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Elemental Composition and Geochemistry of Heavy Oil in Parts of Eastern Dahomey Basin, Southwestern Nigeria

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Abstract
Bituminous tar sand deposit of South-western Nigeria represents the product of in-reservoir transformation of convectional crude oil by microorganisms. The biotransformation of the heavy oil has led to the alteration of both the chemical and physical characteristics of this oil. The change in the chemical composition has posed a great problem to the refineries as feedstock tends to react with refineries components thereby destroying refining plant. Hence the commercial production of these resources has not been encouraged.
Based on this, 14 samples spread across the tar sand belt of the region were taken and subjected to laboratory analysis. Result shows an average elemental composition of Carbon, Hydrogen, Oxygen, Nitrogen, and Phosphorus to be 80%, 8%, 4.5%, 4.1% and 3.9% respectively. This considerable high Nitrogen and Phosphorus content is due to biodegradation which occur in the trap due to untimely harvest of the oil and water washing effect.
Keywords: Bituminous Tar Sands, Biotransformation, Reservoir

Abstract
Bituminous tar sand deposit of South-western Nigeria represents the product of in-reservoir transformation of convectional crude oil by microorganisms. The biotransformation of the heavy oil has led to the alteration of both the chemical and physical characteristics of this oil. The change in the chemical composition has posed a great problem to the refineries as feedstock tends to react with refineries components thereby destroying refining plant. Hence the commercial production of these resources has not been encouraged.
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1. Introduction

Nigeria has a considerable large deposit of natural bituminous tar sand also known as oil sand or oil impregnated sand. The Nigerian tar sand deposits can be found within the confine of the eastern margin of Dahomey basin which lies within a depobelt cutting across three major provinces/States which include: Ogun, Ondo, Edo states in the South-western and South-southern Nigeria respectively **(Fig 1)** also shown in the index.
Tar sand is composed mainly of heavy oil and clays that are rich in mineral and waters. This heavy oil content of tar Sand is commonly called bitumen. In the raw state tar sand is a strictly black viscous black substance.
The total reserve of heavy oil is estimated to exceed 30 billion barrel (Adegoke 1980). Bituminous sand is wide spread in the South-western part of Nigeria in minable, economical quantity.
Despite the inadequate information available on tar sands (Bituminous sands) significant work has been carried out by various workers on the geology, origin, and occurrence, processing and utility of the tar sands.
Nigerian bitumen corporation, (1908-1914), Shell Dancy (1922-1933) Cassey et al (1963); crocket and Westcott (1954); IPCO; (1965); Durham and Pickett) 1966); and others, have confirmed the occurrence of bituminous sands in South Western Nigeria.
Adegoke et al (1976 and 1978) and 1980, Omatsola and Adegoke (1981), Coke (1976) (1982) have also indicated that residual oil occurs in the upper cretaceous sediments which outcrop on the Okitipupa structure. Also information had been presented in papers on the tectonic evolution and Cretaceous stratigraphy of the Dahomey basin.

