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Speciation of Heavy Metals in Water and Channel Sediments of the Lower Mekong River

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Abstract

The speciation of heavy metals in water and channel sediments was investigated along a 680 km reach of the lower Mekong River in Thailand, encompassing 17 sites on the Mekong River and 6 sites on the Mun River, a major tributary. Ten heavy metals—Mn, Fe, Cr, Co, Ni, Cu, Zn, As, Cd, and Pb—were quantified in surface water and riverbed sediments using a modified 4-stage sequential extraction protocol incorporating water-soluble (F1), exchangeable (F2), reducible (F3), and residual (F4) fractions. The resulting geochemical data were evaluated against quality standards, the Risk Assessment Code (RAC), a proposed Modified Risk Assessment Code (MRAC), and the Contamination Factor (CF). Water-soluble extraction (F1) was used to evaluate the proposed MRAC. The surface water quality complies with Thailand's National Standard at all sites. However, localized sediment contamination was identified and can be categorized into five priority groups. The group with the highest priority consists of Cr, Ni, and Cu. The concentrations of these exceeded national sediment quality standards, and surpasses the Probable Effect Concentration (PEC) at several sites, indicating a high probability of adverse ecological effects. Furthermore, MRAC identified them as having a high risk of mobilizing at ambient conditions in the dry season. The Mun River shows no substantial effect on Mekong hydrochemistry, but it may contribute Cr and Ni loading downstream.

Keywords: chemical speciation; sequential extraction; Modified Risk Assessment Code (MRAC); Lower Mekong River

1. Introduction

1.1. Chemical Speciation

The behavior of elements in the environment (e.g., bioavailability, toxicity, and distribution) cannot be reliably predicted based on their total concentration. It has been shown that identifying the binding forms of the chemical species will allow one to truly determine the availability and mobility of the elements in order to understand their chemical behavior and fate [1]. The rule that total elemental concentration alone cannot reliably predict environmental behavior applies universally as a baseline rule, but the strength of the relationship between total concentration and bioavailability varies significantly among different potentially toxic elements (PTEs). For example, cadmium (Cd) and zinc (Zn) are highly mobile and sensitive to pH. In acidic soils, a very low total concentration can still result in high bioavailability and toxicity. The bioavailability of these metals (arsenic, chromium) is severely dictated by their oxidation state, which is controlled by redox potential rather than total concentration. Lead (Pb) binds very strongly to soil organic matter and

Check for updates

Academic Editor: Laura Bulgariu

Received: 17 July 2026
Revised: 21 September 2026
Accepted: 30 September 2026
Published: 2 October 2026

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iron/manganese oxides. While copper has a massive affinity for organic matter, in soils with low organic content, its bioavailability often scales more linearly with total concentrations because it lacks the complex redox-shifting behaviors of elements like chromium [2–4].

While chemical speciation dictates the bioavailability, mobility, and toxicity of elements universally [5,6], these chemical transformations are dynamically governed by the unique environmental conditions of the Lower Mekong River (LMR). Unlike static aquatic systems, the LMR is characterized by a distinct tropical monsoonal pulse, resulting in drastic seasonal fluctuations in discharge, pH, and dissolved organic matter (DOM) [7,8]. During the high-flow wet season, elevated physical weathering injects massive quantities of suspended sediments into the river column. These particulates serve as critical adsorption surfaces and bioavailable ionic forms to less mobile particulate-bound fractions [9]. Conversely, during the low-flow dry season, reduced dilution capacity and increased water residence times can alter pH, temperature, and redox conditions. These shifts potentially remobilize bound contaminants into more toxic, dissolved species [10,11].

Chemical speciation in rivers describes how elements partition among dissolved, colloidal, and particulate forms and among inorganic complexes and organic ligands. These forms control the toxicity, mobility, and bioavailability of nutrients and contaminants such as Cu, As, Se, Pb, Cd, and Fe [12]. The river's chemistry reflects the geology, atmospheric inputs, organic matter, and human activities. There are several key controlling factors on river water speciation. pH and alkalinity cause shifting between free ions, hydroxo, carbonate, phosphate, and chloride complexes [13,14]. Low pH keeps metals dissolved while high pH favors sorption/precipitation. Dissolved or colloidal organic matter effects strong complexation of Cu, Fe, Hg and other metals and causes dominance of organic complexes and colloids [15,16]. Salinity and estuarine mixing alter carbonate/chloride complexes and phase partitioning and can also enhance ecotoxicological risk by changing labile fractions [17]. Mineral weathering and sediment fractions (carbonate, reducible, and residual) control mobility and bioavailability due to exchange at the water–sediment interface [13,18].

Chemical speciation in the Mekong River is shaped by a combination of natural factors, such as hydrological conditions and sediment characteristics, and anthropogenic influences, including dam construction and agricultural practices. Seasonal changes, sediment interactions, and climate variability also play crucial roles in determining the river's chemical dynamics [7]. Although the Mekong River extends across several countries, most chemical speciation studies in the Lower Mekong have focused on the delta region [19–21], while studies of the river reaches through Thailand and the Lao PDR remain lacking. While standard hydrological monitoring exists along the Thailand–Lao PDR reach, existing studies remain limited because they primarily focus on baseline water quality [7]. Consequently, there is a critical knowledge gap regarding the chemical speciation of heavy metals in water and channel sediments relative to the impact on sediment transport in this specific transboundary stretch.

1.2. Sequential Extraction and Risk Assessment

Sequential extraction is widely applied to characterize the chemical speciation of trace metals in riverine sediments and to assess their environmental mobility and bioavailability. This operationally defined approach partitions sediment-bound metals into distinct geochemical fractions, typically including exchangeable, carbonate-bound, reducible, oxidizable, and residual phases. Numerous studies have demonstrated its effectiveness in evaluating metal partitioning and estimating potential bioavailability [22–24].

The classical procedure proposed by Tessier [25] remains one of the most recognized sequential extraction methods. This five-step protocol fractionates trace metals into

exchangeable, carbonate-bound, Fe–Mn oxide–associated, organic/sulfide-bound, and residual fractions. It was originally applied to fluvial sediments for Cd, Co, Cu, Ni, Pb, Zn, Fe, and Mn, demonstrating satisfactory analytical precision and mass balance recovery.

An alternative and widely adopted protocol is the three-stage (plus residual) scheme developed under the European Community Bureau of Reference (BCR), now known as the Standards, Measurements and Testing (SM&T) program [26]. This method separates metals into four operationally defined fractions: (1) acid-soluble/exchangeable (including carbonate-bound species), (2) reducible (associated with Fe–Mn oxides), (3) oxidizable (bound to organic matter and sulfides), and (4) residual [27–29]. The BCR protocol has been extensively validated using river sediments and certified reference materials and is currently one of the most standardized approaches in environmental geochemistry.

Modified schemes have subsequently been proposed to provide greater mineralogical resolution, including differentiation of Mn oxides from Fe oxides, separation of amorphous and crystalline Fe phases, and adaptation for Fe-rich sediments [30,31]. Such refinements improve mechanistic interpretation but may reduce comparability across studies.

In many fractionation protocols, an initial extraction with distilled or deionized water—representing the water-soluble fraction—is sometimes omitted due to typically low extraction yields [32,33]. However, this step targets the truly dissolved and very weakly bound metal species and therefore represents the most immediately mobile and bioavailable fraction [34]. Its inclusion can provide critical insight into short-term environmental risk.

The four general geochemical fractions derived from sequential extraction are widely used to interpret metal speciation and to support river pollution assessment and ecological risk evaluation. The exchangeable/acid-soluble fraction reflects weakly adsorbed species and carbonate-associated metals, which are considered readily mobilizable and directly linked to the Risk Assessment Code (RAC) [35,36]. The reducible fraction represents metals associated with Fe–Mn oxides and is indicative of potential release under reducing conditions [37]. The oxidizable fraction includes metals bound to organic matter and sulfides and provides insight into metal stability under oxidizing environments. The residual fraction, associated with silicate lattices and primary minerals, is generally regarded as geochemically immobile and representative of lithogenic background contributions [29,38]. Operationally, the first two fractions are often considered bioavailable, whereas the latter two are classified as relatively non-bioavailable.

Particle size and mineralogical composition exert strong control over metal partitioning. It has been reported that approximately 92% of the total metals identified via sequential extraction are associated with particles smaller than 53 μm [39]. Clay minerals, in particular, function as major sinks for heavy metals and strongly influence their transport behavior and bioavailability [40]. Promkotra [41] reported higher clay mineral abundance in Mekong River suspended sediments than in riverbed sediments. Such findings highlight the importance of fine particles as vectors for metal transport. Variations in sediment grain size distribution and mineralogy may therefore substantially influence spatial patterns of metal mobility, redistribution, and toxicity in river systems.

Sequential extraction has been extensively applied in environmental risk assessment, including studies of contaminated soils [23], mine waste and acid mine drainage systems [42], estuarine sediments [43], and riverine pollution [36,44,45]. Quantitative risk indices—including the Risk Assessment Code (RAC), Secondary Phase Enrichment Factor (SPEF), Enrichment Factor (EF), and Contamination Factor (CF)—are frequently derived directly from fractionation data to evaluate ecological risk and to distinguish anthropogenic inputs from natural background contributions [35,36].

Another index used to assess the level of risk that contaminants (especially heavy metals) pose to the environment and living organisms is the potential ecological risk index

(RI) [46]. It is commonly used to assess contamination in soil, sediment, or water sources by combining the concentration of contaminants, toxicity, and natural background factors in its calculation [47]. The evaluation is divided into two main levels, ecological risk factor (E_r) and potential ecological risk index (RI). The benefits of this index are to identify which areas are facing contamination problems that are harmful to living organisms, and to indicate which heavy metals or substances are the main culprits causing the most damage. This will provide guidance for relevant agencies to use in managing the environment and planning the remediation of contaminated areas in a targeted manner [48].

