

**TRACE ELEMENT LEVELS IN TERRESTRIAL
AND AQUATIC ENVIRONMENTS NEAR THE
NIGERIA RESEARCH REACTOR***

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ABSTRACT

Soils and river sediments sampled around the vicinity of the Nigeria Research Reactor-1 (NIRR-1) were investigated for their physical properties, morphology, and trace element levels as part of a the reactor pre-operational environmental monitoring campaign. Neutron Activation Analysis (NAA), was chosen as the analytical technique of interest via the k_0 -Standardization method. We identified Fe, Zn, Co, Na, K, Rb, Sc, Cs, Sb, Br, Ba, La, Hf, W, Yb, Cr, U, Th, Lu, Ce, Nd, Ta, and Tb as elements at different concentrations in both matrices. Gold and Zirconium foils were used as the single comparator and thermal neutron flux monitor respectively during the reactor irradiations. The International Atomic Energy Agency (IAEA) Soil-7 was used for the quality control of the measurements to ensure precision of the analytical process, which was found to be better than 5% within the confidence interval specified for each of the elements.

*This project was initially funded by the Centre for Energy Research and Training Ahmadu Bello University, Zaria. The International Atomic Energy Agency (IAEA), Vienna, Austria, is equally acknowledged for an IAEA Fellowship (NIR 99002) to one of us (I. O. B. Ewa) at the Institute of Nuclear Techniques (INT), Technical University of Budapest, Hungary, where the analytical part of the work on k_0 -Standardization was done. We also appreciate the use of the INT facilities for the Monte Carlo evaluation.

INTRODUCTION

The Nigeria Research Reactor-1 (NIRR-1), installed at the Centre for Energy Research and Training, Ahmadu Bello University, Zaria, is the first nuclear reactor in the country. This reactor which was critical on February 3, 2004, is one of the Miniature Neutron Source Reactor (MNSR) type, small, compact, safe with a power output of 30 kW, and neutron flux of about $1.0 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ (SAR, 1999). NIRR-1 is equally a low-hazard research reactor of the tank-in-pool type. The core is immersed in water to a depth of 5.7 m and during normal operations the release of radioactivity to the environment is considered very low below the limits that could cause any radiological impact either to the workers or the environment.

NIRR-1 is a low power research reactor when compared with the Chernobyl and Three Mile Island reactors whose high power-ratings make them capable of supplying sufficient thermal energy output for the generation of electricity. By its design therefore, it is anticipated that NIRR-1 will not pose any serious problems if operated strictly in compliance with internationally accepted regulations and procedures. However, being a nuclear facility, its pre-installation requirements necessitated an investigation of several site characteristics including base-line radiological levels, meteorology, physical properties of the soil, geological survey of the area, seismic state of the region, and levels of trace elements within the reactor environs.

The investigation on the trace element levels became necessary in order to allay fears of any environmental degradation in trace element levels while the reactor is in operation. It is for this reason that a pre-operational campaign of the trace element levels for both terrestrial and aquatic environment surrounding the reactor was undertaken. Soil and sediment samples from the study site were subjected to Instrumental Neutron Activation Analysis (INAA) using the k_0 -Standardization method.

STUDY SITE

The study site is the location of the research reactor within the Samaru savannah plains which could be referred to in the Nigeria Geological Topographic Map Sheet No. 102 SW Zaria, bounded by latitudes $110^\circ 8' \text{ N}$ and $11^\circ 10' \text{ N}$ as well as longitudes $7^\circ 41' \text{ E}$ and $7^\circ 42' \text{ E}$.

EXPERIMENTAL

Sampling

Soil samples were taken around marked points within the vicinity of the reactor building and toward the flood plains where the run-off surface water drains into the Kubanni river. This river drains the entire Samaru plains including the

site where the Nigeria Research Reactor (NIRR-1) is located at the Centre for Energy Research and Training, Ahmadu Bello University, Zaria, Nigeria. Sediment samples from the river were also obtained for analysis by using standard techniques of coring as proposed in IAEA (1970).

Sample Preparation

Soils and sediments were obtained from the sampling sites and transferred to the laboratory. The soils and sediments were dried to constant weight using a low temperature oven maintained at 50°C for two days. Thereafter, both sediment and soil samples were weighed into snap-cap vials, heat-sealed, ready for irradiation. Soil 7 was used as the quality control secondary standard and was prepared in the same manner as the samples.

