccumulation factor (root to soil), Translocation factor (shoot to root) and Accumulation factor (shoot to soil) respectively. HP and PS represents High-accumulator species and Phytostabilisation species, respectively, while 1, 2, and C represents species from Site 1, Site 2 and the Control site respectively, and ND represents Not Detected. Obtained metal concentration in the root, shoot and soil of each plants are presented in Appendix A.

Despite the ASM activities, active mine sites show higher pH than the control sites, which is unusual compared to most related studies (Salami et al. 2003; Sheoran et al. 2010; Oladipo et al. 2014; Petelka et al. 2019). Nevertheless, a previous study by Olabiyi et al. (2009) within the region shows that the soil is characterized by a pH of 4.5. Moreover, low soil pH, low % OC, and low N contents limits cocoa production on old cocoa fields in the country (Ayanlaja 1983). This could have influenced the pH of the control site, since Igila is an old cocoa farm with no record of anthropogenic activities except agriculture. However, obtained pH on the mine sites are comparable to previous studies (Oladipo et al. 2014), and suggest to limit plant growth, biological activity, nutrient availability, and toxicity of the heavy metal contaminants (Sheoran et al. 2010). Soil pH is one of the main factors influencing the mobility and availability of heavy metals to plants (Rieuwerts et al. 1998). Heavy metal solubility and leaching increases as the soil become more acidic (Liu et al. 2004; Yoon et al. 2006), it is therefore an important indicator of potential risk. Since none of the sites shows pH value greater than 6.5, the risk of its mobility and availability is high, with potential transfer to the food chain.

Soil OM positively influences nutrients supply to plant, soil physicochemical properties, as well as the binding and retention ability of metals (Rieuwerts et al. 1998; Sheoran et al. 2010; Mensah et al. 2015). According to Landon, (1991), the obtained OM on all the sites are low, but are within the range of similar related studies (Areola et al. 1982; Abiya et al. 2019). The control site shows the greatest % OM (2.21 %), especially on the topsoil, which could be attributed to its high litter fall from cocoa production (Asiedu et al. 2013). Greater % OM on Site 1 compared to Site 2 can be attributed to the revegetation process the site is undergoing and its abandoned ASM activities, thereby increasing its litter accumulation, unlike Site 2 with ongoing intense ASM activities (Adesipo et al. 2020b). Moreover, Site 1 is occupied by degraded secondary lowland rainforest, which is under regrowth with some relics of original forest capable of supporting rehabilitation of degraded soils.

Following N classification for tropical soils (Landon 1991; Petelka et al. 2019), N values ≤ 0.2 %, ≤ 0.5 %, and ≥ 0.5 % are low, medium, and high, respectively. All sites show high N content typical of cocoa production (van Vliet and Giller 2017) and higher in comparison to other related studies (Eludoyin et al. 2017; Abiya et al. 2019). However, the highest % TN observed on mine Site 1 can be attributed to some N-fixing plant species growing on the site (Adesipo et al. 2020b),

as well as the ongoing agricultural activities which might require fertilizer application. The extremely high EC on mine Site 2 can be attributed to the intense ASM activities and its high clay content limiting the flow of salt on the site, as well as the low landscape condition of the site with a high tendency to accumulate more water (since salt moves with water). Soils dominated by clay minerals such as smectite have a high cation-exchange capacity (CEC) and EC, whereas kaolinite has a low CEC. Unfortunately, there is limited information on the clay minerals on this site. However, soils with high EC (sodic condition) limit soil structure, infiltration or drainage, as well as toxicity to crops. This might also have contributed to the low vegetation on the site compared to other sites (Adesipo et al. 2020b). Previous studies in southwest Nigeria reported available P in most soil series is below the critical level of 8 mg kg⁻¹ (Anetor et al. 2013). However, the very low available P observed on the sites can be attributed to elevated Fe (Okusami et al. 1997 and Soremi et al. 2017). In addition, due to limited mineralization that mining activities have on plant nutrients (Martinez and Motto 2000; Oladipo et al. 2014), the observed low nutrients on the mine sites can be attributed to the ASM activities and the elevated heavy metal concentration.

6.5.2 Soil heavy metal concentration

The total content of Pb, Cd and Cu on Site 1 and 2 exceed the control site: Pb (from 43 – 78 %), Cd (from 36 – 68 %), and Cu (from 72 – 91 %) (Table 12). Similar high concentration differences were observed with Fe, however, low Fe was as well obtained in the topsoil of mine Site 2. Since there are no existing standard threshold values in relation to heavy metal soil contamination in Nigeria, which might be in relation to its influencing factors such as the soil parent materials, there are limits to the extent of its assessment efficiency and comparison. However, standards according to the Finland Ministry of Environment (FME) (Ministry of Environment 2007) and the Maximum Permissible Addition (MPA) of the National Institute for Public Health and the Environment, Netherlands (NIPHEN) (Crommentuijn et al. 1997) were employed accordingly. Concentration of Pb, Cd, and Cu on all the sites exceeds the natural concentration on uncontaminated soil, except Cu on the control site as well as the subsoil of Site 1. However, except Cd on the mine sites, the concentrations of Pb, and Cu are below the threshold level (both FME and NIPHEN), and are within related studies on gold mine sites (Antwi-Agyei et al. 2009; Ekwue et al. 2012; Oladipo et al. 2014; Petelka et al. 2019), except Cd and Fe. The elevated Cd concentration suggest a prompt need for reclamation of these sites, most especially Site 2 with up to 153 % elevated Cd contamination. On Site 2 (Itaganmodi), comparing the result by Salami et al. (2003) and Oladipo