1.3. Objective and Key Approach

The objective of this study is to characterize the spatial distribution and geochemical speciation of toxic heavy metals in surface water and channel sediments of the Mekong River along a 680 km stretch of the river flowing through Thailand. Additional attention is given to the influence of the Mun River, a major tributary that converges with the Mekong near the Thailand–Lao PDR border, where hydrological mixing may substantially modify downstream metal partitioning and risk assessments. Although it was anticipated that hydrological mixing at the Mun River confluence would alter downstream metal partitioning based on established geochemical principles, this study was designed to explicitly test and quantify the extent of these modifications under localized flow conditions.

The key approach is to integrate sequential extraction data with established sediment quality and enrichment indices, i.e., Risk Assessment Code (RAC) and Contamination Factor (CF). By coupling fraction-specific geochemical information with these quantitative risk metrics, this framework links operational speciation directly to environmental hazard evaluation, enabling mechanistic interpretation of toxicity potential rather than relying solely on bulk concentration data.

2. Materials and Methods

2.1. Sampling Sites

Sampling was conducted at seventeen sites along the Mekong River and six sites along the Mun River, as shown on the map in Figure 1 and listed in Table 1. All samples were collected on one single occasion in January of 2025. Based on previous work [49], the hydrochemistry of the upstream (the Upper Mekong River) and downstream (the delta region) areas remains similar between the wet and dry seasons. Sampling locations along the Mekong are denoted by the prefix "MK," while those along the Mun River are designated "MU." The upstream Mekong site, MK01, is located in Nong Khai Province. Sampling proceeded longitudinally downstream to MK16 in Ubon Ratchathani Province, representing the final upstream site before the confluence with the Mun River, as shown in Figure 2. Site MK17 is situated several kilometers downstream of the confluence, allowing evaluation of tributary mixing effects. The total river length between MK01 and MK17 is approximately 680 km.

Mun River samples were collected along the final 90 km-reach upstream from its confluence with the Mekong River. Sites were numbered in reverse longitudinal order, from the downstream site (MU06) at the confluence to the upstream site (MU01) in Nong Khai Province. The cumulative distance reported in Table 1 is calculated sequentially from MK01 to MU01 according to the order of the site listed.

Sampling sites were distributed evenly (every 50 km) across the upper, middle, and lower basins to track spatial trends while avoiding localized pollution from populated, agricultural, or industrial areas. Due to accessibility constraints, sites were restricted to locations near roads or bridges. However, the single downstream station at Kong Chiam

(MK17) cannot fully capture the complex mixing dynamics of the Mekong and Mun rivers, and collecting further downstream samples is unfeasible as those areas lie outside Thailand.

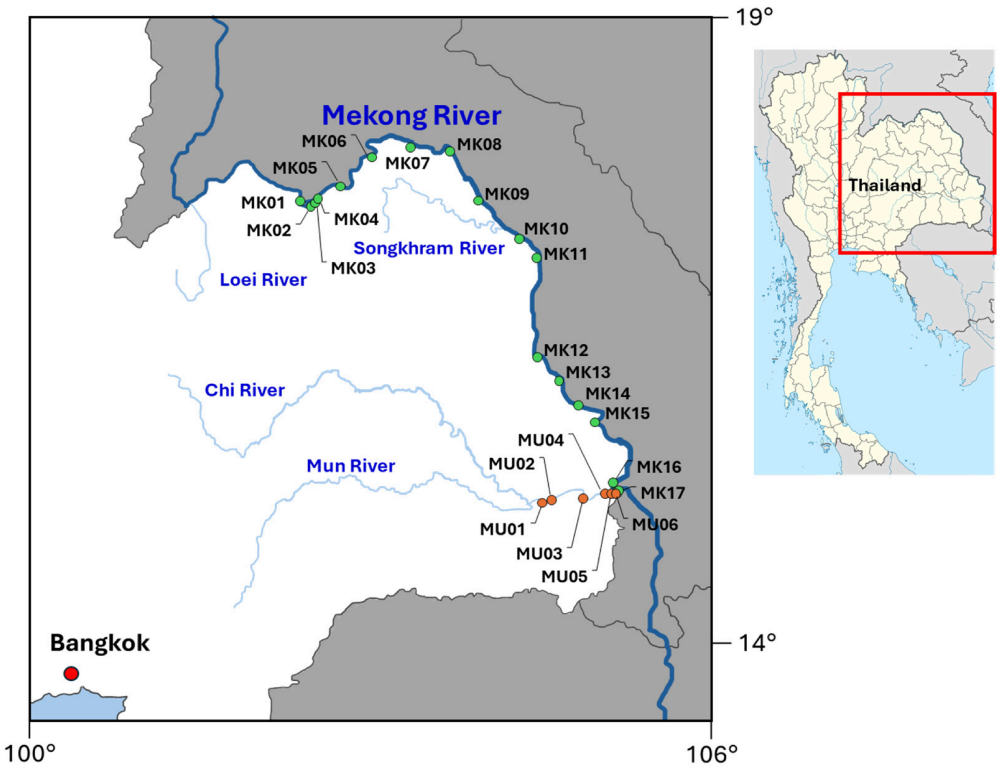


Figure 1. Sampling locations along the Mekong River (MK01–MK17) and Mun River (MU01–MU06) shown in green and orange dots, respectively.

Table 1. Sampling locations along the Mekong River (MK) and Mun River (MU).

	Sample Location	Latitude	Longitude	Cumulative Distance (km)
1	MK01	17°53′55.6″ N	102°36′23.6″ E	0
2	MK02	17°52′33.8″ N	102°42′32.3″ E	29.4
3	MK03	17°53′02.4″ N	102°44′32.7″ E	33.1
4	MK04	17°53′25.8″ N	102°45′30.1″ E	35.0
5	MK05	18°02′38.2″ N	103°04′56.1″ E	79.5
6	MK06	18°18′22.3″ N	103°17′59.1″ E	124.2
7	MK07	18°23′05.2″ N	103°37′59.1″ E	180.7
8	MK08	18°18′27.0″ N	103°59′28.7″ E	227.5
9	MK09	17°58′07.5″ N	104°13′35.4″ E	272.2
10	MK10	17°34′45.9″ N	104°35′44.6″ E	324.7
11	MK11	17°23′10.6″ N	104°47′41.2″ E	356.6
12	MK12	16°32′24.4″ N	104°43′55.1″ E	452.9
13	MK13	16°13′39.0″ N	105°00′47.2″ E	500.7
14	MK14	16°02′34.7″ N	105°13′24.3″ E	535.4
15	MK15	15°56′00.3″ N	105°20′41.2″ E	572.4
16	MK16	15°19′12.6″ N	105°29′50.8″ E	674.2
17	MK17	15°19′12.1″ N	105°33′25.5″ E	680.8
18	MU06	15°18′49.8″ N	105°30′00.8″ E	687.4
19	MU05	15°17′12.4″ N	105°28′03.3″ E	693.1
20	MU04	15°16′20.5″ N	105°27′16.2″ E	695.6
21	MU03	15°14′47.2″ N	105°14′55.1″ E	725.0
22	MU02	15°14′51.0″ N	104°57′49.3″ E	762.2
23	MU01	15°12′14.5″ N	104°48′53.0″ E	780.4

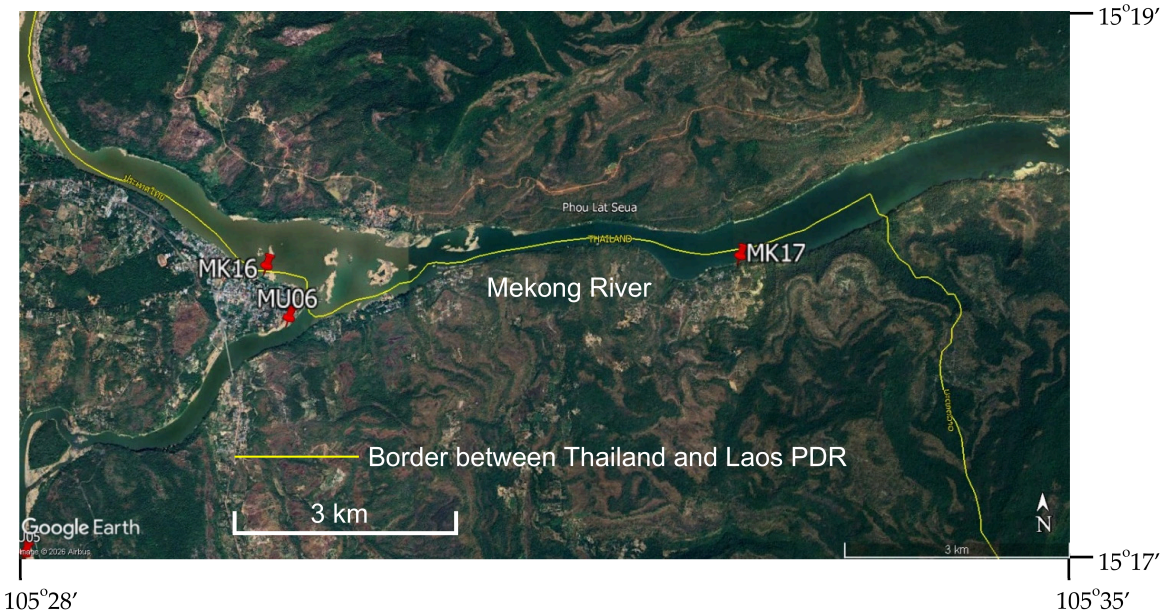


Figure 2. Google Earth map showing the last sampling sites (MK16 and MU06) upstream of the confluence and the sampling site (MK17) downstream of the confluence.