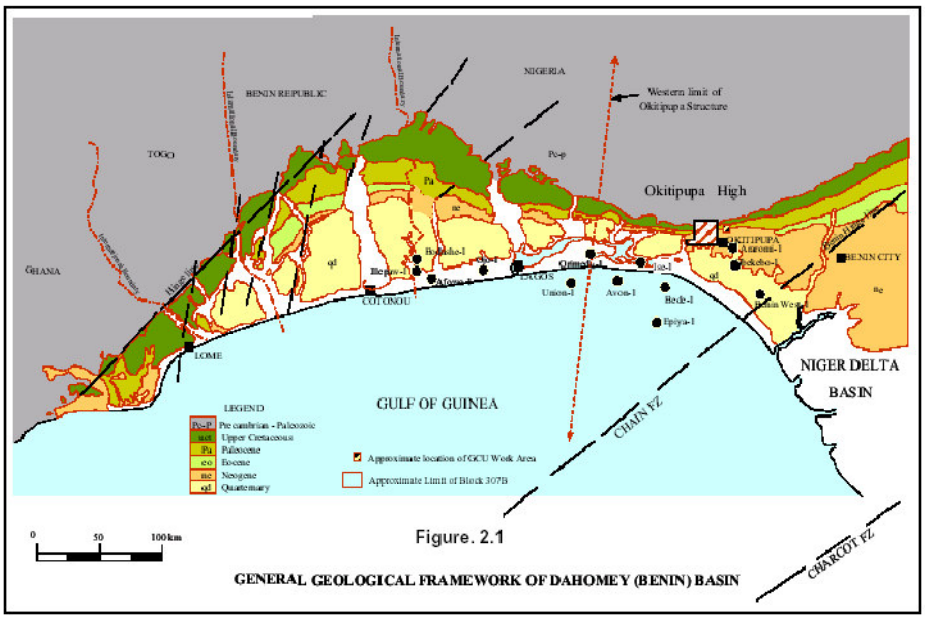

Figure 1: General Geological Framework of the Dahomey Basin. (Modified from Bilman, 1992)

2. Geologic Setting

The origin(s) of the oil in sand either in-situ or from an external source has been described by Oluwole et al (1985); Nwachukwu and Ekweozor (1989).The chemical composition of bitumen extracts from Nigerian oil sand has been worked on by Ekweozor (1985, 1986) with the help of Oluwole, Adegoke, Kehinde, and others.

Studies by the Geological consultancy unit of Obafemi Awolowo University, Ile-Ife in the 1980's have revealed a lot of information on the occurrence and the characteristic of bituminous sand of South-Western Nigeria. Other relevant studies on the bituminous sand have been made by Ako et al (1983) Coke et al (1983); Ekweozor (1990) and Obiajunwa and Nwachukwu (2000) highlighted the relevant aspect of the bituminous sand, exploitation and the associated environmental issues.

These tar sands outcrop in a 29km by 6km belt in the South-western Nigeria from Okitipupa Ridge/western further edge of the tertiary Niger-Delta to the far west of Ijebu-Ode in Ogun State

Various workers such as; Durhan and Pickett (1966), Adegoke et al (1974) have confirmed that tar sands outcrops occur from east of Ijebu-Ode (Ogun State) to Silu through Akotogbo areas in Okitipupa (Ondo State) to Edo State South-western Nigeria a distance of about 110km (**Fig. 2**).

The peasant farmers and hunters in these areas are the main inhabitants who have observed the occurrence of these seepages which over the years have used this material for painting and sealing up of broken fishing vessels among many other uses.

These seepages are observed to be well noticed in areas of road cuts, slopes and low topography where they cut out into rivers wherefore solidified form of tar sand are observed on the floors of rivers flanks or at water fall. Optical structural framework of tar sand shows that the heavy oil content is not in direct contact with the sand grain (Enu 1985).

Solid bituminous sand (tar sand) is formed in a number of ways. These include thermal attraction, microbial degradation, water washing or gas de-asphalting of the fluidly hydrocarbon. Irrespective of its formational mode, bituminous sand is a sedimentary rock attest of the former presence of fluid hydrocarbon in the environment. The occurrence of these deposits in Nigeria has been known since early last century, however intense investigation had commenced and continued from mid 70's till date. The pioneering effort was initiated by the geological consultancy unit of the University of Ife. The geology of these deposits **(Table 1, Fig. 3)**, oil saturation and reserve estimates as well as textural characteristics of the associated sand has been described (Adegoke et al, 1980 and 1981: Enu 1987).

A reservoir is therefore defined as subsurface rock Containing Commercially exploitable quantities of oil and gas because of its porosity and permeability. These parameters are the two major factors that influence a reservoir quality.

It is therefore pertinent to determine the reservoir and other sedimentological characteristics of the deposits such as grain size distribution, porosity and permeability which will assist its future production procedures. Also, our aim of sampling outcrops in this region is to compare variation in elemental components of tar sand, on a regional scale and place it side by side with other works from other tar sand producing countries around the

globe.