et al. (2014), there is an increasing elevation of Pb (2.54, 35.00, and 38.28 mg kg⁻¹), Cd (0.13, 0.20 and 2.33 mg kg⁻¹), as well as Fe (137.27, 296.20 and 537 mg kg⁻¹), respectively. This consistent elevation is similar to previous related studies and can be attributed to the continuous exploitation by the ASM activities, which consequently induce variation in the soil chemical properties (Martinez & Motto 2000; Cooke & Johnson 2002; Oladipo et al. 2014). Iron is not included in the threshold values set by both FME and NIPHEN. Neither is there a related threshold standard on its concentration in Nigeria. However, comparing results on Site 2 to previous studies, there is a percentage increase of 115 % and 81 % between 2003 – 2014 and 2014 – current study, respectively. Apart from the ASM activities, elevated Fe content on all the investigated sites can be attributed to the characteristics of the soil parent material within the southwest region of the country (Oladipo et al. 2014) and higher concentration has been observed in previous studies (Okoya et al. 2011). The high Pb concentration might be related to galena, which is a natural mineral form of PbS (lead sulfide) occurring in gold ores with high concentration of sulfide (Matocha et al. 2001). Cadmium occurs in gold bearing ore as an isometric trace element in sphalerite, which determines its level of concentration. Similar to that is Cu, which occurs alongside gold ores, and distributed in sulfides, arsenites, chlorides, as well as carbonates (Fashola et al. 2016). Health risk of this metal toxicity has been widely discussed. Though both Fe and Cu are trace elements, however, consequences of their toxicity need to be averted. Therefore, prompt remediation of the sites is recommended.

6.5.3 Analysis (heavy metals, soil physicochemical properties)

The PERMANOVA and nDMS analysis of the soil physicochemical properties and total heavy metal showed the significant differences of the sites. The three sites are significantly different, with few similarities existing between Site 1 and Site 2, and Site 1 and the control site, but not between Site 2 and the control. Few of the soil properties with significant difference between Site 1 and Site 2 as obtained from the PERMANOVA result include % TN and EC, while between Site 1 and the control site include % OM, and % TN. Non-existing similarities between Site 2 and the control site indicate the severe impact of the ASM activities on Site 2, while the existing similarities between Site 1 and the control site confirms the ongoing self-rehabilitation of Site 1. Moreover, this can be explained from its floristic association highlighted by Adesipo et al. (2020b). Leaving the mine sites after ASM activities gives the site the opportunity to restore and self-sustain its ecosystem.

6.5.4 Plants heavy metal content and phytoremediation potentials

All the plants showed elevated Pb, Cd and Fe accumulation, but Cu was low except in *Theobroma cacao* leaves on mine Site 1. The elevated Fe can be attributed to the characteristics of the soil parent material in this region, while Pb and Cd can be attributed to the characterized gold ore mine on the sites. Therefore, prompt intervention is necessary to monitor, curb, and remediate the consequences of these illegal ASM activities, most importantly its entry into the food chain. Cases of Pb poisoning outbreak linked to ASM gold processing in the northwestern region of Nigeria, with over 400 deceased and thousands being affected have been reported (Lo et al. 2012; Plumlee et al. 2013; Bartrem et al. 2014). Similar occurrence needs to be averted. Apart from Pb, metals such as Cd which is highly mobile in soil-plant system, with exceptional long biological half-life >20 years can pose serious threat due to its high accumulation potentials in the food chain (Fashola et al. 2016). On the other hand, Cu and Fe are however essential nutrients for plants. In gold ores, Cu is widely distributed in arsenites, sulfides, and chlorides as well as carbonate, while Fe is one of the most abundant metals in the earth crust and all forms of life require it. However, a high concentration of either Cu or Fe is toxic; Fashola et al. (2016) have highlighted their toxic effects.

The high accumulation of the heavy metals in the investigated plants, despite the differences in the bioavailability of the metals (especially Pb, the least; and Cd, the most bioavailable), can be attributed first to the low pH of the soil and the perennial nature of the investigated plants (e.g. *Theobroma cacao*, *Musa sapientum* and *Crinum jagus*). Also, most of the considered plants suggest to have high tolerance for the contaminants and they have been existing on the sites for long time. The plants might be similar to examples of plants with mechanisms to accumulate the contaminants with less influence of the metal toxic effects (Wang et al. 2009; van der Ent et al. 2013; Petelka et al. 2019). Moreover, plants such as *Theobroma cacao* and *Musa sapientum* has deep roots, while *Musa sapientum* has a high-water content which might have also enhanced its high metal accumulation potential. Nevertheless, analysis of the plants secreted water in relation to bioavailability of heavy metals might be of interest. In addition to the plants' high accumulation potentials is their high biomass. This is also true especially for plants such as *Acanthus montanus*, as well as *Crinum jagus*, and *Melochia corchorifolia* which grow best in swamp forest and riverine vegetation (Adesipo et al. 2020b).