2.2. Sampling and Sample Preservation

At each site, approximately 1 kg of surface sediment, 1 L of river water (unacidified), and 1 L of acid-preserved river water were collected. Sediment samples were obtained from the top 5–10 cm using a Van Veen grab sampler at a perpendicular distance of at least 3 m from the water's edge. Deeper sediments exhibit different metal fractionation characteristics, varying by metal and environment. However, samples were collected at or close to the riverbed surface because these sediments are in contact with the flowing river water and carry readily mobile species downstream—particularly since the water-soluble fraction (F1) is of primary interest. To minimize bank-related depositional bias, water samples were collected from at least twice that distance. Flow velocity data was collected during our field investigation. Combined with secondary data on flow velocity and channel geometry, these measurements provide a rough velocity profile for each sampling site. This profile is used to verify that the sampling distance from the riverbank is sufficient to accurately represent the main river channel. A sketch of sampling schematics is provided in Figure 3.

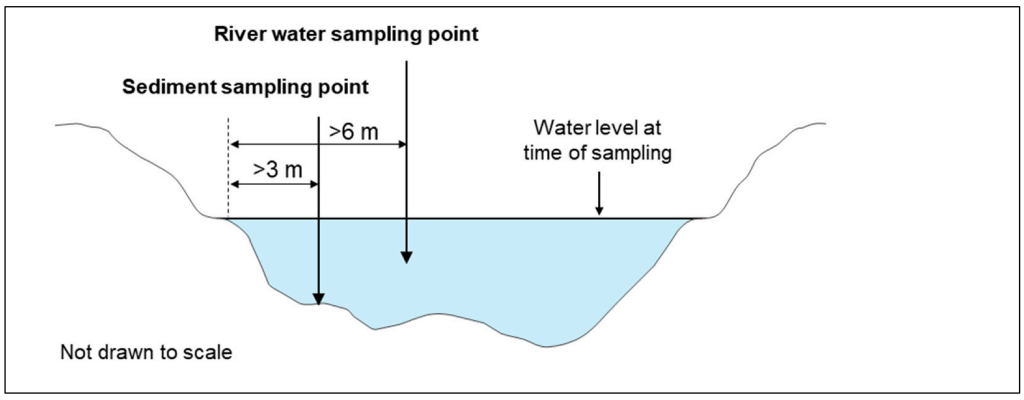


Figure 3. Generalized riverbank morphology showing the sediment sampling point and water sampling point.

In situ measurements of water pH, electrical conductivity (EC), and temperature were conducted immediately upon collection. For dissolved metal analysis, water samples were treated with 1 mL 50% nitric acid (HNO_3) per liter of sample. Parallel untreated samples were collected for ancillary analyses and stored at 4 °C prior to laboratory processing. All sampling campaigns were conducted during the dry season (January 2025) to minimize hydrological variability and dilution effects associated with monsoonal discharge.

2.3. Laboratory Processing

Upon arrival at the laboratory, water samples designated for dissolved-phase analysis were filtered through 0.45 µm membrane filters and stored under refrigerated conditions until chemical analysis. Riverbed sediments collected by the grab sampler were air-dried and sieved through a #100 mesh (149 µm aperture) to remove coarse debris and homogenize particle size prior to analysis. Suspended particulate matter (SPM) was obtained from river water by vacuum filtration using 0.45 µm nylon membrane filters (47 mm diameter). The retained particulate fraction was preserved for further characterization. For the risk assessment, only the riverbed sediments were used.

2.4. Chemical Testing and Analysis

River water and sediment samples were subjected to comprehensive physicochemical and geochemical analyses, as summarized in Table 2.

Table 2. Summary of laboratory testing work.

Sample Type	Resulting Parameter (s)	Method (Standard)/Equipment
River water	Total Dissolved solids (TDS), [mg/L]	Gravimetric Method (APHA Standard 2540C)
	5 Major Anions, [mg/L]: Chloride (Cl^-) Bicarbonate (HCO_3^- + CO_3^-)	Titration
	Nitrate (NO_3^-) Sulphate (SO_4^{2-}) Phosphate (PO_4^{3-})	Lambda 2 Scanning UV-VIS Spectrometer (Perkin Elmer Co. Ltd., Shelton, CT, USA)
	4 Major Cations, [mg/L]: Sodium (Na^+) Potassium (K^+) Magnesium (Mg^{2+}) Calcium (Ca^{2+})	Atomic Absorption Spectrophotometer (AAS, 3300 Perkin Elmer, Shelton, CT, USA)
	10 Heavy Metals [mg/L]: Mn, Fe, Cr, Co, Ni, Cu, Zn, As, Cd, Pb	Atomic Absorption Spectrophotometer (AAS, 3300 Perkin Elmer, Shelton, CT, USA)
River Sediments	10 Heavy Metals, [mg/kg]: Mn, Fe, Cr, Co, Ni, Cu, Zn, As, Cd, Pb	4-Stage sequential extraction/Atomic Absorption Spectrophotometer (AAS, 3300 Perkin Elmer, Shelton, CT, USA)
	Total Heavy Metal Concentration, [mg/kg]	Aqua regia digestion [Hydrochloric acid (HCl) + nitric acid (HNO_3) + Perchloric Acid ($HClO_4$)]/Atomic Absorption Spectrophotometer (AAS, 3300 Perkin Elmer, Shelton, CT, USA)
	Mineral types and relative concentration, [%]	X-Ray Diffraction
Suspended River Sediments	Mineral types and relative concentration, [%]	X-Ray Diffraction

Water samples were analyzed for Total Dissolved Solids (TDS) following the American Public Health Association Standard Method 2540C [50]. Major anions and cations were quantified using standard instrumental procedures, together with ten trace metals: Mn, Fe, Cr, Co, Ni, Cu, Zn, As, Cd, and Pb. These elements were selected based on their environmental relevance, toxicity potential, and prevalence in fluvial systems influenced by mixed lithogenic and anthropogenic inputs.

Sediment samples were analyzed for the same ten metals using a four-stage sequential extraction protocol to determine operationally defined geochemical fractions. Total recoverable metals were independently determined via aqua regia digestion to assess overall metal burdens and to evaluate the recovery efficiency of the sequential extraction procedure.

Both surface sediments and suspended particulate matter were characterized by X-ray diffraction (XRD) using a D8 Advanced, Bruker AXS Co., Ltd., Karlsruhe, BW, Germany, CuK α radiation (λ = 1.5418 Å) generated at 40 kV and 40 mA, scanning range between 4–70°, with a step size of 0.02° at a rate of 0.2° 2θ per minute. Phase identification was performed through comparison with established diffraction reference databases [51]. Semi-quantitative analysis from the diffraction pattern was used to estimate the relative percentage of mineral phases, enabling determination of the overall mineral composition of the sediments which might reflect the geogenic source of the metals.

Metal concentrations in aqueous extracts and digests were measured using Atomic Absorption Spectrophotometry (AAS; PerkinElmer AAnalyst 3300, Springfield, IL, USA). Validation was performed using the standard reference material (SRM) NIST 2711A (Montana II Soil) [52]. The analysis results showed good recovery and accuracy for most components, with deviations from the NIST certificate values below 10%. The instrument detection limits for each element are provided in Table 3. For the surface water, an analytical chemical standard addition procedure was performed by a triplicate test using a minimum concentration limit of two orders of magnitude below the detection limit of AAS or until the concentration was quantified by using the variance of the x-intercept, derived from the residual standard deviation of the regression line. Therefore, the concentrations of some metals can be reported even though they are below the detection limit of the instrument.

Table 3. Detection limit for the Atomic Absorption Spectrophotometer (AAS).

Element	Concentration (mg/L)	Element	Concentration (mg/L)
Na	0.012	Co	0.12
Mg	0.0078	Ni	0.14
K	0.043	Cu	0.077
Ca	0.092	Zn	0.018
Cr	0.078	As	1.0
Mn	0.052	Cd	0.028
Fe	0.10	Pb	0.45

Analytical quality control included repeated tests, calibration with multi-element standards, and verification against procedural blanks. The final values reported and used in the analysis are averaged from at least 3 repeated tests with values within 0.5% of the mean.

2.5. Sequential Extraction

Sequential chemical extraction was conducted to partition particulate Mn, Fe, Cr, Co, Ni, Cu, Zn, As, Cd, and Pb into operationally defined geochemical fractions. The four-stage protocol employed in this study is summarized in Table 4 and was designed to enhance resolution of the most labile metal species relative to conventional three-stage schemes.

Table 4. Sequential extraction steps and target phase.

Extraction Step and Resulting Fraction	Extraction Reagent	Nominal Target Phase
F1–Water soluble	Distilled de-ionized water	Soluble salts and very weakly adsorbed ions
F2–Exchangeable	Ammonium acetate ($NH_4CH_3CO_2$)	Absorbed ions and carbonates
F3–Reducible	Hydroxylamine hydrochloride ($[NH_3OH]Cl$) and Acetic acid (CH_3COOH)	Fe, Mn
F4–Residual	Hot nitric acid (HNO_3)	Metals bound in lithogenic minerals

Unlike the commonly applied BCR-type protocol, the present method incorporates an initial deionized water extraction step (F1) to isolate the truly water-soluble and weakly adsorbed species representing the most immediately mobile fraction. The subsequent stages were as follows.

Compared to Tessier's method [25], our approach features three main differences. First, the introduction of a water-soluble fraction (F1), which is omitted in Tessier's method (where the first step is assigned to the exchangeable fraction). Second, we combined the exchangeable and carbonate-bound fractions into a single extraction step (F2). Finally, we excluded the organic matter-bound fraction extraction. Three points form the rationale for our method. The water-soluble fraction (F1) was first investigated to assess the readily mobile species, which dissolve upon contact with water alone [6]. Second, the exchangeable and carbonate-bound fractions were combined to evaluate the species susceptible to mobility under changing pH conditions. Lastly, the extraction of the fraction bound to organic matter was omitted due to the negligible organic matter content in the sediments.

