Scientific Knowledge Group

ISSN: 3068-9538

Research Article

Journal of Environmental Sciences and Plant Research

Trace Level Determination, Bioaccumulation and Health Risk Assessment of Bromine in Leaves and Roots of Selected Medicinal Plants from Akwa-Ibom State, Nigeria Using Instrumental Neutron Activation Analysis

Moses Ukiri[1,2*], Emmanuel Joseph[2] and Adamu N Baba-Kutigi[2]

[1]*Department of Physics, Federal College of Education (Tech), Gusau, Zamfara State, Nigeria*

[2]*Department of Physics, Federal University Dutsin-Ma, Katsina State, Nigeria*

[*]Corresponding author:

[1,2*]Moses Ukiri, [1]Department of Physics, Federal College of Education (Tech), Gusau, Zamfara State, Nigeria.

[2]Department of Physics, Federal University Dutsin-Ma, Katsina State, Nigeria. Email: m.ukiri_pg1840@fudutsinma.edu.ng

ABSTRACT

The increasing use of medicinal plants in primary healthcare has raised concerns regarding the accumulation of toxic trace elements and their associated health risks. Bromine (Br), a non-essential halogen with potential toxicological significance, has been poorly studied in medicinal plants from coastal regions of sub-Saharan Africa. This study investigated the concentration, bioaccumulation, and health risks of bromine in selected medicinal plants and soils from Akwa Ibom State using Instrumental Neutron Activation Analysis (INAA), a highly sensitive, reliable, and non-destructive analytical technique for trace-level bromine determination in botanical matrices of Five selected medicinal plant species and corresponding soil samples, were analyzed using the Nigerian Research Reactor-1 (NIRR-1) under short and long irradiation conditions. Quality assurance was achieved using certified reference materials IAEA-336 and IAEA-158, with satisfactory Z-score values (±2), confirming analytical accuracy and precision. Bromine concentrations ranged from 0.85 – 13.50 mg/kg in leaves, 1.25 – 9.68 mg/kg in soils, and 1.31 – 7.11 mg/kg in roots. Higher concentrations in leaves indicated enhanced translocation and accumulation in aerial tissues. Bioaccumulation Factor (BAF) values ranged from 0.17 to 8.80, with Plant 3 and Plant 4 showing strong accumulation potential (BAF > 1). Estimated Daily Intake (ADI) values ranged from 0.00419 to 0.06653 mg/kg/day. Target Hazard Quotient (THQ) values ranged from 1.05 to 16.63, all exceeding the safe limit of 1, indicating potential non-carcinogenic risks, while Target Carcinogenic Risk (TCR) values (4.52×10^{-3}–4.66×10^{-2}) exceeded acceptable USEPA limits, suggesting possible long-term carcinogenic concerns. The study demonstrates that medicinal plants from coastal environments may accumulate bromine to hazardous levels and validates INAA as a reliable technique for trace-level bromine determination in botanical matrices. The findings provide baseline scientific data for environmental monitoring, herbal medicine regulation, and public health risk management in Nigeria and other developing countries heavily reliant on traditional medicine.

Keywords: Bromine, Medicinal Plants, INAA, Bioaccumulation Factor, Health Risk Assessment, Nigeria.

Received: May 27, 2026;
Accepted: June 03, 2026;
Published: June 10, 2026

Introduction

Medicinal plants remain a primary source of healthcare for over 80% of the population in sub–Saharan Africa, including Nigeria [1,2]. In Akwa Ibom State, the use of herbal remedies for chronic ailments such as diabetes, malaria, and hypertension is deeply embedded in local culture [3,4]. However, Environmental contamination of medicinal plants by toxic trace elements has become a major global public health concern due to increasing industrialization and environmental pollution [5,6]. Therefore, the safety of these botanicals with respect to trace element contamination has received far less attention than that of essential and toxic metals, hence, several studies have shown that trace element mobility and translocation are strongly influenced by plant physiology, soil chemistry, and environmental

Citation: Ukiri M, Joseph E, & Baba-Kutigi AN (2026) Trace Level Determination, Bioaccumulation and Health Risk Assessment of Bromine in Leaves and Roots of Selected Medicinal Plants from Akwa-Ibom State, Nigeria Using Instrumental Neutron Activation Analysis. J Envir Sci Plant Res 2: 1-10.

conditions [7,8]. In particular, the halogen bromine (Br), whose environmental levels are elevated in coastal regions with high salinity and industrial activity like Akwa-Ibom state, remains largely unmonitored in Nigerian medicinal plants [9-11].