Unfortunately, there are limited amount of research on the normal range of mineral nutrients in some of the investigated plants on uncontaminated soils. Since *Theobroma cacao* and *Musa sapientum* are food crops with high potential to enter the food chain, comparison with related studies is necessary (Lockard & Asomaning 1964; Anhwange et al. 2009; Araujo et al. 2017; Assa et al. 2018). The level of Cu is within the normal nutrient range, while Pb, Cd and Fe are above. Araujo et al. (2017) highlighted that variations in Fe, Cu, and Cd as well as Mn, Zn, and Ba in cacao beans are in relation to the cropping system. Similar to that is the high range of Cd noticed by Arevalo-Gardini et al. (2017) in the species of cacao grown in Amazonas, Piura as well as the Tumbes regions in Peru. The Cd accumulation in *Theobroma cacao* is species related (for both the leaves and beans). Adequate screening of low metal accumulator of *Theobroma cacao* genotypes for safe production is therefore recommendable. Apart from the species, this variability factor might be true for other investigated metals as well. In addition, variation for within-species distribution of the heavy metals in the plants due to compartmentalization and translocation in the vascular system, which is poorly considered in most related studies (Kim et al. 2003).

Theobroma cacao and *Musa sapientum* are food crops and are not recommended for remediation purposes (Bansah & Addo 2016). However, all the plant species showed highaccumulating potentials of Pb. *Chromolaena odorata*, *Crinum jagus*, *Melanthera Scanetenes*, and *Palisota ambigua* showed high-accumulating potential of Cd, while *Acanthus Monthanus*, *Crinum jagus* and *Chromolaena odorata* showed high-accumulating potential for Cu. Most of these investigated plants are yet to be considered for phytoremediation by other authors, except *Chromolaena odorata* which has been efficiently confirmed to accumulate Pb (Tanhan et al. 2007; Wilberforce 2015; Jampasri et al. 2016) and Cd (Fati 2011), while *Melochia corchorifolia* was found efficient for As (Idris et al. 2016). None of the plants meets threshold criteria for hyperaccumulators. However, a review of the threshold criteria is necessary; some of this has been suggested by van der Ent et al. (2013). The increasing demand for remediation in tropical regions, requires further investigation of plant phytotoxicity. Nevertheless, the accumulation potential of *Crinum jagus* is significantly high for all the metals, this is similar to the observations of (Salami et al. 2003). Interest in exploring its phytoremediation potentials is high, and it is a novel recommendable plant species for the tropics. Its remediation potentials can be employed with other remediation techniques such as bioremediation with agents such as bacterial, fungi, and algae.

6.6 Conclusions and recommendations

Due to the ASM activities, tailing soils at the gold mine sites in southwestern Nigeria are characterized by elevated Pb, Cd, Fe, and Cu more than the control site, low nutrient, high heterogeneity and clay content. The elevated metal content of the mine site is also traceable to its acidic condition (below pH 6.5). However, Site 1 showed self-rehabilitation potential, and with no further ASM activities; the ASM induced adverse effects on the sites might be reduced. Cd on the mine sites exceeds recommendable threshold limits of both FME and NIPHEN. In comparison to previous studies, there is a consistent increase in the heavy metal contaminants, therefore prompt remediation of the sites is necessary. Effective approaches and policies to curb the ASM activities are necessary, this can be backed-up by empowering the youths, trace its supply chain, and discourage its illegal source of income. In addition, the economy needs to be stabilized with practicable conservation and management strategies that can deter the continuation of the ASM activities and enhance appropriate reclamation. More so, there is need to establish comprehensive threshold standards within this region. Moreover, due to limited access to the sites, the process the artisanal miners employ in processing the gold is not clear, this is however necessary, especially in case of cyanide. Nevertheless, determination of other related heavy metals such as As, Hg, Ni, Zn, and Cr, is important.

According to threshold criteria for defining hyperaccumulators, none of the plants shows hyperaccumulating potential. However, all the plants show high-accumulating potential for Pb, while *Chromolaena odorata*, *Crinum jagus*, *Melanthera Scanetenes* and *Palisota ambigua* are high-accumulators for Cd, and only *Chromolaena. odorata*, *Acanthus monthanus* and *Crinum jagus* are high-accumulators for Cu. Most importantly is *Crinum jagus*, which showed high-accumulating potential for all the metals, with significant high accumulator factors of 8.71, 37.47, 1.08, and 29.38 for Pb, Cd, Fe, and Cu, respectively. It is a recommendable novel plant for all forms of remediation, and can be employed in climatic adaptable regions around the world. In addition, further studies on the plant with high heavy metal concentration is necessary to ascertain if it can attain hyperaccumulator threshold. Also, other similar viable plants for phytoremediation are to be explored in the tropics.

7. Synthesis

7.1 Conclusions

In line with the objectives of this research, a comprehensive advancement to reclamation of post-mining sites was considered on international scale and practically on national scale; taking Nigeria as an example. On the international scale, a conceptual model for evaluating reclamation progress was developed. While on national scale, practical approach in respect to the state-of-the-art research gaps in crude oil exploration and gold mining in Nigeria were studied. To summarize the objectives, outcomes and outlooks covered in this research, a diagrammatic representation of the research summary is presented in Figure 25 below.