Irradiation

The soil, sediment, and quality control reference standards were all subjected to 8-hour irradiations at the WWR-Research Reactor of the Technical University of Budapest, Hungary. This reactor rated at 100 kW operates at a full neutron flux of $2 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$. Gold was used as the comparator standard while zirconium foils were used as flux monitors during the irradiation. At the end of irradiation both samples and standards were cooled for a period of 10 days and counted with an HpGe (vertical dip-stick) detector for 30 minutes.

The SAMPO 90 (Logion, 1993) program was used for the spectral acquisition in order to obtain the specific intensities of the radionuclides of interest. The k_0 -Standardization method was used for the calculations of the element concentrations based on the following theoretical concepts.

Concentration Measurements by k_0 -Standardization

For ideal spectra, the evaluation of the concentration of elements of interest in the samples using the k_0 -Standardization method could be obtained using the expression below (De Corte, Simonits, DeWispelaere, & Hoste, 1987):

$$\text{Conc (ppm)} = \frac{I_{sp} \varepsilon_{\gamma}^* \{f + Q_o^*\}}{I_{sp}^* k_0 \varepsilon_{\gamma} \{f + Q_o\}} \quad 1.0$$

(Gold-comparator data with an asterisk)

where the specific intensity $I_{sp} = \frac{N_p}{t_m \cdot S \cdot D \cdot C \cdot m}$ and

N_p = net peak counts, t_m = measurement time, m = sample weight

k_0 = constant for gold, ε_{γ} = detector efficiency

S = saturation factor = $1 - e^{-\lambda t_r}$

$D = \text{decay factor} = e^{-\lambda t_d}$

$C = \text{counting factor} = \frac{(1 - e^{-\lambda t_c})}{\lambda t_c}$ and $\lambda = \frac{\ln 2}{T_{1/2}}$

$t_r = \text{irradiation time}, t_d = \text{decay time}, t_c = \text{counting time}$

$Q_o = \frac{I_o}{\sigma_{th}}$; I_o denotes the resonance integral, σ_{th} is the thermal absorption cross-section

However, since we obtained non-ideal spectra for this work, corrections for the neutron spectrum parameters were made for the concentration of the elements determined using the expression also proposed by De Corte et al. (1987) in Eqn. 2.0:

$$\text{Conc (ppm)} = \frac{I_{sp} \varepsilon_{\gamma}^* \{f + Q_o^*(\alpha)\}}{I_{sp}^* k_o \varepsilon_{\gamma} \{f + Q_o(\alpha)\}} \quad 2.0$$

where:

$f = \text{the thermal to epithermal flux ratio and}$

$\alpha = \text{a measure for the deviation of the epithermal neutron fluence rate distribution from the } 1/E \text{ shape}$

The neutron spectrum parameters f and α in Eqn. 2.0 were determined for the reactor channels using the usual relation as given in Eqn. 3.0:

$$f = \frac{\phi_{th}}{\phi_{epi}} = Q_o (R_{Cd} - 1) \quad 3.0$$

where:

ϕ_{th} and ϕ_{epi} are the thermal and epithermal neutron fluxes at the reactor measurement channel and R_{Cd} the Cadmium ratio

The nuclear data for the gold comparator and zirconium flux monitor used during the analysis are given in Table 1.

Table 1. Nuclear Data Used for Gold and Zirconium Foil Monitors

Nuclide	E_{γ} (keV)	Half-life (s)	$Q_o (I_o/\sigma_{th})$
^{198}Au	411	232 934	15.71
^{95}Zr	724	5 532 192	5.05
	756	5 532 192	5.05
^{97}Zr	743	60 264	248.0

Full Energy Peak Efficiencies (FEPE) for all the gamma energies of interest was obtained using the Monte Carlo Method (Breismeister, 1993) as described earlier in Ewa and colleagues (2001) and was validated using the standard sources since the latter could not take into account all the experimental gamma energies required for all elements evaluated.

RESULTS AND DISCUSSION

The soil showed a typical morphology which is characteristic of tropical ferruginous soils of the group *Alfisols* (Foth, 1984); with an ustic moisture regime leading to hard concretions arising from the presence of iron minerals. This eventually leads to a soil color (see Table 2), within the hue range of 10 YR based on the Munsell Colour Chart (Miller & Donahue, 1997).