Bromine is a non-essential trace element that, at low doses, can displace iodine in the thyroid gland and interfere with endocrine function [12,13]. Chronic dietary exposure to elevated bromine has been linked to neurotoxicity, renal injury, and thyroid disorders [14,15]. While bromine is used as a flame retardant and as a soil fumigant, its natural occurrence in coastal alluvial soils, typical of Akwa Ibom State, can be significantly augmented by anthropogenic inputs such as waste incineration and pesticide residues [16-20]. Despite these concerns, no systematic survey of bromine concentrations in medicinal plants from the Akwa-Ibom State has been published. However, while Nigerian medicinal plants have been screened for various elements, no study has reported bromine concentrations in plants harvested from Akwa Ibom State [21-23]. The unique pedological and hydrological conditions of this coastal zone, which include high soil salinity, organic matter content, and proximity to the Atlantic Ocean, are most likely to influence bromine uptake [24,25]. Baseline occurrence data are therefore urgently needed. Furthermore, Routine determination of bromine in plants by ICP-MS or AAS often suffers from spectral interferences and incomplete digestion [26,27]. INAA bypasses these issues by using neutron irradiation and gamma-ray spectroscopy without chemical dissolution. However, the method has been rarely applied to bromine in Nigerian medicinal plants; most INAA studies in the region have focused on heavy metals [28,29]. Hence, a validated INAA protocol for bromine in this matrix is a methodological prerequisite. Bioaccumulation factors (BAF = concentration in plant/concentration in soil) are essential for understanding the mobility and risk of an element [30-32]. For bromine, published BAF values range from 0.2 to 3.5 depending on plant species and soil type [16,33-35]. No such data exist for any medicinal plant species from Nigeria based on available information at our disposal. Without BAF estimates, it is impossible to predict which plant parts (roots vs. leaves) pose the greatest bromine exposure risk, a critical deficit for traditional medicine where both aerial and underground parts are used [36,37]. To date, only two studies have performed a dietary risk assessment of bromine from medicinal plants: one from Italy and one from Algeria [14,15]. Both used INAA, but none were conducted in sub-Saharan Africa. Nigerian populations frequently consume herbal decoctions daily for weeks or months, yet no hazard indices (HI) or tolerable daily intake (TDI) comparisons for bromine have been computed. Children are particularly vulnerable because of their lower body weight and higher relative intake [38-40]. This research challenge leaves the Nigerian National Agency for Food and Drug Administration (NAFDAC) without evidence-based limits for bromine in traditional herbal products. In addition, Individual studies have either measured trace elements in Nigerian plants or assessed health risks of metals, but none have combined (i) trace-level bromine determination by INAA, (ii) soil-to-plant bioaccumulation analysis, and (iii) a probabilistic health risk assessment for both adults and children [41-44]. Such an integrated framework is needed for regulators to set science-based safety standards [45,46].

Notably, the analytical determination of bromine at trace levels in botanical matrices is challenging; however, Instrumental neutron activation analysis (INAA), a highly sensitive, non-destructive multi-element analytical technique avoiding the digestion-related limitations of ICP-MS and AAS, has been proven to offer the advantages of minimal sample preparation, high sensitivity (detection limits often below 0.1 mg kg^{-1}), and freedom from matrix effects [47,48]. INAA has been successfully applied to halogens in plant materials from India, Brazil and Italy, but its use for bromine determination in West African medicinal plants has been limited to only a handful of studies [14,21,22,49,50]. Furthermore, no Nigerian study has integrated bromine determination, soil-to-plant bioaccumulation assessment, and human health risk evaluation in medicinal plants. Therefore, this study investigates trace-level bromine concentrations, bioaccumulation behavior, and associated health risks in selected medicinal plants from Akwa Ibom State, Nigeria, using INAA.

Material and Method

Study Area

The study was conducted in Ikot Akpaden, located in Akwa Ibom State within the south-south region of Nigeria (Figure 1). The area lies between longitude 7°46′22″E and latitude 4°37′38″N at an elevation of approximately 185 m above sea level, covering about 322.35 km² (Media Nigeria, 2022). Mkpat Enin is the second-largest Local Government Area in the state and forms part of the industrial belt extending through Eastern Obolo, Etinan, Oruk Anam, Onna, and Ikot Abasi. The region is characterized by coastal swamps and the Mkpat Enin creek system. Agriculture is the major occupation of the inhabitants, who are predominantly Ibibio-speaking people distributed across four clans and 87 villages, with an estimated population of 178,036 based on the 2006 census (Media Nigeria, 2022). Major agricultural products include palm fruits, cassava, coconut, plantain, and vegetables, while the area is also endowed with natural resources such as crude oil, natural gas, limestone, iron ore, salt, magnesium, and gypsum.

