

Natural radioactivity and trace metals in crude oils: implication for health

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Abstract Crude oil samples were collected from six different fields in the central Niger Delta in order to determine their natural radioactivity and trace element contents, with the aim of assessing the radiological health implications and environmental health hazard of the metals, and also to provide natural radioactivity baseline data that could be used for more comprehensive future study in this respect. The activity concentrations of the radionuclides were measured using a well, accurately calibrated and shielded vertical cryostat, Canberra coaxial high-purity germanium (HPGe) detector system, and the derived doses were evaluated. The metal concentrations were determined by the graphite furnace atomic absorption spectroscopic (GFAAS) method. The

radionuclides identified with reliable regularity belong to the decay series of naturally occurring radionuclides headed by ^{238}U and ^{232}Th along with the non-decay series radionuclide, ^{40}K . The averaged activity concentrations obtained were $10.52 \pm 0.03 \text{ Bq kg}^{-1}$, $0.80 \pm 0.37 \text{ Bq kg}^{-1}$ and $0.17 \pm 0.09 \text{ Bq kg}^{-1}$ for ^{40}K , ^{238}U and ^{232}Th , respectively. The equivalent doses were very low, ranging from 0.0028 to $0.012 \text{ mSv year}^{-1}$ with a mean value of $0.0070 \text{ mSv year}^{-1}$. The results obtained were low, and hence, the radioactivity content from the crude oils in the Niger delta oil province of Nigeria do not constitute any health hazard to occupationally exposed workers, the public and the end user. The concentrations of the elements (As, Cd, Co, Fe, Mn, Ni, Se and V) determined ranged from 0.73 to 202.90 ppb with an average of 74.35 ppb for the oil samples analysed. The pattern of occurrence of each element agreed with the earlier studies from other parts of the Niger Delta. It was obvious from this study and previous ones that the Niger Delta oils have low metal contents. However, despite the low concentrations, they could still pose an intrinsic health hazard considering their cumulative effects in the environment. Also, various studies on the impact of oil spillage and activities of oil exploration and production on organisms in the immediate environment suggest this.

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Table 1 Activity concentration of radionuclides (Bq kg⁻¹) in Niger Delta oils

Sample location	⁴⁰ K	²³⁸ U	²³² Th
Field A	6.49 ± 0.77	ND	0.17 ± 0.09
Field B	10.60 ± 1.25	ND	0.034 ± 0.02
Field C	2.24 ± 0.28	0.39 ± 0.16	0.09 ± 0.05
Field D	19.60 ± 2.32	0.47 ± 0.27	0.30 ± 0.16
Field E	14.13 ± 1.71	0.63 ± 0.36	0.25 ± 0.14
Field F	19.73 ± 2.53	1.29 ± 0.69	ND
Range	2.24–19.73	ND–1.29	ND–0.25
Mean	10.52 ± 1.03	0.80 ± 0.37	0.17 ± 0.09

ND: not detected

radionuclides present, and it is also present in all the oil samples in the area. The activity concentration of ⁴⁰K ranged from 2.24 ± 0.28 to 19.73 ± 2.53 Bq kg⁻¹ with a mean value of 10.52 ± 1.03 Bq kg⁻¹. The higher concentration of ⁴⁰K compared to ²³⁸U and ²³²Th is consistent with Ahrens (1957), who noted that the activity of ⁴⁰K in sedimentary rocks depends on the relative amounts of feldspar, mica and clay minerals that make up the mineral-aggregate sediments. The high concentration of ⁴⁰K could be attributed to the presence of feldspar and clay that characterises the formations in the Niger Delta (Whiteman 1982).

The range of the specific activity for the series ²³⁸U varies from ND to 1.29 Bq kg⁻¹, with a mean value of 0.80 ± 0.37 Bq kg⁻¹. It is below detectable limits in fields A and B. It is the second highest contributor to the total activity in the area.

The least contribution to the total activity in the area is made by ²³²Th, with concentrations ranging from complete absence to 0.25 Bq kg⁻¹ and a mean of 0.17 ± 0.09 Bq kg⁻¹, and it is below detectable limits in field F. In contrast to ²³⁸U, ²³²Th is highly insoluble under all geochemical conditions. This means that it will have been more difficult to mobilize ²³²Th than to mobilize ²³⁸U from the source from which they get into the oil even if they had occurred with the same concentration in the source material. This agrees with the NCRP (1987) that uranium is more mobile than thorium, and would appear to explain the observation that U levels are more than Th in the oil samples. Figure 1 shows the contribution of each radionuclide in each sample.

