Mathematically Aided Risk Assessment of Crude Oil Contamination in Ogoni, Nigeria

Part 1. Geo-ecological Characterization of the Pollution

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Abstract

Mathematical modeling can support the environmental risk assessment and decision making processes. Soil contamination caused by crude oil in the Ogoni region, Nigeria, is qualitatively described in part 1 to understand expected mathematical results. A mathematical-statistical analysis following in part 2 characterizes quantitatively the 33 contaminated sites as entire ecological complex. The single sites are studied in part 3 by classifying multivariate mathematical models to derive precise information about kind and degree of contamination at every surveyed spill site.

The geological structure of the Ogoni subsoil and the composition of the upper soil layers are summarized. In this context, the unprotected aquifers are discussed which are essential for the supply of the local population with potable water. The crude oil exploited within and transported through this region for decades will be characterized to understand and interpret results of data processing. Reference will be taken also to the extensive research about negative effects of crude oil contamination on people, fauna and flora.

Oil companies have carried out environmental remediation measures, mainly by land farming. These activities are partly unfinished. Therefore, numerous oil spills are still an environmental hazard. In 2007, the Nigerian Federal Government has invited the United Nations Environment Program (UNEP) to explore the remaining crude oil contaminations in the compartments soil and groundwater to prepare final clean-up measures. This project is finished now. The mathematical data processing presented within this three-part contribution will be understood as part of this survey.

Geographical and Geological Outline of Ogoni

Ogoni, the home of Ogoni people, is an area of the Niger River delta and is part of the Rivers State, Federal Republic of Nigeria, subdivided in several Local Governmental Areas (LGAs). The delta covers 24,000 km² in which 30 millions of people are living (Fig. 1). It consists mainly of wetland and involves the four zones coastal barrier islands (not to be considered here), mangrove swamps, freshwater swamps, and lowland rainforest, creeks, deltaic tributaries, flood plains. A satellite photo (Fig. 2) published by Google maps [15] imparts an imposing impression of the former habitat in Ogoni. This unique ecosystem in the tropics was originally characterized by an extremely high biodiversity and a wide belt of rainforest. According to the dense population in Ogoni, the original environment is widely displaced by agricultural areas and other vulnerable goods of public interest like villages and their infrastructure (roads, hospitals, schools, hand dug groundwater wells etc.).

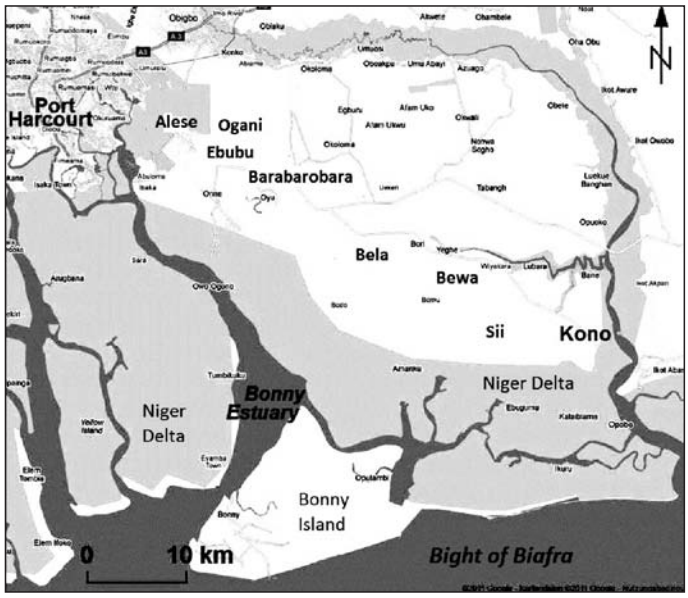

Fig. 1 General map of Ogoni; basic layer from [15]
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The Niger Delta region was a Cretaceous triple junction leading to sea floor spreading within the Atlantic Ocean and a structural zone of weakness in the Benin trough: the old Gondwana continent began to break and the South America plate drifted towards west. At the same time, the intermittent breaching by marine waters of a southern land barrier called Walvis Ridge took place [5]. The stratigraphic sequence in the studied area is built up by an interbedding of paralic sandy and clayey layers deposited since the Late Cretaceous age (Fig. 3). The oldest member in this sequence is the marine Eocene–Oligocene overpressed mud or shale of the Akata formation. Recently, it will be understood as the source of Nigerian petroleum originated from deposited organic substances. The hydrocarbons migrated into reservoir sands of the hanging paralic Agbada formation with a thickness of 300 to 4500 m [6, 21]. Lawrence et al.