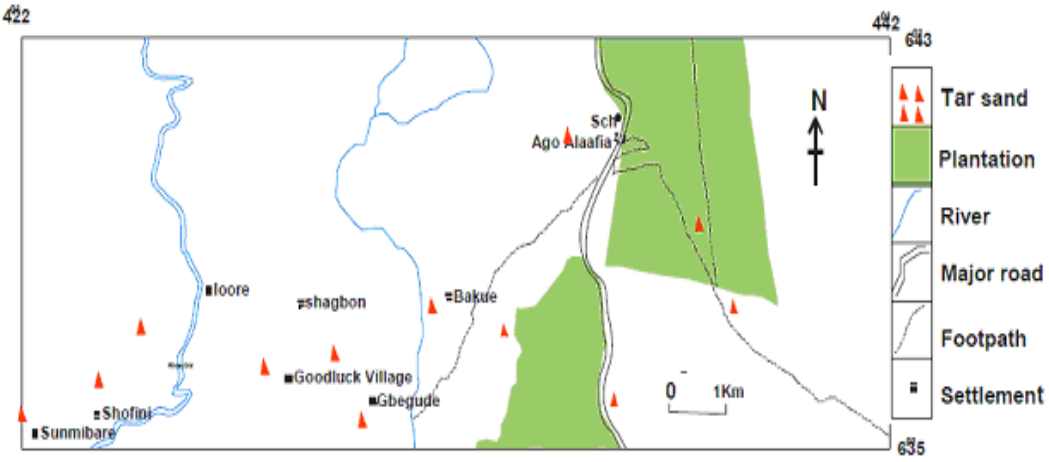

Figure 2: Map showing sampling points

Table 1: Stratigraphic Data Of Eastern Dahomey Basin (Adapted And Modified From Various Authors)

Jones and Hockey (1964)		Omatsola and Adegoke(1981)			Agagu (1985)	
	Age	Formation	Age	Formation	Age	Formation
Quaternary	Recent	Alluvium			Recent	Alluvium
Tertiary	Pleistocene - Oligocene Eocene Paleocene	Coastal plain sand Ilaro Ewekoro	Pleistocene- Oligocene Eocene Paleocene	Coastal Plain sand Ilaro Oshosun Akinbo Ewekoro	Pleistocene- Oligocene Eocene Paleocene	Coastal Plain sands Ilaro Oshosun Akinbo Ewekoro
Cretaceous	Late Senonian	Abeokuta	Maastrichtian - Neocomian	Araromi Afowo Ise	Maastrichtian - Neocomian	Araromi Afowo Ise
Precambian Crystalline Basement Rocks						

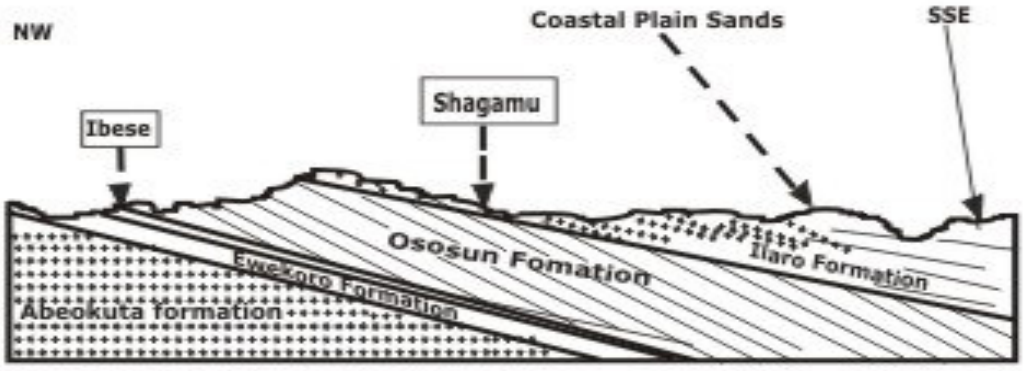

Figure 3: Generalized Stratigraphy succession of Dahomey basin (After Adegoke 1969)

3. Methodology

The reconnaissance survey conducted revealed areas with different boundaries (Longitude $6^0$35.601'E to $6^0$41.961'E and Latitude $4^0$40.146'N to $4^0$13.093' N) covering Loore, Lumogo, Ago-Alaye, Ago-Titun, Oke **(Fig 2)**. Representative samples were collected at random from outcrops investigated using materials made of aluminium which made it possible to acquire a contamination free samples before it was sent to the laboratory

for geochemical analysis.
However the procedure for the chemical analysis include weigh of 10g of the sample, mixed with 10ml pentane and poured into a conical flask with the aid of a funnel fixed with a filter paper, then the collected filtrates were analysed.
The result present a variation in composition spread across the study area which may be typical of difference in biodegradation rate of elemental composition of the asphaltenes content of the heavy crude oil. The percentage composition of the major elements namely Carbon, Hydrogen, Oxygen, Nitrogen and Phosphorus average 80, 8, 4.4, 4.2 and 4.0 respectively supports the high hydrocarbon content, which suggests the effect of immature biogenic material in the reservoir rock. The high hydrocarbon content suggest a high producibility grade also with a decrease in hydrocarbon content from the Ogun arm to the Ondo arm it further supports a higher producibility of the Ogun tar sand deposit relative to those of Ondo areas.

