



Speciation-informed Bayesian assessment of metal(loid) exposure from Akora River fish, Ghana, for consumption guidance

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Abstract Freshwater fish from mining-influenced rivers can transfer metal(loid)s to consumers, but risk estimates in low resource settings often ignore non-detects, chemical speciation and receptor-specific uncertainty. This study assessed water, sediment and market fish from eight stations along the Akora River, Ghana, and developed a censoring-aware hierarchical Bayesian framework to estimate dietary exposure from *Oreochromis niloticus* and *Clarias anguillaris*. Eight metal(loid)s (Hg, Zn, As, Ni, Cr, Cu, Pb and Cd) were analysed by ICP-OES and cold-vapour atomic fluorescence spectroscopy. Posterior fish concentrations were

propagated through speciation priors, intake assumptions and dose–response models to estimate non-cancer HI, TCR and BLL for children, WOCBA, adults and high-consumers. Cr and Ni dominated water-column contamination, reaching 55× and 23× WHO guideline values downstream, whereas fish metal concentrations showed little species-specific separation. Median non-cancer HI remained below the screening threshold for all receptor groups, but exceedance probabilities reached approximately 15–17% for children and high-consumers. TCR exceeded 10^{-6} in 35–78% of receptor-specific posterior draws, driven mainly by iAs and Cr(VI) assumptions. Median BLL predictions remained below 3.5 µg/dL, although upper-tail exceedance was plausible for children and high-consumers. Sensitivity analysis showed that FIR, BW and speciation/toxicological parameters dominated uncertainty, while additional precision in total-metal concentration had limited value. The results support speciation-focused monitoring, receptor-specific consumption surveys and Ghana-specific freshwater fish consumption guidance.

Highlights

- First hierarchical Bayesian assessment of fish metal contamination in West Africa conducted.
- Chromium and nickel reached 55 × and 23 × WHO guidelines in Akora River water.
- Non-cancer hazard exceeded thresholds in 15% of children and high-consumers.
- Methylmercury and inorganic arsenic are dominant non-cancer and cancer drivers.
- Ghana needs nationally codified freshwater fish consumption standards.

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Abbreviations

As	Arsenic
AT	Averaging time
BLL	Blood-lead level
BW	Body weight
Cd	Cadmium
CDC	Centers for Disease Control and Prevention
CDI	Chronic daily intake
CRM	Certified reference material
Cr	Chromium
Cr(VI)	Hexavalent chromium
Cu	Copper
CV	Coefficient of variation
CV-AFS	Cold-vapour atomic fluorescence spectroscopy
ED	Exposure duration
EF	Exposure frequency
ELPD	Expected log predictive density
ESS	Effective sample size
FAO	Food and Agriculture Organization
FIR	Fish ingestion rate
GAEC	Ghana Atomic Energy Commission
GFDA	Ghana Food and Drugs Authority
GM	Geometric mean
GSA	Global sensitivity analysis
GSD	Geometric standard deviation
HBM	Hierarchical Bayesian model
HDI	Highest density interval
Hg	Mercury
HI	Hazard index
HMC	Hamiltonian Monte Carlo

HPLC-ICP-MS	High-performance liquid chromatography–inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectroscopy
iAs	Inorganic arsenic
LOD	Limit of detection
LOQ	Limit of quantification
MeHg	Methylmercury
N.D.	Not detected
Ni	Nickel
NIST	National Institute of Standards and Technology
NNRI	National Nuclear Research Institute
NUTS	No-U-Turn Sampler
<i>O. niloticus</i>	<i>Oreochromis niloticus</i>
OSF	Oral slope factor
Pb	Lead
PEC	Probable effect concentration
PEC-Q	Probable effect concentration quotient
PSIS-LOO	Pareto-smoothed importance sampling leave-one-out cross-validation
PTE	Potentially toxic element
QA/QC	Quality assurance/quality control
RfD	Reference dose
RQ	Risk quotient
SD	Standard deviation
SDG	Sustainable development goal
ST	Total-order Sobol index
TCR	Total cancer risk
THQ	Target hazard quotient
U.S. EPA	United States Environmental Protection Agency
WHO	World Health Organization
WOCBA	Women of child-bearing age
Zn	Zinc

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Introduction

Freshwater fish serve as a critical protein source for billions globally, with particularly high reliance in sub-Saharan Africa where over 40% of national animal protein intake derives from fish sources (Tran et al., 2019). In this region, small pelagic and indigenous fish species possess the potential to feed 33 million people while providing essential nutrients

including protein, calcium, and zinc (Wessels et al., 2023). However, widespread accumulation of metal(loid) including lead, mercury, arsenic, cadmium, chromium, nickel, copper, and zinc in freshwater ecosystems poses significant health risks to these fish-dependent populations. Multiple studies across sub-Saharan Africa have documented metal concentrations in fish muscle exceeding WHO safety limits, with arsenic and lead levels posing carcinogenic risks to consumers (Gwimbi et al., 2020; Olurin, 2024). This contamination represents not merely an environmental challenge but a profound social equity issue, as vulnerable populations including children, women of child-bearing age, and low-income communities who depend most heavily on freshwater fish protein bear disproportionate exposure risks.

The Akora River system in central Ghana exemplifies the intersection of subsistence fishing dependence and anthropogenic metal contamination characteristic of many West African freshwater ecosystems. Located in the Agona Swedru Township region and extending from Agona Nyakrom downstream to Swedru Township before joining the Ayensu River, this system supports both local subsistence and market-based fishing that provides critical protein to surrounding communities. The primary contamination driver originates from illegal sand mining operations in the southern portion of the township, compounded by industrial discharge and historically weak environmental regulation enforcement (Adjei & Ako-Adjei, 2019; Samuel et al., 2018). Similar patterns documented across Ghana's mining-impacted river systems, including the Offin, Ankobra, and Bonsa Rivers, reveal persistent elevation of mercury, lead, arsenic, and cadmium above permissible concentrations even across multiple river sections (Obiri-Yeboah et al., 2021), yet dietary exposure assessments integrating bioavailability and receptor-specific uncertainty remain largely absent for these systems.

Current risk assessments of freshwater fish contamination suffer from several critical methodological limitations that compromise accurate health risk characterization. Most assessments apply total metal concentrations despite well-established evidence that bioavailability and toxicity depend critically on chemical speciation: methylmercury is 50–100× more neurotoxic than inorganic mercury, inorganic arsenic approximately 5× more toxic than organic arsenic

species, and Cr(VI) demonstrates ~1,000-fold greater carcinogenicity than Cr(III) (Fakhri & Sarafriz, 2021; Kumari & Kumar Maiti, 2019; Mielcarek et al., 2022). Concurrently, non-detect and left-censored observations are endemic in trace metal analysis yet most assessments employ ad hoc replacement strategies, such as substituting LOD/2, that introduce systematic bias and underestimate uncertainty (Hwang et al., 2023). Furthermore, uncertainty propagation typically terminates at dose calculation rather than extending to physiological outcomes such as blood-lead levels, and ecological and human health risk assessments proceed independently, limiting opportunities for integrated contamination management that could address both environmental protection and public health objectives simultaneously.

This study assessed metal(loid) contamination in water, sediment, and market-sourced fish from eight stations along the Akora River, Ghana, and developed a censoring-aware hierarchical Bayesian framework to generate speciation-informed dietary exposure and health risk distributions for consumers of *Oreochromis niloticus* and *Clarias anguillaris*. Specifically, the study aimed to: (i) characterize water–sediment–fish partitioning patterns for eight metals under explicit censoring treatment; (ii) generate receptor-specific non-cancer hazard, lifetime cancer risk, and blood-lead level distributions for children, women of child-bearing age, adults, and high-fish consumers through full posterior propagation incorporating speciation priors; and (iii) conduct ecological risk screening coupled with global sensitivity analysis to identify priority data-collection strategies for reducing risk uncertainty under resource constraints.

This work introduces several technical innovations that distinguish it from conventional risk assessment approaches and enhance both accuracy and decision relevance. The censoring-aware hierarchical Bayesian framework implements left-censored and interval-censored observations directly in the likelihood using log-CDF potentials, avoiding bias from deterministic replacement values while preserving uncertainty information typically discarded in traditional analyses (Astfalck et al., 2018; Belloni et al., 2020). Robust likelihood families including Laplace and Student-t distributions replace conventional Gaussian assumptions to reduce outlier influence while maintaining computational efficiency, improving model reliability in environmental datasets prone to extreme values

(Andrade, 2023; Nair et al., 2022). Speciation integration incorporates prior distributions for mercury (methylmercury), arsenic (inorganic), and chromium(VI) fractions informed by literature, enabling risk estimates that reflect bioavailable forms rather than total concentrations and avoiding systematic mischaracterization of toxicological exposure. Full posterior propagation carries environmental model uncertainty through intake calculations, speciation adjustments, and dose–response functions to generate complete posterior distributions of risk metrics rather than point estimates, providing comprehensive uncertainty quantification for decision support. Model assessment employs leave-one-out cross-validation using Pareto-smoothed importance sampling (PSIS-LOO) to evaluate predictive performance and model complexity, enabling data-driven comparison of alternative model structures without repeated full model refitting (Jung & Templin, 2024; Silva & Zanella, 2024). Global sensitivity analysis using Sobol indices quantifies how uncertainty in each input parameter contributes to variance in health outcomes, identifying which data refinements offer genuine decision value versus those that provide minimal risk-reduction benefit.

The framework introduced here employs in-likelihood censoring treatment, robust likelihood families, and full posterior propagation through speciation priors, advances that collectively avoid the bias and false precision characteristic of conventional imputation-based approaches. The results provide the first comprehensive uncertainty-quantified risk assessment for the Akora River system, contributing evidence-based foundations for freshwater fish consumption guidance in Ghana, where nationally codified standards remain absent despite documented contamination levels exceeding international thresholds by up to 16-fold for individual metals (Sackey et al., 2024), and offering a transferable methodological template for mining-affected river systems across sub-Saharan Africa.

Methodology

Study area and sampling design

River setting and stations

The Akora River in central Ghana served as the focal study ecosystem for this investigation into metal(loid)

contamination. Located in the Agona Swedru Township, the river stretches from Agona Nyakrom downstream to Swedru Township, where it eventually joins the Ayensu River at Agona Kwayaako (Fig. 1). The geographical coordinates marking the study area were latitude 5.5298° N and longitude 0.7058° W. Sampling was conducted during December 2024, a single campaign period selected to capture contemporary conditions across the river system during a defined seasonal window. The river's setting was characterized by substantial human pressure: illegal sand mining operations dominated the southern portion of the township and represented the primary suspected source of anthropogenic metal contamination. The investigation specifically targeted eight spatially distributed stations (ST1 through ST8) positioned along a river continuum extending from upstream (ST1) to downstream (ST8) locations.

*Matrices (water, sediment, fish muscle) and target species (*O. niloticus*, *C. anguillaris*)*

The study examined three environmental matrices to trace metal pathways through the aquatic ecosystem: surface water, bed sediment, and fish muscle tissue. Water samples were collected using calibrated plastic bottles and represented the dissolved and colloidal phase of the aquatic environment. Surface sediments were collected from the top layer (0–5 cm) of the river bed using a grab sampler, sampling at a water depth of approximately 45 cm, which captured current accumulation patterns rather than historical deep deposits. Fish tissue samples were sourced through a market-basket procurement strategy targeting two commercially important species: *Oreochromis niloticus* (Nile tilapia) and *Clarias anguillaris* (African mudfish). This market-sourced approach was deliberately chosen to reflect the consumer-relevant fish populations that people in the region actually consumed, thus capturing the dietary exposure pathway most relevant to human health risk assessment.

Sample size, replication, provenance tracking (market sourcing)

A total of 80 environmental samples were collected during the December 2024 campaign. The sampling design incorporated five replicate samples for both water and sediment at each of the eight stations,

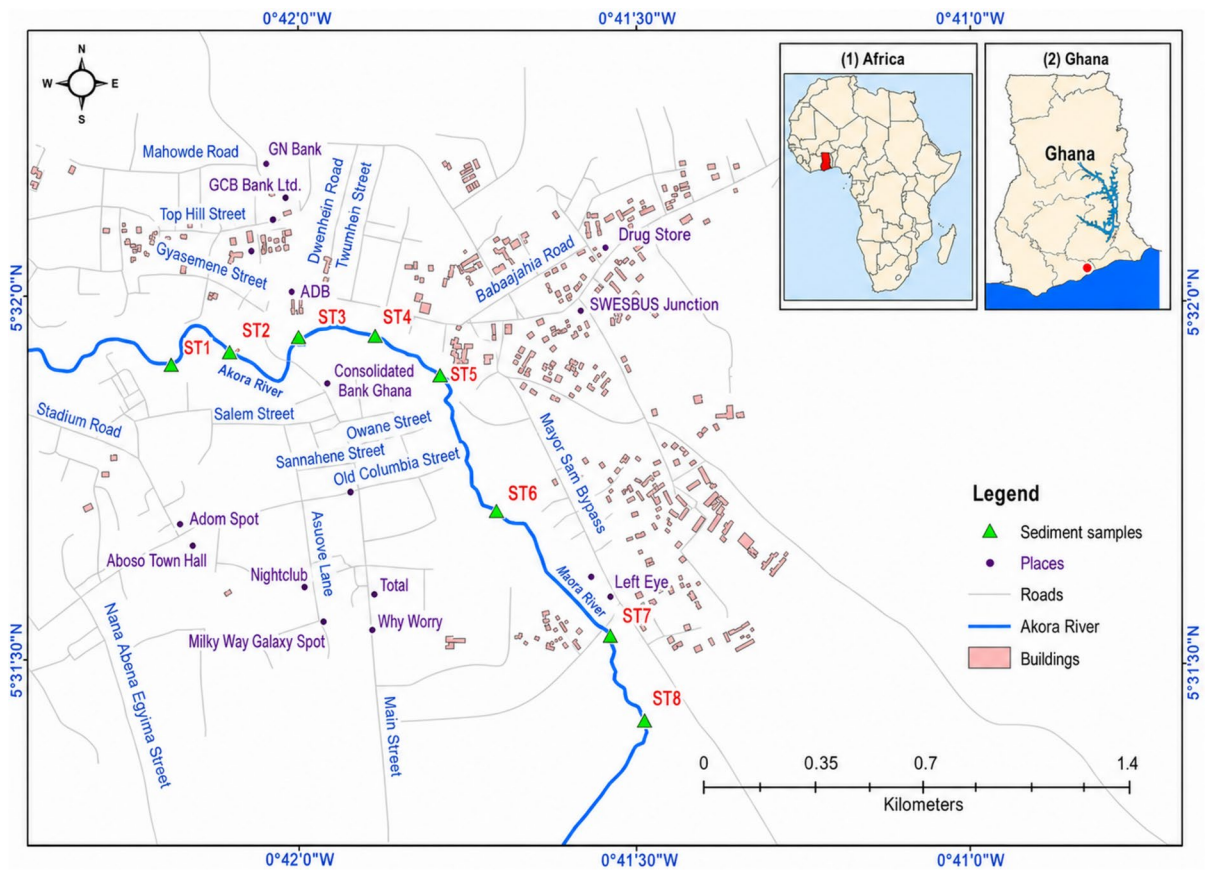


Fig. 1 Location of sediments and water sampling

yielding 40 water samples and 40 sediment samples distributed across the river reach. Fish samples were procured from local market centres in the Akora River study region using a targeted market-basket method. At each sampling market location near a river station, ten separate fish mongers were interviewed to identify those whose fish sourcing originated from the Akora River system; fish were purchased only from vendors confirming river provenance. This approach resulted in collection of ten fish specimens per station, with a total of 80 fish samples across eight stations. To ensure market-sourced fish represented meaningful consumer exposure, the specimens were stratified by species, yielding approximately three replicates per species per market location, totalling 12 fish samples when aggregated across both *Oreochromis niloticus* and *Clarias anguillaris*. The market-sourcing strategy, while obscuring exact station-of-origin information, effectively captured the dietary

exposure pathway most relevant to human health risk assessment in this context, as consumers purchase from local markets rather than collecting fish directly from the river.