Sediment samples were air-dried at room temperature, gently disaggregated, and sieved through a #60 mesh to ensure homogeneity. A representative subsample (20.0 ± 0.1 g) was weighed for extraction. Each stage employed a sediment-to-solution ratio of 1:5 by weight. Ratios of 1:2, 1:5, and 1:10 were tested. However, the 1:5 ratio was selected and provided optimal analyte recovery. The suspension was agitated using a mechanical shaker for 1 h to ensure sufficient reagent–solid interaction. Following each extraction step, the mixture was filtered and the supernatant was collected for metal analysis. The solid residue was retained and subjected to the subsequent extraction stage under identical sediment-to-solution conditions until the completion of F4.

To evaluate procedural reliability, the cumulative concentration of metals obtained from sequential extraction ($\sum$Fi) was compared with total concentrations derived from aqua regia digestion. Recovery efficiency (%) was calculated according to:

$$\text{Recovery } (\%) = \frac{\text{F1} + \text{F2} + \text{F3} + \text{F4}}{\text{Concentration } (\text{Aqua Regia})} \times 100\% \quad (1)$$

where

- F1 (Water-soluble fraction): Extraction with distilled deionized water to determine readily soluble and weakly bound ions.
- F2 (Exchangeable fraction): Extraction using ammonium acetate ($NH_4CH_3CO_2$) targeting metals associated with carbonate phases and exchangeable sites.
- F3 (Reducible fraction): Extraction with hydroxylamine hydrochloride ($[NH_3OH]Cl$) in acetic acid (CH_3COOH) to dissolve metals associated with reducible Fe–Mn–Al oxide phases.

- F4 (Residual fraction): Digestion with hot nitric acid (HNO_3) heated on a hot plate to 380 °C for at least 30 min to release metals structurally incorporated within resistant lithogenic minerals.

2.6. Soil Type Classification

The riverbed sediments were sieved according to ASTM C136 [53]. For materials finer than 75 microns, a wet sieve was performed according to ASTM C117 [54]. Liquid and plastic limit tests were conducted following ASTM D4318 [55]. Finally, the soil type was classified according to ASTM D2487 [56].

2.7. Quality and Risk Assessment

2.7.1. Water Quality Guidelines

Heavy metal concentrations in river water samples were determined and compared with the National Surface Water Quality Standard [57]. This standard, established under Thailand's Enhancement and Conservation of National Environmental Quality Act B.E. 2535 (1992), defines quality classes for natural surface waters. We applied the criteria for Surface Water Type 2 (waters receiving anthropogenic discharges and used—after basic treatment—for consumption, aquatic life conservation, fisheries, and recreation), the most stringent class relevant to this study. These national standards were chosen based on Thailand's regulatory framework, environmental management, and specific water body uses. Additionally, heavy metal assessments were aligned with international limits by comparing minimum contaminant levels against WHO and USEPA guidelines.

2.7.2. Sediment Quality Guidelines

Sediment metal concentrations (aqua regia digestion) were evaluated against the National Surface Water Sediment Quality Standard [58], which sets limits to protect benthic organisms while accounting for bioavailability and long-term human-health effects. We also compared our results to consensus-based sediment quality guidelines [59], which define a Threshold Effect Concentration (TEC; below which adverse effects are unlikely) and a Probable Effect Concentration (PEC; above which adverse effects are likely).

Of the 10 metals analyzed, six (Cr, Ni, Cu, As, Cd, and Pb) are listed in the national sediment standard [58], and seven (Cr, Ni, Cu, Zn, As, Cd, and Pb) are covered by the consensus sediment guidelines [59] (Table 5).

Table 5. Surface Water Sediments Quality Standard [57] and the sediment quality guidelines [58] for metals that were investigated in this study.

Element	Surface Water Sediments Quality Standard (mg/kg) [57]	Consensus-Based Sediment Quality Guidelines [58]	
		TEC (mg/kg)	PEC (mg/kg)
Mn	n/a	n/a	n/a
Fe	n/a	n/a	n/a
Cr	43.4	43.4	111
Co	n/a	n/a	n/a
Ni	23	22.7	48.6
Cu	31.5	31.6	149
Zn	n/a	121	459
As	10	9.79	33
Cd	1	0.99	4.98
Pb	36	35.8	128

Note: n/a denotes values that are not specified by the standard or guidelines.

2.7.3. Risk Assessment Code (RAC)

The Risk Assessment Code (RAC) is a classic criterion used for evaluating the ecological risks of pollutants based on the proportion of heavy metals obtained from sequential extraction [60]. The RAC value is the ratio between the concentration of the exchangeable fraction and the total concentration from all fractions with units in percentage as follows:

$$\text{RAC } (\%) = \frac{F_{\text{exchangeable}}}{F_{\text{total}}} \times 100\% \quad (2)$$

where $F_{\text{exchangeable}}$ is the exchangeable and carbonate-bound (acid-soluble) fractions (F1 + F2), and F_{total} is the total metal concentration (F1 + F2 + F3 + F4).

Values of the RAC are interpreted as: RAC $\leq$ 1%, no risk; 1% < RAC $\leq$ 10%, low risk; 10% < RAC $\leq$ 30%, moderate risk; 30% < RAC $\leq$ 50%, high risk; 50% < RAC, very high risk.

2.7.4. Modified Risk Assessment Code (MRAC)

In this paper, we propose a Modified Risk Assessment Code (MRAC) in order to investigate heavy metals fractions that are extremely at risk. MRAC is served as the initial proposal and exploratory application of the index. This is done by comparing the water-soluble fraction (F1) to the total metal concentration as follows:

$$\text{MRAC } (\%) = \frac{\text{F1}}{\text{F1} + \text{F2} + \text{F3} + \text{F4}} \times 100\% \quad (3)$$

where F1 is the water-soluble fraction, F2 is the exchangeable fraction, F3 is the reducible fraction, and F4 is the residual fraction. The interpretation of the risk still follows that of the original RAC.

In environmental geochemistry and risk assessment frameworks, the exclusion of the exchangeable fraction (F2) in favor of focusing solely on the water-soluble fraction (F1) is typically justified by the specific operational definitions and exposure pathways the model intends to simulate. The water-soluble fraction (F1) consists of ions already dissolved in the soil pore water. It is instantly available for plant uptake, leaching, and runoff without any change in environmental conditions. The exchangeable fraction (F2) is bound to soil particles by weak electrostatic forces. It requires ion exchange processes (e.g., changes in ionic strength or pH) to desorb into solution. The traditional Risk Assessment Code (RAC) considers both (F1) and (F2) together as the highly mobile fraction to represent a worst-case scenario. Grouping F1 and F2 overestimates immediate environmental toxicity. In ambient, stable field conditions, the exchangeable fraction remains bound to the solid phase and does not actively migrate or exert toxic pressure.

2.7.5. Contamination Factor (CF)

The Contamination Factor (CF), originally adopted by Hakanson [46], is a widely applied index for assessing pollution risk based on sequential extraction results. The values are employed to distinguish anthropogenic contributions from natural geogenic background levels. It is defined as the ratio of the sum of non-residual fractions to the residual fraction of a given heavy metal (*i*), referred to as the Individual Contamination Factor (ICF) as proposed by Fernandes [61]. The Global Contamination Factor (GCF) is subsequently calculated as the sum of the ICF values for all analyzed metals in each sediment sample, as expressed in the following equations [62],

$$\text{ICF} = \frac{\text{F1} + \text{F2} + \text{F3}}{\text{F4}} \quad (4)$$

and

$$GCF = \sum_{i=1}^{n} ICF_i \quad (5)$$

The values of ICF and GCF can be interpreted as follows [63]: ICF $\leq$ 1 and GCF $\leq$ 6, low risk; 1 < ICF $\leq$ 3 and 6 < GCF $\leq$ 12, moderate risk; 3 < ICF $\leq$ 6 and 12 < GCF $\leq$ 24, moderately high risk; ICF > 6 and GCF > 24, high risk. All elements do not contribute equally to the ecological risk, because ICF and GCF measure total chemical abundance, not biological toxicity. These indices (ICF, GCF) only measure the degree of enrichment relative to baseline levels. They do not factor in how toxic a specific element is to living organisms. Neither ICF nor GCF accounts for biological toxicity. A high ICF for a relatively harmless element contributes heavily to the GCF, while a lower (but highly toxic) ICF for chromium or cadmium poses a much greater actual environmental threat. By the way, ICF and GCF can be evaluated together as low risk, moderate risk, moderately high risk, and high risk.

3. Results and Analysis

3.1. Sediment Type

Based on the Unified Classification System (ASTM D2487), the riverbed sediments of the Mekong are classified as poorly graded sand with silt (SP-SM) with an average D50 (particle size corresponding to 50% finer on the cumulative particle size distribution curve) at 0.165 mm. The Mun River is mainly silty sand (SM) in the upstream section, then becomes poorly graded sand with silt (SP-SM) downstream of the Sirindhorn Dam. Figure 4 shows the particle size distribution for sediments collected at MK-12, which is a representation of the Mekong riverbed sediments in this study. This classification represents the predominant or most common sediment type found in each respective river or river section.

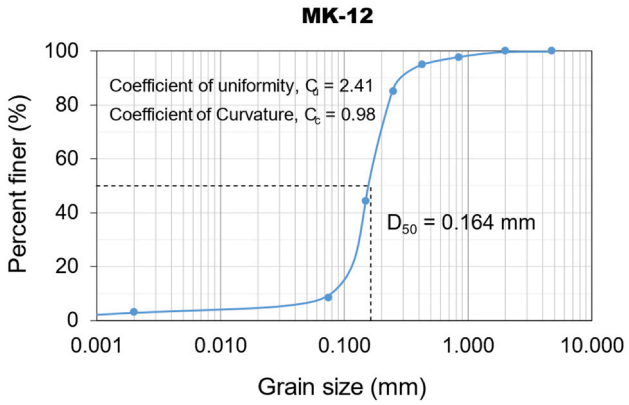


Figure 4. Particle size distribution curve for MK-12, showing characteristics typical of the Mekong riverbed sediments in this study.