The report of Mokobia et al. (2006) on the radioassay of some Nigerian fossil fuels (coal and

bitumen) showed a strong correlation between the levels of metals and radionuclides in the fossil fuels. The higher the concentrations of metals was, the higher the specific activity concentrations of radionuclides in the fossil fuels (Figs. 2 and 3). Bitumen had higher ²³⁸U and ²³²Th contents compared to their contents in coal. It then follows that the low specific activity concentrations found in these crude oils are a result of their low metal contents.

Arogunjo (2002) gave the distribution of radionuclide activities in soils and sediments from the Niger Delta region; the soils and sediments were not necessarily contaminated by oil spills. According to his work, the activity concentrations of K within the region ranged from 13.4 ± 0.7 Bq kg⁻¹ at IgboKoda to 127.8 ± 0.8 Bq kg⁻¹ in Calabar. The activity concentrations of ²³⁸U within the region ranged from 10.8 ± 2.0 Bq kg⁻¹ at the Imo river flow station to 26.7 ± 1.5 Bq kg⁻¹ at Otujememi, while that of the activity of ²³²Th ranged from 11.0 ± 2.2 Bq kg⁻¹ at Ovu-Kokori to 30.5 ± 1.9 Bq kg⁻¹ at Ekulama. The mean activity concentrations for ⁴⁰K, ²³⁸U and ²³²Th are 34.8 ± 20.4 Bq kg⁻¹, 16.2 ± 3.7 Bq kg⁻¹ and 24.4 ± 4.7 Bq kg⁻¹, respectively. The activity concentration of ⁴⁰K accounts for the highest rate of 46.1% compared to the 21.5% and 32.4% for ²³⁸U and ²³²Th, respectively. The highest contribution from ⁴⁰K is also reflected in this study. However, ²³²Th has a higher contribution than ²³⁸U, unlike what is obtained in the oil samples analysed where the contribution from ²³⁸U is higher than that of ²³²Th. This can be explained from the standpoint that

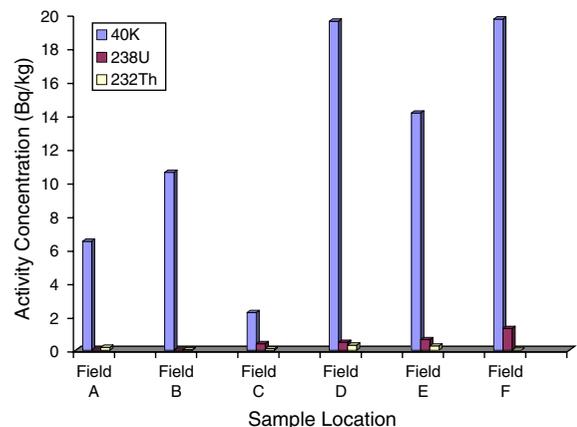


Fig. 1 Illustration showing the contribution of each radionuclide in each sample

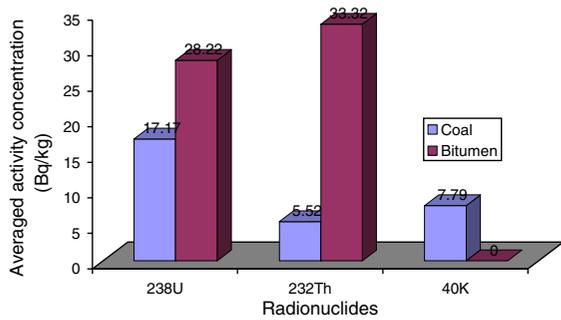


Fig. 2 Averaged activity concentration of some Nigerian fossil fuels (after Mokobia et al. 2006)

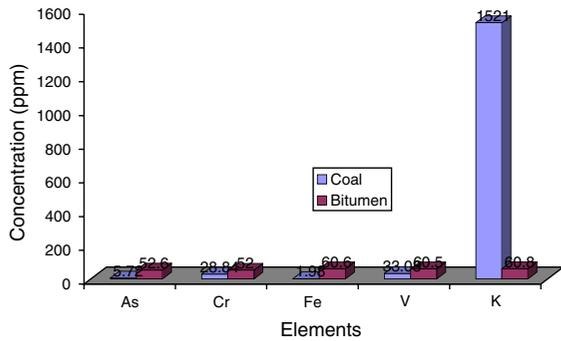


Fig. 3 Averaged elemental composition of Nigerian fossil fuels (ppm) (from Mokobia et al. 2006)

thorium is insoluble under all geochemical conditions, and as a result, it would have been less easily removed or mobilised from the source material than uranium.