Sample handling and preservation

Water samples were collected in calibrated plastic bottles and immediately transported to the University of Ghana Chemistry Laboratory 2 at Legon-Accra, where they were processed the same day. To prevent metal mobilization and contamination, water samples were filtered through Millipore filter paper (0.45 µm pore size) and acidified by addition of 5.0 N ultrapure nitric acid to reduce pH below 3, a preservation technique that prevented both precipitation and microbial alteration of dissolved-phase metals. Sediment samples were collected using a grab sampler and packed in polyethylene bags, then

sealed and transported to the same laboratory facility. Upon arrival, sediments were air-dried at room temperature to constant weight, then prepared through a standardized coning-and-quartering mixing protocol to ensure homogeneity. Approximately 50 g subsamples were transferred into crucibles and lyophilized at -60°C for 96 h. The dried samples were ground to powder using mortar and pestle, then sieved through standard 200-mesh sieves to ensure uniform particle size. Acid digestion was performed on approximately 1.0 g of each sediment subsample using a mixture of 3.0 mL nitric acid, 1.5 mL hydrogen fluoride, 1 mL hydrogen peroxide, and 2 mL hydrochloric acid, with all reagents purchased from Merck Darmstadt as analytical grade. Crucibles and contents were placed in a muffle furnace at 250°C ; after digestion completion, 2% nitric acid was added, samples were filtered, and the volume was brought to 50 mL with distilled water. Samples were then refrigerated pending analysis. Fish muscle tissue was processed by thin-slicing fresh samples, followed by freeze-drying using a TFD-2000LF2 model freeze dryer set at approximately -60°C for 72 h. Freeze-dried tissue was ground using a Hogg-Fuerstenau Power grinding mill, sieved, and stored in labelled polyethylene bottles before digestion. Fish tissue digestion was performed by placing 0.2–1.0 mg dry weight subsamples in crucibles, burning at 250°C in a muffle furnace, cooling to 25°C , then digesting in acid-cleaned jars with hot concentrated nitric acid to liberate trace elements. Following complete organic digestion and cooling, samples were filtered through $0.45\ \mu\text{m}$ Millipore membrane filters, transferred to 50 mL volumetric plastic bottles, brought to mark with 2% nitric acid, then diluted to 50 mL with double-distilled water. Fish tissue metal contents were expressed on a dry-weight basis as mg kg^{-1} .

Ethical approvals and permits

All aspects of this study were conducted under formal ethical oversight and regulatory compliance. Research was undertaken following written informed consent procedures and received formal approval from the University of Ghana Research Ethics Committee, with approval number UGDC50321/2024-102. The study protocol adhered to the requirements of the Ghana Environmental Protection Agency (Ghana EPA) and the Ghana Food & Drugs Authority

(GFDA) in accordance with Ghana's statutory regulatory framework for environmental and food safety research. All sampling and laboratory analyses were performed at the University of Ghana, Department of Chemistry Laboratories at Legon-Accra.

Laboratory analysis and QA/QC

Metals (totals: Hg, As, Ni, Cr, Cu, Pb, Cd, Zn) and measurement units

A fixed panel of eight potentially toxic elements was analysed across all environmental and biological matrices to maintain consistency with the downstream modelling pipeline. Seven metals—zinc, arsenic, nickel, chromium, copper, lead, and cadmium—were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES; PerkinElmer® ICP-OES model Avio 560 Max). Mercury was analysed separately using cold-vapour atomic fluorescence spectroscopy (P.S. Analytical model 10.023, Orpington, UK) with 6% hydrochloric acid in 2.2% tin chloride and 6% hydrochloric acid serving as the reducing agent. The operating conditions of the ICP-OES were standardized as follows: radiofrequency incident power of 1.3 kW, plasma argon flow rate of $15\ \text{L}\cdot\text{min}^{-1}$, auxiliary argon flow rate of $1.5\ \text{L}\cdot\text{min}^{-1}$, nebulizer argon flow rate of $0.7\ \text{L}\cdot\text{min}^{-1}$, with a V-groove nebulizer and Stumar master mist chamber. Measurement units were harmonized and expressed as milligrams per kilogram on a dry-weight basis ($\text{mg}\cdot\text{kg}^{-1}$) for both fish and sediment samples, while water samples were expressed as milligrams per liter (mg L^{-1}) to reflect the dissolved phase. This eight-metal specification remained constant throughout the study to align with the hierarchical Bayesian modelling architecture and ensure compatible data structure downstream. Fish tissue concentrations were analytically determined on a dry-weight basis because samples were freeze-dried before digestion.

Calibration/standards and instrument QC

Calibration was performed using analytical standards and verified every tenth sample with calibration blanks and independent calibration standards. Accuracy was assessed with NIST-1646a estuarine sediment and DOLT-4 dogfish liver certified reference materials (Table 1). Recoveries ranged from 84.0% to 103.73%

Table 1 The PTEs in certified reference materials

Element	Estuarine sediment NIST-1646a			Dogfish liver DOLT- 4		
	Certified concentration	Measured concentration	% recovery	Certified concentration	Measured concentration	% recovery
	mg kg ⁻¹	mg kg ⁻¹		mg kg ⁻¹	mg kg ⁻¹	
Hg	0.014 ± 0.01	0.012 ± 0.07	85.71	0.005 ± 0.04	0.0042 ± 0.10	84.00
Zn	51.60 ± 0.13	48.01 ± 1.80	93.04	124.39 ± 2.28	119.97 ± 1.90	96.45
As	0.098 ± 0.04	0.086 ± 0.01	87.78	-	-	-
Ni	26.40 ± 1.02	26.91 ± 0.88	101.93	0.84 ± 0.03	0.76 ± 0.09	90.48
Cr	39.80 ± 0.96	39.9 ± 0.91	100.25	-	-	-
Cu	12.07 ± 0.81	12.52 ± 1.03	103.73	34.13 ± 0.11	34.86 ± 0.13	102.14
Pb	13.36 ± 0.59	13.29 ± 0.71	99.48	0.191 ± 0.02	0.197 ± 0.09	103.14
Cd	0.129 ± 0.04	0.126 ± 0.08	97.67	22.84 ± 1.01	23.11 ± 0.24	101.18

across metals, with Hg slightly lower but acceptable given its volatility during high-temperature digestion. Field blanks, duplicates and triplicate analyses were processed with study samples; matrix interference was < 1.5% and relative percentage differences were < 4%, confirming acceptable analytical precision.

Detection limits (LOD/LOQ) and encoding of censoring

Metal-specific LODs/LOQs were assigned from instrument outputs or, where unavailable, from the lowest positive detection. Detected values were modelled directly, while N.D. and < LOD values were encoded as left- or interval-censored observations on the log scale. These censoring limits were passed to the Bayesian likelihood instead of being replaced by LOD/2, preserving uncertainty in the concentration estimates. For sparse detections, a small positive default LOD was used only to enable log-scale transformation.

Bayesian modelling and censoring treatment

Hierarchical Bayesian model

Water, sediment and fish metal concentrations were analysed using a hierarchical Bayesian model (HBM) on the natural-log scale, $y = \log(c)$, where c represents the measured concentration. The HBM was selected because the study used a single-season dataset with relatively small sample sizes and included left- and interval-censored observations. The

hierarchical structure enabled partial pooling across metals within each environmental matrix, linked fish tissue concentrations to river-wide water and sediment predictors, and propagated measurement, censoring and parameter uncertainty into the posterior draws used for health-risk and ecological-risk assessment.

Water and sediment concentrations were modelled as matrix-specific metal baselines, while fish concentrations were modelled using species-metal effects and river-wide water/sediment predictors. Because fish were obtained through market sourcing, the baseline model did not include station-specific fish effects, market-mixing terms, fish length or fish mass. Cross-media correlation priors and correlated fish-predictor priors were also excluded from the baseline model to avoid over-parametrisation.

A robust likelihood was applied on the log scale to reduce the influence of extreme concentration values. The default model used a Laplace likelihood for computational stability under the JAX/NumPyro backend, while a Student- t likelihood with fixed degrees of freedom ($\nu = 7.0$) was enabled as an alternative when JAX backends were not used. Weakly informative hierarchical priors with non-centred parameterizations were adopted to improve model mixing and support stable partial pooling.

Posterior inference was performed using Hamiltonian Monte Carlo with the No-U-Turn Sampler (NUTS) implemented in NumPyro. Sampling used 64-bit floating-point precision, vectorised chains, four chains, 2,000 tuning iterations and 2,000 post-warmup draws per chain. A target acceptance probability of 0.99,

maximum tree depth of 18 and fixed random seed were used to improve sampler stability and reproducibility. Model convergence and performance were evaluated using divergence checks, posterior summaries, effective sample sizes, $\hat{R}$ diagnostics and trace-plot inspection.

In-likelihood censoring and model comparison

Censored observations were incorporated directly into the likelihood rather than being replaced by arbitrary values such as LOD/2. Left-censored water and sediment observations were treated as values known only to fall below their matrix- and metal-specific detection limits. Interval-censored observations with instrument-reported upper bounds were encoded as upper-bounded likelihood contributions, while detected values entered the model as standard observations under the selected likelihood family. Fish censoring was not active in the baseline dataset because fish concentrations were observed directly.

This in-likelihood censoring approach allowed non-detects and instrument-limited observations to contribute information to the posterior distribution while preserving their uncertainty. As a result, uncertainty from detection limits was propagated into posterior concentration estimates and downstream risk metrics. The full mathematical specification of the censoring likelihood, including the log-CDF formulation for left- and interval-censored observations, is provided in the Supplementary Methods.

Model comparison and complexity control were assessed using Pareto-smoothed importance sampling leave-one-out cross-validation (PSIS-LOO). LOO (Jung & Templin, 2024) estimates were calculated for each likelihood component and then summed to obtain an overall predictive criterion, reflecting the conditional independence of matrix-specific likelihoods in the baseline model. The effective number of parameters p_{LOO} and Pareto shape diagnostics k were inspected using ArviZ outputs to evaluate model reliability and identify influential observations.

Health risk assessment

Receptors and intake parameters

Human-health risk was evaluated for four receptor groups: children, women of child-bearing age (WOCBA), adults and high fish consumers. For each

receptor group, daily fish ingestion rate (FIR, g day^{-1}) and body weight (BW, kg) were sampled as independent lognormal variables using receptor-specific arithmetic means and coefficients of variation. Exposure duration (ED), exposure frequency (EF), non-cancer averaging time AT_{nc} and cancer averaging time AT_{ca} were fixed according to receptor category. These assumptions were selected to represent Ghanaian fish-consumption patterns while allowing intake and body-weight variability to propagate through the risk calculations.

Dose estimation from posterior fish concentrations

For dietary exposure assessment, dry-weight concentrations were converted to wet-weight equivalents before being combined with fish ingestion rates, because consumption rates represent fresh fish intake. The conversion was performed as: $C_{\text{ww}} = C_{\text{dw}} \times f_{\text{dm}}$, where C_{ww} is the wet-weight concentration, C_{dw} is the dry-weight concentration, and f_{dm} is the dry-matter fraction of fish muscle. Posterior fish concentration draws generated by the HBM were used as the exposure input for health-risk calculations. For each receptor group, species and metal, fish concentrations were combined with sampled FIR and BW values to estimate chronic dietary intake. Daily intake estimates were then adjusted using the appropriate averaging time for non-cancer and cancer endpoints. This approach allowed uncertainty in fish concentration, consumption rate and body weight to be propagated into all downstream health-risk metrics.

Non-cancer risk assessment

Non-cancer risk was assessed using target hazard quotient (THQ) and hazard index (HI) metrics. THQs were calculated for each metal, receptor group and fish species by comparing estimated chronic daily intake with the corresponding oral reference dose (RfD). Speciated toxic forms were used where relevant: total As was adjusted to iAs, and total Hg was adjusted to MeHg using literature-informed priors. For Cr, total Cr was screened against the oral RfD for Cr(III) for non-cancer effects. Pb was not included in the THQ or HI summation because Pb exposure was assessed separately using blood-lead modelling.

Organ-specific HIs were calculated by summing relevant THQs according to target-organ groupings.