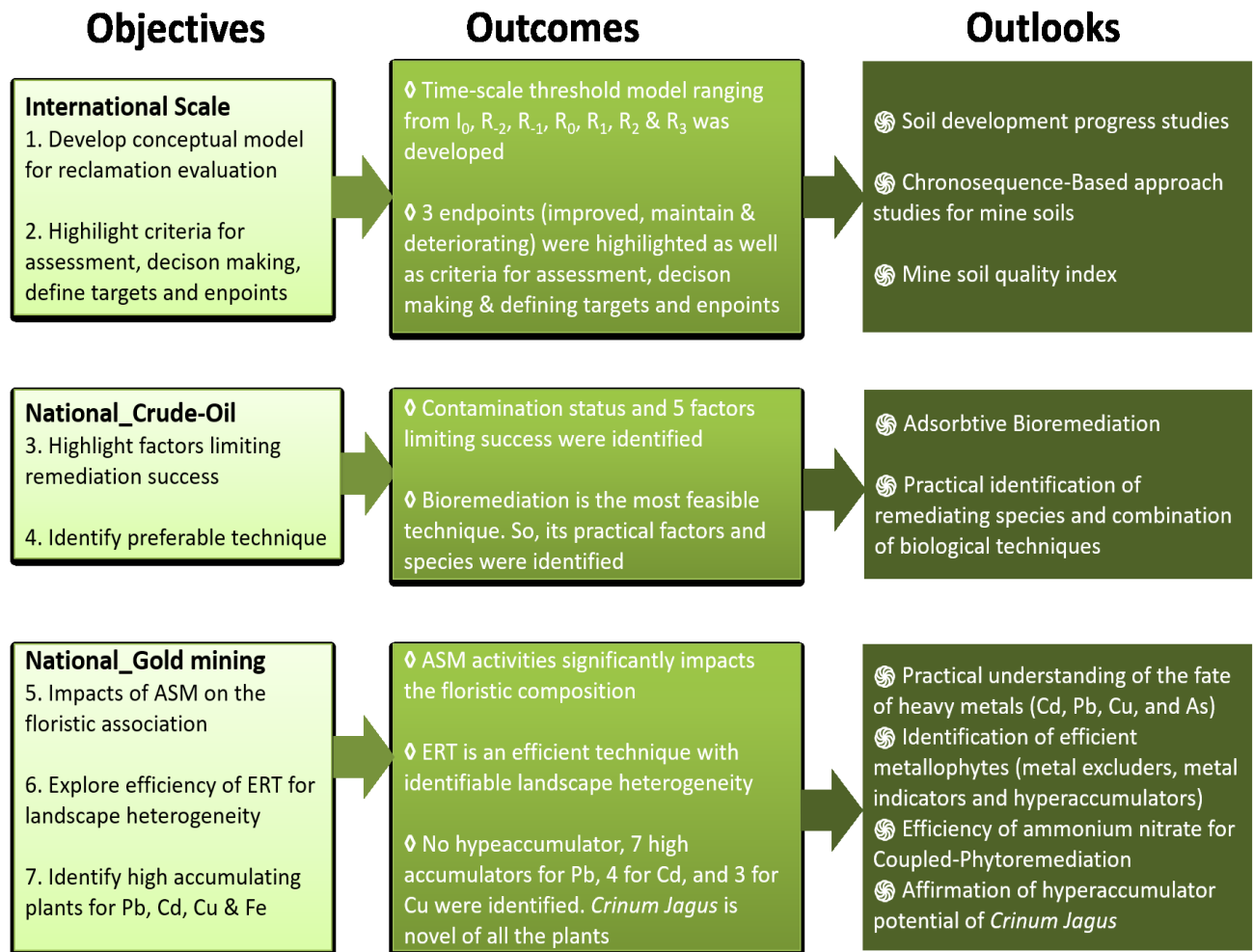


Figure 25: A comprehensive summary of the research objectives, outcomes and outlooks.

The developed conceptual threshold model presents identifiable step-by-step threshold stages representing what level(s) has been crossed and level(s) to be crossed. Along the reclamation progress ladder, continual status assessments and decision-making is necessary at each threshold level. Decisions on land-use, endpoints and sustainable management along each threshold stage should efficiently involve relevant multidisciplinary stakeholders. Although the model presents defined threshold stages, however, there could be some overlapping which depend on the site's condition and the identified influencing drivers (positive and negative drivers). This is because identification of some threshold indicators does not explicitly adapt probability of a perfect condition. Representation of key attributes and functional groups give a picture of threshold attainment, what to be identified, monitored and improved while climbing the reclamation success ladder. Therefore, it is necessary to be flexible. In addition, considerations of sites biological sustainability are essential and should remain a fundamental criteria guiding land use decision making.

From a broader perspective, “mining” in relation to the developed threshold model is not limited to extraction of minerals or geological materials. It entails all forms of resources extraction from the ecosystem, and this makes the model also applicable to several degraded ecosystems. The developed model is recommended for adoption in both national and international regulations monitoring reclamation progress. It is capable of assessing, evaluating, documenting, and monitoring the overall long-term success of post-mine sites reclamation process. Future studies focus on the threshold values, measurements, assessments and its harmonization in detail.

On the national scale with Nigeria in focus, the status of mining and reclamation in the country in relation to the developed threshold model showed that almost all Nigerian mine sites are below the minimum threshold level R_0 . The sites are heavily contaminated and pose high risk of entry into the food chain. Also, the biological diversity of the sites has been altered. Several invasive species have been introduced and widely spread. Moreover, the landscape homogeneity and the soil lithology have been subjected to severe disturbance with identifiable uncovered pit holes and foreign substance. All these limit the sites accessibility, safety, erodibility, sustainability, aesthetic values as well as the soil physicochemical properties, which are preliminaries for reaching the minimum threshold (R_0). Although despite the ASM impacts, most of the sites are in use for farming, whereby there exist some R_1 (soil/abiotic conditions) and R_2 (biological) threshold

indicators, however, the vulnerability of the sites limits them to R_0 . This ranges from contamination, floristic composition, and landscape heterogeneity as further concluded below.