All the radionuclides have far lesser activity concentrations in the oils than in the rocks/sediments in the region. Many occurrences of metalliferous minerals are associated with petroleum liquids or altered petroleum in the form of viscous liquids or solids. The significant concentration of metals in many oils and oil-field brines suggests that transportation of metals in petroleum as stable organo-metallic complexes is an important process in certain types of ore genesis (Sverjensky 1984). The radionuclides of ²³⁸U, ²³²Th and ⁴⁰K must have been from the organic matter-rich predominantly shale source rocks in the area or from when petroleum liquids that have migrated up dip from mature source rocks and encountered oxygenated aqueous geothermal fluids rich in uranium by circulating through permeable sandstones in the region. Progressive oxidation of the migrated petroleum would be accompanied by the

formation of stable organo-metallic compounds or ligands, such as organo-uraniferous complexes.

Bell (1960) suggested that the bitumens in Nigeria could have extracted their uranium and thorium from the host rocks and that he found no evidence to suggest that petroleum acts as an ore-forming fluid. It is therefore most probable that the uranium and thorium contents of the crude oils are from the source rocks in the Niger Delta and must have complexed with the crude oil.

Absorbed dose rate

The absorbed dose rates in air calculated from the radioactivity concentration of each sample are given in Table 2. Radiation emitted by a radioactive substance is absorbed by any materials it encounters, dead or living cells. Every kilogram (kg) of material absorbs some energy (joule or J). The unit J kg⁻¹ is used for the measurement of the absorbed dose. In radiation protection, the unit is called the gray (Gy).

The corresponding absorbed dose rates have been calculated using the relationship derived by Beck et al. (1966), which is given as

$$D = 0.042 A_{c(K)} + 0.429 A_{c(U)} + 0.666 A_{c(Th)}$$

where D is in nGy h⁻¹ and represents the absorbed dose rate in air due to the specific activity concentration of A_{c(U)}, A_{c(Th)} and A_{c(K)} in Bq kg⁻¹, respectively. The values of D ranged between 0.32 and 1.38 nGy h⁻¹ with a mean of 0.85 nGy h⁻¹, which is on the very low side of normal background radiation (Ajayi et al. 1996). Normal background radiation ranges approximately between 30 and 70 nGy h⁻¹ (UNSCEAR 1993).

Table 2 Gamma dose rates in the sample locations deduced from the radionuclides in the samples

Sample location	Absorbed dose rate (nGy h ⁻¹)	Equivalent dose (mSv year ⁻¹)
Field A	0.39	0.00342
Field B	0.45	0.00395
Field C	0.32	0.00281
Field D	1.23	0.0108
Field E	1.03	0.00903
Field F	1.38	0.0121

The absorbed dose rate itself does not give an indication of possible biological effects until it is converted into the equivalent dose, which is measured in Sievert (Sv). The absorbed dose rate is multiplied by a radiation-weighting factor, which is 1 for gamma radiation and 20 for alpha radiation because 1 Gy of alpha radiation is about 20 times more severe than 1 Gy of gamma radiation. Using 365.25 days as the total number of days in a year, Table 3 shows the calculated absorbed dose rate in nGy h⁻¹ and the corresponding equivalent dose rate in mSv year⁻¹. The equivalent dose ranges from 0.0028 to 0.012 mSv year⁻¹ with a mean of 0.0070 mSv year⁻¹. Comparing the results with the dose limit set by the ICRP, one notes immediately that the values are all far lower than the normal background for humans. The values are far below the harmful limit for humans handling or exposed to the crude oil.

Trace metals in crude oils

A wide range of metals have been determined in crude oils, especially the Niger Delta oil. However, few of the metals that are pertinent to objectives of this study will be considered.

It is evident from various studies that the Niger Delta oils have low metal contents (Oluwole et al. 1993; Asuquo et al. 1995; Akinlua and Torto 2006), especially nickel and vanadium contents, compared with Venezuelan crude oil (Stacy 1994), which is a characteristic feature of oils derived from organic matter of strong terrestrial input.