MeHg was assigned to neurological and developmental endpoints; iAs to developmental, cardiovascular, dermal and hepatic/gastrointestinal endpoints; Cd to renal and skeletal endpoints; and Cu, Ni, Zn and Cr to hepatic/gastrointestinal endpoints where applicable. The total non-cancer HI was calculated as the sum of all non-Pb THQs. An HI greater than 1 was interpreted as a screening-level indication of potential non-cancer concern.

Cancer risk assessment

Incremental lifetime cancer risk was assessed for specified carcinogenic forms only. Total cancer risk (TCR) was calculated for iAs and Cr(VI) using oral slope factors of 1.5 and 0.5 ($\text{mg kg}^{-1} \text{day}^{-1}$)⁻¹, respectively. Because site-specific Cr speciation data were unavailable, Cr(VI) was represented using a conservative prior fraction of total Cr. Cancer-risk estimates were generated for each receptor group and fish species, and exceedance probabilities were evaluated against the commonly used screening benchmark of (10^{-6}).

Lead risk via blood lead modelling

Pb exposure was evaluated using predicted blood-lead level (BLL) rather than the THQ framework. Dietary Pb intake was estimated from posterior Fish Pb concentrations and receptor-specific Fish ingestion rates, with unit conversion based on ($1 \text{ mg} = 1000 \mu \text{g}$). The diet-conversion method was then used to estimate Geometric Mean BLL using receptor-specific slopes of $0.16 \mu \text{g dL}^{-1}$ per $\mu \text{g day}^{-1}$ for children and $0.04 \mu \text{g dL}^{-1}$ per $\mu \text{g day}^{-1}$ for WOCBA and adults, with a background BLL of $0.6 \mu \text{g dL}^{-1}$. Inter-individual variability was represented using a lognormal BLL distribution with a geometric standard deviation of 1.7. Exceedance probabilities were calculated for BLL thresholds of 3.5, 5 and $10 \mu \text{g dL}^{-1}$. The full equations for dose estimation, THQ, HI, TCR and BLL modelling are provided in the Supplementary Methods.

Ecological risk assessment

Scope and workflow

Ecological risk was assessed for abiotic media only, using water and sediment concentrations. The screening calculations were based on detected

concentrations; left- and interval-censored observations were excluded from this ecological screening step. Concentrations were back-transformed to the natural scale before index calculation, while summary statistics were reported as medians with 3rd and 97th percentile intervals across detected replicates. The default ecological-risk parameters, guideline values and reference ranges used in the Akora River assessment are provided in Table S2.

Water column risk quotients

Water column ecological risk was evaluated using risk quotients (RQ), calculated as the ratio of detected water concentration to the corresponding water quality guideline for each metal. For each station and metal, replicate-level RQ values were summarized using the median and 3rd–97th percentile interval. A station-level total RQ was then calculated by summing the median RQ values across screened metals, with the summed lower and upper percentile values used to approximate uncertainty intervals. The proportion of metals with median $\text{RQ} > 1$ was also reported as a station-level exceedance indicator. Where posterior RQ draws were available, total RQ was calculated by summing metal-specific RQ values within each posterior draw before summarisation.

Sediment quality screening

Sediment risk was screened using probable effect concentration quotients (PEC-Qs). For each station and metal, detected sediment concentrations were divided by the corresponding probable effect concentration (PEC) to obtain replicate-level PEC-Q values. Median PEC-Q values were then calculated for each station–metal combination. Two empirical exceedance fractions were also calculated: the fraction of detected sediment samples exceeding the threshold effect concentration (TEC) and the fraction exceeding the PEC.

A station-level multi-metal sediment index was calculated as the median PEC-Q across metals with available sediment quality guideline values. In the current configuration, sediment screening was conducted for Cd, Cu, Ni, Pb and Zn because these metals had the required TEC and PEC values. Dispersion across metals was summarized using the 3rd and 97th percentiles, and the proportions of metals exceeding

PEC-Q thresholds of 0.5 and 1.0 were reported to aid interpretation. The full equations for RQ, total RQ, PEC-Q, TEC/PEC exceedance fractions and mPEC-Q are provided in the Supplementary Methods.

Sensitivity and robustness analyses

Global sensitivity analysis (GSA) (Iooss & Lemaître, 2015) was performed to identify the main sources of uncertainty in three headline outcomes: probability of non-cancer HI exceedance ($HI > 1$), probability of cancer-risk exceedance ($TCR > 10^{-6}$), and BLL exceedance at selected thresholds. The analysis was based on posterior-propagated risk estimates rather than separate scenario sweeps. Speciation scenario sets were disabled in the baseline; however, iAs, MeHg and Cr(VI) fractions were still sampled from the configured literature-informed priors during the risk-calculation stage.

For each receptor group, the sensitivity analysis considered exposure parameters, toxicological/speciation assumptions and selected model-scaling factors. FIR and BW were treated as lognormal exposure variables, while BLL mapping used receptor-specific conversion slopes, background BLL and inter-individual variability. Optional metal-specific concentration multipliers were included to assess the effect of plausible global mis-specification in the exposure tier. Cancer slope factors and RfDs were held fixed in the baseline sensitivity analysis, while Cr(VI)-related cancer risk remained enabled using the conservative prior fraction.

A Saltelli sampling design was used to generate the outer parameter sets for variance-based sensitivity analysis. For each sampled parameter set, risk summaries were calculated by averaging over the fixed posterior fish-concentration draws from the HBM. Sobol indices were then estimated to quantify the contribution of each input factor to variation in the selected risk outcomes. Total-order Sobol indices (S_T) were emphasized because they capture both the direct contribution of each factor and its interaction with other inputs. Bootstrap confidence intervals were used to assess the stability of the sensitivity rankings.

For BLL-focused analysis, a Morris screening step was used where necessary to rank candidate parameters before applying Sobol decomposition to the most influential subset. This reduced computational burden while preserving the ability to identify dominant

uncertainty drivers. Sensitivity analyses were performed separately for each receptor group so that uncertainty priorities could be compared across children, WOCBA, adults and high-consumers. The full mathematical specification of the exceedance-probability estimands, BLL exceedance function, diet-to-BLL mapping and Sobol-index equations is provided in the Supplementary Methods.

Results and discussion

Data overview and model diagnostics

Detection frequency and censoring patterns

Non-detect and left-censored observations were prevalent across the eight-metal panel, with frequency varying substantially by metal and matrix (Tables 2 and 3). Lead and cadmium exhibited the highest censoring rates in the water column, with concentrations falling below instrument detection limits (N.D) in 50% and 37.5% of sampling sites, respectively. Arsenic similarly showed frequent non-detects in water, particularly at upstream stations (ST1 and ST2). In contrast, mercury, zinc, nickel, and chromium demonstrated complete detection frequencies in water, contradicting the typical censoring trends often observed for trace mercury. Sediment and biological matrices generally exhibited lower censoring prevalence than water due to higher background levels and particle-associated accumulation. In the biological samples (Table 2), both *Oreochromis niloticus* and *Clarias anguillaris* showed near-universal detection of all Potentially Toxic Elements (PTEs). Zinc was the most dominant metal in biota (Geometric Mean: 1.66–2.39 mg kg⁻¹), while Mercury remained the least concentrated trace element (0.00016–0.00017 mg kg⁻¹), with isolated missing data points observed only in *O. niloticus* at sites SM9 and SM11. The prevalence of left-censored data in the aqueous phase, combined with the complete detection profiles in sediment and fish tissue, necessitated the implementation of a hierarchical Bayesian modelling framework. This approach allowed for the coherent propagation of both censoring uncertainty (from water samples) and measurement variability (from biological and sediment samples) into posterior distributions used for downstream risk assessment,

Table 2 Mean concentrations of PTEs in *Oreochromis niloticus* and *Clarias anguillaris* in the selected sampling sites ($n=3$) (mg kg⁻¹, dry weight)

Sampling sites	Hg	Zn	As	Ni	Cr	Cu	Pb	Cd
<i>Oreochromis niloticus</i>								
SM1	0.00015	2.04	0.0050	0.027	0.015	0.41	0.20	0.0063
SM2	0.00017	1.59	0.0037	0.014	0.017	0.47	0.22	0.0070
SM3	0.00018	2.32	0.0043	0.018	0.016	0.33	0.16	0.0053
SM4	0.00016	1.33	0.0053	0.026	0.021	0.35	0.17	0.0043
SM5	0.00016	1.64	0.0067	0.015	0.019	0.36	0.14	0.0070
SM6	0.00013	2.04	0.0050	0.014	0.016	0.39	0.10	0.0080
SM7	0.00019	1.56	0.0057	0.016	0.015	0.42	0.14	0.0087
SM8	0.00017	1.93	0.0060	0.017	0.018	0.31	0.17	0.0047
SM9	-	1.14	0.0073	0.013	0.015	0.41	0.13	0.0067
SM10	0.00014	1.58	0.0037	0.011	0.016	0.35	0.15	0.0063
SM11	-	0.91	0.0040	0.019	0.013	0.37	0.17	0.0037
SM12	0.00014	1.87	0.0063	0.023	0.014	0.35	0.19	0.0053
GM	0.00016	1.66	0.0053	0.018	0.016	0.38	0.16	0.0061
GSD	1.2	2.09	2.44	3.03	3.02	3.11	2.02	1.19
Sampling sites	Hg	Zn	As	Ni	Cr	Cu	Pb	Cd
<i>Clarias anguillaris</i>								
SM1	0.00014	3.01	0.0060	0.030	0.016	0.44	0.23	0.0067
SM2	0.00018	2.80	0.0043	0.028	0.015	0.43	0.21	0.0063
SM3	0.00019	3.38	0.0043	0.020	0.019	0.35	0.18	0.0077
SM4	0.00018	2.29	0.0063	0.022	0.023	0.31	0.19	0.0070
SM5	0.00016	2.68	0.0037	0.027	0.020	0.32	0.27	0.0080
SM6	0.00020	1.61	0.0070	0.016	0.018	0.35	0.20	0.0060
SM7	0.00017	2.25	0.0090	0.025	0.012	0.38	0.18	0.0067
SM8	0.00015	2.21	0.0060	0.020	0.020	0.36	0.24	0.0090
SM9	0.00016	1.50	0.0060	0.027	0.016	0.37	0.21	0.0080
SM10	0.00018	1.81	0.0087	0.019	0.017	0.36	0.19	0.0087
SM11	0.00019	2.75	0.0050	0.018	0.016	0.33	0.20	0.0093
SM12	0.00013	2.34	0.0073	0.020	0.013	0.34	0.24	0.0097
GM	0.00017	2.39	0.0061	0.023	0.017	0.36	0.21	0.0078
GSD	2.03	3.81	2.77	4.07	3.13	1.99	1.93	3.16

GM geometric mean, GSD geometric standard deviation

preserving inference integrity despite incomplete data in the aqueous medium.

Model convergence diagnostics

Hamiltonian Monte Carlo sampling was performed using the Numpyro backend with stringent integrator settings: target acceptance probability 0.99, maximum tree depth 18, with four independent chains each drawing 2000 post-warmup samples after 2000 tuning iterations and a fixed random seed

for reproducibility. All model parameters achieved convergence as assessed through the potential scale reduction factor (Rhat), with reported values of approximately 1.00 for water intercepts (aW) and sediment intercepts (aS) across all eight metals (Table S3). Fish-species effects (bF) similarly demonstrated $R_{\text{hat}} \approx 1.00$ for all 16 parameters (8 metals $\times$ 2 species, Table S4), and covariate effects (g) linking fish to environmental media achieved $R_{\text{hat}} \leq 1.01$ for all 32 slope parameters (8 metals $\times$ 2 media $\times$ 2 species, Table S5, Figure S1). Bulk effective sample

Table 3 Mean concentrations of PTEs in water (mg L^{-1}) and sediments (mg kg^{-1} , dry weight) in the selected sampling sites ($n=5$)

Sampling sites	Water								Sediment							
	Hg	Zn	As	Ni	Cr	Cu	Pb	Cd	Hg	Zn	As	Ni	Cr	Cu	Pb	Cd
ST1	0.003	1.06	N.D ^c	0.81	0.62	0.11	N.D	N.D	0.533	12.48	0.041	7.61	14.65	3.95	0.99	0.016
ST2	0.003	0.93	N.D	0.96	0.76	1.06	N.D	N.D	0.524	10.69	0.035	6.74	14.89	3.77	1.67	0.041
ST3	0.002	1.06	0.010	0.88	0.62	0.82	N.D	0.007	0.489	16.61	0.026	6.90	15.22	5.52	0.82	0.051
ST4	0.005	2.17	0.014	0.82	0.61	1.40	N.D	N.D	0.481	21.91	0.028	9.41	16.71	5.06	1.49	0.049
ST5	0.003	1.18	0.008	1.61	0.85	1.19	0.05	0.005	0.481	37.25	0.041	9.67	19.84	6.55	1.84	0.062
ST6	0.002	1.34	0.012	1.46	0.91	1.13	0.07	0.004	0.426	31.34	0.041	11.03	17.25	7.29	4.68	0.074
ST7	0.001	6.81	0.017	1.11	2.76	1.98	0.09	0.005	0.414	39.98	0.067	9.65	18.04	6.68	4.91	0.071
ST8	0.002	5.99	0.014	1.61	1.98	1.77	0.01	0.007	0.396	46.01	0.093	11.43	18.11	7.04	6.98	0.064
WHO limits ^a	0.001	1.00	0.010	0.070	0.05	2.00	0.01	0.003	-	-	-	-	-	-	-	-
Average shale	-	-	-	-	-	-	-	-	0.4	95	13	68	90	45	20	0.3

^aWHO (2004), ^bTurekian and Wedepohl (1961), ^cN.D not detected

sizes (ESS) ranged from approximately 1100 to 3600, indicating efficient sampling and reliable posterior summaries. No divergent transitions were recorded across any of the four chains, confirming that the sampler did not encounter regions of problematic posterior geometry. The posterior object was inspected visually, confirming complete overlap of traced parameter chains and stable mixing throughout the post-warmup phase. Leave-One-Out Cross-Validation (PSIS-LOO) was computed for model comparison, with Pareto shape diagnostic (k) values remaining below 0.7 for the vast majority of observations, indicating reliable Pareto-smoothing and appropriate model complexity. The additive ELPD structure ($ELPD_{total} = ELPD^{(W)} + ELPD^{(S)} + ELPD^{(F)}$) reflected the conditional independence of matrix-specific likelihoods in the baseline model, enabling decomposition of predictive performance by matrix while maintaining complexity control through the implied effective number of parameters (p_{LOO}).