4. Result And Interpretation

The results obtained, from the laboratory analysis of the bituminous sands, from the different locations, within the investigated region are presented in **Table 2** below.
From the result obtained through chemical analysis of the asphaltenes content of the tar sand enrichment of Nitrogen, Oxygen, Phosphorus and Carbon was observed. The enrichment of Nitrogen, Carbon and Hydrogen compound in the bitumen are evident of thermal immaturity and likewise incomplete thermal evolution of virgin convectional crude oil or microbial transformation of convectional crude oil. It could be as a result of biodegradation which does not require oxygen but the solution or alteration of minerals in the water lag that occur in the area of seepage. Also the presence of this tar sand belt within the Afowo formation which is a transition zone may be a likely source for this enrichment. Other support of this hypothesis arises from several independent observations.
Table 2: Showing the Elemental Composition of the Bituminous Sands.

S\N	Location	Sample code (N=14)	Longitude	Latitude	C (%)	H (%)	O (%)	N (%)	P (%)
1	**Ogun Arm**	OG LOC. 10	06^0,35,786'E	004^0,15,171'N	80.6	8.6	1.4	5	4.3
2	**Ogun Arm**	OG LOC. 9	06^0,35,750'E	004^0,15,157'N	83	8.9	5	5.9	4.4
3	**Ogun Arm**	OG LOC. 8	06^0,35,601'E	004^0,13,093'N	77.5	9.4	5.1	6.5	1
4	**Ogun Arm**	OG LOC,7	06^0,41,961'E	004^0,16,563'N	80.1	8.8	2.9	3.7	4.4
5	**Ogun Arm**	Lumogo	06^0,41,798'E	004^0,16,378'N	82.2	6.7	3	3	5.2
6	**Ondo Arm**	SHG.A1	06^0,38,521'E	004^0,40,105'N	81.2	9	3	4.5	2.3
7	**Ondo Arm**	SHG.A2	06^0,38,473'E	004^0,40,045'N	80.3	7.3	5.1	4.4	2.9
8	**Ondo Arm**	SHG.B1	06^0,38,693'E	004^0,40,205'N	78.2	6.8	6.1	2.7	6.1
9	**Ondo Arm**	AGT.	06^0,39,482'E	004^0,39,780'N	80.8	8.2	4.1	5.5	1.4
10	**Ondo Arm**	OKE.3	06^0,38,500'E	004^0,39,439'N	79.3	7.6	5.5	2.1	5.5
11	**Ondo Arm**	N -14	06^0,40,216'E	004^0,23,351'N	77.1	8.3	5.6	3.5	5.6
12	**Ondo Arm**	N -18	06^0,40,729'E	004^0,23,593'N	80.9	8.8	3.7	4.9	2.2
13	**Ondo Arm**	N -20	06^0,40,702'E	004^0,26,202'N	79.9	7.2	5	1.4	6.5
14	**Ondo Arm**	N -5	06^0,40,995'E	004^0,30,116'N	78.6	6.4	6.4	5	3.6
		Minimum	-	-	**77.1**	**6.4**	**1.4**	**1.4**	**1.0**
		Maxmum	-	-	**83.0**	**9.4**	**6.4**	**6.5**	**6.5**
		Mean	-	-	**80.0**	**8.0**	**4.4**	**4.2**	**4.0**
		Median	-	-	**80.2**	**8.3**	**5.0**	**4.5**	**4.4**
		SD	-	-	**1.7**	**1.0**	**1.4**	**1.5**	**1.8**

The result present a variation in composition spread across the study area which may be typical of difference in biodegradation rate of elemental composition of the asphaltenes content of the heavy crude oil. The percentage composition of the major elements namely Carbon, Hydrogen, Oxygen, Nitrogen and Phosphorus average 80, 8, 4.4, 4.2 and 4.0 respectively supports the high hydrocarbon content, which suggests the effect of immature biogenic material in the reservoir rock. The high hydrocarbon content suggest a high producibility grade also with a decrease in hydrocarbon content from the Ogun arm to the Ondo arm it further supports a higher

producibility of the Ogun tar sand deposit relative to those of Ondo areas.