For the crude oil contaminated sites, bioremediation (phytoremediation) remains the most preferable remediation technique. This is also applicable to the gold mine sites. However, adequate knowledge and considerations of its discussed factors that influences in-situ implementation is recommendable. These include site condition, plant characteristics, agronomic measures, cost estimation, operation maintenance, the aftermath of harvested plants, and regulatory standards. For the heavily contaminated sites, phytoremediation can be employed as final 'polishing-step' after some conventional clean-up techniques. Also, combination of techniques (especially biological) such as dendroremediation, vermiremediation, etc. is recommended. Provision for effective remediation and monitoring approaches needs to be made in Nigeria national laws. A transparent and robust stakeholder's engagement process capable of admitting its complex dynamics and decision making is necessary. Also, is the establishment of methods and standards within Nigeria context. Adopting other foreign standards may be ineffective on the long run. And to ease the fund stress, development of sustainable funding mechanisms from both the operators and sales of petroleum can help. The remediation potentials of most identified species is poorly studied, its considerations in future research is important. More so, the highlighted factors and listed species are not limited to Nigeria; it is widely applicable to other tropical regions globally.

On the gold mine sites, the results showed that the floristic compositions of the three experimental sites have been altered. These impacts can be attributed to the intense agricultural colonization and human activities on the sites in time past. However, the species richness, life form patterns, as well as floristic composition of the mine sites showed significant influence of the ASM activities with the introduction of identifiable exotic species. It could be deduced that the mine sites had not only been stressed but had also been greatly disturbed. This can be largely traced to the ASM activities and on-going farming activities which involves pollution, deforestation and exposure of the forest soils to direct sunlight. The stress decreases the biodiversity of the species while the disturbance increases its productivity. The washing and processing of the mined gold might have also influenced the substrate conditions of the mine sites which act as an 'environmental sieve' especially for the groundwater. Strategies to curb the ASM activities is important, also,

comprehensive species identification and database of the tropical species is necessary. Especially with the unidentifiable species encountered in this study.

The efficiency of ERT as a geophysical technique for characterizing the heterogeneity landscape of post-mining sites was confirmed. The results show high landscape disturbances with significant vertical and horizontal lithological disturbances. Foreign material and inappropriate uncovered pits were also detected on the sites. This lithological heterogeneity causes variations in the soil-use properties (such as soil texture) and behavioural qualities (such as infiltration) thereby limiting agricultural potentials. Adequate ploughing and organic amendment is therefore recommended. Top-soiling could be efficient, but its large-scale application and financial demands is not feasible, especially in Nigeria. More so, other geophysical techniques such as ground penetrating radar (GPR), complex resistivity (CR) with better resolutions and more investigating depths could be employed.

Results of the sites soil properties and identification of high accumulating plant species showed that tailing soils at the gold mine sites are characterized by elevated Pb, Cd, Fe and Cu. Also are its low nutrient, high heterogeneity and clay content. However, Site 1 (abandoned site) evidently show self-rehabilitation potentials if there are no further ASM activities. This is true in relation to its pH condition and return of native plant species. All the nine investigated plants show high-accumulating potential for Pb, while *Chromolaena odorata*, *Crinum jagus*, *Melanthera Scanetenes* and *Palisota ambigua* are high-accumulators for Cd, and only *Chromolaena odorata*, *Acanthus monthanus* and *Crinum jagus* are high-accumulators for Cu. Although none of the plants meets the international threshold criteria for defining hyperaccumulators, which has been suggested in this study to be revisited, the most notable of the investigated plants is *Crinum jagus*. *Crinum jagus* showed high-accumulating potential for all the metals, with significant high accumulating factors of 8.71, 37.47, 1.08, and 29.38 for Pb, Cd, Fe, and Cu, respectively. This values are significantly high in comparison to other related studies. It is a recommendable novel plant for all forms of remediation, and can be employed in climatic adaptable regions around the world. More so, its hyperaccumulating potentials at higher heavy metal concentrations can be ascertained in future research. Similarly, identification of more potential plants in the tropics is necessary. The mine sites show a consistent increase in its total heavy metal content, so, effective approaches to discourage ASM activities is necessary. Likewise, a comprehensive threshold standards guiding

pollution and contamination in Nigeria is promptly important. In addition is the determination of other related heavy metals on the sites, especially mercury, which the ASM miners might have been using.

In a haze, it is urgently necessary to put an end to the ongoing farming activities on the mine sites in Nigeria. All the farm products are to be discarded to avert its entry into the food chain. Effective approaches and policies that can curb ASM activities are very important. More so, provision to enact necessary standards and monitoring regulations in the national environmental law is promptly needed. The economy needs to be stabilized with adequate youth empowerment, which can discourage ASM activities and its illegal source of livelihood.

7.2 Limitations

In the course of this research, the limitations that were encountered, which could have enhanced the outcome of this study are highlighted below.

International scale

- i. Inaccessibility to adequate database that can be employed to define each threshold and adequately ascribe values for the identified threshold indicators.