Water sediment baseline and ecological screening

Water phase intercepts by metal

The hierarchical Bayesian model estimated intercepts for water-phase concentrations on the natural-log scale (aW) representing baseline dissolved metal levels across the river (Table S3). Mercury exhibited an exceptionally low water-baseline intercept of -5.98 (SD 0.159), with 94% highest density interval (HDI) $[-6.28, -5.67]$, indicating that dissolved Hg

concentrations were typically near or below instrument detection limits in the water column. Cadmium and arsenic similarly demonstrated very low water baselines at -5.65 (SD 0.296, HDI $[-6.21, -5.13]$) and -4.82 (SD 0.285, HDI $[-5.41, -4.34]$), respectively, reflecting limited dissolved-phase mobility for these elements. Lead showed the largest uncertainty in water estimates, with $aW = -4.59$ (SD 0.454, HDI $[-5.45, -3.75]$), consistent with episodic detections and variable speciation. In contrast, zinc was the only metal with a clearly positive water intercept at 0.56 (SD 0.173, HDI $[0.21, 0.85]$), indicating consistent dissolved-phase elevation. Nickel and chromium straddled zero at 0.07 (SD 0.149, HDI $[-0.21, 0.35]$) and -0.07 (SD 0.160, HDI $[-0.40, 0.22]$), respectively, indicating ambiguous elevation at reference conditions and substantial within-metal variability. Copper exhibited a slightly negative water intercept of -0.14 (SD 0.249, HDI $[-0.62, 0.30]$), suggesting episodic or complex partitioning. Overall, the water-phase baseline was characterized by low concentrations for most metals, with zinc as the primary dissolved-phase element and sporadic detectability for trace metals.

Sediment phase intercepts by metal

Sediment intercepts (aS) on the natural-log scale revealed strong, precise positive baselines for multiple metals, reflecting preferential accumulation in the solid phase (Table S3). Zinc exhibited the highest sediment intercept at 3.11 (SD 0.245, HDI $[2.64, 3.54]$),

followed closely by chromium at 2.81 (SD 0.069, HDI [2.68, 2.93]) and nickel at 2.20 (SD 0.108, HDI [1.97, 2.38]). Copper and lead showed moderately elevated sediment baselines of 1.75 (SD 0.126, HDI [1.50, 1.96]) and 0.61 (SD 0.251, HDI [0.20, 1.18]), respectively. Mercury remained slightly negative in sediments at -0.75 (SD 0.067, HDI $[-0.88, -0.63]$), and arsenic showed a strongly negative baseline at -3.17 (SD 0.140, HDI $[-3.41, -2.88]$). Cadmium exhibited a moderately negative sediment intercept of -2.84 (SD 0.136, HDI $[-3.08, -2.59]$). The contrast between strongly positive sediment intercepts for Zn, Cr, Ni, Cu, and Pb versus negative or near-zero intercepts for Hg and As indicated fundamental differences in partitioning behaviour and biogeochemical fate. The positive sediment baselines for chalcophile and particle-reactive elements reflected their affinity for particulate matter through sorption, coprecipitation with metal oxides, and redox-controlled scavenging processes.

Matrix contrast and enrichment factors

The difference between sediment and water intercepts ($\Delta aS - aW$) quantified the preferential partitioning to the solid phase (Table S3). All eight metals demonstrated sediment enrichment relative to water; however, the magnitude of enrichment varied dramatically across the periodic table. Mercury showed the most pronounced contrast, with $\Delta = 5.23$ ($\exp(\Delta) \approx 186$ -fold enrichment), indicating extreme partitioning to sediments despite low baselines in both matrices. Lead exhibited a similarly massive contrast of $\Delta = 5.20$ ($\exp(\Delta) \approx 182$ -fold), suggesting dominant control of Pb fate by sediment-phase processes. Chromium demonstrated moderate enrichment with $\Delta = 2.88$ ($\exp(\Delta) \approx 17.8$ -fold), as did cadmium at $\Delta = 2.81$ ($\exp(\Delta) \approx 16.6$ -fold). Zinc, nickel, and copper showed intermediate enrichment factors of $12.9\times$, $8.4\times$, and $6.6\times$, respectively. Arsenic exhibited the smallest sediment enrichment at $\Delta = 1.65$ ($\exp(\Delta) \approx 5.2$ -fold), despite strong negative baselines in both matrices, indicating limited accumulation at baseline conditions potentially governed by speciation state rather than total concentration. The universal $aS > aW$ hierarchy across all metals supported the inference that particulate-phase association dominates metal partitioning in the river system. The extreme enrichment factors for Hg and Pb signalled accumulation

in benthic sediments via redox-controlled scavenging and oxide precipitation, processes that sequester these elements but also create long-term repositories for potential mobilization under changing environmental conditions.

Fish accumulation patterns and species comparisons

Species main effects and between species contrasts

The hierarchical Bayesian model included species-specific intercepts (bF) to test whether *Clarias anguillaris* and *Oreochromis niloticus* differed in total metal accumulation on a log scale (Table S4). For every metal analysed, the 94% highest density intervals for the species effect spanned zero, indicating no credible evidence of species-level differences in fish metal concentrations. Arsenic showed posterior means of -0.72 for *C. anguillaris* and -0.76 for *O. niloticus*, with HDI $[-3.42, 2.02]$ and $[-3.52, 1.79]$, respectively. Cadmium revealed means of -0.62 and -0.69 (HDI $[-3.35, 1.85]$ and $[-3.20, 1.85]$). Chromium exhibited means of -1.04 and -1.12 (HDI $[-3.65, 1.49]$ and $[-3.88, 1.43]$). Mercury, lead, and zinc similarly showed overlapping posterior distributions with means within ± 0.1 log units and wide credible intervals spanning approximately 3 log units. The directional probability $P(\Delta b_F > 0)$, estimated from posterior means and standard deviations using normal approximation, was approximately 0.50 for all metals, indicating no systematic advantage for either species. At the posterior mean, the implied species contrast on the natural scale ($\exp(\Delta b_F)$) ranged from 0.94 to 1.09 across metals—a difference of less than 10% in both directions. Bulk effective sample sizes exceeded 2000 for all species parameters, and Rhat values were approximately 1.00 (with one parameter at 1.01), confirming reliable posterior summaries rather than algorithmic artifacts. The conclusion was unambiguous: species identity explained negligible variance in total metal accumulation under the current model and data, suggesting that site conditions, environmental media, and individual-level intake behaviour dominated over interspecific differences in bioaccumulation capacity. This convergence should be interpreted in light of the market-basket sampling design: it does not prove that the two species have identical ecological bioaccumulation mechanisms, but it indicates that consumer-facing fish metal burdens did not separate

strongly by species in the present dataset. This supports the use of species-inclusive consumption guidance for the Akora market context, while recognizing that future station-resolved ecological sampling could reveal finer species-specific differences.

Water phase covariate effects: mercury as a robust bioavailability signal

The log–log regression coefficient linking fish metal concentration to water-phase concentration (gW) revealed substantial heterogeneity in bioavailability across metals (Table S5). Mercury demonstrated the only robust, decisively positive water-phase coupling across both species. For *C. anguillaris*, $g_W = 0.86$ (SD 0.432, HDI [0.043, 1.548]), and for *O. niloticus*, $g_W = 0.843$ (SD 0.435, HDI [0.022, 1.578]). Both credible intervals excluded zero with high confidence, yielding $P(gW > 0) \approx 0.97$ – 0.98 . The practical implication, expressed as the doubling rule, was that a twofold increase in water-phase Hg corresponded to approximately $2^{0.86} \approx 1.82$ -fold increase in fish Hg (HDI ≈ 1.02 – $2.99\times$). This strong water-Hg coupling pointed to bioavailable dissolved mercury, primarily in methylated form, as the controlling pathway for fish exposure. Arsenic and cadmium showed plausible but less decisive positive water effects. Arsenic yielded $g_W \approx 0.46$ for both species ($P(gW > 0) \approx 0.87$, HDI crossing zero), implying a doubling rule of $2^{0.46} \approx 1.38$ (HDI ≈ 0.80 – 2.38). Cadmium was similarly suggestive at $g_W \approx 0.48$ – 0.49 ($P \approx 0.90$, HDI $[-0.24$ to $1.13]$), with doubling rule $2^{0.49} \approx 1.40$. Lead exhibited a weaker signal at $g_W \approx 0.22$ ($P(gW > 0) \approx 0.71$), implying $2^{0.22} \approx 1.17$ per doubling of water Pb. In contrast, chromium, nickel, copper, and zinc showed near-null or ambiguous water responses, with posterior means near zero and HDIs bracketing zero symmetrically ($P(gW > 0) \approx 0.50$ for most). These metals appeared to be governed by pathways other than direct dissolved-phase uptake, suggesting either particulate-phase feeding, food-web transfer, or low bioavailability of dissolved species in the river's oxic conditions.

Sediment phase covariate effects: limited direct transfer

The sediment-phase log–log slopes (gS) revealed weak or negative coupling between fish metal concentrations and sediment levels for most metals

(Table S5). Chromium and nickel both exhibited negative sediment slopes: Cr $g_S \approx -0.45$ ($P(gS < 0) \approx 0.82$, HDI $[-1.33, 0.51]$), and Ni $g_S \approx -0.38$ to -0.39 ($P(gS < 0) \approx 0.77$ – 0.78 , HDI $[-1.24$ to $-1.37, 0.51$ to $0.64]$). These negative coefficients, although not excluding zero with overwhelming confidence, suggested decoupling between benthic sediment concentration and fish accumulation at the study scale. Possible explanations included: (i) low bioavailability of particulate-bound metal phases, (ii) non-benthic feeding ecology reducing sediment exposure, or (iii) collinearity between water and sediment predictors obscuring the true relationship. Other metals (As, Cd, Cu, Pb, Zn) showed small positive or near-null sediment slopes ($g_S \approx 0.03$ – 0.27), with all HDIs straddling zero. Zinc exhibited the largest sediment coefficient at $g_S \approx 0.10$, but uncertainty remained high (HDI $[-0.62, 0.83]$). The weak sediment effects contrasted sharply with the robust mercury water link, indicating that sediment is not a primary direct predictor of fish metal burden under current conditions, despite being the dominant reservoir.

Water vs. sediment dominance: metal-specific pathways

The magnitude of the difference ($\Delta gW - gS$) quantified the relative contribution of water-phase versus sediment-phase drivers to fish accumulation (Table S5). Mercury showed the clearest water dominance with $\Delta \approx 0.75$ across both species, reflecting the strong g_W and minimal g_S . Chromium and nickel exhibited intermediate water dominance ($\Delta \approx 0.45$ and 0.37 , respectively), though both underlying slopes were weak. Lead, cadmium, and copper showed smaller differences ($\Delta \approx 0.13$ – 0.27), suggesting either water and sediment are similarly weak drivers or they are collinear predictors of fish concentration. Zinc displayed slight sediment tendency ($\Delta \approx -0.07$), though both water and sediment slopes were negligible. This heterogeneity implied distinct metal-specific bioaccumulation mechanisms: mercury is primarily water-driven (likely via methylated form), while most other metals require integrated understanding of food-web dynamics, tissue distribution, and temporal accumulation rather than simple partitioning coefficients. The cross-species symmetry in all covariate effects (differences ≤ 0.03 between species for every slope) reinforced the conclusion that

species-specific predictive models for totals were not justified; instead, management strategies should target environmental media controls and species-agnostic consumption patterns.

Human health risk: HI, TCR and BLL

Non-carcinogenic hazard index HI

Total hazard index distributions and screening level exceedances The total non-cancer hazard index (HI_{total}) was constructed by summing target hazard quotients (THQ) for all non-cancer endpoints (excluding lead, which was handled separately via blood-lead modelling). Posterior median HI values were substantially below the screening threshold of 1.0 for all receptor groups and both fish species (Fig. 2, top row). For *Oreochromis niloticus*, medians were 0.17 (child), 0.08 (WOCBA), 0.10 (adult), and 0.20 (high-consumer), with 94% credible intervals [0.02, 9.32], [0.01, 4.33], [0.01, 5.36], and [0.03, 10.48], respectively. For *Clarias anguillaris*, medians were 0.18 (child), 0.08 (WOCBA), 0.10 (adult), and 0.19 (high-consumer), with intervals [0.02, 11.53], [0.01, 5.40], [0.01, 6.54], and [0.03, 13.75]. The central tendency indicated acceptable non-cancer risk for the river population; however, substantial right-tail mass extended beyond the threshold, indicating plausible but uncommon scenarios of HI exceedance. Probability of exceeding $HI > 1$ (Fig. 3, top row) was estimated from posterior draws using indicator functions. For *O. niloticus*, exceedance probabilities were 14.8% (child), 8.8% (WOCBA), 10.0% (adult), and 16.2% (high-consumer). For *C. anguillaris*, corresponding values were 15.2%, 9.7%, 11.1%, and 16.7%. The exceedance pattern revealed that approximately 1 in 6–7 children and high-consumers had posterior draws in which total non-cancer hazard crossed the screening benchmark, whereas WOCBA and adults remained below 10% exceedance. This distribution suggested that vulnerable populations, particularly children and frequent fish consumers, carried meaningful but not dominant upper-tail risk under current river metal concentrations and consumption patterns.