The plastic soil structure consolidates the soil aggregates into iron-pan formations. The implication and advantage of this soil structure within the context of trace element migration within the soil strata is that the soil structure will assist in slowing down the rate of spread of trace elements into the soil environment through leaching in the event of any leakage of the reactor steel vessel. This may not be the case if the soil structure were to be loose and sandy without clay as a soil binder.

Twenty-four elements were determined in this work (see Table 3) and could be classified according to their elemental levels as trace (Ce, Co, Cr, Eu, Hf,

Table 2. Morphology of a Typical Soil Environment Profile
Near the Reactor Site

Horizon	Depth (cm)	Description
O-A1	0-10	Brown (10 YR 7/2) dry, loose, weak medium, sub-angular blocky structure, slightly hard, few quartz gravel, wavy boundary
AE	10-30	Pale brown (10 YR 8/3), light loam, clay, medium sub-angular blocky structure, dry, slightly hard, few quartz gravels, clear wavy boundary
A2	30-50	Very pale brown (10 YR 8/3), mottled reddish brown, light loam, clay, moderate medium sub-angular blocky structure, few dead organic debris, gradual boundary
B2t	50-70	Very pale brown (10 YR 8/3) mottled dark brown, reddish yellow fine sandy loam, plastic clay, moderate medium sub-angular blocky structure merging to next horizon

Table 3. Trace Element Data Determined for Soil and Sediments
Near the Nigeria Research Reactor (NIRR-1).
(All units are in ppm ($\mu\text{g}/\text{gm}$) unless as stated)

Elements	Terrestrial (Soil) Mean (σ)	Aquatic (River sediments) Mean (σ)
Ce	58.1 (0.7)	94.52 (0.48)
Co	2.04 (0.3)	5.56 (0.01)
Cr	31.71 (1.9)	54.12 (3.9)
Eu	0.625 (0.005)	1.1 (0.02)
Fe (wt. %)	0.82 (0.01)	1.37 (0.01)
Hf	35.41 (0.4)	27.98 (0.65)
K (wt. %)	1.455 (0.005)	1.6 (0.2)
La	26.46 (0.02)	44.73 (0.24)
Na	921.04 (0.1)	1069 (1.5)
Nd	20.21 (5.9)	23.5 (2.8)
U	4.43 (0.2)	6.27 (0.08)
Th	15.48 (0.5)	20.40 (0.89)
Rb	71.66 (2.1)	103.5 (0.2)
Sb	1.31 (0.1)	0.26 (8.5)
Sc	3.65 (0.1)	7.40 (0.2)
Tb	0.66 (0.07)	0.995 (0.11)
Zn	6.2 (0.2)	10.57 (5.4)
Lu	0.585 (0.005)	0.64 (0.04)
Yb	3.55 (0.2)	4.15 (0.09)
W	1.55 (0.4)	1.6 (0.1)
Ba	610.02 (11.7)	650.95 (11.05)
Br	0.765 (0.065)	0.98 (0.02)
Cs	1.4 (0.08)	3.55 (1.5)
Ta	2.12 (0.07)	1.75 (2.5)

σ = Standard Deviation

La, Nd, U, Th, Rb, Sb, Sc, Tb, Lu, Yb, W, Br, Cs, Ta, Zn), minor (Na, Ba) and major (Fe, K) elements. The list of the elements measured was limited to those for which the *k*-factors have been pre-determined by the laboratory at the time when the measurements were carried out.

From Table 3 one could see a general enrichment in the concentration of some of the elements notably K and Na in the aquatic environment when compared to that of the soils. The plausible reason for this could be as a result of an increase in the leachable elements in the river sediments emanating from composite fractions in the natural geochemical state of the upstream detritals and upland soils.

Human activities such as application of phosphate fertilizers and herbicides by farmers cultivating the upland part of the basin, as well as the dumping of refuse from the University and Samaru communities upstream could equally have played a contributory role to this build-up. These detritals are usually drained into the river-bed during the rainy-seasons by surface run-off aided by gravity whose competence is determined by the steep landform of the basin.