Cobalt concentration ranged from 1.08 to 14.18 ppb (Table 3). The low values are comparable with those obtained from other parts of the Niger Delta (Oluwole et al. 1993; Akinlua and Torto 2006) (Table 4). Arsenic has concentration values from 3.74 to 9.13 ppb (Table 4), which is consistent those obtained from other parts of the Niger Delta and is also comparable with the arsenic content of Venezuelan oil (Oluwole et al. 1993; Stacy 1994; Akinlua and Torto 2006) (Table 4). Iron concentration ranged from 1.62 to 202.90 ppb (Table 3). Iron is the predominant transition metal in these oils, as it is for other Niger Delta oils (Oluwole et al. 1993; Akinlua and Torto 2006) (Table 4). Concentration of manganese ranged from 6.40 to 22.93 ppb (Table 3). The low values are in agreement with those other

Table 3 Trace metal data of central Niger Delta oil

Sample	As	Cd	Co	Fe	Mn	Ni	Se	V
Field A	9.13 ± 0.001(1.57)	47.68 ± 0.001(0.07)	14.18 ± 0.005(3.36)	202.90 ± 0.068(4.22)	7.22 ± 0.008(4.24)	152.71 ± 0.017(6.08)	0.90 ± 0.000(2.11)	48.51 ± 0.001(0.98)
Field B	6.03 ± 0.002(4.27)	4.70 ± 0.011(6.12)	8.69 ± 0.003(2.82)	171.87 ± 0.028(1.88)	6.40 ± 0.003(1.80)	117.03 ± 0.005(2.20)	0.80 ± 0.001(7.80)	59.94 ± 0.002(3.04)
Field C	3.74 ± 0.002(5.54)	1.01 ± 0.003(6.84)	1.28 ± 0.000(3.14)	160.27 ± 0.070(5.05)	15.66 ± 0.018(4.25)	45.23 ± 0.004(4.63)	0.87 ± 0.001(7.97)	38.55 ± 0.002(3.86)
Field D	7.34 ± 0.003(5.03)	2.21 ± 0.001(0.58)	1.08 ± 0.001(7.04)	163.97 ± 0.005(0.33)	15.95 ± 0.015(3.73)	29.58 ± 0.004(6.58)	1.09 ± 0.000(4.09)	37.73 ± 0.000(1.02)
Field E	5.08 ± 0.001(2.95)	2.90 ± 0.002(1.82)	1.12 ± 0.001(4.79)	159.83 ± 0.044(3.16)	15.34 ± 0.007(1.80)	29.16 ± 0.001(1.80)	0.73 ± 0.000(2.39)	32.62 ± 0.002(5.48)
Field F	5.59 ± 0.000(0.36)	3.34 ± 0.004(2.96)	3.18 ± 0.001(3.39)	1.62 ± 0.091(6.36)	22.93 ± 0.004(0.72)	72.36 ± 0.000(0.72)	0.79 ± 0.000(0.47)	43.61 ± 0.002(4.57)

Concentrations are presented in ppb; values in parenthesis refer to the %RSD

Table 4 Comparison of trace metal data of Niger Delta oils

Metal	This study (ppb)	Oluwole et al. (1993) (ppm)	Asuquo et al. (1995) (ppm)	Akinlua and Torto (2006) (ppb)
As	3.74–9.13	0.001–0.33	–	–
Cd	1.01–47.68	–	–	–
Co	1.08–14.18	0.008–0.99	–	0.15–7.34
Fe	1.62–202.9	3.40–9.54	0.20–0.42	23.38–259.12
Mn	6.40–22.93	0.023–0.76	0.02–0.10	0.29–18.65
Ni	29.16–152.71	0.54–5.71	0.20–0.82	2.34–76.13
Se	0.73–0.90	0.022–0.101	–	–
V	32.62–59.94	0.054–1.06	0.65–1.30	2.74–44.37
Cu	–	–	0.05–0.08	0.77–53.78
Pb	–	–	0.02–0.07	9.00–941.20

parts of the Niger Delta (Oluwole et al. 1993; Asuquo et al. 1995; Akinlua and Torto 2006) (Table 3). Concentrations of nickel and vanadium range from 29.16 to 152.71 ppb and 32.62 to 59.94 ppb, respectively (Table 3). These low values of Ni and V are consistent with those obtained for other parts of the Niger Delta (Oluwole et al. 1993; Asuquo et al. 1995; Akinlua and Torto 2006) (Table 4). Selenium has concentration values from 0.73 to 1.09 ppb (Table 3). These values are comparable with those obtained for other parts of the Niger Delta (Oluwole et al. 1993) (Table 4). Cadmium concentration ranged from 1.01 to 47.68 ppb (Table 3).