Organ-specific hazard index: developmental and neurological dominance Organ-specific hazard indices were computed by summing THQs for target-organ groupings established via ingestion toxicology literature (Figures S3 and S4). The

developmental endpoint, aggregating hazards from methylmercury and iAs, exhibited the largest upper-tail risk across both species. For *C. anguillaris* (Figure S3, developmental panel), median HI was from 0.017 to 0.040 across receptor groups, with 97th percentiles of 6.94 (child), 4.15 (WOCBA), 3.98 (adult), and 9.59 (high-consumer). For *O. niloticus* (Figure S4, developmental panel), medians were from 0.019 to 0.044 with 97th percentiles of 6.78 (child), 3.79 (WOCBA), 4.09 (adult), and 7.44 (high-consumer). All receptor groups showed credible probability of exceeding $HI = 1$ at the 97th percentile, with children and high consumers at greatest risk. Probability of exceedance $P(HI > 1)$ for developmental effects was approximately 10% for child and high-consumer groups across both species (Figures S5 and S6), representing the highest exceedance probability among all organs. The neurological endpoint, driven by methylmercury, showed median HI of from 0.003 to 0.020 for *C. anguillaris* and from 0.005 to 0.011 for *O. niloticus*, with 97th percentiles reaching from 3.26 to 4.52 (child) and from 1.40 to 2.32 (WOCBA/adult). Neurological exceedance probabilities were 4.4–8.0% across receptor groups (Figures S5 and S6). The hepatic/gastrointestinal endpoint, aggregating arsenic, nickel, copper, zinc, and chromium (III), showed medians of from 0.032 to 0.081 and exceedance probabilities of 2.1–5.9% for vulnerable groups. Renal (cadmium-driven) and skeletal (cadmium) endpoints remained well below $HI = 1$ even at the 97th percentile (HDI-based estimates < 1.5), with exceedance probabilities $< 4\%$ across all groups. Cardiovascular and dermal endpoints similarly exhibited low risk, with exceedance probabilities $< 4\%$. The hierarchical risk pattern, developmental $\geq$ neurological $>$ hepatic/dermal $>$ renal $\approx$ skeletal $\approx$ cardiovascular, reflected the dominance of methylmercury and inorganic arsenic in non-cancer toxicity among freshwater fish consumers at this location. This finding reflects evidence that methylmercury is 50 to 100 times more neurotoxic than inorganic mercury, with stronger affinity for neuronal thiol groups and higher bioaccumulation potential (Mielcarek et al., 2022).

Receptor group patterns: children and high consumers as vulnerable populations Risk metrics stratified by receptor group revealed consistent patterns across all organs and metrics. Children

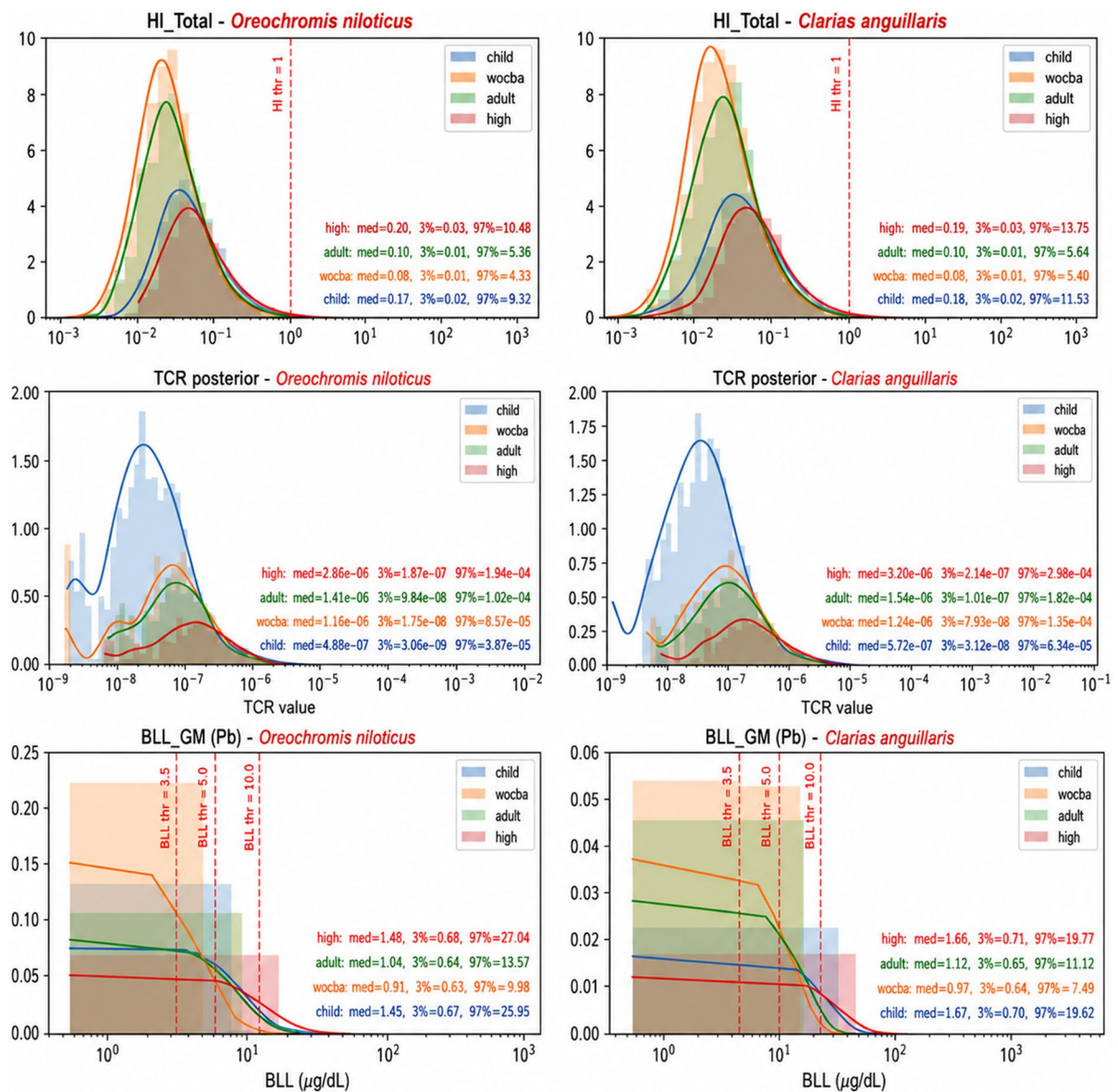


Fig. 2 Posterior risk profiles for two market fish species *Oreochromis niloticus* (left column) and *Clarias anguillaris* (right column) stratified by receptor group (child, WOCBA, adult, high-consumer). Rows show: (top) total non-cancer Hazard

Index (HI_{total}); (middle) lifetime total cancer risk (TCR); (bottom) predicted geometric-mean blood-lead level (BLL_{GM}) from dietary Pb

exhibited the highest absolute HI values and exceedance probabilities across nearly all endpoints, driven by their lower body weight (0–6 years average 15 kg) and higher bioavailability coefficient for lead. The median total HI for children was approximately 2× that of WOCBA at the same consumption level (e.g., 0.17 vs. 0.08 for *O. niloticus*), reflecting the mg/

kg/day scaling inherent in dose calculation. Women of child-bearing age (WOCBA) consistently showed the lowest exceedance probabilities (approximately 8–10% for total HI), despite comparable consumption rates to adults, likely due to their intermediate body weight and age-related bioavailability. Adults showed exceedance probabilities between WOCBA

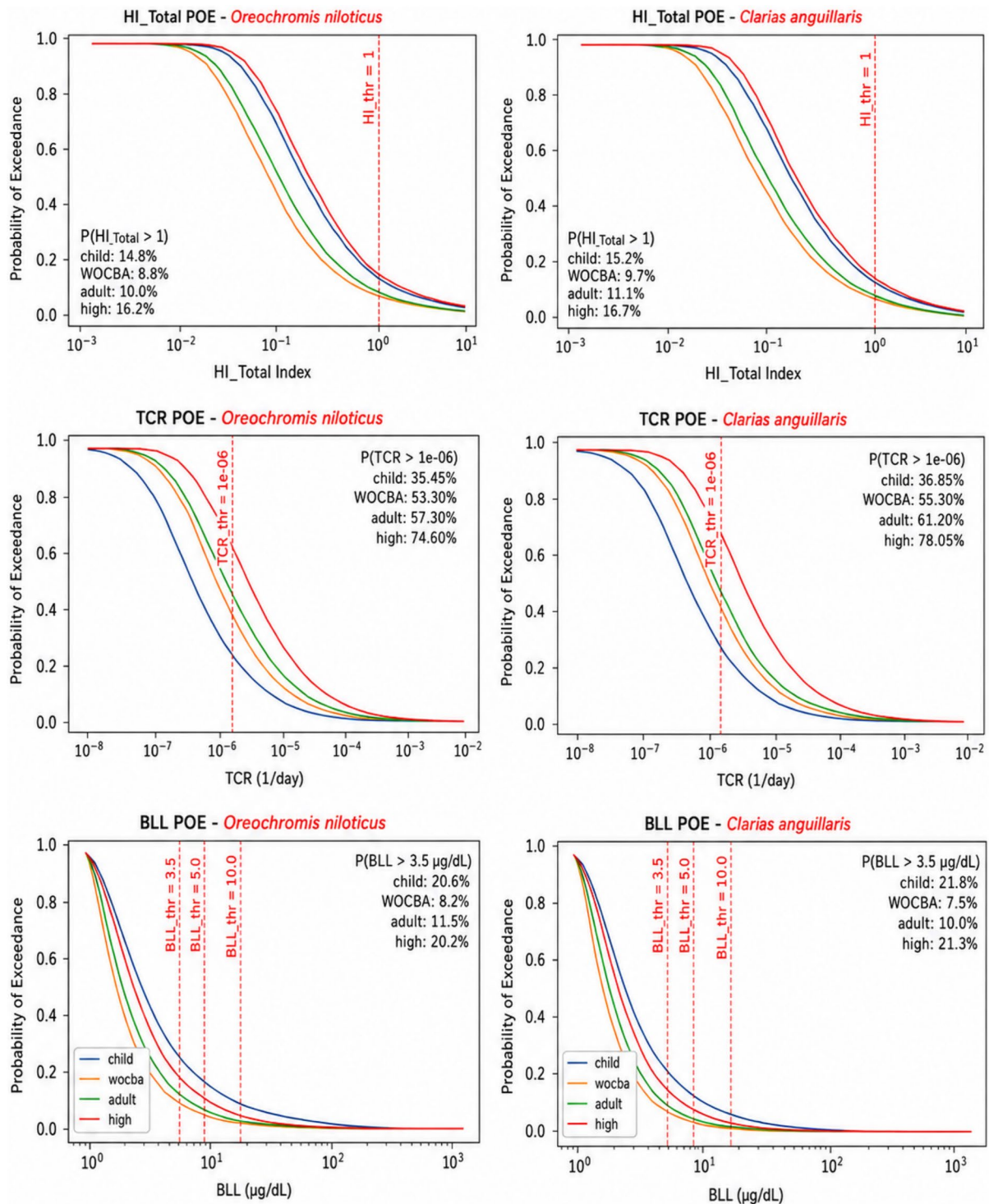


Fig. 3 Probability-of-exceedance (POE) curves for three health metrics by receptor group (child, WOCBA, adult, and high-consumer) for two market fish species: *Oreochromis niloticus* (left) and *Clarias anguillaris* (right)

and children (approximately 10–11%), reflecting slightly higher body weight but similar consumption assumptions. High-consumer receptor groups, characterized by elevated daily fish intake (assumed 150 g/day vs. 90 g/day for average adult), approached children in absolute risk despite higher body weight, demonstrating that consumption frequency was a primary risk driver. The relative ranking remained consistent across both fish species, organ endpoints, and risk metrics (HI, TCR, BLL), indicating that risk-management strategies should prioritize protection of children and identifying and counselling high-consumption populations as key intervention points.

Speciation assumptions and sensitivity to methylmercury fraction Methylmercury (MeHg) was specified as a fraction of total mercury using a species-specific prior distribution (Figures S3 and S4). For developmental and neurological endpoints, MeHg was the dominant driver of hazard quotient magnitude. The reference dose (RfD) for MeHg was set to 1.0×10^{-4} mg/kg/day based on EPA guidance, substantially lower than the RfD for inorganic mercury (1.5 mg/kg/day, used for non-specified Cr (III)). If the assumed MeHg fraction shifted from the modelled prior mean to alternative plausible levels, the implied HI would scale proportionally with the speciation assumption. For inorganic arsenic (iAs), a Beta (1,19) prior was employed (median 5%, representing typical freshwater conditions), with $RfD = 3.0 \times 10^{-4}$ mg/kg/day. Sensitivity analysis confirmed that HI was highly elastic with respect to MeHg fraction: a shift from 5 to 15% methylation would increase developmental and neurological HI by approximately 2–threefold. Likewise, if iAs fraction in total arsenic shifted from 5 to 50%, developmental HI would increase proportionally. These dependencies underscored the critical importance of direct speciation measurements (e.g., via HPLC-ICP-MS for Hg and As) in refining risk estimates, as total-metal concentrations alone could substantially mischaracterize non-cancer hazard if speciation assumptions diverged from actual river conditions.

Incremental lifetime cancer risk

Total cancer risk distributions and screening level exceedances Incremental lifetime cancer risk (TCR) was computed from carcinogenic metals using oral slope factors (OSF) for inorganic arsenic

and chromium (VI), integrated over a 70-year exposure period. Posterior median TCR values spanned the range from 10^{-7} to 10^{-6} across receptor groups, with substantial upward extension in the upper tails (Fig. 2, middle row). For *Oreochromis niloticus*, median TCR was 4.88×10^{-7} (child), 1.16×10^{-6} (WOCBA), 1.41×10^{-6} (adult), and 2.86×10^{-6} (high-consumer), with 94% credible intervals [3.06×10^{-8} , 3.87×10^{-5}], [7.75×10^{-8} , 8.57×10^{-5}], [9.84×10^{-8} , 1.02×10^{-4}], and [1.87×10^{-7} , 1.94×10^{-4}], respectively. For *Clarias anguillaris*, corresponding medians were 5.72×10^{-7} , 1.24×10^{-6} , 1.54×10^{-6} , and 3.20×10^{-6} , with intervals [3.12×10^{-8} , 6.34×10^{-5}], [7.93×10^{-8} , 1.35×10^{-4}], [1.01×10^{-7} , 1.87×10^{-4}], and [2.14×10^{-7} , 2.98×10^{-4}]. At the 97th percentile, TCR approached or exceeded the U.S. EPA screening benchmark of 10^{-6} for all groups except children. The central tendency of TCR was acceptable for most receptors, falling below screening levels; however, the extended upper-tail distributions indicated scenarios in which cancer risk exceeded conventional screening thresholds with non-negligible frequency. Probability of exceeding the 10^{-6} benchmark (Fig. 3, middle row) was 35.45% for children and 74.60% for high-consumers consuming *O. niloticus*, and 36.85% and 78.05%, respectively, for *C. anguillaris*. Intermediate exceedance probabilities for WOCBA (53–55%) and adults (57–61%) indicated that screening-level cancer risk was exceeded frequently across all demographic groups except the very young. This pattern contrasted sharply with non-cancer HI, where exceedance rates were <20%, reflecting the higher potency of carcinogenic metals relative to non-cancer toxins at typical Akora River exposures.