3.2. Hydrochemistry of Surface Water

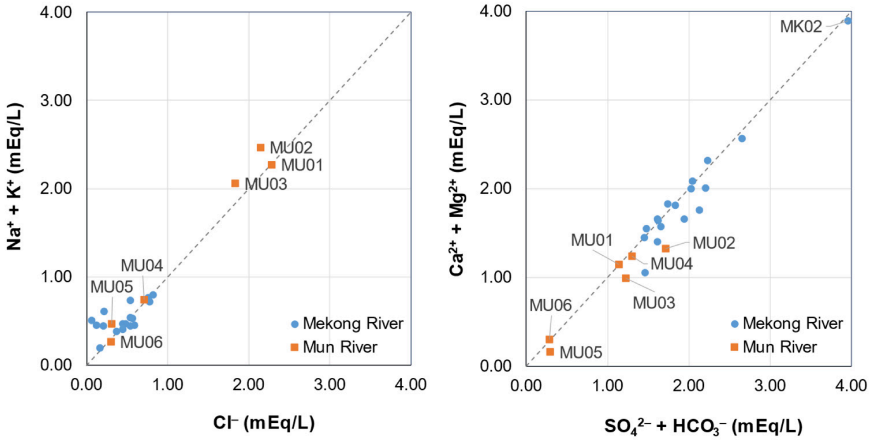
The physicochemical parameters of surface water are summarized in Table 6. Overall, the pH, electrical conductivity (EC), and total dissolved solids (TDS) in the Mekong River exhibit limited spatial variability. Similarly, water samples from the Mun River show relatively consistent values along the river course. However, the Mun River displays slightly lower average pH, EC, and TDS than the Mekong River, with markedly reduced values near the confluence (MU06; pH 5.90, EC 70.0 µS/cm, TDS 40.0 mg/L).

Major anions and cations were quantified in all samples. The scatter plot of ($Na^+ + K^+$) versus Cl^- (Figure 5a) indicates a slight enrichment of alkali cations relative to chloride in both rivers, as most data points plot above the 1:1 line. In contrast, the ($Ca^{2+} + Mg^{2+}$)

versus (SO_4^{2-} + HCO_3^-) plot (Figure 5b) shows a minor excess of anions, with most samples plotting below the 1:1 line.

Table 6. Summary of surface water physical properties.

River	pH			EC (µS/cm)			TDS (mg/L)		
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Mekong	7.00	8.89	7.75	205.4	570.0	300.41	120.0	350.0	191.03
Mun	5.90	7.42	6.73	70.0	334.5	222.83	40.0	200.0	133.83



(**a**) (**b**)

Figure 5. Scatter plots between major cations and anions from water samples of Mekong and Mun Rivers showing (**a**) $Na^+ + K^+$ versus Cl^- and (**b**) $Ca^{2+} + Mg^{2+}$ versus $SO_4^{2-} + HCO_3^-$.

No clear spatial trend is observed for Mekong River samples in either plot, except for MK02, which deviates markedly in the ($Ca^{2+} + Mg^{2+}$) versus ($SO_4^{2-} + HCO_3^-$) relationship. In contrast, the Mun River samples cluster into two distinct groups: upstream sites (MU01–MU03) and downstream sites (MU05–MU06) relative to the Sirindhorn Dam and Pak Mun Dam, indicating a substantial shift in hydrochemical composition across the regulated reach.

The relative abundance of major cations in the Mekong River follows the order $Ca^{2+} > Na^+ > K^+ > Mg^{2+}$, whereas in the Mun River the order is $Na^+ > Ca^{2+} > K^+ > Mg^{2+}$. Both rivers consist of major anions in the same order from $HCO_3^- > Cl^- > SO_4^{2-} > PO_4^{3-} > NO_3^-$. Spatial variations along the Mekong River (0–680.8 km) show generally stable ion concentrations, with notable fluctuations only in Mg^{2+} and PO_4^{3-}. In contrast, the Mun River exhibits a pronounced decrease in all major cations and anions downstream of the Sirindhorn Dam (Figure 6).

Despite distinct hydrochemical differences in the lower Mun River prior to its confluence, no substantial change is observed at MK17, which is located downstream of the confluence. The Mekong River maintains hydrochemical characteristics comparable to upstream sites, indicating the limited influence of the Mun River on the main channel chemistry under the sampled conditions. The massive discharge volume of the Mekong rapidly and overwhelmingly dilutes the Mun River's output. The chemical signature at site MK17 remains statistically continuous with upstream mainstream baselines.

Hydrochemical facies were further evaluated using a Piper diagram (Figure 7). The classifications are summarized in Table 7. The Mekong River is characterized as a Ca-HCO_3 type, while the Mun River exhibits a predominant Na-Cl facies, consistent with the ion balance trends observed in Figure 5a. Downstream of the Sirindhorn Dam (from MU04 onward), the water type shifts slightly, reflecting increased contributions from Ca^{2+} and

HCO_3. Nevertheless, at MK17 downstream of the confluence, the Mekong River retains its Ca-HCO_3 facies, indicating a negligible alteration of its overall hydrochemical signature.

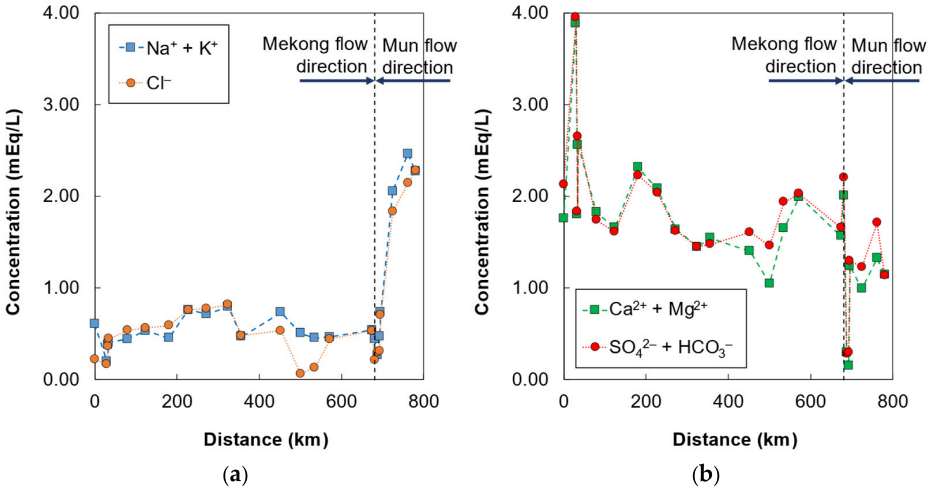


Figure 6. Spatial distribution of major cations and anions, (**a**) $Na^+ + K^+$ and Cl^- as a function of distance, and (**b**) $Ca^{2+} + Mg^{2+}$ and $SO_4^{2-} + HCO_3^-$ as a function of distance. The vertical dashed line represents MK17 which is a site on the Mekong River located downstream from the confluence of the Mekong and Mun rivers.

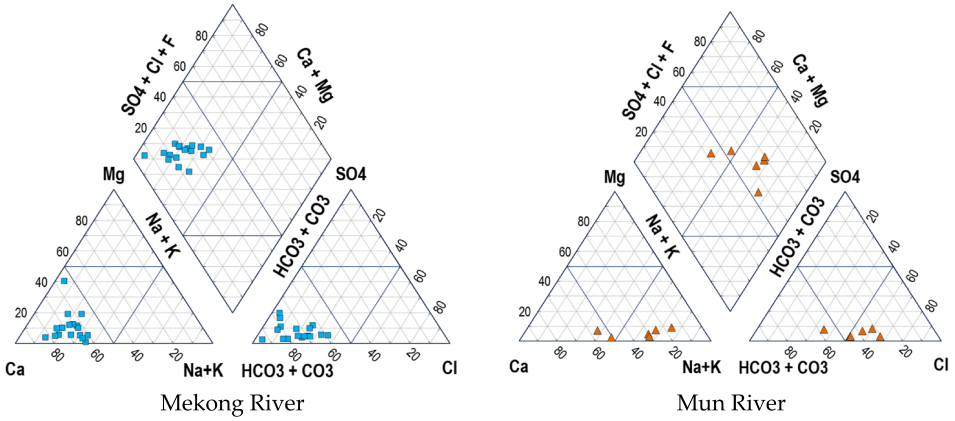


Figure 7. Piper plot showing the hydrochemical facies of surface water samples collected from the Mekong River and Mun River.

Ten heavy metals (Mn, Fe, Cr, Co, Ni, Cu, Zn, As, Cd, and Pb) were quantified in sediments collected from 23 sites using a sequential extraction procedure. The method's performance was evaluated by comparing the cumulative concentrations of the sequential extraction with total concentrations obtained by aqua regia digestion. Zn in sample MK14 and Cr in sample MU06 exhibited unsatisfactory recoveries because of local matrix interferences in the sampling site and were therefore excluded from further analysis. After exclusion, the mean recovery was 92.88% (Table 8), indicating good agreement between the two methods and supporting the reliability of the fractionation results.

Pb and As were below the detection limits in all four operationally defined fractions across the 23 sediment samples. Although the remaining eight metals were detected, in the majority of the samples, only minor proportions were associated with the first fraction (F1). This distribution is consistent with the extraction protocol, in which deionized water was used in F1 to target readily mobile and weakly adsorbed species. However, at some locations, the proportion of F1 is significant for Cr, Ni, and Cu (Figure 8). This presence of metals in F1 suggests low immediate mobility and bioavailability under ambient conditions.

Table 7. Physical properties and hydrochemical facies of surface water samples of the Mekong River (MK) and Mun River (MU).