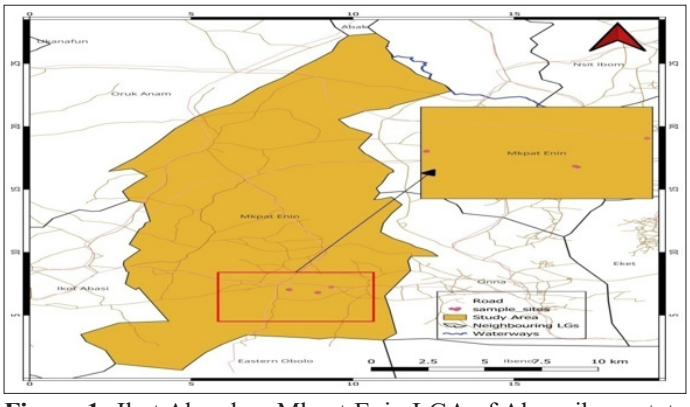

Figure 1: Ikot Akpaden, Mkpat Enin LGA of Akwa-ibom state Map

Sample Collection

Fresh samples of five medicinal plants, including leaves and roots, were collected from the study area together with corresponding rhizosphere soil samples. Plant tissues were separated immediately after collection to assess elemental

distribution between roots and leaves. Sampling locations were geo-referenced using Global Positioning System (GPS) coordinates, and sample collection was conducted under the supervision of a curator from the Department of Botany, Akwa Ibom State University.

Sample Preparation

The medicinal plant samples (leaves and roots) were identified and authenticated by a curator from the Department of Botany, Akwa Ibom State University. Samples were washed with distilled water, air-dried under ambient conditions, pulverized using an agate mortar, and sieved to a 150 µm particle size to ensure homogeneity. The powdered samples were oven-dried at 45 °C for 24 h, cooled in desiccators, and representative sub-samples (0.250–0.300 g) were weighed and heat-sealed in polyethylene bags for irradiation. Similarly, soil samples were air-dried, pulverized, sieved through a 2 mm mesh, and oven-dried at 105 °C to constant weight. Representative sub-samples (0.150–0.250 g) were weighed and sealed in clean polyethylene vials before analysis.

Elemental analysis was carried out using the Nigerian Research Reactor-1 (NIRR-1), a 30.5 kW swimming pool-type reactor. Samples were irradiated under thermal neutron fluxes and analyzed using a High Purity Germanium (HPGe) gamma-ray spectrometer coupled with an ORTEC multichannel analyzer and WINSPAN 2004 software for elemental identification and quantification. Quality assurance was achieved using certified reference materials IAEA-336 and IAEA-158, which were prepared and irradiated under the same conditions as the samples. Elemental concentrations were calculated and expressed in mg/kg. The prepared plant and soil samples were stored in clean polyethylene containers before irradiation, and each powdered sample was accurately weighed and sealed in clean polyethylene vials for neutron activation analysis.

Apparatus

Elemental analysis was carried out using the Nigerian Research Reactor-1 (NIRR-1), a 30.5 kW swimming pool-type reactor. Samples were irradiated under thermal neutron flux conditions and analyzed using a high-resolution High Purity Germanium (HPGe) gamma-ray spectrometer (ORTEC HPGe detector) coupled with ORTEC multichannel analyzers and WINSPAN 2004 software for elemental identification and quantification. Elemental concentrations were determined by comparing the gamma-ray energies and intensities of the samples with certified reference materials and known standards, and results were expressed in mg/kg. For quality assurance and validation of the Instrumental Neutron Activation Analysis (INAA) procedure, certified reference materials IAEA-336 and IAEA-158, whose concentrations are shown in Tables 1 and 2, were prepared under the same conditions as the plant and soil samples. The standards and samples were heat-sealed in pre-cleaned polyethylene vials and irradiated under short and long irradiation regimes using thermal neutron fluxes of 5×10^{11} and 2.5×10^{11} n cm^{-2} s^{-1}, respectively.

Sample Procedure

The irradiation involves two processes covering short-lived nuclides and long-lived nuclides, described by Jonah et al. For the analysis of short-lived nuclides requiring shorter irradiation times of 1 minute and 5 minutes for both geological and biological samples, polythene vials are placed in the 7cm3 rabbit capsules-a larger transport device that travels from the laboratory into the reactor by an air-driven pneumatic transport system into the outer irradiation channel B4, where the neutron spectrum is 'soft' to eliminate corrections due to nuclear interferences caused by threshold reactions, notably Mg in the presence of Al; Al in the presence of Si; and Na in the presence of P [51]. This is so because the proximity of the inner channels of MNS reactors to the core leads to a relatively higher ratio of fast-to-thermal neutrons. For elements requiring longer irradiation times (i.e., long-lived activation products), samples wrapped in polythene films are packed in a stack inside the 7cm3 rabbit capsules and sealed for irradiation. The samples were irradiated for 6 hours at an average thermal neutron flux of 5 × 10^11 ncm-2s-1 in the small irradiation channels A1, B2, and B3 of the same facility, taking advantage of the maximum value of thermal neutron flux in this inner channel.