National scale

- ii. Despite the research advancement in phytoremediation internationally, identification of efficient species and practical studies of its influencing factors is poor in Nigeria.
- iii. Access to the mine sites is limited and risky. The ASM miners are fierce, crooked, illegal, consistently increasing, without control or pattern and desperate. They sometimes become dangerous and defensive to also save their lives. This also hinders knowledge of the chemicals the miners use for gold ores washing and processing.
- iv. For the floristic association studies, there are limited related prior studies on the sites and in Nigeria at large, which could serve as basis for this study. For example, despite consultation with the Herbarium of the Obafemi Awolowo University, online portal of The Plant List, and African Plant Database, some plants could not be identified.
- v. Access to the ERT equipment and other geophysical equipment was challenging and demanding. Geophysics department of the hosting university has just two (2) ERT

equipment, which were accessible after several weeks of waiting and intensive usage for departmental projects.

- vi. There are few national threshold standards regarding contaminants in Nigeria. Threshold standards of other international nations were employed in this study. Similarly, other necessary database such as the soil properties, which could enhance this study were not available.
- vii. There are several other potential high accumulating plants identifiable on the mine sites, which were not accessed due to financial constraints. Also is the affirmation of *Crinum jagus* as a potential hyperaccumulator based on international threshold criteria.

7.3 Outlooks

The outcomes of this study generate some outlooks, which are proposed to have significant contributing potentials for future research studies. Although there are more outlooks possibilities, however, three research focus were selected and developed. These include (1) the soil development process from the developed conceptual model, (2) crude oil remediation by adsorbent bioremediation and (3) identification of optimum heavy metals accumulation potential in the tropics. Below are the categorized topics, which are also presented in respect to both the international and the national scales considered in this study. They are presented as concise summarized ideas with relevant references for further studies and basis as proposals for future research projects.

International scale

1. Soil development process and mine soil quality index

A major concern raised in reclamation related studies is the understanding of the relationship between conceptual framework (general knowledge of how ecosystem works and the factors) and the on-ground application (applicable methodologies in specific situation) and establishing a balance between them (Hobbs & Harris 2001). This is important to ensure that the concept guides specific actions while the on-ground experiences generate definite feedback to refine or reaffirm the concept. More so, ecosystem is dynamic, reclamation targets cannot be based on static standards. For specificity, a major interesting outlook from the developed conceptual model in this study (Session 2) is the threshold scale 1 (R_1), i.e. the soil development process of post-mining site

substrates. Chronosequence-based approaches are well known valuable tools for understanding the rates and direction of soil changes and landscape evolution in the pedological characteristics (Mukhopadhyay & Maiti 2018). On this basis, the preliminary objective of the future research is to do a comprehensive study of mine soil dynamics and acquire adequate data. Examples of previous related studies include carbon sequestration (Ussiri & Lal, 2007), soil nitrogen and carbon accumulation (Stahl et al. 2003; Knops & Tilman 2000), deposition rates, soil chemistry and pedogenic thresholds (Eger et al. 2012), as well as soil phosphorus speciation (Jun et al. 2013). This can be effectively achieved by identification of specific soil quality indicators, which are of interest and enhance defining and evaluating mine soils substrates progress and success. Here, the parameters considered are categorized below.

- Physical parameters: texture analysis, coarse fraction, bulk density, porosity, water holding capacity, and the soil moisture content.
- Chemical parameters: pH, electrical conductivity, organic carbon, available N and P, exchangeable Mg, Na, K and Ca, cation exchange capacity, as well as base saturation.
- Biological parameters: dehydrogenase activity, soil microbial biomass carbon, soil respiration, and mycorrhizal association.

With these identified indicator parameters, the second research objective is to establish a comprehensive mine soil quality index (MSQI) and develop mine soil substrate model, which can help to ascertain recovery stages and characteristics. Most existing indices for soil quality and fertility are for agricultural soils; little or none exists for mine soils. Existing methods for soil quality estimation include simple additive soil quality index SASQI (Amacher et al. 2007), weighted additive soil quality index WASQI (Masto et al. 2008) and statistics-based model SBM (Doran & Parkin 1997; Mukherjee & Lal 2014). Threshold values for SASQI were primarily from literature review and expert's opinion, and the summation of these individual index values are used to estimate the soil quality index. But for WASQI, linear scoring function is used to assign unit less score ranging values from 0 to 1. While for SBM, Principal Component Analysis is used to create minimum set of data, which reduce the indicator load in the model and avoid data redundancy. Unlike SASQI and WASQI which are subject to expert's opinion and previous studies, SBM is more objective, using statistical tools involving multiple correlation, factor, and

cluster analyses, thereby averting potential biasness and data redundancy with the use of minimum data set. Here, combination of both SBM and SASQI will be harnessed in developing.

National scale

2. Adsorptive bioremediation of crude oil contaminated sites

Bioremediation remains the prospective method identified in this study for the Niger Delta region of Nigeria. Though much emphasis was laid on phytoremediation (for the low crude oil contaminated sites), its success on heavily contaminated sites might be hampered by the excessive toxicity thresholds for microbial degraders, site specificity, and the treatment period. Here, adsorptive bioremediation is proposed as further research outlook prior to or in combination with phytoremediation. Adsorptive bioremediation has gained scientific attention over the years (Melkozerov et al. 2011; Vasilyeva et al. 2020), but the adsorbents are in most cases removed from the environment after use and separately disposed or recycled. The residual concentrations mostly exceed legal limits or threshold values. Therefore, in the second remediation steps, the contaminated media further needs other in-site, on-site or off-site remediation methods. The state-of-the-art adsorptive bioremediation aims at prospective development of cost-effective alternative adsorbents, in which the oil-binding agents remains in the soil after use without being disposed and later serves as degradation accelerating surfactant source, fertilizer, and as soil improver. As a progressive innovative research development, the Institute for Oil and Gas of the Siberian Federal University Krasnoyarsk in further cooperation with the Zentrales Analytisches Labor (ZAL) of BTU Cottbus-Senftenberg, developed a urea resins adsorbent (oil binding agents) called Unipolymer-M.