Fig. 2 Sensible scenery at Kwawa near Kono, LGA Khana, Ogoni; basic layer from [15]
(Image © GeoEye; Image © 2011 TerraMetrics; © 2011 Google)

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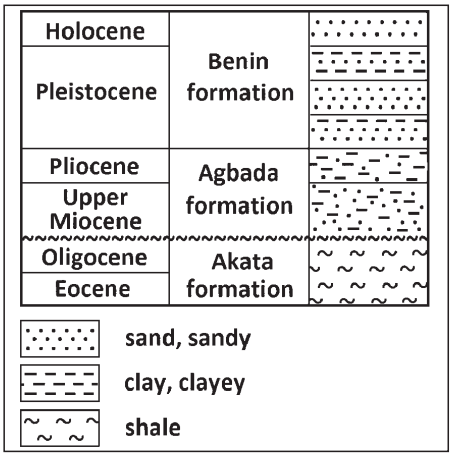

Fig. 3 Principal geological profile of South Nigeria, not scaled

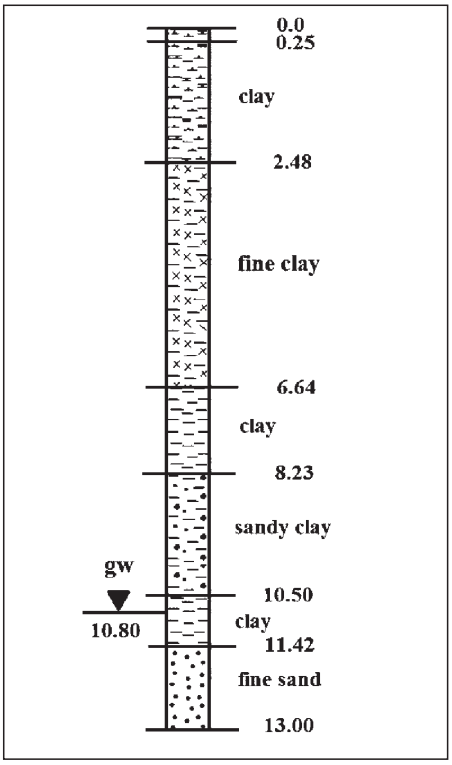

Fig. 4 Well log Okuluebu-Ogale, LGA Eleme; data from [14]

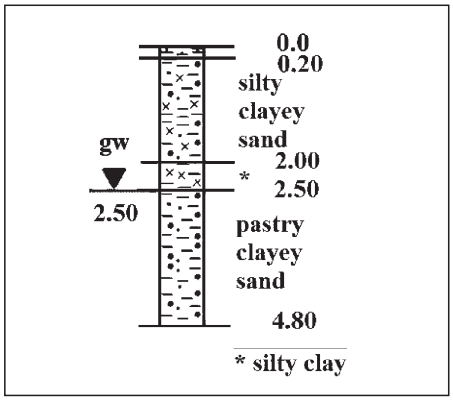

Fig. 5 Well log Kpite S, LGA Tai; data from [14]

[20] reported about the tectonic conditions connected with the oil genesis. After the late Pleistocene transgression to the north followed a regression. The canyon-like Niger Delta began to grow towards south out to the continental shelf, the Gulf of Guinea. The Niger River has continued the deposition of muddy, clayey and mainly sandy sediments in its delta during the Holocene developing the Benin formation which is up to 2100 m thick. These sediments contain also masses of organic material that can change to crude oil in the course of time [8]. The superficial subsoil of the region is "generally dominated by fine-grained silts and clays which are inter-bedded with subordinate and discontinuous sand layers all laid down by the River" (Berthet, Holmes & Vogel, 2010). These unconsolidated sediments are between nearly 10 (beach ridge river zone) and 45 m (NE area) thick.