Quality Assurance

To evaluate the accuracy and reliability of the INAA method, two certified reference materials (CRMs) of biological and geological origin, IAEA-336 and IAEA-158, were irradiated and analyzed alongside the samples, with results presented in Tables 1 and 2. Method validation was assessed using Z-score statistics to determine the level of agreement between measured and certified values. Generally, Z-score values within ±2 indicate satisfactory analytical accuracy and precision. Most evaluated elements showed acceptable Z-score values, confirming good agreement between the measured and certified concentrations and demonstrating the reliability of the analytical procedure.

Table 1 Quality assessment of the INAA results based on the comparison of measured and certified values in (mg/kg) of the Irradiated Standard of IAEA 336

Elements	IAEA 336			
	This Work Value	Certified Value	Z-score	95%Confidence Interval
Mg	626±55.72	-	-	-
Cl	199.8±38	190.0±30	0.52	-
Mn	63.00±0.819	63±7	0.00	56 - 70
Na	320±5.44	320±40	0.00	280 - 360

K	1840±150.88	1840±200	0.00	1640 - 2040
Al	680±±12.92	680±110	0.00	570 - 790
Sm	0.1062±0.0033	0.106±0.014	0.02	0.092 - 0.120
La	0.66±0.0228	0.66±0.10	0.00	0.56 - 0.76
Ca	2668±266.8	-	-	-

Table 2: Quality assessment of the INAA Results(mg/kg) based on comparison of measured and certified values of IAEA 158for Geological sample

Elements	IAEA This Work Value	IAEA Certified Value	IAEA SD	IAEA Z-score	95% Confidence interval
Al	50440±353	51800±2400	1320.39	-1.03	536 — 58,864
Ba	1029±42.22	1028±28	33.33	0.03	941 — 1,121
Co	9.20±0.28	9.2±0.90	0.00	0.00	7.03 — 11.35
Cr	74.4±2.83	74.6±8.2	2.86	-0.07	6 — 88.4
Eu	1.08±0.16	1.079±880	0.10	0.01	0.978 — 1.218
Sm	4.79±0.02	4.94±0.52	0.39	-0.38	01 — 5.27
Zn	140±11.48	140.6±18	12.00	-0.05	122.4 — 159.6

Data Analysis (Z-score, BAF, EDI, THQ, TCR)

The chemical elemental concentration was determined in Comparison with the known masses and concentration of elements in standard reference material using equations (1) and (2):

$$W_s = \frac{W_{st} N e^{\lambda td(s)}}{N_{st} e^{\lambda td(st)}} \quad (1)$$

$$ButC = \frac{W_s}{M} = \frac{M_{st} C_{st} e^{\lambda td(s)}}{M N_{st} e^{\lambda td(st)}} \quad (2)$$

where; C = concentrations of elements in the samples in µg/g

Cst = certified values of the concentrations of elements in the standard in µg/gN

= net photo peak area of radionuclide of interest in the sample N_{st}

= net photo peak area of radionuclide of interest in standard

Ws= weight of unknown element in samples irradiated

$W_{st} = M_{st}C_{st}$ = known weight of the element in the amount standard irradiated M

= mass of the samplesM_{st} = mass of standards td(s)

= decay time before counting of samplestd(st)

= decay time before counting of X the standardsλ

= decay constant for radionuclide of interest

To determine the laboratory performance, we determine the parameter of the Z-score and the ratio of the determined value to the certified andnon-certified value. Z-score was calculated according to the following equation [52].

$$Z - score = \frac{X_{lab} - X_{Ref}}{n - 1} \quad (3)$$

where

XLab, XRef, and σRef are the laboratory result, the reference value, and the uncertainty with the reference value, respectively. Based on the Z-score value, the laboratory performance is evaluated as satisfactory if |Z|-score ≤ 2, questionable for 2 < |Z|-score < 3, and unsatisfactory for |Z|-score ≤3.