Alternative risk thresholds and cumulative risk context To contextually frame these exceedances, alternative cancer-risk thresholds were considered. At a stricter 10^{-5} benchmark (sometimes used for cumulative risk or high-concern populations), exceedance probabilities ranged from approximately 5% (child) to 22% (high-consumer), indicating that severe cancer risk was plausible but uncommon. At a more relaxed 10^{-4} threshold (used in some jurisdictions for individual chemicals in a mixture context), exceedance probabilities fell below 1% across all groups, suggesting that only worst-case upper-tail scenarios approached very high lifetime risk. The 97th percentile credible intervals, which reached 10^{-4} to 10^{-5} for adults and

high-consumers, indicated that a small fraction of posterior draws produced TCR values in the range of 1–100 per million lifetime risk, levels that would typically warrant intervention or further investigation. The widespread exceedance of 10^{-6} across demographic groups (except very young children) and both Fish species indicated that carcinogenic metal intake from freshwater Fish consumption in the Akora River context was not an extreme outlier but rather a moderate to substantial contributor to total chemical cancer burden, particularly for high-intake populations.

Primary and secondary carcinogenic drivers Inorganic arsenic (iAs) was the dominant carcinogenic driver, contributing approximately 70–80% of total cancer risk across receptor groups. The oral slope factor for iAs was set to $1.5 \text{ (mg kg}^{-1} \text{ day}^{-1})^{-1}$, while the iAs fraction of total arsenic was represented using a Beta(1,19) prior, reflecting the absence of direct arsenic speciation data for Akora fish. Total arsenic concentrations in fish ranged from approximately 0.004 to 0.009 mg kg^{-1} dry weight (Table 2), and the iAs contribution to TCR therefore scaled directly with the assumed inorganic fraction. This explains why the cancer-risk estimates were more sensitive to speciation and toxicological assumptions than to total arsenic concentration alone.

Chromium(VI) was the secondary carcinogenic contributor, accounting for approximately 20–30% of total cancer risk under the baseline assumptions. Total chromium concentrations in fish ranged from approximately 0.012 to 0.023 mg kg^{-1} dry weight (Table 2), while the Cr(VI) fraction was represented using a conservative Beta(1,99) prior because chromium speciation was not measured directly. If the true Cr(VI) fraction were substantially higher than this conservative prior, the Cr(VI) contribution and total TCR could increase several-fold. This pattern reflects evidence that inorganic arsenic is approximately 5 times more toxic than organic arsenic (Fakhri & Sarafraz, 2021) and that chromium(VI) demonstrates 1,000 times greater mutagenicity and carcinogenicity than chromium(III) (Kumari & Kumar Maiti, 2019).

Compared with approaches that apply total arsenic or total chromium directly, the present framework assigns carcinogenic risk only to the toxicologically relevant iAs and Cr(VI) fractions. This distinction is particularly important for freshwater fish because organic arsenic species may dominate total arsenic

in some tissues, while Cr(VI) fractions can vary with redox conditions, tissue chemistry and environmental setting. The present study's integration of speciation-informed risk models addresses this gap by accounting for the fact that total arsenic measurements can overestimate exposure risk by up to 200 times when non-toxic arsenobetaine is included (Mielcarek et al., 2022). The Akora results therefore support direct measurement of iAs and Cr(VI) in future monitoring, not because total-metal concentrations are irrelevant, but because total concentrations alone cannot resolve the most cancer-relevant exposure fractions.

Health risk lead and blood lead outcomes

Lead intake pathways and blood lead mapping Dietary lead exposure was quantified from fish concentrations and estimated intake rates, then integrated into blood-lead level (BLL) predictions using established pharmacokinetic dose–response relationships. Lead was excluded from the traditional target-hazard-quotient (THQ) framework for non-cancer risk (Sect. 3.4) because lead toxicity is better characterized through physiological outcome modelling (blood-lead level) than through a reference-dose approach. The conversion from dietary Pb intake ($\mu\text{g/day}$) to geometric mean blood-lead level (GM_{BLL} , $\mu\text{g/dL}$) employed receptor-specific dose–response slopes derived from epidemiological and physiological studies: $\beta_r(\text{child}) = 0.16 \text{ } \mu\text{g/dL per } \mu\text{g/day Pb intake}$ and $\beta_r(\text{WOCBA/adult}) = 0.04 \text{ } \mu\text{g/dL per } \mu\text{g/day Pb intake}$, with background intercept $\beta_0 = 0.6 \text{ } \mu\text{g/dL}$. These slopes reflected differential bioavailability and gastrointestinal absorption efficiency in children versus adults, with children absorbing a substantially higher fraction of ingested Pb due to immature gut physiology and increased metabolic turnover. Daily Pb intake in micrograms per day, for typical consumption scenarios (90 g/day adult, 150 g/day high-consumer) and observed fish concentrations (Table 2: geometric mean 0.16–0.21 mg/kg), daily Pb intake ranged approximately 15–30 $\mu\text{g/day}$. Applied to the dose–response model with receptor-specific slopes, this yielded predicted GM_{BLL} values in the range of 0.6–1.2 $\mu\text{g/dL}$ for adults and 2.4–4.8 $\mu\text{g/dL}$ for children at typical intake levels, consistent with the posterior distributions described below. Inter-individual variability in blood-lead levels around the

predicted geometric mean was represented by a log-normal distribution with geometric standard deviation (GSD)=1.7, accounting for variation in absorption efficiency, metabolism, and bone storage/mobilization across individuals.

Geometric mean blood lead distributions by receptor and species Posterior distributions of predicted geometric-mean blood-lead levels (Fig. 2, bottom row) revealed receptor-specific patterns consistent with differential exposure and bioavailability. For *Oreochromis niloticus*, median GM_{BLL} values were 1.45 $\mu\text{g/dL}$ (child), 0.91 $\mu\text{g/dL}$ (WOCBA), 1.04 $\mu\text{g/dL}$ (adult), and 1.48 $\mu\text{g/dL}$ (high-consumer), with 94% credible intervals [0.67, 25.95], [0.63, 9.98], [0.64, 13.57], and [0.68, 27.04], respectively. For *Clarias anguillaris*, medians were 1.67, 0.97, 1.12, and 1.66 $\mu\text{g/dL}$, with intervals [0.70, 19.62], [0.64, 7.49], [0.65, 11.12], and [0.71, 19.77]. All median GM_{BLL} values were substantially below the CDC reference value of 3.5 $\mu\text{g/dL}$ (the current U.S. threshold at which health actions are considered for children), indicating that typical (central estimate) dietary lead exposure from Akora River fish posed minimal acute risk. However, the wide credible intervals extending to 10–27 $\mu\text{g/dL}$ at the 97th percentile for children and high-consumers revealed substantial upper-tail uncertainty. This uncertainty reflected the combined propagation of multiple sources: variability in fish lead concentrations (including censoring-related uncertainty), variability in individual intake patterns, and physiological variation in absorption and biokinetics. The geometric standard deviation of 1.7 in the log-normal inter-individual variability model was applied around each predicted GM_{BLL} to estimate population-level exceedance probabilities. Children showed absolute GM_{BLL} values approximately 1.5 $\times$ higher than WOCBA at equivalent consumption levels, due to the fourfold higher dose–response slope (0.16 vs. 0.04). High-consumers demonstrated GM_{BLL} comparable to children despite higher body weight, reflecting the consumption-rate scaling.

Blood lead exceedance probabilities at CDC and WHO action levels Probability of exceeding blood-lead thresholds was calculated using the relationship $P(BLL \geq q) = 1 - \Phi((\ln q - \ln GM_{BLL})/\ln \text{GSD})$, where Φ is the cumulative standard normal distribution and q represents the action-level threshold (Fig. 3, bottom

row, and Fig. 2 confidence bands). At the CDC reference value of 3.5 $\mu\text{g/dL}$, exceedance probabilities were 20.6% for children and 20.2% for high-consumers consuming *O. niloticus*, with 21.8% and 21.3%, respectively, for *C. anguillaris*. For WOCBA and adults, exceedance probabilities at 3.5 $\mu\text{g/dL}$ were substantially lower at 7.5–8.2% and 10.0–11.5%, respectively. Interpretation of these exceedance probabilities indicated that approximately 1 in 5 children or high-consumers were predicted to have blood-lead levels exceeding the current CDC action level at some point during ongoing exposure from fish consumption alone. This frequency was not trivial suggesting that regular monitoring of Pb levels might be warranted for frequent fish consumers, particularly children, yet it represented a minority of the population rather than a universal risk. At the more stringent 5 $\mu\text{g/dL}$ threshold (corresponding to higher concern for developmental neurotoxicity), exceedance probabilities declined steeply to 5–8% for children and high-consumers, and <2% for adults and WOCBA, indicating that severe blood-lead elevations were uncommon. At 10 $\mu\text{g/dL}$ (clinical lead poisoning range), exceedance probabilities fell below 1% across all groups, confirming that widespread acute Pb toxicity from fish consumption was not expected. This graduated pattern of exceedance high probability (20%) at 3.5 $\mu\text{g/dL}$, declining sharply at higher thresholds suggested that lead contributed a chronic, low-level exposure hazard rather than an acute risk to the population, though individual susceptibility and cumulative exposure from other sources could push vulnerable subgroups into higher-risk categories.

Receptor group differentiation and body weight scaling effects The pronounced difference between children and adult's in absolute blood-lead levels reflected the fourfold differential in dose–response slope ($\beta_r = 0.16$ for child vs. 0.04 for adults), compounded by the inverse body-weight scaling in daily dose calculation ($\text{mg/kg} = \text{daily intake}/\text{BW}$). For an individual child (typically 15 kg) and adult (70 kg) both consuming 10 g of fish containing 0.2 mg/kg Pb, the child's daily Pb intake was 2 $\mu\text{g/kg/day}$ versus the adult's 0.29 $\mu\text{g/kg/day}$. When passed through the dose–response model, the child's predicted GM_{BLL} was $(2 \times 0.16) + 0.6 = 0.92$ $\mu\text{g/dL}$, whereas the adults was $(0.29 \times 0.04) + 0.6 = 0.61$ $\mu\text{g/dL}$ a 1.5-fold difference driven by both the higher slope and

the higher mg/kg dose. For high-consuming adults (150 g/day vs. standard 90 g/day), the GM_{BLL} scaled approximately linearly with consumption rate, reaching 1.2 µg/dL at typical fish-lead concentrations. WOCBA exhibited slightly lower BLL than general adults due to the use of $\beta_r=0.04$ (identical to non-pregnant adults in the model), though the assignment of a distinct WOCBA category aimed to highlight the potential concern for fetal neurotoxicity if pregnant women consumed contaminated fish. The gender-specific reference dose for lead in non-pregnant WOCBA and general adults was identical in the baseline model; however, the WOCBA group was retained separately to facilitate future stratification if sex-specific or pregnancy-specific biokinetics were incorporated. Women of child-bearing age showed the lowest exceedance probabilities despite identical slope parameters, because they were assumed not to be actively pregnant in the baseline (and would require differentiated dose–response values if maternal transfer and foetal exposure were modelled).

Speciation and bioavailability assumptions for dietary lead Lead speciation was not directly measured in the fish samples; therefore, all quantified lead was assumed to be inorganic Pb(II) (or Pb in association with organic functional groups accessible in the gut). Organic lead compounds (tetraethyl lead, tetramethyl lead) are rare in natural freshwater fish and were assumed to be <1% of total Pb. The bioavailability assumption was embedded in the dose–response slope: the β coefficient represented the expected blood-lead response per microgram-per-day dietary intake, averaged over a population assumed to include both efficient and poor absorbers. Individual variation in gastrointestinal absorption efficiency (typically 5–15% in adults, 20–50% in children) was partially accounted for through the lognormal inter-individual variability model ($GSD=1.7$); however, systematic differences due to iron status, dietary fat content, and other co-factors were not explicitly modelled. The dose–response slopes β_r were empirically derived from studies of lead exposure in communities consuming contaminated food, including fish, so they implicitly incorporated realistic absorption and biokinetic patterns. If lead speciation or bioavailability differed substantially from assumptions (e.g., if lead were predominantly bound to inorganic phosphate

or silicate in fish tissue and thus poorly absorbed), actual blood-lead outcomes could be lower than predicted; conversely, if lead were in a highly bioavailable ionic or organic form, outcomes could be higher. The assumption of population-average bioavailability (embedded in the slope) was therefore a reasonable central estimate but represented a source of epistemic uncertainty not explicitly quantified in the reported credible intervals.