4.1. Hydrogen Enrichment

The enrichment of hydrogen can be associated to the fact that hydrogen is reactive, mobile and cannot be permanently retained in the subsurface. It is likely to be actively produced within the reservoir adjacent to source beds or diffusing upward from depth. Thus the high hydrocarbon content is strongly suspected to be formed during thermal maturation of organic matter.

It can be deduced from analysis that the concentration of the hydrocarbon content of heavy oils in the Ogun arm is considerably higher than those of the Ondo region. Hence, since the hydrocarbon constituent of heavy oil determines its grade, and the higher the hydrocarbon content suggesting a higher quality. With respects to these suggested deduction, if qualitative exploration is to be carried out, pinning of mines on the Ogun region will be of more economic value.

Table 3: Comparison of Concentrations of the Nigerian tar sand as reported by various workers**.**

	Ekweozor and Nwachukwu.1989		**Oluwole *et al*., 1989**		**This Study**	
Element	Mean	Numbers of Samples	Mean	Numbers of Samples	Mean	Numbers of Samples
Carbon	85.7	4	85.7	6	80	**14**
Hydrogen	10.7	4	10.7	6	8	**14**
Nitrogen	0.5	4	0.5	6	4.2	**14**
Chlorine	0.1	4	0.1	2	-	**14**
Oxygen	1.72	14	1.72	6	4.4	**14**

Also, comparing this to previous works (Oluwole et al (1985) and Ekweozor and Nwachukwu (1989), in the asphaltenes extract analysis, it was observed that there is a significant and continuous decrease in the C and H content while N and O shows an appreciable enrichment **(Table 3)**. This is typical of biodegradation effect, (Ekweozor and Nwachukwu (1989)) since this is the fraction of crude oil that most unequivocally provides evidence of microbiological transformation. When comparison of the result was made with others from other parts of the world, increased and improved properties were observed with those of Athabasca Canada which raised a big question in our minds. Since Canada produce lube oil from their oil sand, then Nigerian tar sands would produce a high quality of lube oil for both domestic consumption as well as a for export thereby boosting its economy.

Table 4 Summary of Elemental composition at a glance from different sources**.**

ELEMENTS	ATHABASCA OIL SAND **(UNITAR 1984)**	NIGERIAN OIL SAND FROM VARIOUS AUTHORS **(EKWEOZOR & NWAACHUKWU 1989)**	NIGERIAN Oil SAND FROM THIS WORK
C	**83.6**	**85.7**	**80**
H	**10.3**	**10.7**	**8.0**
N	**0.5**	**0.5**	**4.1**
O_2	**1.0**	**1.7**	**4.5**
P	**-**	**-**	**3.9**

The asphaltenes content of heavy crude oil together with the resins content contain polar component more than 50% of the whole heavy crude fraction. Oluwole et al (1985) and Ekweozor and Nwachukwu (1989) have also reported high value from the non-hydrocarbon portion of the Nigerian tar sand. In contrast, convectional crude oil contains less than 10% of this fraction.

5. Conclusion

Producibility of heavy oil depend more on the hydrocarbon content such as; the higher the hydrocarbon content, the higher its Producibility. Hence pinning of any mines should be preceded by the geochemical analysis of the asphaltenes content and with positive results, Nigerian tar sands are good for mining but as suggested be this research, better Producibility can be accorded to the Ogun region than that further north in Ondo. This is because of its high hydrocarbon content.

Nigerian tar sands as revealed by this work and other previous works of Ekweozor and Nwachukwu (1989) and Oluwole et al (1985), should be well exploited and also other method of exploration and processing should be tested and employed. Apart from its use for road construction, lube oil and other petrochemicals can also be distilled from these heavy oil deposits thus properly utilizing it as being it is being explored in other parts of the world.

As a result of variation in the elemental components which is due to the level of degradation, more physio-

chemical work if carried out would make up for the differences between Nigerian tar sands and its Athabasca counterpart in its viscosity difference (i.e. viscosity of Nigerian tar sands is higher than Athabasca deposit (Ekweozor and Nwachukwu (1989).

6. Recommendation

This research has shed more light on the Nigerian heavy oil deposits and apart from its use for road construction, lube oil and other petrochemicals can also be distilled from these heavy oil deposits thus utilizing its resource maximally as it is being done in other parts of the world but further studies should be carried out on this and other physio-chemical characteristics of the Nigerian tar sands. Basically work should be done on its viscosity as it has posed a big problem for refining processes when used as field stocks.