Bioaccumulation Factor (BF)

The bioaccumulation process occurs through uptake, bioavailability, bioconcentration, and biomagnification. Bioaccumulation can be comprehended as a metabolically active process by which living organisms absorb chemical elements, especially toxic ones, in their intracellular space using importer complexes that create a translocation pathway through the lipid bilayer (i.e., microorganisms). Once inside the intracellular space, the heavy metals (HM) can be sequestered by proteins and peptide ligands (i.e., storage systems in plants) [53]. Bioaccumulation was determined using the equation below

$$BAF = \frac{C_{plant}}{C_{soil}} \quad (4)$$

Estimated Daily Intake

Estimated Daily Intake (EDI)(Exposure dose) of Heavy Metals

The estimated average daily intake (EDI) depends on both the metal concentration in plants and the dose of consumption of the individual herbs. The EDIs of some trace and toxic elements were calculated according to the mean concentration of each element in each plant and the consumption rate. The EDI for human exposure to heavy metals was calculated using the equation below, which was recommended by Zheng et al. [54].

$$EDI = \frac{EF \times ED\ IR \times C_{element}}{B_{weight} \times AT} \quad (5)$$

where: EDI – the estimated average daily intake (mg·kg^{-1} from BW/d);

C – the calculated Br concentration in plants (mg·L-1 or mg·kg^{-1});

IR – the daily ingestion rate per capita, is 0.52 kg/d [55];

ABS – the absorption coefficient (=1), [54];

EF – the exposure frequency was set to 180 days per year.
ED – is the exposure days over a lifetime (50 years) [56].
BW– the body weight, the average adult body weight was considered to be 70kg [57];
AT – is the average lifetime (day) (AT = 60 years·365 days per year)d [58].
Where EF is the exposure frequency (180 days/a;a=annum), ED is the exposure duration, IR is the ingestion rate of herbs (0.52kg/d), $C_{element}$ is the concentration in the herbs (mg/kg), AT is the average time for non-carcinogens (365 x ED days), and B_{weight} is the person's body weight (70kg).

Target Hazard Quotient (THQ-non Carcinogenic)
The target hazard quotient (THQ) is defined as the ratio of exposure to the toxic element and the reference dose, which is the highest level at which no adverse health effects are expected. The reference dose is specific to the trace element being assessed. The THQ describes the noncarcinogenic health risk posed by exposure to the respective toxic element. If the THQ is<1, then non-carcinogenic health effects are not expected. If, however, the THQ is>1, then there is a possibility that adverse health effects could be experienced. A THQ exceeding 1 is not a statistical probability that adverse non-carcinogenic health effects will occur. THQ is given by the expression below

$$THQ = \frac{E_{FR}XE_dXF_{IR}XC}{Rf_D \times BWcXAT_n} \times 10^{-3} \quad (6)$$

Where E FR is the exposure frequency to the trace element, Ed is the exposure duration (70 yrs), FIR is the food ingestion rate in grams per day for the respective food item, C is the concentration in wet weight of the trace element in the given food item, RfD is the oral reference dose of the trace element inμg/g/day, BWa is the reference body weight of 70kg and ATn is the averaged exposure time (365 days 70yrs) and 10−3 is the unit conversion factor.

Target Carcinogenic Risk (TCR-carcinogenic)
The target cancer risk (TCR) is used to assess the potential risk associated with exposure to carcinogenic agents throughout the life-time exposure period. Instead of an oral reference dose, as is used for the determination of THQ, an oral slope factor is utilized. This factor determines, along with the dose of the carcinogen, the probability of excess cancer risk over the lifetime of the exposed individual. The equation for TCR is:

$$TCR = \frac{E_{FR}XE_DXF_{IR}XCXCPS_o}{BWcXAT_c} \times 10^{-3} \quad (7)$$

where EFR is the exposure frequency to Bromine, ED is the exposure duration (70 yrs), FIR is thefood ingestion rate ingrams per day for the respective food item, C is the concentration in wet weight of the trace element in the given food item, CPS O is the oral cancer slope factor for in organicarsenic of 1.5 (mg/kg)/day, Bwa is the reference body weight of 70kg, ATc is the averaged exposure time to the carcinogen (365days*70yrs) and 10−3 is the unit conversion factor.

Results and Discussion

Results

The trace elemental composition of five selected medicinal leaves (MPL), plant roots (PR), and soil sample (SS) was determined using INAA, as presented in Table 3. The results reveal significant variations in elemental concentrations among the different sample matrices, reflecting the influence of soil composition and plant uptake mechanisms. In this present study, the range of concentrations of trace-elements of Bromine in leave, roots and soil samples determined as shown in Table 4, hence the fellows:0.85-13.50 mg/kg, 1.25-9.68 mg/kg and 1.31-7.11 mg/kg, with highest concentration of trace-level of Bromine found in the leaves, followed by the soil, and the least concentration of trace-level of Bromine found in the roots part of the medicinal plants.