Sample ID	Cumulative Distance (km)	pH	EC (µS/cm)	TDS (mg/L)	Hydrochemical Facies
MK01	0	7.56	307.6	220	Ca-HCO_3
MK02	29.4	7.36	570.0	350	Ca-HCO_3
MK03	33.1	7.85	303.1	190	Ca-HCO_3
MK04	35.0	7.67	323.0	211	Ca-HCO_3
MK05	79.5	7.85	312.0	223	Ca-HCO_3
MK06	124.2	7.80	293.4	190	Ca-HCO_3
MK07	180.7	8.23	277.0	161	Ca-HCO_3
MK08	227.5	7.00	358.0	202	Ca-HCO_3
MK09	272.2	7.76	302.0	192	Ca-HCO_3
MK10	324.7	7.60	227.0	120	Ca-HCO_3
MK11	356.6	7.65	263.6	160	Ca-HCO_3
MK12	452.9	7.70	280.0	200	Ca-HCO_3
MK13	500.7	8.89	205.4	130	Ca-HCO_3
MK14	535.4	7.80	222.2	138	Ca-HCO_3
MK15	572.4	7.88	312.0	200	Ca-HCO_3
MK16	674.2	7.71	220.5	150	Ca-HCO_3
MK17	680.8	7.40	330.1	211	Ca-HCO_3
MU06	687.4	5.90	70.0	40	Ca-Cl
MU05	693.1	6.93	80.0	50	Na-Cl
MU04	695.6	7.42	256.7	160	Ca-HCO_3
MU03	725.0	7.20	317.8	200	Na-Cl
MU02	762.2	6.02	278.0	153	Na-Cl
MU01	780.4	6.89	334.5	200	Na-Cl

Table 8. Recovery of heavy metals by aqua regia digestion (92.88% mean recovery with 95% CI).

Sample ID	Cd	Co	Cr	Cu	Fe	Mn	Ni	Zn
MK01	-	88.58	77.76	77.81	97.86	86.29	91.19	99.93
MK02	-	99.99	98.81	94.75	93.02	91.34	91.76	92.29
MK03	-	90.91	92.93	84.41	97.33	90.13	-	94.79
MK04	-	88.16	86.76	86.70	96.38	94.40	74.47	90.70
MK05	-	86.40	96.90	91.74	93.08	93.39	-	92.34
MK06	-	87.11	98.98	89.53	96.26	87.20	97.96	88.06
MK07	-	91.91	97.77	97.73	88.51	99.01	-	92.83
MK08	-	95.08	92.70	90.68	93.59	92.45	-	94.82
MK09	-	99.02	96.27	95.65	98.19	91.96	97.75	95.53
MK10	-	99.73	94.91	-	98.39	96.65	-	97.90
MK11	-	95.24	99.91	87.57	92.10	98.83	95.45	93.82
MK12	97.21	91.64	98.76	97.22	98.32	93.07	92.22	97.29
MK13	-	97.00	94.40	90.48	94.72	97.56	84.04	96.52
MK14	-	83.92	75.76	86.13	96.98	98.26	81.63	N/A
MK15	92.82	89.50	95.67	97.70	93.19	93.65	99.25	96.44
MK16	-	90.63	67.74	87.05	97.12	94.47	-	-
MK17	-	-	97.73	76.14	90.11	85.91	98.82	95.00
MU06	-	97.14	N/A	93.75	94.75	90.68	-	97.22
MU05	-	91.43	93.54	83.33	93.54	98.31	-	92.69
MU04	-	91.37	91.17	99.72	93.92	97.39	92.05	-
MU03	-	-	88.12	98.16	96.27	91.07	-	92.34
MU02	-	90.88	97.04	90.63	88.89	85.68	91.91	96.59
MU01	-	86.24	91.41	95.24	94.24	90.32	87.54	95.95
SRM 2711A	98.21	97.71	96.85	95.54	98.32	95.95	97.64	99.32
(mean ± aq SD)	1.11	1.50	0.92	0.88	1.24	1.22	0.85	0.53

Notes: N/A denotes values that are not available. CI is confidence interval. Hyphens represent values below the detection limit. Standard Reference Material (SRM): NIST 2711A Montana II soil [52].

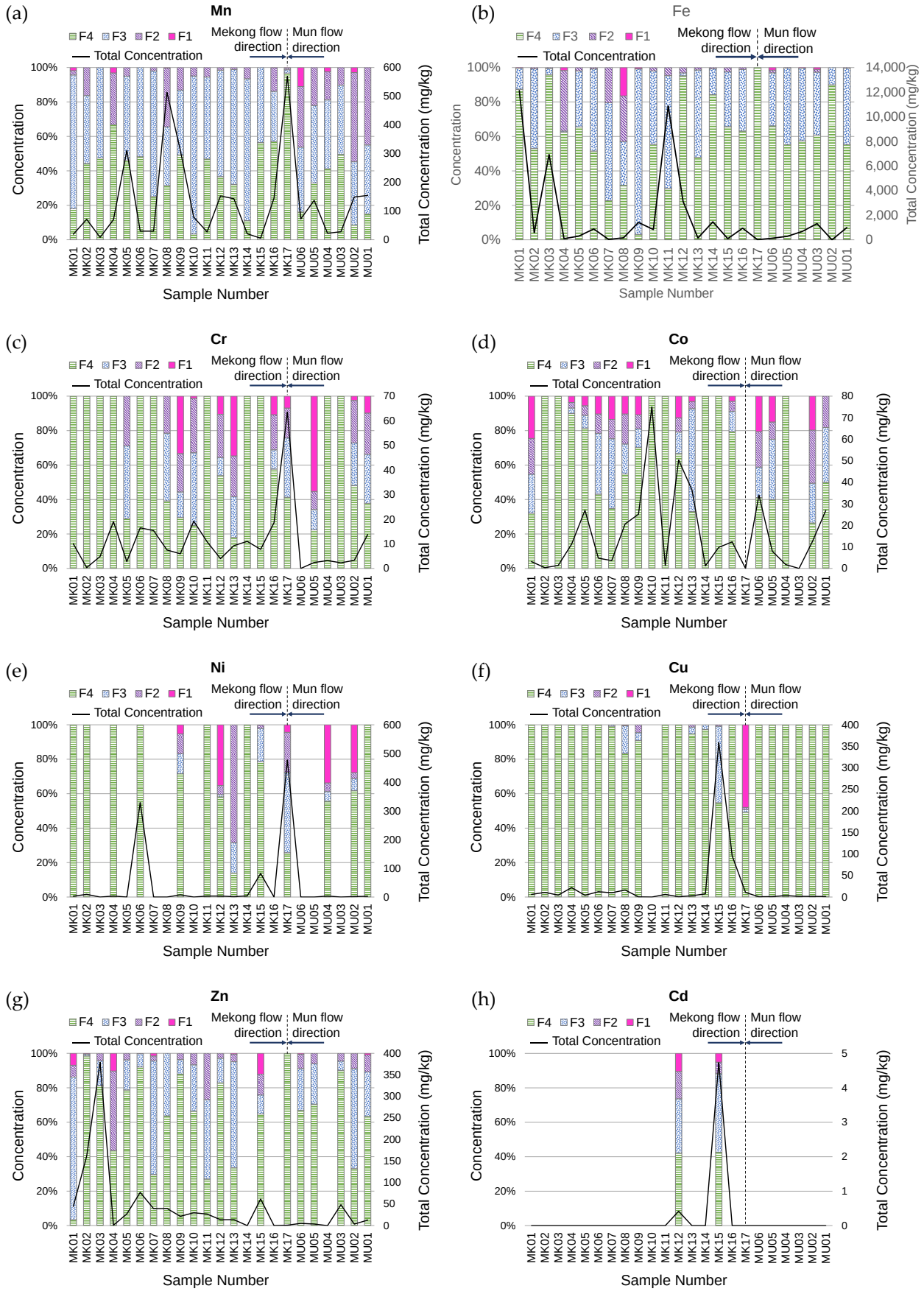


Figure 8. Metal concentrations obtained from sequential extraction (F1–F4) for (**a**) Mn, (**b**) Fe, (**c**) Cr, (**d**) Co, (**e**) Ni, (**f**) Cu, (**g**) Zn, and (**h**) Cd.

3.3. Water Quality

The same ten heavy metals (Mn, Fe, Cr, Co, Ni, Cu, Zn, As, Cd, and Pb) were analyzed in surface water samples. Co, As, Cd, and Pb were below detection limits at all sites. Fe and Mn were consistently detected across the 23 sampling locations, whereas Cr, Ni, Cu, and Zn were detected sporadically. Measured concentrations were compared with the national surface water quality standard for Type 2 water bodies, defined as waters receiving anthropogenic discharge and designated for consumption after basic treatment, aquatic life conservation, fisheries, and recreation [57]. As summarized in Table 9, concentrations of Mn, Ni, Cu, and Zn were below the prescribed limits at all sites. Parameters not regulated under the standard are indicated as "n/a".

Table 9. Concentrations of 6 heavy metals in the Mekong and Mun river water compared to the National Surface Water Quality Standard for Surface Water Type 2 [57].

Element	Type 2 Surface Water Quality Standard [53]	Mekong River (n = 17)		Mun River (n = 6)	
		Mean	Standard Deviation	Mean	Standard Deviation
Mn	1.0 (mg/L)	0.260	0.248	0.160	0.109
Fe	n/a (mg/L)	0.675	0.479	0.345	0.127
Cr	n/a (µg/L)	3.117	1.141	4.000	0.000
Ni	100 (µg/L)	5.450	1.717	-	-
Cu	100 (µg/L)	6.300	0.000	-	-
Zn	1000 (µg/L)	3.980	3.129	5.450	0.450

Note: Hyphens represent values below the detection limit.