The soil in the Niger Delta region consists of very dense clayish or loamy sediments with high silt content and relatively little coarser fractions. It is influenced by tropical rainfalls and a relatively high groundwater table that leads to physical and chemical alterations of their composition. The lying of a relatively thin layer of topsoil with high organic content is dominated by silty and clayey strata down to the groundwater table occurring in a depth between about 2 and 13 m (Tables 1 and 2; Figs. 4 and 5). The soil can be described as hydromorphous. It is formed quite uniform without a distinct vertical profile. This is typically for young, alluvial sediments in the tropics [12, 35]. The intergranular space has disappeared in the hydromorphous soil and a reducing milieu seems to diminish the natural degradation of organic compounds. According to the classification used by the US Dept. of Agriculture (USDA) the soil in the delta can be named "inceptisol" or more precisely "entisol", the younger formation with its suborder "fluvent" [36]. Fluvent correlates with "fluvisol" according to the FAO soil taxonomy [12].

The groundwater in the Niger Delta is, first of all, connected with the Benin formation. The aquifer is productive and multi-layered. The upper aquifer is semi-confined [6]. Amajor [2] described the regional lithostratigraphic and hydraulic situation for the upper 0 to –300 m of the Benin formation where groundwater is abstracted in the Rivers State. The aquifers are predominantly developed within sand beds with minor clay, lignite, and conglomerate intercalations. The regional groundwater flow in the Niger Delta is directed towards south. The transmissivity measured for the aquifers ranges from 1.05×10^{-2} to 11.3×10^{-2} m^{2}s^{-1}. The groundwater quality is very good and compares favorably with WHO standards for drinking water in all areas not influenced by human activities. The soil and the upper aquifer are not protected against any dangerous impacts from the surface. The characteristic of the Niger Delta groundwater described by Berthet et al. [7] points to a certain dilemma with respect to impacts of pollutants: "In the wetlands areas the groundwater table is often very shallow and less than 0.5 m below ground level and often perched on impermeable silt and clay layers. The depth to the water table in the superficial deposits of the delta plain area is slightly deeper but generally less than 5 m. Groundwater in the superficial deposits is not considered by the authorities as a strategic water source through a combination of limited storage capacity, saline intrusion and pollution sources on the surface introducing contaminants such as organics and iron." The upper aquifer is commonly used by the local population in hand dug wells.

Table 1 **Groundwater well log Alukere-Ebubu 01, LGA Eleme; data from [14]**

Depth (m)	Lithology	Characteristics	Hydrocarbons
0.00–0.32	organic matter soil	brownish-black	no
0.32–2.28	clay	brownish	no
2.28–7.52	silty clay	brownish	no
7.52–8.53	sandy clay	bright-yellowish brown – light gray	no
8.54	groundwater level		
8.53–9.84	silty sand	light gray – pale yellow	no
9.84–12.00	fine sand	yellow-orange	no

Crude Oil Contamination in the Niger Delta

Nigeria as an OPEC member takes the 15th place in the world oil production. The country produced 2.211 million b/d in 2009 [35]. Rich oil reserves are concentrated in the delta of the Niger river. Ogoni as part of the delta is located southeast of Port Harcourt and covers about 1000 km^2. Crude oil was produced between 1958 and 1993 in several small and scattered fields. Many wells have been drilled and an extensive network of pipelines has been installed to transport the crude oil to the terminal. Although the production has stopped in Ogoni years ago, oil spills are caused by corroding pipelines, inadequate equipment, partly careless handling during the oil production and activities

Table 2 **Groundwater well log Kwawa 01, LGA Khana; data from [14]**

Depth (m)	Lithology	Characteristics	Hydrocarbons
0.00–0.50	organic soil	dark yellowish-brown	smell
0.50–1.00	silty sandy clay	light bluish gray	strong smell
1.00	groundwater level		
1.00–4.50	silty sandy clay	light bluish gray	strong smell