Implication for health

The absolute concentrations of these metals are generally low and below the guideline limits of these metals in effluent from the petroleum industry. However, they could still pose intrinsic health hazards considering their cumulative effects in the environment. The metals can enter the environment by accidental oil spills or through combustion products of the refined crude oil. A number of crude oil spills occur each year. Between 1976 and 1986, about 1.8 million barrels of crude oil were spilled into the land, swamp and offshore environments in Nigeria (Ifeadi and Nwankwo 1987). In recent years, a far greater volume than the above was spilled into the environment through the acts of sabotage.

Most remediation processes employed in the cleanup of oil spills involve degradation of the organic constituents; the metals may not degrade the same way as the organics do and may remain for an indefinite

period of time. Hence, more incidents of oil spills will increase the concentrations of the metals in the environment. It is also known that certain organisms have the ability to accumulate and biomagnify metals (Osuji and Onojake 2004; Davies et al. 2006).

Many case studies have shown the effects of pollution of the environment by petroleum in Nigeria. The toxicity of treated petroleum effluent from one of the refineries in Nigeria was tested by Oladimeji and Onwumere (1987), and they reported that fish accumulated trace metals at a rate a hundred-fold higher than what was in the effluent. They concluded that the results of chemical analysis may be misleading and recommended integrated studies that involve ecological monitoring of receiving waters to determine the effect on the biota. Osuji and Onojake (2004) reported enhanced levels of the trace heavy metals Ni, Cu and Pb, which are normal constituents of crude oil, in the soils of oil-spill-polluted sites compared to a geographically similar, unaffected area located 50 m from each contaminated site. They further stated that the enhanced levels of these metals in the soils may result in enhanced absorption by plants, which may bring about possible bioaccumulation by such plants and the animals that depend on them for survival, and all of these may lead to toxic reactions along the food chain. This also may bring about eventual adverse consequences for humans. Davies et al. (2006) reported a study on bioaccumulation of heavy metals in water, sediment and periwinkles (*Tympanotonus fuscatus var radula*) from Elechi Creek, Niger Delta. The study showed that the sediment accumulated more heavy metals than the water, while the periwinkles

accumulated more of these metals than the sediment. This also further emphasizes the ability of animals to bioaccumulate metals, which could be of far lower concentration in the environment. Concentrations of trace metals (lead, iron, copper and zinc) in crops harvested in some oil-prospecting locations in Nigeria were estimated (Hart et al. 2005).

The study revealed higher concentrations of metals in various food crops harvested from the industrialized areas (oil-prospecting locations) compared to the non-industrialized area. These findings were indicative of industrial pollution from oil prospecting. They concluded that although the essential elements are beneficial to humans and plants, when found in excessive amounts well above the levels normally found in food, they can prove detrimental to health, particularly when they exist in commonly consumed food crops.

Conclusions

Specific activity of radionuclides present in crude oils obtained from the Niger Delta were identified and quantified. Their equivalent doses were determined so as to assess the health impact on humans. The results of the study indicated that the radionuclides identified belong to the naturally occurring decay series headed by ^{238}U and ^{232}Th as well as the single-decay type, ^{40}K . The average specific activity contents of ^{238}U , ^{232}Th and ^{40}K in the oil samples in the study area have values that agree with those reported by previous workers in various environmental samples, such as soil, rock, building materials, water and foodstuffs, etc. The study also showed that the radionuclides present differ in quantity from location to location. This might be due to the heterogeneity of the environments in which the radionuclides are deposited since it could be greatly influenced by the type of mineral or source rock, as well as other factors. The assessment of health impact due to gamma radiation of the study reveals that it is safe for people to handle or use the oil because of its very low radioactivity level. However, long exposure may pose an intrinsic health hazard.

Trace metal concentrations of central Niger Delta oils were determined using the graphite furnace atomic absorption spectroscopic method. The concentrations of the metals were relatively low, which is

a characteristic feature of oils from other parts of the Niger Delta and oils derived from organic matter of strong terrestrial input. Despite the low concentrations, they could still pose an environmental hazard because of their cumulative effects in the environment as a result oil spills and other means by which metals in oil enter the environment and also the ability of some organisms to accumulate and bio-magnify some metals. A number of studies from the Niger Delta have confirmed this.

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