Unipolymer-M has an open coarse-pore structure, 100 % biodegradable and buoyancy. Other considered criteria in its developments include contaminants free, spontaneous ignition under environmental temperature (-25+300 °C), influence on the physicochemical and biological properties of both soil and water, and other regulated properties such as oil retention, coarse fraction, density (4-25 kg/m³), sorbent capacity (43-67 g oil/g sorbent), sorption rate (0.8-1.5 mm oil/s), desorption (0 %), etc. Its basic materials include minerals (e.g. expanded perlite, clay minerals like vermiculite, glauconite), biopolymers (such as sawdust, thermally expanded peat, straw), synthetic polymers (such as Lavsan, polypropylene, urea resin), expanded graphite, as well

as combined mineral and organic coating. While Unipolymer-M is a welcomed innovative approach, there are a number of scientifically open questions yet to answer. This include its influence in the environment, especially, its soil physicochemical effects (soil improver), P- and N- fertilizing influence, degradation increasing effects as a microbial co-substrate and as a surfactant source if left in the soil and in addition the influence of plant exudates. Moreover, development of recommendable application rate for each country's Federal Environmental Agency considering its influencing factors is necessary. These are further research questions proposed to be answered in future studies. The research is planned as collaboration between Germany (BTU Cottbus-Senftenberg), Russia (Siberian Federal University Krasnoyarsk) and Nigeria (IEES Obafemi Awolowo University and the National Oil Spill Detection Agency).

As a basis for further research, stating few preliminary knowledge is necessary, especially its influence as fertilizers, degradation rate, and soil improver. In agriculture, urea is used as slow acting nitrogen fertilizers, which develop its effects through microbial degradation. Existing related studies on its use as fertilizers, degradation process, nitrogen release and the enzyme involved has been widely studied (Alexander & Helm 1990; Aarnio et al. 1996; Jahns & Kaltwasser 2000; Elliot & Fox 2014). This makes the use of urea based Unipolymer-M potentially efficient. In relation to the degradation efficiency of Unipolymer-M, similar to section 3.4 and 3.5 of this study, degradation rates of crude oil and its products in environmental media varies, it depends on the abiotic framework condition, existing microflora, as well as the bioavailability of the hydrocarbon itself. The biodegradation can be accelerated by addition of surfactants (e.g. BioVersal), inoculation, or stimulation of the indigenous soil microflora. Contrarily, hydrocarbons also serve as material and energy source by soil organisms and their bioremediation potentials depends on adaptability of the microbial communities (Zucchi et al. 2003; Margesin et al. 2007). Regarding the influence of Unipolymer-M as soil improvers, synthetic and biopolymers are commonly used as soil improvers. They increase the cation exchange capacity, soil aeration and reduce structural effects such as silting up and compaction. On the other hand, for the bioremediation adsorbents, the hydrophilic surfaces as appropriate for oil binding agents enhances water absorption inhibiting the effects of wetting such as surface runoff, erosion, formation of flow path, which characterized most abandoned exploration site. Typical example of such absorbent is Polyacrylates. Use of urea resins based Unipolymer-M is therefore hypothesized to improve water

retention capacity, infiltration, aggregate stability, and reduces surface runoff and storage density, crust formation etc., which are crucial for heavy rainfall regions such as the Niger Delta Nigeria.

3. Optimum heavy metals accumulation influence

Despite the research advancements in heavy metals bioremediation around the world, yet, there are identifiable research gaps necessary for effectiveness. Here, the research interest is understating the fate of heavy metals in the lixisols and ferrasols regions of Nigeria and identification of efficient metallophytes (i.e. metal excluders, metal indicators or hyperaccumulators) preferable for multiple heavy metals in the tropics.

Complex varieties of abiotic and biotic processes such as adsorption unto/desorption from mineral surfaces, incorporation in precipitates/co-precipitates, dissolution of minerals, plants and microbe's interactions, etc. influence the speciation and distribution of heavy metals in the environment (Rao et al. 2008). These reactions are affected by factors such as pH, nature of the sorbents, organic and inorganic ligands, root exudates, etc. Taking Cadmium (Cd) for example, it is governed by various physicochemical processes in the soil. It exist as Cd^{2+} , $Cd(OH)_2(aq)$, $Cd(OH)_3^-$, $Cd(OH)_4^{2-}$, as well as $CdCO_3$ in aquatic systems while in soil, it may occur as cationic such as $CdCl^+$, $CdOH^+$, as well as $CdHCO_3^+$, and as anionic such as $CdCl_3^-$, $Cd(OH)_4^{2-}$ and $Cd(HS)_4^{2-}$. Cd occurs in complexes with various organic acids in soil solution and might be retained in the soil through precipitation and adsorption reactions. In the presence of anions such as S^{2-} , CO_3^{2-} , OH^- and PO_4^{3-} precipitation is suggested predominant while sorption at surfaces of soil minerals might occur by both specific and nonspecific processes. Cd precipitate to minerals such as octavite ($CdCO_3$), CdO or $Cd(OH)_2$ in oxidizing environments and alkaline soils (Elbana 2013). While this advanced knowledge exists, especially with different heavy metals and on different soils, the fate of these metals in the lixisols and ferrasols regions of Nigeria remain largely unknown. Major chemical components of Lixisols are $CaCO_3$ and $MgCO_3$, which play important role in the biogeochemical process of heavy metals. Quantifying the proportion of the heavy metals bound to soil constituents help to understand the behavior and fate in the soils. In addition to that is the introduction of "coupled phytoremediation" (Khalid et al. 2014), which describes use of two successive approaches involving efficient selection of chelating agent along with hyperaccumulating species. Considering ammonium sulphate for example, ammonium ion enhances mobility of metals whereas the acidic radical (i.e. sulphate) inhibits its mobility. As a

future research, ammonium nitrate suggests efficient. It liberates NH_4^+ and NO_3^- (basic and acidic radicals) that both enhance heavy metals mobility either through chelating process or its related pH properties. This is a novel research objective for future study.