3.4. Sediment Quality

Total metal concentrations determined by aqua regia digestion were used to assess sediment quality against the National Surface Water Sediment Quality Standard [58] and the consensus-based sediment quality guidelines, including the Probable Effect Concentration (PEC) [59]. Among the 17 sites along the Mekong River, sediment metal concentrations exceeded the national sediment quality standard at four locations and surpassed the PEC at three locations (Tables 10 and 11). High levels of Cr and Cd were localized to a single site, whereas Cu and Ni were repeatedly detected across two and three separate sites, respectively. In contrast, none of the sediment samples from the Mun River exceeded either benchmark.

The concentrations of copper (Cu), chromium (Cr), and nickel (Ni) at the sampling sites can be explained by both natural-hydrological conditions and anthropogenic factors. First, natural and hydrological conditions have a major effect on sediment quality, especially at MK16 and MK17. There are two major effects, confluence dynamics (Mun and Mekong Rivers), and geographical sink. These sites are located right at the mouth of the Mun River where it empties into the Mekong River. The confluences naturally act as heavy sediment traps. When the fast-flowing waters of two major rivers meet, the current abruptly slows down. This reduction in velocity causes suspended particles and bound contaminants to drop out of the water column and settle heavily into the bottom sediment. As a geographical sink, they sit at the downstream end of the massive Mun River Basin (which drains a huge portion of Northeast Thailand). They serve as the ultimate geological sink for everything carried downstream.

Moreover, the specific anthropogenic influences are localized human impacts from the cumulative upstream load as well as localized border activities. Localized cross-border trade and tourism at MK02-MK03 (Nong Khai) and MK06 (Bung Kan) or points of leniency in the border crossing—which is an official cross-border trading checkpoint between Thailand and Laos—are a busy border district and a prominent tourist destination. The constant

movement of cargo boats, passenger ferries, and local border markets creates localized pollution from fuel discharges, antifouling paints, and improper waste disposal.

Table 10. Mekong (MK) and Mun (MU) River sediment samples with heavy metal concentrations above the National Surface Water Sediments Quality Standard [54].

Sample No.	Concentration from Aqua Regia Digestion (mg/kg)
MK06	Ni (335.57)
MK15	Ni (82.54)/Cu (367.17)/Cd (5.10)
MK16	Cu (110.00)
MK17	Ni (482.97)/Cr (65.00)

Table 11. Mekong (MK) and Mun (MU) River sediment samples with metal concentrations above the Threshold Effect Concentration (TEC) and the Probable Effect Concentration (PEC) [59].

Sample No.	Concentration from Aqua Regia Digestion (mg/kg)	
	Between TEC and PEC	Above PEC
MK02	Zn (174.78)	none
MK03	Zn (399.95)	none
MK06	none	Ni (335.57)
MK15	none	Ni (82.54)/Cu (367.17)/Cd (5.10)
MK16	Cu (110.00)	none
MK17	Cr (13.85)	Ni (482.97)

3.5. Environmental Risk Assessment

3.5.1. Risk Assessment Code (RAC) Results

From 17 sampling sites on the Mekong, 15 sites are at moderate risk, high risk, or very high risk (Table 12). Specifically, 12, 7, and 3 sites are at moderate risk, high risk, and very high risk, respectively. Each of these sites are at risk from different metals. From the Mekong sediments, the metal with the most frequent appearance at moderate risk or higher is Cr (8 sites), followed by Co (7 sites), and Mn (5 sites). The frequent appearance of these three metals is similarly observed in the Mun River, although the frequency is in the opposite order, i.e., Mn > Co > Cr. MK17, which is downstream from the confluence of Mekong and Mun Rivers, shows an unusually high risk from Cu, although this metal is no risk at all in the Mun river sediments and appears only once with low risk at MK09, much farther upstream. Moderate risk is mostly caused by a combination of several metals. However, the highest risk categories are driven by just one or two metals. The copper (Cu) risk spike at MK17 in Khong Chiam, Ubon Ratchathani, is driven by its location at the Mun–Mekong River confluence. Localized activities release heavy metals that get trapped in bottom sediments; their re-suspension causes a sudden surge in dissolved Cu concentrations.

3.5.2. Modified Risk Assessment Code (MRAC) Results

Using the adapted MRAC assessment, it appears that several sites (MK09, MK12, MK13, MK17, MU04, and MU05) are worrisome (Table 13). This result represents the metal fraction available without pH adjustment, providing a clear indication of the high proportion of the F1 fraction for Cr, Ni, and Cu that appears in Figure 8. The water-soluble fraction represents the un-bonded or loosely bound metals, making them immediately active in aquatic environments [64,65].

Table 12. Risk Assessment Code for potentially toxic elements in sediments from the Mekong River (MK) and Mun River (MU).

Sample No.	Risk Assessment Code			
	Low Risk 1% < RAC ≤ 10%	**Moderate Risk** 10% < RAC ≤ 30%	**High Risk** 30% < RAC ≤ 50%	**Very High Risk** 50% < RAC
MK01	Mn	Zn	Co	
MK02		Mn		
MK03				
MK04	Co		Mn, Fe	Zn
MK05	Mn, Fe	Cr, Co		
MK06		Co		
MK07	Mn, Zn	Fe, Co		
MK08		Cr, Co	Mn, Fe	
MK09	Cu, Zn	Mn, Co, Ni		Cr
MK10	Mn, Fe, Zn		Cr	
MK11	Mn, Fe	Zn		
MK12	Mn, Fe, Zn	Co, Cd	Cr, Ni	
MK13	Mn, Fe, Co, Cu, Zn			Cr, Ni
MK14 [a]	Mn			
MK15	Fe, Ni	Zn, Cd		
MK16	Fe, Co	Mn	Cr	
MK17	Mn	Cr, Ni	Cu	
MU06 [b]	Fe, Zn		Mn, Co	
MU05	Zn	Mn Co		Cr
MU04		Mn	Ni	
MU03	Fe, Zn	Mn		
MU02	Zn	Cr	Ni	Mn, Co
MU01		Co, Zn	Mn, Cr	

Notes: [a] Zn was not included in the analysis. [b] Cr was not included in the analysis.

Table 13. Modified Risk Assessment Code for potentially toxic elements in sediments from the Mekong River (MK) and Mun River (MU) showing sampling sites that are at high and very high risk.

Sampling Site	Modified Risk Assessment Code	
	High Risk 30% < MRAC ≤ 50%	**Very High Risk** 50% < MRAC
MK09	Cr	
MK12	Ni	
MK13	Cr	
MK17	Cu	
MU04	Ni	
MU05		Cr

3.5.3. Risk of Individual Metals

According to the assessment based on the Global Contamination Factor (GCF), there are no sites on the Mekong at very high risk. The worst condition was at a high-risk level, found at 3 sites (MK01, MK09, and MK10) and a moderately high risk at 1 site (MK13). At the high-risk sites, the Individual Contamination Factor (ICF) metals that are of concern are Zn (MK01) and Mn together with Fe, which appear frequently across several sampling sites, as shown in Table 14 and Figure 9. The trend of Fe > Zn > Mn reflects their dominant contribution to contamination factors. This order is driven by the high natural abundance of Fe and Mn in the Earth's crust alongside the widespread industrial input of mobile Zn, which closely associates with iron chemistry.

Table 14. Risk assessment of heavy metals in Mekong and Mun River sediments according to their Individual Contamination Factor (ICF) and Global Contamination Factor (GCF).

Sample No.	Individual Contamination Factor (ICF) *			Global Contamination Factor (GCF)	
	Moderate Risk	Moderately High Risk	High Risk		
MK01	Co	Mn	Zn	34.82	High risk
MK02	-	Fe	-	6.14	Moderate risk
MK03	-	Fe	-	4.03	Low risk
MK04	-	-	-	0.92	Low risk
MK05	Fe	Mn	-	5.42	Low risk
MK06	-	-	Fe	8.72	Moderate risk
MK07	Fe	-	-	3.00	Low risk
MK08	-	Fe	Mn	15.24	Moderately high risk
MK09	-	Mn	Fe	437.66	High risk
MK10	-	-	Mn Fe	30.00	High risk
MK11	-	-	Fe	256.67	High risk
MK12	Mn Fe	-	-	4.54	Low risk
MK13	Fe	Mn	-	6.07	Moderate risk
MK14 [a]	Mn Fe	-	-	4.40	Low risk
MK15	Cu	-	-	4.12	Low risk
MK16	Mn	Fe	-	6.78	Moderate risk
MK17	-	-	Ni	14.96	Moderately high risk
MU06 [b]	-	Mn	-	4.97	Low risk
MU05	Mn Fe	-	-	5.33	Low risk
MU04	-	Fe	-	5.37	Low risk
MU03	-	-	Fe	8.80	Moderate risk
MU02	-	-	Mn	16.38	Moderately high risk
MU01	-	-	Mn Fe	17.47	Moderately high risk

Notes: * Metals with low risk are not shown in this table. [a] Zn was not included in the analysis. [b] Cr was not included in the analysis. Hyphens indicate absence of the risk posed by any metals.