Environmental impact assessment (EIA) studies should also be carried so as to ascertain the influence of exploration and exploitation of bitumen on the environment as well as the inhabitant of the area where deposits occur.

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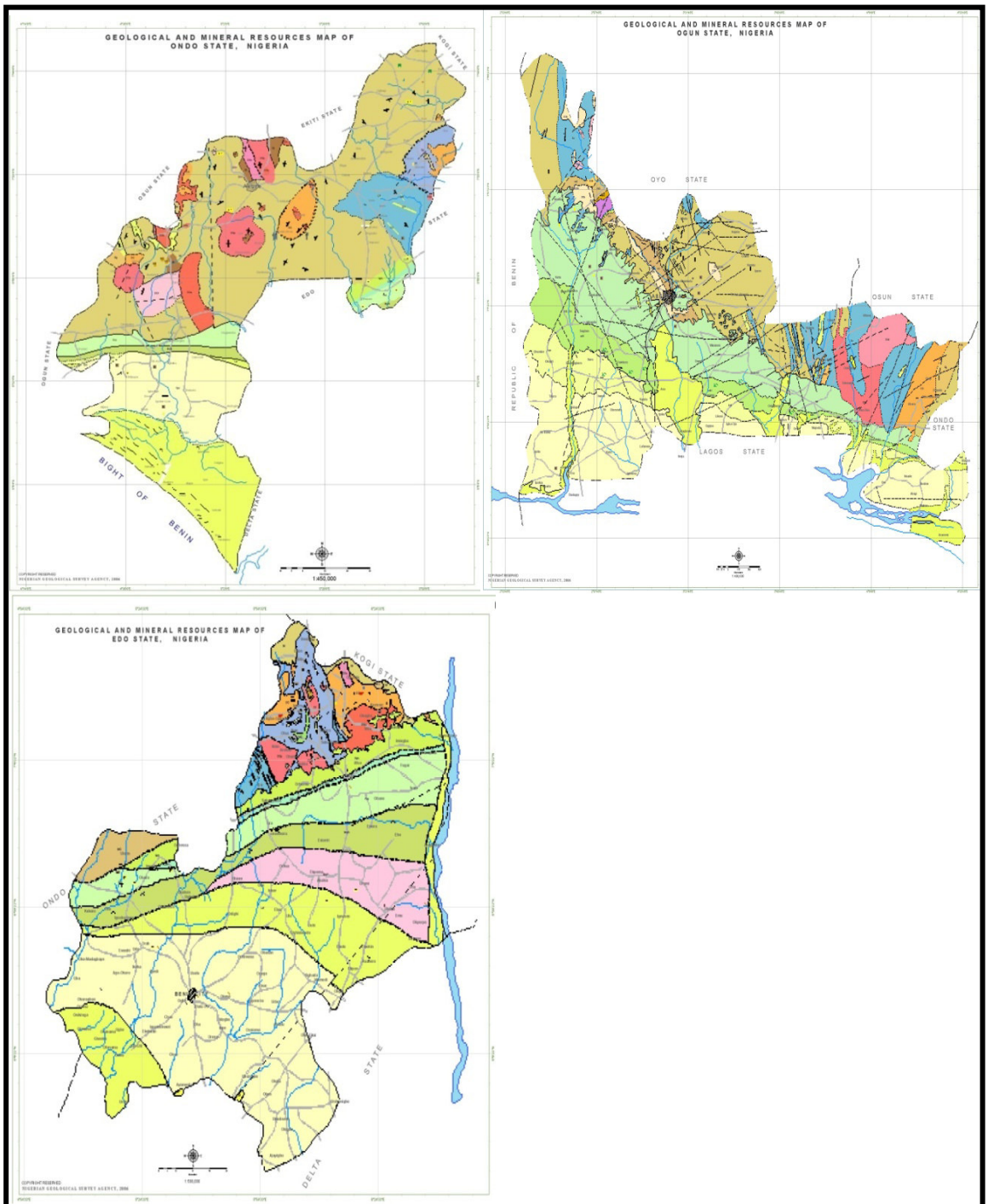
APPENDIX I



Maps of states been covered by the Tar sand belt

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