Table 3: Bromine Concentration, Bioaccumulation, and Health Risk Indices of Selected Medicinal Plants from Akwa Ibom State, Nigeria. Values are expressed as Mean ± Standard Error of Mean (SEM), n = 3.

Sample Code	Plant Part	Bromine in Plant (mg/kg)	Bromine in Soil (mg/kg)	BAF	ADI	THQ	TCR
MPL1	Leaf	0.85 ± 0.04	5.01 ± 0.41	0.17	0.00419	1.05	2.93×10^{-3}
PR1	Root	3.28 ± 0.07	5.01 ± 0.41	0.65	0.01617	4.04	1.13×10^{-2}
MPL2	Leaf	3.15 ± 0.06	9.44 ± 0.30	0.33	0.01553	3.88	1.09×10^{-2}
PR2	Root	5.86 ± 0.13	9.44 ± 0.30	0.62	0.02889	7.22	2.02×10^{-2}
MPL3	Leaf	13.50 ± 0.20	1.55 ± 0.17	8.71	0.06653	16.63	4.66×10^{-2}
PR3	Root	1.31 ± 0.05	1.55 ± 0.17	0.85	0.00646	1.62	4.52×10^{-3}
MPL4	Leaf	11.00 ± 0.10	1.25 ± 0.15	8.8	0.05421	13.55	3.79×10^{-2}
PR4	Root	7.11 ± 0.14	1.25 ± 0.15	5.69	0.03503	8.76	2.45×10^{-2}
MPL5	Leaf	5.60 ± 0.07	9.68 ± 5.30	0.58	0.0276	6.9	1.93×10^{-2}
PR5	Root	1.80 ± 0.09	9.68 ± 5.30	0.19	0.00887	2.22	6.21×10^{-3}

MPL=medicinal plant, PR= plant root in mg/kg BAF=Bioaccumulation Factor, ADI= Annual Daily Intake, THQ= Target hazard quotient (THQ-non carcinogenic), TCR= Target Carcinogenic risk

Table 4: Descriptive Statistics of Bromine Concentration

Parameter	Leaves (mg/kg)	Roots (mg/kg)	Soil (mg/kg)
Range	0.85 – 13.50	1.31 – 7.11	1.25 – 9.68
Mean	6.82	3.87	5.39
Median	5.60	3.28	5.01

Discussion

Bromine Distribution in Soil, Leaves and Roots

The concentration of Bromine (Br) across the studied medicinal plants revealed marked variability between plant compartments and soil matrices. Bromine levels ranged from 0.85–13.50 mg/kg in leaves, 1.31–7.11 mg/kg in roots, and 1.25–9.68 mg/kg in soil, reflecting heterogeneous environmental distribution and plant uptake behaviour. The higher concentrations observed in leaves relative to roots in several plant species indicate efficient translocation of bromine to aerial tissues, likely driven by transpiration streams and atmospheric deposition processes. This pattern is consistent with previous findings that halogens and trace elements tend to accumulate in metabolically active tissues such as leaves [59-61].

Furthermore, the presence of bromine in soil–plant systems may arise from both natural geochemical sources and anthropogenic activities, including agrochemical application and environmental contamination [62-64]. Similar distribution trends have been reported in medicinal plants cultivated in contaminated environments [65,66].

Bioaccumulation Factor (BF)

The calculated Bioaccumulation Factor (BAF) values ranged from 0.17 to 8.80, indicating both low and extremely high MPL3 and MPL4 leaves exhibited BAF values greater than 8, indicating accumulation potential among the studied plants. Notably, suggesting a strong bioaccumulation capacity. According to established criteria, BAF > 1 indicates active uptake and accumulation of elements from soil into plant tissues [67,68]. Elevated BAF values indicate enhanced transfer efficiency of bromine from soil to plant tissues and may reflect differences in elemental bioavailability and physiological uptake mechanisms [69,70]. Furthermore, such high accumulation capacity may be attributed to plant-specific physiological traits, including root absorption efficiency and internal transport mechanisms [71,72]. Similar high BAF values have been reported in medicinal and edible plants grown in contaminated soils, raising concerns about food-chain transfer [53,73]. Conversely, BAF values <1 observed in some samples suggest limited uptake efficiency, possibly due to low bioavailability of bromine in soil or plant exclusion mechanisms [74,64].