Table 3 **Constituents of crude oil and content in wt%**

Constituent	Formula	Description and environmental hazards	wt% [16]
Alkanes, aliphatic hydrocarbons or paraffins (aliphatics)	C_nH_{2n+2}	frequently toxic aliphatic n-paraffins and their derivates iso-paraffins: saturated hydrocarbons with chains of C: small amounts of dissolved "solution gases" as methane, ethane, propane and butane; liquid constituents as pentane, hexane, heptane, octane … hexadecane [5 to 16 C atoms]; solid matters as paraffin wax [18 to 25 C atoms; 6%] and bituminous asphaltic or asphaltenes [more than 35 C atoms; 6%]. Substances are not, weekly, or moderately water polluting.	between 15 and 60%, average 30%.
Aromatic hydrocarbons (aromatics)	$C_6H_{6-n}R_n$	toxic and carcinogenic unsaturated hydrocarbons with 1 or more six-carbon or benzene-ring(s) of C and radicals R; e. g. benzene, naphthalene, phenanthrene, subordinated also ethylbenzene, toluene, xylenes. Moderately to strongly water polluting.	between 3 and 30%, average 15%.
Cycloalkanes (naphthenes)	$C_nH_{2(n+1-r)}$	relatively harmless and weekly water polluting, saturated hydrocarbons with 1 or more ring(s) of C: monocyclic (r=1; as cyclopropane, cyclobutane, cyclopentane, cyclohexane) and polycyclic (r>1; as bicyclo-octane) substances.	between 30 and 60%, average 49%.
Phenols	$C_6H_5(OH)$ $C_6H_4(OH)R$	possibly mutagen and cancerogenic, water polluting unsaturated hydrocarbons with 1 bencene ring and at least 1 substituting OH group, e. g. phenol and cresols (with radical R).	
Naphthenic acids	mixture	an unspecific mixture consisting of unsaturated polycyclic hydrocarbons consisting of 2 or more bencene-rings with 9 to 20 C atoms as cyclopentyl and cyclohexyl carboxylic acids: aggressive metal corroding substances, hazardous to water and irritant to skin.	varying contents measured by TAN (Total Acid Number)
Resines	mixture	an unspecific mixture of notably liquid, adhesive organic carboxylic acids without specific dangerous potential.	
Alkanals (aldehydes)	COH-R	hydrocarbons with a COH core and a radical R (aliphatic or aromatic) group, e. g. benc-aldehyde: causes crucial adverse effects following inhalative exposure, is partly carcinogen and water polluting.	traces
Alkanthiols (mercaptans)	C_nH_{2n}+1SH	sulfur containing toxic alkanes with SH group; extremely water polluting liquid mixtures.	traces
Metal bearing porphyrin complexes	complexed $[C_4H_4NH]$ rings with Fe, Cu, V, Ni, or Mo	aromatic heterocyclic macrocyclic hydrocarbons consisting of four modified pyrrole subunits (5-membered C4H4NH rings) where the metal atoms are centered towards the interior N atoms. Harmless, close to nature substances within the light oil fraction.	traces

where pipelines were tapped to extract oil illegally. Crude oil transporting pipelines are the major contaminant sources for oil spills in Ogoni. The often elongated shape of such oil spills is caused by a higher transmissivity which forms a preferential pathway for crude oil along pipelines where soil has been loosened by excavation to put down pipelines.

Consequently, crude oil sank into subsoil, contaminated surface and groundwater and polluted the ecologically sensible wetlands and important farmland.

The crude oil composition covers nearly 500 compounds. Every crude oil is characteristic and a fingerprint for the respective source. Table 3 informs about the main compounds of crude oil. For details, see also [29]. Oyekunle & Famakin describe Nigerian crude oil in more detail, however related to the physical properties viscosity and gravity [27].

The Nigerian crude oil belongs to the group of light sweet oils (L. S. Crude). The attribute sweet means less than 0.5% sulfur (bound to mercaptans) and the attribute light describes a low specific gravity due to a high portion of light hydrocarbon fractions and low wax content. The gravity of light crude oil is less than 0.870 corresponding to >31.1 API°. Usually, crudes will be named by their export terminal or depot (here: Bonny island); therefore, the name of the Ogoni crude oils is Bonny light crude oil (BLCO). It is produced in Ogoni by Shell and Chevron concessions [10]. A detailed analysis was made by Onyema & Ajike [25]. They compared the composition of Tertiary Niger Delta crude oils and concluded that they contain the important compartment light hydrocarbons heptane (C_7, LHs): *n*-heptane, isoalkanes, cyclopentanes and cyclohexanes and they "were shown to mature and exhibit high six ring preference (6 RP). .Heptane ratio allowed two distinct oil sets to be discriminated. C_7 LH invariance among the crude oils, although relatively constant, separated the Niger Delta oils into two source-related families: terrigenous for the Western oil and marine for the Central and Eastern subtype. Similar patterns followed by the Central and Eastern oils were different from the Western further affirming two homologous sources for crude oils in the Tertiary Niger Delta." The Niger Delta oils are frequently gassy and they have a high content of solved gas.

Table 4 shows the chemical analysis of Bonny light crude oil published by Chevron Corp. [9].