The quality control measurement using an IAEA reference standard given in Table 4 were in good agreement with the prescribed confidence level justifying the accuracy of the technique used.

Our work also revealed the presence of seven rare earth elements (La, Ce, Nd, Eu, Tb, Yb, Lu) known to remain unique as a group in their geochemical environments (Ewa, Elegba, & Adetunji, 1996; Henderson, 1984). It was observed that some of these rare earth elements (Ta, Yb, Lu) showed marginal variation in concentrations. The reason for this may be attributed to their natural stability in aquatic environments. In the same vein, La, being the first element in the contracting series showed an appreciable enrichment. This is consistent with the general trend of La in any geochemical environment. Additionally, the similarity in the chemical behavior of the rare earth elements can be explained in terms of partial fractionation promoted by several petrological and mineralogical processes (Henderson, 1984). The thorium-uranium (Th/U) ratios for the terrestrial and aquatic environments were 3.5 and 3.3 respectively. These results are consistent with values for sedimentary environments as obtained by other workers (Adams & Weaver, 1958; Orajaka, 1986; Senftle & Keevil, 1947). The lower value for the sediments (3.3) is in agreement with the geochemical theory of the lowering of the sedimentary line beneath the igneous line (Dim, Ewa, & Ikpokonte, 2000; Galbrath & Saunders, 1983; Orajaka, 1986; Senftle & Keevil, 1947).

We identified K, a major element both in the soil and sediment although relatively enriched in the sediments. This increase may be attributed to farmer's application of the NPK fertilizers for soil amendment purposes. The presence of Fe in substantial concentration (0.82%) in the soil is suggestive of the presence of iron rich minerals responsible for the hard-pan concretions during the dry seasons (Ewa, Oladipo, Dim, & Mallam, 2000). It is for this reason that the soils assume the usual fragipan texture and color associated with the ferruginous

Table 4. Quality Control Data on the Measurement of IAEA Standard Soil 7

Element	This work Mean (σ)	95% Confidence Interval	IAEA values ^a (IAEA)*(Status)*Units
Ce	60.8 (7.7)	50-63	61.0 (R)
Co	8.5 (0.17)	8.4-10.1	8.9 (R)
Cr	75.4 (0.1)	49-74	60.0 (R)
Eu	1.0 (0.01)	0.93-1.3	1.0 (I)
Fe (wt. %)	25.6 (0.7)	25.2-26.3	25.7 (I)
Hf	6.6 (1.1)	4.8-5.5	5.1 (R)
K (wt. %)	11.5 (0.6)	11.3-12.7	12.1 (I)
La	26.0 (0.1)	27-29	28.0 (R)
Na (wt. %)	2.2 (0.1)	2.3-2.5	2.4 (R)
Nd	29.1 (1.7)	22-34	30.0 (I)
U	2.8 (0.3)	2.2-3.3	2.6 (R)
Th	7.9 (0.1)	6.5-8.7	8.2(R)
Rb	55.7 (2.3)	47-56	51.0 (R)
Sb	1.8 (0.2)	1.4-1.8	1.7 (R)
Sc	7.7 (0.1)	6.9-9.0	8.3 (R)
Tb	0.7 (0.1)	0.5-0.9	0.6 (I)

Note: All units are in ppm (mg/kg) except as stated.

^aI = Information, R = Recommended

Source: IAEA (2001, pp. 36-37).

tropical soils. Physico-chemical reactions must have assisted the sedimentation and enrichment process, while the debris-inundated, alluvial upstream-discharge supported the thick Kubanni river bed-load sediments as the river meanders through the flood-plains of the basin flowing gently at a distance of roughly 2 km away from the reactor site.

CONCLUSION

This work has provided the pre-operational baseline trace element data for terrestrial and aquatic environments near the NIRR-1 facility. Now that the reactor is in full operation, continuous environmental measurement is being made and will be bench-marked with respect to this work on a regular basis. Our measurements will give assurance to the university community and Samaru dwellers of the inherent safety of NIRR-1 and will be a valid proof of the non-degradation of the terrestrial and aquatic environments with respect to their elemental composition during the reactor operation. Infiltration as it relates to the soil-water permeability and naturally occurring radioactivity of these soils has been studied in another work and will be the subject of future publication on the terrestrial soils surrounding the reactor.

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