Average Daily Intake (ADI)

The estimated Average Daily Intake (ADI) values ranged from 0.00419 to 0.06653 mg/kg/day, indicating varying exposure levels depending on plant species and concentration. Higher ADI values observed in MPL 3 and MPL 4 leaves are directly linked to elevated bromine concentrations and high BF values. ADI is a key metric used to quantify human exposure to contaminants through dietary intake, and it is strongly influenced by concentration, ingestion rate, and exposure duration [75,76]. Comparable studies have demonstrated that elevated contaminant concentrations in medicinal plants significantly increase ADI values, particularly in populations with high reliance on herbal remedies [77-79]. Given that medicinal plants are frequently consumed without strict dosage control, this raises concerns regarding chronic exposure [80].

Non-Carcinogenic Risk Assessment (THQ and HI)

Chronic exposure modeling using THQ has been widely employed in environmental toxicology studies to evaluate potential non-carcinogenic health effects associated with contaminated food and medicinal plants [32]. The Target Hazard Quotient (THQ) values for bromine ranged from 1.05 to 16.63, with all values exceeding the safety threshold of THQ = 1, indicating potential non-carcinogenic health risks. THQ values greater than unity imply that the estimated exposure exceeds the reference dose, potentially leading to adverse health effects over time [81,82]. The highest THQ values were recorded in MPL 3 and MPL 4 leaves, which correspond to their elevated bromine concentrations and bioaccumulation capacity.

Carcinogenic Risk (TCR)

The Total Cancer Risk (TCR) values ranged of Br in this present study range from4.52×10-3 to 4.66×10-2. These values exceed the acceptable risk range of 10^{-6}–10^{-4}, indicating a potential carcinogenic concern. However, it is important to emphasize that bromine is not widely recognized as a primary carcinogenic element, and limited toxicological data exist regarding its cancer slope factor [83,84]. Therefore, the calculated TCR values have been interpreted as conservative estimates rather than definitive cancer risks. Nevertheless, elevated TCR values highlight the need for caution, as prolonged exposure to contaminated plant materials may contribute to long-term health risks [85,86]. Hence, long-term dietary exposure to contaminated plant materials may contribute to cumulative carcinogenic risk through food-chain transfer mechanisms [39].

Enhanced Multi-Panel Figure (BF, THQ and TCR)

Figure 2 shows the enhanced multi-panel visualization presents an integrated assessment of bioaccumulation (BF), non-carcinogenic risk (THQ), and carcinogenic risk (TCR) of bromine in leaves and roots of selected medicinal plants. The combined representation provides a comprehensive overview of elemental transfer dynamics and associated human health risks, which is essential for environmental toxicological interpretation. From Figure 2, the integrated assessment presented in the figure demonstrates substantial variability in bioaccumulation factor (BF), target hazard quotient (THQ), and total cancer risk (TCR) among the investigated medicinal plant samples, as shown in Figure 2, indicating differential elemental uptake, translocation, and associated human health implications. The markedly elevated BF values observed in MPL 3 and MPL 4 suggest strong accumulation potential of toxic elements in the leaves relative to roots and soil, confirming that foliar tissues act as major sinks for elemental deposition and translocation. This pattern is consistent with recent findings that medicinal plants cultivated in contaminated environments exhibit enhanced metal accumulation in aerial tissues due to higher metabolic

activity and transpiration-driven transport mechanisms [87,88]. Furthermore, the THQ results reveal that several samples, particularly MPL 3, MPL 4, PR 4, and MPL 5, exceeded the safe threshold value of 1, indicating possible non-carcinogenic health risks associated with prolonged consumption of these medicinal plants. The elevated THQ values imply chronic exposure concerns, especially for populations relying heavily on herbal preparations as primary healthcare alternatives. Similar observations have been reported in recent environmental toxicology studies where persistent ingestion of contaminated medicinal plants contributed significantly to cumulative dietary exposure and organ toxicity risks [89,90]. In addition, the TCR values, even on logarithmic scale representation, demonstrate that MPL 3 and MPL 4 possess comparatively higher carcinogenic potentials than other samples, suggesting that continuous exposure may increase lifetime cancer susceptibility beyond acceptable regulatory limits. This elevated carcinogenic tendency may be linked to the accumulation of carcinogenic trace elements such as As, Cd, Cr, and Pb, which are known to induce oxidative stress, DNA damage, and cellular dysfunction in exposed populations. The comparatively lower BF, THQ, and TCR values recorded in MPL 1, MPL 2, and PR 5 indicate relatively safer phytochemical utilization and reduced contaminant mobility within these plant systems. Overall, the figure confirms that elemental bioaccumulation strongly influences both non-carcinogenic and carcinogenic health outcomes, emphasizing the necessity for continuous environmental monitoring, strict quality control of medicinal plants, and implementation of phytoremediation-informed cultivation practices to minimize toxicological risks associated with herbal medicine consumption.