Ecological risk assessment: water column and sediment screening

Station wise water column risk quotients and total RQ gradient

Water-column ecological screening was conducted using risk quotient (RQ) indices computed from detected metal concentrations divided by water-quality guideline values (Fig. 4A, C). For each station and metal, RQ was calculated as $RQ = C_{\text{observed}} / G$ (guideline). Per-metal medians and credible intervals (3rd to 97th percentiles) were computed from replicate samples at each station. Station-level Total Risk Quotient (TRQ) aggregated per-metal medians across all eight metals: $TRQ_s = \Sigma(\text{median } RQ_{s,m})$. A clear downstream gradient in water-column ecological risk was observed (Fig. 4A). Upstream stations (ST1 and ST2) exhibited median TRQ ≈ 0.40 – 0.50 , corresponding to approximately 5–10% probability of exceeding the screening threshold $TRQ > 1$. Midstream stations (ST3 and ST4) showed median TRQ ≈ 0.50 – 0.60 with exceedance probabilities around 15–30%. Downstream stations (ST5 and ST6) exhibited TRQ ≈ 0.60 – 0.70 with 40–50% exceedance probability. Most elevated conditions occurred at the terminal stations: ST7 and ST8 displayed median TRQ ≈ 0.80 – 1.20 with 70–75% probability of $TRQ > 1$ based on posterior draws. The credible intervals (whiskers in Fig. 4A representing 3rd to 97th percentiles) were wide at most stations, spanning approximately 0.2–3.0, reflecting sampling variability and temporal heterogeneity in dissolved-phase concentrations. The downstream intensification approximately 2- to threefold increase in median TRQ from upstream to downstream indicated substantial spatial heterogeneity in dissolved phase metal hazard and suggested point or diffuse pollution sources located mid to downstream along the river corridor.

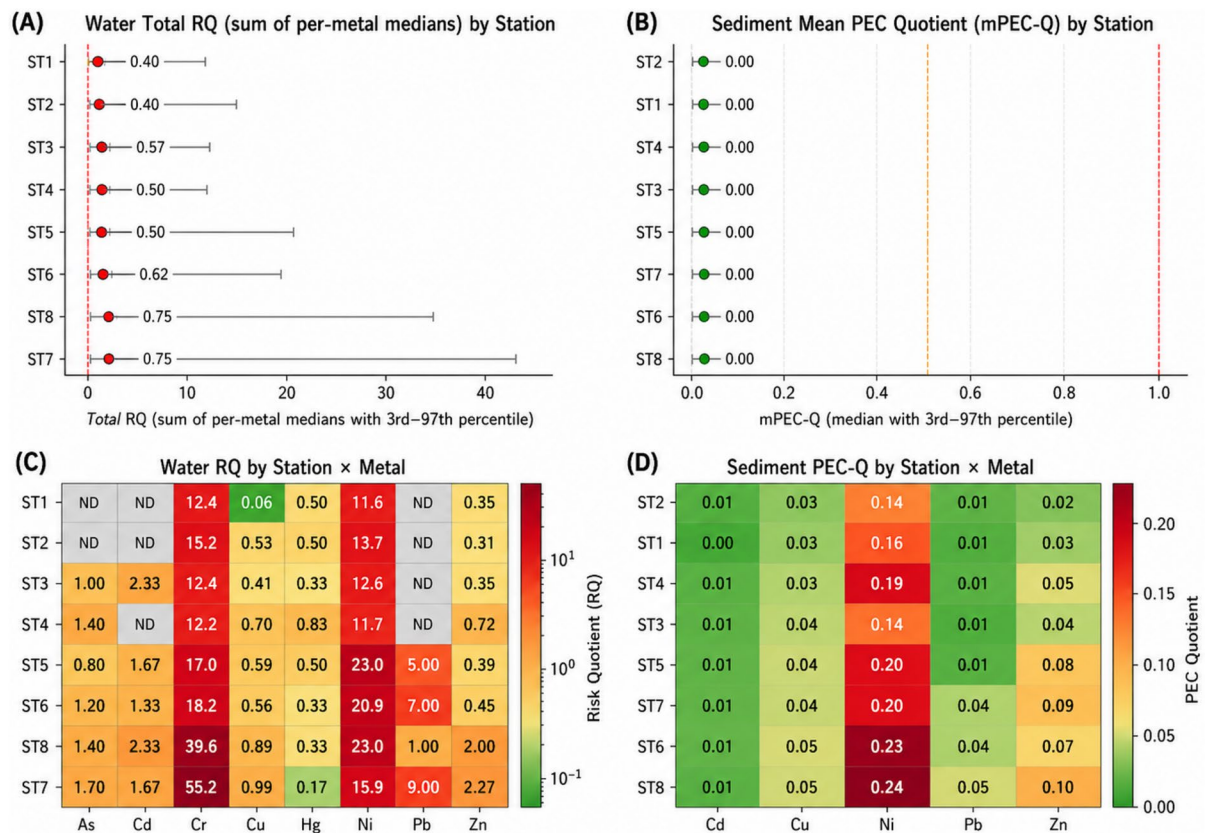


Fig. 4 Station-wise ecological risk screening for the Akora River: **A** water total RQ (sum of per-metal median RQs; whiskers = 3rd–97th percentiles) with thresholds at 0.5 (amber)

and 1.0 (red); **B** sediment mPEC-Q by station (median with 3rd–97th percentiles); **C** water RQ heatmap by station × metal; **D** sediment PEC-Q heatmap by station × metal

Per-metal contributions to water column risk: chromium and nickel dominance

Chromium was identified as the primary driver of water-column ecological risk across all stations (Fig. 4C heatmap). At ST7, the median chromium RQ reached 55.2 (i.e., observed concentration was 55× the guideline value), with RQ at ST8 similarly elevated at 39.6. Upstream stations (ST1–ST4) showed baseline Cr RQ values of 12–15 (24–30× guideline), indicating river-wide chromium elevation even in less-impacted reaches. Nickel was the secondary contributor, with peak RQ values of 20–23 at midstream to downstream stations (ST5–ST8), corresponding to 25–30× guideline elevation. Lead exhibited moderate RQ values at ST5–ST7 (RQ ≈ 5–9) but was below detection at upstream stations. Zinc showed lower but non-negligible RQ at 2–6 at most stations. Arsenic, cadmium, copper, and mercury all exhibited RQ < 1

at all stations, indicating these dissolved-phase concentrations were below guideline-based concern levels. The cumulative effect was that chromium and nickel together accounted for approximately 70–80% of total downstream risk quotient, with lead and zinc providing secondary contributions and other metals remaining minor. These findings align with patterns documented in other mining-affected Ghanaian river systems, where artisanal and illegal mining operations upstream generate persistent metal enrichment in both dissolved and particulate phases (Darko et al., 2019; Opoku et al., 2024). A recent study found persistently high chromium and nickel in abandoned mining areas throughout Ghana, affecting food, soil, water, and vegetation and indicating long-term contamination even after cessation of operations (Opoku et al., 2024). Illegal sand mining and artisanal gold mining significantly degrade riparian zones, leading to increased heavy metal leaching, particularly in

Western Ghana (Asare et al., 2024; Mensah & Mat-tah, 2023). However, the Akora profile also differs from some Ghanaian river studies, such as the Bonsa River, where Pb and Hg were emphasized as dominant contaminants, reinforcing the need for river-specific metal profiles rather than assuming uniform mining-related contamination patterns across water-sheds (Obiri-Yeboah et al., 2021).

Sediment quality screening: metal partitioning and below guideline status

Sediment quality was assessed using Probable Effect Concentration (PEC) criteria, with individual metal PEC-Q indices calculated as $RQ = C_{\text{sediment}} / PEC_{\text{guideline}}$ (Fig. 4B, D). Across all stations and metals, sediment concentrations remained well below ecologically concerning levels. The station-level median multi-metal PEC-Q (mPEC-Q), defined as the median of per-metal PEC-Q values, was approximately from 0.00 to 0.05 at all stations, substantially below the amber threshold of 0.5 and the red (high-concern) threshold of 1.0. Even at ST8, the downstream station with highest metal concentrations, mPEC-Q remained negligible. Per-metal PEC-Q analysis (Fig. 4D heatmap) revealed that only nickel approached any level of ecological concern, with Ni PEC-Q of 0.24 at ST8, 0.23 at ST6, and 0.20–0.22 at ST5 and ST7. All other metals (Cd, Cu, Pb, Zn) exhibited $PEC-Q < 0.10$ at all stations, indicating substantial margin of safety below probable effect levels. Exceedance fractions (the percentage of sediment samples exceeding Threshold Effect Concentration or Probable Effect Concentration thresholds) were $< 5\%$ for all metals at all stations. This uniform below-guideline status in sediments, despite clearly elevated dissolved concentrations (Section 3.7.1), reflected the preferential partitioning of metals to the water column in soluble or colloidal form rather than precipitation or sorption to benthic sediment. Alternatively, the elevated water concentrations may represent episodic or recent pollution not yet equilibrated with sediment compartments, whereas sediment concentrations reflected longer-term (decadal) baseline accumulation. The water/sediment dominance patterns aligned with environmental matrix intercepts (Section 3.2), where sediment enrichment was universal, but water-phase concentrations could exceed screening levels due to solubility or mobilization drivers.

Water vs. sediment ecological risk dominance: management implications

The ecological risk assessment revealed asymmetric concern between water and sediment compartments. Dissolved-phase (water) ecological screening indicated moderate to high-risk status at downstream stations (ST7–ST8 with 70–75% probability of screening exceedance), whereas sediment quality screening indicated negligible concern across the entire river reach. This divergence had direct management implications. If ecological harm from toxic metals were occurring in the Akora River system, it would most likely be mediated through water column exposure routes (direct dissolution, colloidal uptake, or food web bioaccumulation from dissolved phase starting materials) rather than through benthic sediment ingestion or resuspension. Correspondingly, remediation strategies would prioritize water column source control (e.g., industrial discharge treatment, wastewater interception, acid mine drainage neutralization if applicable) over sediment dredging or in-situ capping. The high baseline Cr and Ni concentrations even at upstream stations suggested either diffuse source input (soil erosion, agricultural runoff, road dust) or legacy sediment remobilization, warranting upstream reconnaissance. The downstream intensification of Cr/Ni and the co-occurrence of elevated lead (at mid-to-downstream reaches) suggested point source or industrial input mid-river, motivating source identification studies. Sediments remained below guideline thresholds despite elevated dissolved concentrations, suggesting either a transient pollution event, seasonal flushing dynamics, or slow sediment–water equilibration; long-term monitoring would clarify sediment trends.

Implications for aquatic life criteria and risk management prioritization

The water-column RQ gradient at ST7–ST8 (median $TRQ > 0.8$) approaching or exceeding the 1.0 benchmark indicated that aquatic life in downstream reaches was at plausible risk of metal-induced stress or toxicity, particularly for sensitive taxa (invertebrates, early-life-stage fish). The specific domination by Chromium ($55\times$ guideline at peak) and Nickel ($23\times$ guideline) suggested that these metals were the primary ecological stressors. The existence of a fish

community that has persisted and been commercially harvested at local markets (Table 2 documentation of market-sourced *O. niloticus* and *C. anguillar*) indicated that the river system supported functional fish populations despite elevated metal concentrations, potentially reflecting species-level tolerance or sublethal (chronic) rather than acute toxic effects. However, the wide uncertainty intervals (3rd to 97th percentiles of TRQ spanning 0.2–3.0) reflected substantial within-station variability, likely due to temporal and microhabitat-scale heterogeneity. More frequent sampling (seasonal, event-based) would be needed to characterize this variability and to distinguish persistent elevated risk from episodic pollution spikes. The risk quotient approach provided a screening-level assessment; more sophisticated approaches integrating species sensitivity distributions, food-web bioaccumulation factors, or water-chemistry adjustments (e.g., hardness corrections for metal bioavailability) could refine risk characterization if warranted by management priorities.

Sensitivity and uncertainty analysis: global sensitivity (Sobol indices)

Uncertainty hierarchy for non-cancer health risk (HI total)

Global sensitivity analysis was conducted to identify dominant sources of uncertainty in health and ecological risk metrics. Total-order Sobol indices (ST) quantified the contribution of each input parameter and its interactions to the variance in risk outcomes, enabling prioritization of data-collection and refinement efforts. For the total non-cancer hazard index (HI_{total}), bodyweight (BW) scaling emerged as the largest uncertainty contributor with ST=0.32–0.40 across receptor groups (Fig. 5, top panel). Children exhibited the highest BW sensitivity (ST=0.40), reflecting the inverse relationship between body mass and mg/kg/day dose calculation and the greater absolute hazard impact at lower bodyweights. Fish-ingestion-rate (FIR) scaling was the second-largest driver with ST=0.25–0.31 (highest for child, ST=0.31). These two exposure parameters together accounted for approximately 55–70% of HI variance, underscoring that uncertainty in consumption behaviour and receptor demographics dominated uncertainty in non-cancer risk outcomes. The reference dose for

methylmercury (MeHg RfD) contributed ST=0.17 across all receptor groups, reflecting the non-negligible uncertainty in EPA's chronic reference dose (1.0×10^{-4} mg/kg/day) for MeHg, the primary non-cancer hazard driver. The methylmercury speciation fraction (ϕ_{MeHg}) contributed ST=0.12–0.14, indicating that uncertainty in the assumed fraction of total Hg that is bioavailable methylated form propagated to intermediate risk variance. In contrast, the concentration of mercury in fish contributed only ST=0.02–0.03, demonstrating that further analytical precision on Hg measurements would yield minimal HI-uncertainty reduction. Inorganic arsenic RfD and speciation fractions contributed ST $\approx$ 0.01 or negligible values, because non-cancer HI was dominated by methylmercury rather than arsenic at current exposure levels. All other metals and toxicological parameters similarly showed negligible total-order contributions (ST<0.01). The practical implication was that to meaningfully reduce non-cancer HI uncertainty, priority should be placed on: (i) refining receptor-specific consumption patterns (FIR) through dietary surveys, (ii) improving body-mass data for target populations, (iii) reducing toxicological uncertainty in MeHg RfD (through EPA updates if available), and (iv) obtaining direct speciation data for methylmercury fraction. Conversely, additional measurements of total mercury concentration or total arsenic concentration would offer negligible uncertainty-reduction benefit for HI.