In addition, globally, only about 400 hyperaccumulators has been identified for Cd, As, Ni, Zn and Mn, other heavy metals including Pb, Cu, Cr, Hg are largely limited (Adesipo et al. 2020c). For future study, *Crinum Jagus* is hypothesized as a potential hyperaccumulator for several heavy metals. While its experimental confirmation is necessary and proposed as future research outlook, there are several other species yet to be identified in the tropics. As described by Rascio & Navari-Izzo (2011), two most evident hypothesis explaining hyperaccumulators are “elemental defense” (stating that plants hyperaccumulate heavy metals as a defense mechanism) or “joint effects” (stating that heavy metals can operate in concert with organic defensive compounds leading to enhanced plant defense overall). Hyperaccumulators are significant for their enhanced heavy metal uptake, faster root-to-shoot translocation, high potential of detoxifying and sequestration of great amount of heavy metals in vacuoles or cell walls of the plant’s leaves. This can be attributed to constitutive overexpression of genes encoding transmembrane transporters with members’ examples such as ZIP, HMA, MATE, YSL, and MTP families. On this basis, the research objective further focuses on identification of hyperaccumulating potential of *Crinum jagus* alongside other species to be identified in the tropic. Also, investigate the species biological, biochemical, ecological, physiological as well as molecular mechanisms related to multiple heavy metals hyperaccumulation.

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Appendix A

Appendix A: Concentration of metals in the considered plants in $\mu\text{g g}^{-1}$

Plants	Metals	Shoot	Root	Soil	BCF	TF	AF
Site 1							
<i>Chromolaena odorata</i>	Pb	59.40	22.20	36.90	0.60	2.68	1.61
	Cd	2.90	1.80	1.23	1.46	1.61	2.36
	Fe	599.7	236.4	637.20	0.37	2.54	0.94
	Cu	7.50	2.50	36.12	0.07	3.00	0.21
<i>Melochia corchorifolia</i>	Pb	78.70	49.10	36.90	1.33	1.60	2.13
	Cd	1.40	0.30	1.23	0.24	4.67	1.14
	Fe	233.00	ND	637.20	ND	ND	0.37
	Cu	1.40	7.20	36.12	0.20	0.19	0.04
<i>Melanthera scandens</i>	Pb	91.70	62.90	36.90	1.71	1.46	2.49
	Cd	5.00	1.60	1.23	1.30	3.13	4.07
	Fe	575.60	ND	637.20	ND	ND	0.90
	Cu	3.50	4.00	36.12	0.11	0.86	0.10
Site 2							
<i>Chromolaena odorata</i>	Pb	70.50	41.6	38.28	1.09	1.70	1.84
	Cd	4.60	2.20	2.33	0.94	2.09	1.97
	Fe	ND	ND	537.00	ND	ND	ND
	Cu	28.60	6.20	34.50	0.18	4.61	0.83
<i>Palisota ambigua</i>	Pb	64.20	63.90	38.28	1.67	1.01	1.68
	Cd	5.90	3.00	2.33	1.29	1.97	2.53
	Fe	ND	ND	537.00	ND	ND	ND
	Cu	29.50	17.00	34.50	0.49	1.74	0.86

<i>Pteris togoensis</i>	Pb	64.90	41.00	38.28	1.07	1.58	1.70
	Cd	5.90	2.20	2.33	0.94	2.68	2.53
	Fe	449.30	ND	537.00	ND	ND	0.84
	Cu	3.20	7.50	34.50	0.22	0.43	0.09
Control site							
<i>Chromolaena odorata</i>	Pb	43.5	35.8	8.34	4.29	1.22	5.22
	Cd	2	0.6	0.83	0.72	3.33	2.41
	Fe	405.2	8.9	584.6	0.02	45.53	0.69
	Cu	19.8	3.3	3.24	1.02	6.00	6.11
<i>Acanthus montanus</i>	Pb	60.90	16.30	8.34	1.95	3.74	7.30
	Cd	0.90	1.70	0.83	2.05	0.53	1.08
	Fe	326.10	ND	584.6	ND	ND	0.56
	Cu	56.30	47.10	3.24	14.54	1.20	17.38
<i>Crinum jagus</i>	Pb	72.60	45.40	8.34	5.44	1.60	8.71
	Cd	31.10	0.90	0.83	1.08	34.56	37.47
	Fe	629.30	ND	584.60	ND	ND	1.08
	Cu	95.20	39.50	3.24	12.19	2.41	29.38

Dedication

This study is dedicated unto GOD Almighty and My Parents; Engr. Adebile Jeremiah Adesipo and Deaconess Sabainah Oyenike Adesipo who both died on August 15, 2020 and March 23, 2018 in the course of this study.