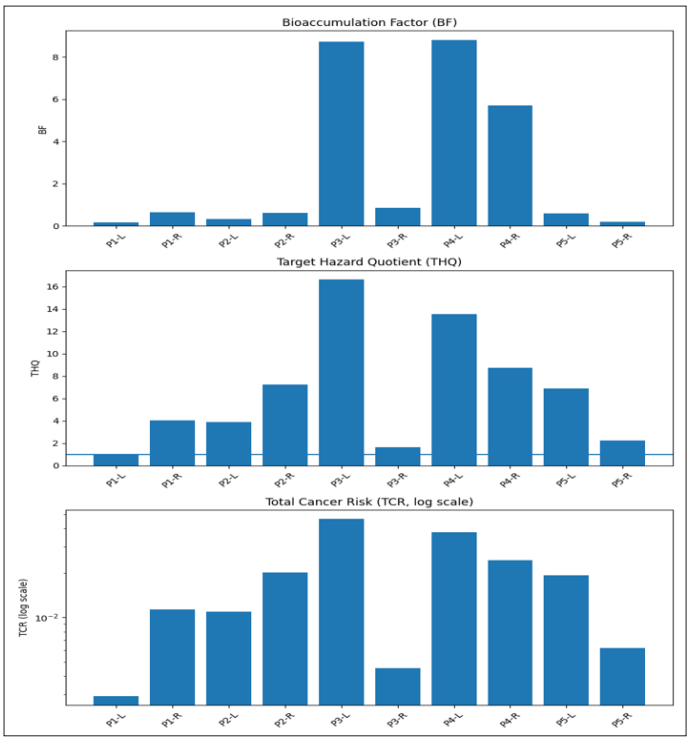

Figure 2: Bioaccumulation factor BAF, THQ, and TCR of bromine in leaves and roots of selected medicinal plants showing enhanced accumulation in MPL 3 and MPL 4.

Comparative Analysis with Previous Studies

The findings of this study are consistent with several recent investigations on contaminant accumulation in medicinal plants. For instance, studies conducted in Nigeria and other developing regions have reported THQ values greater than 1, indicating potential health risks associated with herbal plant consumption [65,66]. Similarly, global assessments have shown that medicinal plants grown in contaminated soils often exhibit elevated BF and ADI values [71,59].

Environmental and Public Health Implications

The elevated BAF, THQ, HI, and TCR values observed in this study suggest significant soil-to-plant transfer of bromine and potential human health risks. This is particularly important in developing countries, where up to 80% of the population relies on medicinal plants for primary healthcare [80]. The presence of contaminants in these plants may therefore have widespread public health implications. Environmental contamination of soil plays a crucial role in determining plant uptake of trace elements [91,62]. Hence, Environmental contamination of agricultural soils has been recognized as a major pathway for trace element accumulation in edible and medicinal plants [92,10]. Consequently, monitoring and regulation of medicinal plant cultivation areas are essential to minimize exposure risks [93].

Conclusion

This study successfully determined the trace-level concentration, bioaccumulation characteristics, and potential health risks of bromine in selected medicinal plant leaves, roots, and associated soils collected from Akwa Ibom State, Nigeria, using Instrumental Neutron Activation Analysis (INAA). The analytical procedure demonstrated high precision and reliability through the use of certified reference materials and satisfactory Z-score validation, confirming the suitability of INAA for trace elemental determination in complex biological and geological matrices. The results revealed significant variations in bromine concentrations among leaves, roots, and soils, with leaves generally exhibiting higher accumulation levels than roots. This observation suggests enhanced translocation of bromine to aerial plant tissues, likely influenced by physiological transport mechanisms and environmental deposition processes. The elevated Bioaccumulation Factor (BAF) values observed in some medicinal plants, particularly Plant 3 and Plant 4, indicate strong bromine uptake capability and substantial soil-to-plant transfer potential [94-98]. The health risk assessment further revealed that all calculated THQ values exceeded the permissible safety threshold of unity (THQ > 1), indicating potential non-carcinogenic health risks associated with prolonged consumption of these medicinal plants. Additionally, the calculated TCR values exceeded the recommended USEPA acceptable risk range, suggesting possible long-term carcinogenic implications under chronic exposure conditions. These findings raise important environmental and public health concerns, especially in regions where medicinal plants constitute a major component of primary healthcare delivery. Overall, this study provides the first comprehensive baseline dataset on bromine contamination, bioaccumulation, and associated health risks in medicinal plants from Akwa Ibom State, Nigeria. The findings contribute significantly to the existing body of knowledge on trace element contamination in herbal medicines and highlight the urgent need for continuous monitoring, environmental regulation, and the

establishment of permissible bromine limits in medicinal plant products in Nigeria [99-102].

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