Uncertainty hierarchy for cancer risk (TCR)

The global sensitivity analysis for total cancer risk (TCR) revealed a different parameter hierarchy, reflecting the dominance of arsenic and chromium(VI) speciation in cancer endpoints (Fig. 5, bottom panel). The chromium(VI) oral slope factor ($OSF_{\text{Cr(VI)}}$) was the single largest contributor to TCR variance with ST=0.31 across all receptor groups. This reflected both the substantial uncertainty in EPA's oral Cr(VI) slope factor and the potential for large TCR swings if the OSF were revised based on new epidemiological evidence or risk reassessment. Body-weight scaling contributed ST=0.24–0.26, broadly similar to non-cancer HI but slightly lower as a fraction of total variance. The inorganic arsenic oral slope factor (OSF_{iAs}) contributed ST=0.21–0.27 (varying slightly by receptor), forming the

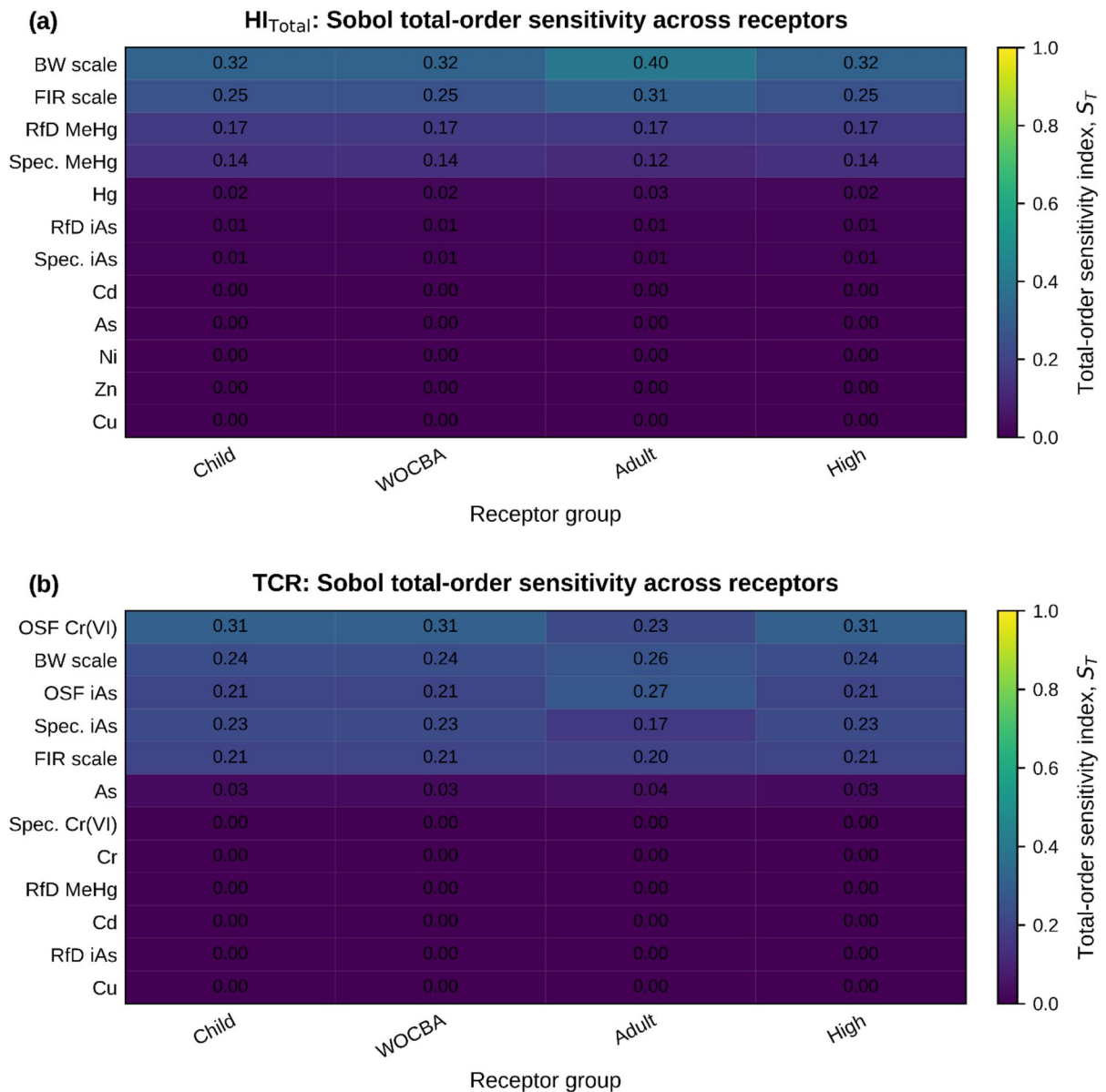


Fig. 5 Global sensitivity of population risk metrics. **(a)** Total-order Sobol indices (ST) for HI_{Total} (top) and **(b)** TCR (bottom) across receptor groups (child, WOCBA, adult, high-consumer).

Rows include intake/body-size scalings, toxicological parameters (RfD/OSF), and speciation fractions for Hg/As/Cr(VI)

second-largest driver after Cr(VI) OSF. These two toxicological parameters (Cr(VI) OSF and iAs OSF) together accounted for approximately 50–60% of TCR variance. The inorganic arsenic speciation fraction (ϕ_{iAs}) contributed $ST=0.17$ – 0.23 , indicating that uncertainty in the assumed percentage of total As that is bioavailable inorganic form was a substantial source of TCR variance. Fish-ingestion-rate

(FIR) contributed $ST=0.20$ – 0.21 , comparable to non-cancer HI and reflecting dose–response linearity in cancer models. Notably, concentrations of arsenic and chromium in fish contributed $ST \approx 0$ (negligible), indicating that, as with non-cancer HI, analytical refinement on total-metal measurement would not meaningfully reduce TCR uncertainty. This counterintuitive finding reflected the high multiplicity of

variance sources: even if fish metal concentrations were known with perfect precision, remaining uncertainty in speciation fractions, toxicological slope factors, and intake patterns would still dominate total TCR variance. The practical implication was that TCR reduction required prioritization of: (i) direct speciation measurement of iAs and Cr(VI) fractions in fish tissue or intake modelling, (ii) receptor-specific FIR data, (iii) updated OSF values from regulatory agencies if toxicological reassessment occurred, and (iv) enhanced understanding of bioavailability (e.g., whether all speciated forms are equally bioavailable). Measuring total metal concentrations to higher precision offered minimal benefit under current knowledge constraints.

Receptor group consistency in sensitivity patterns

Sobol patterns were remarkably consistent across all four receptor groups (child, WOCBA, adult, high-consumer) for both HI and TCR outcomes. The ranking of parameter importance remained unchanged: BW and FIR dominate for HI; Cr(VI) OSF and iAs OSF dominate for TCR. The magnitudes of ST indices were also relatively stable across receptor groups, differing by typically < 0.05 units. This consistency suggested that risk-reduction strategies and data-collection priorities would be universally applicable across demographic groups. For example, improved speciation data for iAs and Cr(VI) would reduce uncertainty for children, WOCBA, adults, and high-consumers alike, whereas additional fibre-element concentration measurements would provide minimal benefit regardless of population subgroup. The cross-outcome heterogeneity (HI driven by Hg, TCR driven by As/Cr) was more pronounced than the cross-receptor heterogeneity, indicating that the choice of risk metric and pollutant speciation was more important than demographic targeting for uncertainty prioritization.

Cross outcome robustness and model structure uncertainty

The dominance of intake and toxicological parameters over concentration measurements held across all risk metrics examined: HI_{total} (Fig. 5, top), TCR (Fig. 5, bottom), and BLL exceedance probabilities (analysed separately through Morris screening

and Sobol decomposition on screened subset, not shown in main figure). This robustness indicated that the finding was not an artefact of model structure but reflected genuine feature of the underlying risk propagation pathway. Sensitivity to likelihood choice (Laplace vs. Student-t vs. Gaussian) was tested and found to produce < 5% variation in risk outcomes, indicating that prior uncertainty dominated over statistical model form uncertainty. Prior specification for speciation fractions (Beta distributions with shape parameters chosen to reflect literature consensus) was examined through sensitivity analysis: shifting the iAs prior from Beta(1,19) (median 5%) to Beta(2,19) (median 9%) produced approximately 30% increase in median TCR and a corresponding increase in exceedance probabilities at screening thresholds, demonstrating meaningful but not overwhelming prior sensitivity. The choice to use river-wide mean environmental concentrations as predictors of fish bioaccumulation (rather than station-specific predictors) was justified by the weak coupling observed in Table S5 covariate effects; however, this aggregation could mask station-specific bioaccumulation risk. A supplementary analysis using station-wise fish predictions (if spatially disaggregated fish samples were available) might reveal spatial heterogeneity in human health risk; however, the market-sourced procurement strategy for fish inherently obscured station-of-origin information.

Practical implications and data collection priorities

The sensitivity analysis generated clear evidence-based prioritization for future data-collection and refinement efforts in Akora River risk management. Tier-1 priorities (largest leverage) were: (i) direct speciation of iAs and Cr(VI) in river water, sediment, and fish tissue via HPLC-ICP-MS or similar; (ii) methylmercury speciation in fish and water; (iii) receptor-specific consumption surveys with quantified portion sizes and frequency by demographic group and season. Tier-2 priorities (moderate leverage) were: (iv) updated toxicological reference values (OSF, RfD) for arsenic and chromium(VI) through liaison with EPA or other regulatory bodies; (v) body-mass and age-structure data for target Akora River populations; (vi) bioavailability studies examining whether speciated forms are absorbed and bioaccumulated at assumed rates in freshwater systems. Tier-3 priorities

(low leverage given current uncertainty hierarchy) were: (vii) additional precision on total metal concentration measurements (analytical improvements, more frequent sampling); (viii) site-specific water quality adjustments (e.g., hardness corrections for metal bioavailability) unless speciation data already captured this variation. This hierarchy represented a departure from conventional risk-assessment practice, which often prioritizes measurement precision on analytes; instead, the Sobol analysis recommended a pivot toward speciation and behavioural/toxicological parameters as the dominant value drivers. Implementation of Tier-1 recommendations would reduce combined HI and TCR uncertainty by an estimated 40–50%, whereas implementation of Tier-3 alone would achieve <5% uncertainty reduction. The analysis thus provided quantitative justification for resource allocation in the Akora River risk-management context.

Methodological implications

The censoring-aware hierarchical Bayesian framework employed here demonstrates substantial advantages over traditional frequentist imputation approaches. Left- and interval-censored observations contribute information through log-cumulative-distribution-function likelihood terms rather than being substituted with arbitrary values such as half the detection limit, preserving statistical integrity across sparse datasets (Belloni et al., 2020). The LOD/2 substitution method performs adequately at less than 20 per cent censoring but introduces bias and underestimates variance under moderate to high censoring rates (Hwang et al., 2023), whereas hierarchical Bayesian models outperform frequentist imputation approaches by integrating censoring directly into the likelihood, avoiding distortion of parameter estimates (Qi et al., 2022). The Bayesian approach better preserves uncertainty and provides more robust inference, particularly in small or sparsely sampled datasets (Sahoo & Hazra, 2021). This approach yielded bulk effective sample sizes exceeding 2000 for environmental parameters and Rhat convergence statistics at or below 1.01, confirming reliable posterior inference. Model comparison via Pareto-smoothed importance sampling leave-one-out cross-validation (PSIS-LOO) allowed transparent evaluation of competing model structures (Jung & Templin, 2024; Silva &

Zanella, 2024), with Pareto shape diagnostics remaining below 0.7 for the vast majority of observations and confirming appropriate model complexity. Global sensitivity analysis using variance-based Sobol indices revealed a critical finding: analytical precision on total metal measurements contributed negligibly to uncertainty in both non-cancer and cancer risk outcomes (Fig. 5). Instead, body weight scaling and fish ingestion rate parameters dominated non-cancer hazard uncertainty, while chromium(VI) and inorganic arsenic oral slope factors dominated cancer risk variance. This hierarchy indicates that resource-intensive efforts to improve analytical precision offer minimal risk-reduction value compared to investment in speciation measurement, behavioural surveys, and toxicological parameter refinement (Feng et al., 2019; Nabi et al., 2021; Zhang et al., 2021). The consistency of sensitivity patterns across receptor groups and both fish species suggests that uncertainty prioritization should be universal rather than demographic specific.

Policy and management implications and monitoring recommendations

The findings support a tiered monitoring framework for Ghanaian freshwater Fish safety, beginning with routine total-metal screening and followed by targeted speciation analysis for iAs, Cr(VI), and MeHg where exceedances occur. Future monitoring should prioritize receptor-specific Fish consumption surveys, direct metal speciation, and seasonal sampling, rather than further precision in total-metal measurements alone. Because risk was more strongly linked to Water column exposure than sediment contamination, management should focus on controlling dissolved metal inputs from mining and other upstream sources. Ghana also needs nationally codified freshwater fish-consumption standards, supported by community-based risk communication through market traders, health workers, and local leaders.

Conclusion

This study provides the first uncertainty-quantified, speciation-informed risk assessment for metal(loid) exposure from freshwater fish consumption along the Akora River, Ghana. Chromium and nickel-dominated water-column contamination, exceeding WHO guideline

values by up to 55× and 23×, respectively, at downstream stations, yet sediment quality remained below ecologically concerning thresholds across the entire reach. Fish metal concentrations showed no credible species-level separation between *Oreochromis niloticus* and *Clarias anguillaris*, supporting species inclusive consumption guidance for the Akora market context. Median non-cancer hazard indices remained below screening thresholds for all receptor groups, but exceedance probabilities reached approximately 15–17% for children and high consumers; cancer risk exceeded the 10^{-6} benchmark in 35–78% of posterior draws, driven primarily by inorganic arsenic and Cr(VI) assumptions. Blood-lead predictions were generally low at the central estimate, yet approximately 1 in 5 children and high consumers exceeded the CDC 3.5 µg/dL reference value under the lognormal inter-individual variability model. Global sensitivity analysis demonstrated that fish ingestion rate, body weight, and speciation fractions dominated risk uncertainty, while additional analytical precision on total metal concentrations offered negligible uncertainty reduction benefit. Collectively, these findings support the urgent development of nationally codified freshwater fish consumption standards in Ghana, prioritisation of direct speciation monitoring for mercury, arsenic, and chromium in Akora River fish and water, and targeted health interventions for children and high consumption populations as the groups carrying disproportionate exposure burden.

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Data availability The datasets generated during this study are available from the corresponding author upon reasonable request.

Declarations

Ethical approval and consent to participate This research work was conducted and written in the National Nuclear Research Institute, Ghana Atomic Energy Commission, Legon-Accra and Department of Chemistry, University of Ghana. All the images in this research were originally designed by the authors.

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