Crude oil is composed of numerous hazardous substances (Table 3). Subsoil contamination caused by crude oil can be distinguished by their qualitative and quantitative characteristics. Kind and degree of such pollution is depending on the amount of spilled oil, the primary composition of the impacting substance, on the duration of impact, on the local soil properties inclusively water saturation and their ability to migrate. The oil is nearly insoluble in water but swims up

as a thin film on the groundwater water surface and covers soil grains without phase boundary. Due to this property, essential micro-organisms in subsoil are not aerated, soil functions will be stopped and all higher forms of animal life will die ([37]). Drinking water taken from contaminated wells is poisonous and dangerous to health. Oil spills are also contaminating farmland, fishing water, natural habitats (like the remnants of the mangrove forest), and last but not least villages. After years, volatile compounds evaporate, whereas remaining substances stay as insoluble tar and tar oil in the soil.

Ayotamuno et al. reported that crude oil and products as well contaminate the unprotected upper aquifers in Rivers State and especially in Ogoni area [6]. Eyong, et al. showed that shellfish exposed to crude oil contaminated water is significantly toxic and dangerous to health [11]. Farombi et al. described the influence of BLCO on the human fertility and concluded that it is measurably dangerous, although crude oil is commonly used also by the local population in folklore medicine [13]. Another study [18] shows that oil spillage and gas flaring in the Niger Delta region is reducing the population of birds as well. Originally, there were more than 900 species of birds. Many of them are not endemic in the delta anymore. The detrimental influence of crude oil to Guinea pigs was studied in [26]. The toxicity of Bonny light crude oil against Freshwater shrimps (*Desmocaris trispinosa)* was proved in [22]. The authors stated a high toxicity compared even with the influence of an oil dispersant (Nalco-D4106) on the shrimps; an additive of the dispersant brought into the test arrangement, however, was able to reduce the toxicity of oil.

Revitalization Measures

In general, oil-exploring companies try to minimize any soil and groundwater pollution. Thus, in [1] an environmental management plan is described valid for the recovery of the Diebu Creek deposit by the Shell Petroleum Development Company of Nigeria Ltd. (SPDC). Nevertheless, soil and water contamination is occurring often.

Clean-up activities, mainly by excavation, land farming and backfilling of (partially) degraded soil, took place in the investigated area since years. The results are reported in [7] as follows: "SPDC has a substantial history related to the remediation of oil spills. In August 2007 SPDC reported that 1002 of 1062 pre-2005 'legacy' sites had been remediated: all 224 sites contaminated in 2005 had been remediated; all but 13 of sites contaminated in 2006 had been remediated and 45 of 225 sites contaminated in the first six months of 2007 had been remediated. .In August 2007 therefore a total of 253 contaminated sites remained to be remediated. SPDC report that about 30% of oil spill incidents have been accompanied by deliberately set fires resulting in the presence of burnt residues on many impacted sites. SPDC procedures specify that the remediation of oil spills shall be carried out seamlessly and timely to return the environment to a 'safe and fit for purpose condition' and to meet the Nigerian Department of Petroleum Resources Environmental Guidelines and Standards for Petroleum Industry in Nigeria (EGASPIN) (VIII-F1) intervention level…The remediation intervention level of TPH is soil is set by this standard at 5000 mg/kg (ppm). All remediation processes are approved by the Department of Petroleum Resources EGASPIN and all remediation actions are preceded by a Risk Based Corrective Action assessment of the impacted site. Earlier impacted sites may exist where TPH levels still exceed the current intervention value of 5000 mg/kg." The short report issued by Shell [28] quoted that 282 sites were remediated in Nigeria during 2010.

Monitored natural attenuation can be considered as one of the possible strategies to revitalize contaminated subsoil. Studies made from several experts have shown that a remarkable microbiological degradation in the estuarine microcosm is ongoing. Amund & Akangbou investigated four different types of Nigerian crude oil and reasoned that microbes listed in their contribution reduce the original oil concentration in soil to 15 to 45 wt% in the course of 10 weeks [3]. The concrete reduction rate is depending on the oil type. The role of crude oil utilizing bacteria *Bacillus sp.*, *Pseudomonas sp.*, *Vibrio*, *Micrococcus* and *Alcaligenes* as aerobic heterotrophs was studied in [19]. They stated that the total extent of crude oil degradation by these organisms ranged from 26.7% to 43.3% – depending on the primary concentration of oil in soil and on the season – after 16 days and that especially hydrocarbons with C_{14} up to C_{32} were degraded. High rates of biological degradation of BLCO applying *Pseudomonas aeruginosa* cultures to clean-up soil were also measured [23]. These results were confirmed by investigations of other authors as [3, 4]. They point to concrete possibilities to reduce the degree of pollution in subsoil by suitable measures based on land farming and microbiological degradation. Furthermore, Ibekwe et al. [17] showed that an addition of organic nutrient in form of poultry manure to soil material contaminated by crude oil supports the biodegradation measurably (enhanced biodegradation). The oil concentration was reduced to 70–60% within seven weeks. However, these results from tests in laboratories do not correspond with the strong presence of volatile hydrocarbons even on old spill sites. It is obvious that there are existing differences between natural and the laboratory conditions.

The United Nations Environment Program (UNEP) was invited by the Nigerian Federal Government in 2007 to undertake an environmental assessment of Ogoni and to determine the appropriate levels of remediation needed to rehabilitate the land to a condition that is environmentally acceptable. UNEP experts analyzed the present state of contaminated sites [32]. "The first step to making the land cleaner is to carry out the environmental assessment which will determine the nature and extent of the oil contamination. Only once the results of the assessment are known UNEP will be able to make recommendations for a clean-up program" [31]. UNEP is working together with the Rivers State University of Science and Technology, the Nigerian government officials at national and Rivers State level, traditional rulers, local landowners, laboratories and many other stakeholders [33]. Well logs to describe the soil composition have been made by FUGRO Nigeria Ltd. [14]. Chemical analyses applied in this contribution were made by a UK laboratory on request of UNEP.

In the frame of this program, 12 total exploration fields, 116 drilled wells and five flow stations operating during the last 50 years in Ogoni have been compiled [30]. Meanwhile,

Table 4 **Rounded average composition of Nigerian Bonny Light crude oil (from [9])**

Constituent	Content (vol-%)	Thereof aromatics (vol-%)	Thereof naphthenes (vol-%)
Butanes and lighter	0.9		
Light gasoline	4.3		
Light naphtha	13.7	1.7	7.3
Heavy naphtha	10.1	1.5	6.7
Kerosene	13,3	2.7	8.3
Atmospheric gas oil	22.7		
Light vacuum gas oil	16.8		
Heavy vacuum gas oil	13.3		
Vacuum residuum	5.0		
Asphaltenes	0.003		
Sulfur (wt-%)	*0.16*	–	–
V (ppm)	*0.42*	–	–
Ni (ppm)	*4.16*	–	–

UNEP has uncovered numerous spill sites in Ogoni. Over 300 potentially contaminated sites have been identified within the four Ogoni LGA [24] supported by a Shell data base. The aim of any remediation measures is to revitalize the Ogoni subsoil based on a differentiated analysis the sites and kind and degree of their pollution.

The final UNEP report compiling the results of several scientific disciplines was released in August 2011 [34]. The report records severe impact on the environment due to crude oil and oil product contamination. The report summarizes that 200 locations were examined by the UNEP team, 122 km of pipeline rights of way were surveyed. Groundwater and soil pollution has been investigated at 69 contaminated sites. The assessed situation is described as "catastrophic". The period necessary to clean-up all sites was estimated with 25 to 30 years. UNEP recommends set up a special fund for Ogoni to finance this project.

This contribution as well as the following two parts of the mathematical analysis (OilGas Magazine, in press) will supplement the UNEP report, specify its results mathematically and will show a way to manage a great amount of analytical data in the frame of a risk assessment in a mathematical objective and easy way.

Conclusion

Methodology. Any mathematically aided environmental risk assessment requires a preceding study of the natural situation in the investigated sites to avoid later misinterpretations of more or less "abstract" mathematical results. This includes also a certain prior knowledge about location, extension, embedding and effects of previous remediation measures as well including the chemical composition of crude oil which has impacted soil and groundwater.

Incorrect results regarding scientifically based conclusions are programmed if this recommendation will be neglected because usually an uncritical thought of absolute correctness is connected with any mathematically computed quantitative result. Only a critical discussion and a comparison with the real ecological situation lead to realistic information about any kind of contamination.

The authors would like to thank the Nigerian colleagues performing thorough field work at Ogoni to prepare the data basis and UNEP for the systematic survey of oil spills and contaminated sites in the studied region. They are also grateful that is was possible to introduce a satellite photograph regarding the Kwawa region published by Google Maps in the World Wide Web.

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