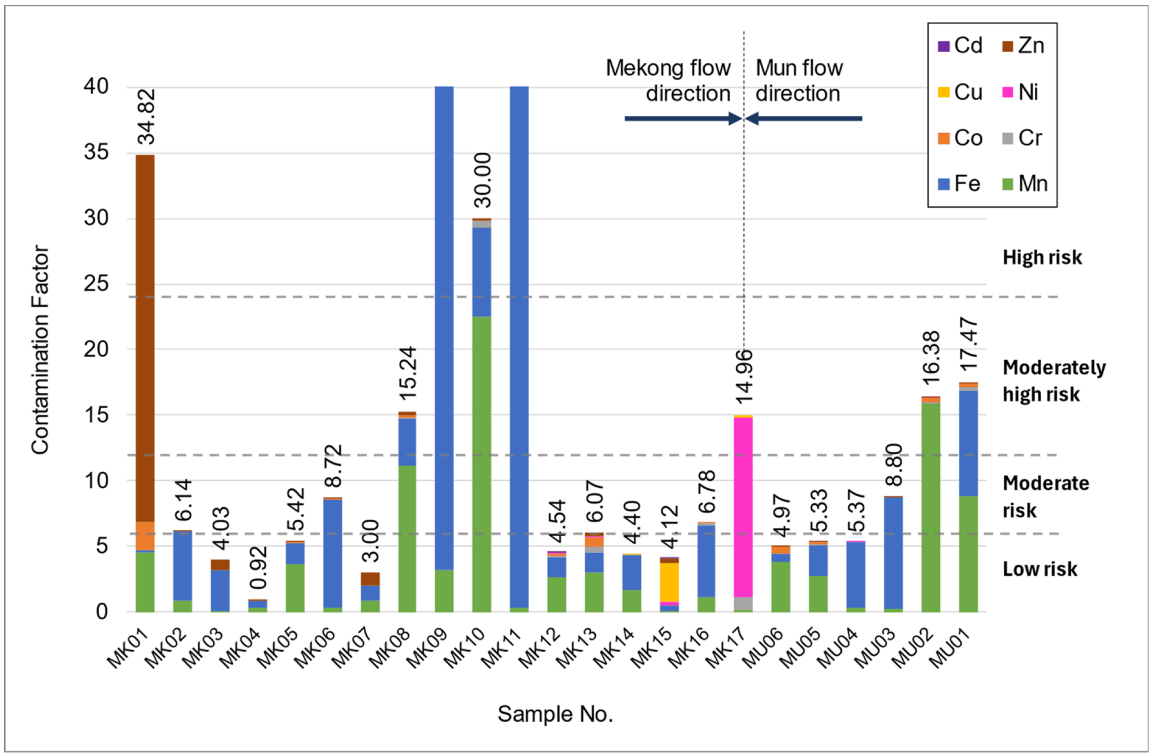


Figure 9. Contamination Factor (CF) for Mekong River (MK) and Mun River (MU) sediments. Stacked items in each column are the Individual Contamination Factor (ICF) for each heavy metal. The numbers at the top of the columns are the Global Contamination Factor (GCF) for each site. Horizonal dashed lines separate the 4 levels of GCF.

3.6. Sediment Mineralogy

A semi-quantitative analysis for the mineral composition of riverbed sediments and suspended sediments from 23 locations was obtained from X-Ray Diffraction. A total of 11 minerals were identified as listed in Table 15. Figure 10 shows XRD diffractograms for river sediments and suspended sediments from a selected site (MK03). Table 16 presents the average values of mineral composition of sediments from the riverbed and suspended sediments of the Mekong and Mun rivers. The results show that quartz is the main composition in the riverbed sediments, averaging 88.21% for the Mekong River and 94.56% for the Mun River. In the suspended sediments of the Mekong, the average quartz content is much smaller (53.46%) compared to that in the riverbed, while the average total clay minerals content (a sum of Kaolinite, Montmorillonite, Vermiculite, Biotite, Muscovite, and Chlorite) is significantly higher (35.98%) compared to that in the riverbed (9.53%). A similar occurrence is observed in the Mun River, where the average total clay minerals content is much higher in the suspended sediments than in the riverbed. However, the riverbed sediment of the Mun River consists of a very small amount of clay minerals (average at 3.99%). Kaolinite is the dominant clay mineral in the sediments of both rivers. Overall, the mineral composition of the sediments in both rivers are almost the same, except for vermiculite, which is absent from all Mun river samples.

Table 15. Names and abbreviations of minerals identified from the riverbed sediments and suspended sediments.

Abbreviation Names	Minerals	Chemical Formulae
Qz	Quartz	SiO_2
K	Kaolinite	$Al_2Si_2O_5(OH)_4$
Mont	Montmorillonite	$Na_{0.2}Ca_{0.1}Al_2Si_4(OH)_2(H_2O)_{10}$
Ver	Vermiculite	$Mg_{1.8}Fe^{2+}_{0.9}Al_{4.3}SiO_{10}(OH)_2{\cdot}4(H_2O)$
Bio	Biotite	$KMg_{2.5}Fe^{2+}_{0.5}AlSi_3O_{10}(OH)_{1.75}F_{0.25}$
Mus	Muscovite	$KAl_3Si_3O_{10}(OH)_{1.8}F_{0.2}$
Chl	Chlorite	$(Mg_5Fe^{2+})_5(Al_2Si_3)O_{10}(OH)_8$
Cal	Calcite	$CaCO_3$
He	Hematite	Fe_2O_3
Py	Pyrite	FeS_2
Do	Dolomite	$CaMg(CO_3)_2$

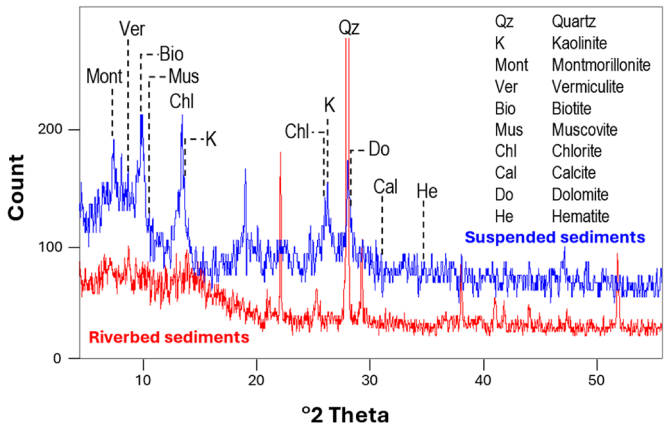


Figure 10. Comparison between diffractograms of riverbed sediments and suspended sediments from MK03.

Table 17 shows the Pearson correlation coefficients (r) between each extracted fractions (F1 to F4) of the 8 heavy metals and the amount of clay minerals from the riverbed sediments. For most metals, there appears to be no correlation with the amount of clay minerals. Two

strong and positive correlations were found (significant 2-tailed at the 0.01 level) between the F2 fractions of Fe and Zn and the amount of montmorillonite with r values of 0.551 and 0.566, respectively. Additional positive correlations that are worth noting (significant 2-tailed at the 0.05 level) are between the F2 fraction of Fe and total clay minerals (r = 0.454) and between the F3 fraction of Fe and Montmorillonite (r = 0.467).

Table 16. Average values of mineral composition of sediments from the riverbed and suspended sediments of the Mekong and Mun rivers.

Sediment Source and Type	Qz (%)	Clay Minerals (%)							Other Minerals (%)
		K	Mont	Ver	Bio	Mus	Chl	Total	
Mekong riverbed	88.21	3.59	1.69	0.77	1.51	1.63	1.09	9.53	1.98
Mekong suspended	53.46	12.03	6.25	3.55	6.21	5.77	5.80	35.98	11.52
Mun riverbed	94.56	1.37	0.85	-	0.75	0.53	0.60	3.99	1.45
Mun suspended	56.01	12.51	6.21	2.85	6.28	4.42	5.53	34.68	10.33

Notes: Qz = Quartz, K = Kaolinite, Mont = Montmorillonite, Ver = Vermiculite, Bio = Biotite, Mus = Muscovite, Chl = Chlorite. Other minerals = a sum of Calcite, Hematite, Pyrite, and Dolomite.

Table 17. Pearson Correlation Coefficient (r) between chemical fractions (F1–F4) and amount of clay minerals in the riverbed sediments.

	Pearson Correlation Coefficient (r)		
Concentration (mg/kg)	Kaolinite (%)	Mont (%)	Total Clay Minerals (%)
F1 Mn	−0.172	−0.287	−0.279
F2 Mn	−0.192	−0.108	−0.240
F3 Mn	−0.239	−0.151	−0.356
F4 Mn	−0.094	−0.341	−0.086
F1 Fe	−0.117	0.017	−0.184
F2 Fe	0.287	0.551 **	0.454 *
F3 Fe	0.227	0.467 *	0.376
F4 Fe	0.209	0.366	0.208
F1 Cr	−0.227	−0.419	−0.290
F2 Cr	−0.149	−0.412	−0.201
F3 Cr	−0.140	−0.428 *	−0.148
F4 Cr	0.006	−0.028	0.182
F1 Co	−0.050	0.028	−0.245
F2 Co	−0.229	−0.160	−0.402
F3 Co	−0.302	−0.273	−418 *
F4 Co	−0.076	−0.001	−0.183
F1 Ni	−0.053	−0.328	−0.019
F2 Ni	−0.055	−0.347	−0.010
F3 Ni	−0.049	−0.329	0.013
F4 Ni	0.006	−0.138	0.032
F1 Cu	−0.054	−0.350	−0.012
F2 Cu	0.071	0.290	0.356
F3 Cu	0.077	0.308	0.361
F4 Cu	0.175	0.337	0.414 *
F1 Zn	0.127	0.289	0.357
F2 Zn	0.142	0.566 **	0.456 *
F3 Zn	0.051	0.384	0.251
F4 Zn	0.398	0.294	0.449 *
F1 Cd	0.123	0.367	0.379
F2 Cd	0.129	0.374	0.381
F3 Cd	0.093	0.328	0.369
F4 Cd	0.100	0.337	0.371

Notess: * Correlation is significant at the 0.05 level (2-tailed). ** Correlation is significant at the 0.01 level (2-tailed).

On the contrary, a Pearson correlation analysis between the concentration of heavy metals and the amount of clay minerals from suspended sediments appear to have no correlation at all.

4. Discussion

4.1. Ecological Risk Implications

4.1.1. Immediate Threats

Among the 17 sites along the Mekong River, Cr, Ni, Cu, and Cd exceeded the national sediment quality standard at four locations (Table 10), and the PEC at three locations (Table 11). The exceedance of the PEC indicates a high probability of adverse biological effects on benthic organisms, suggesting that these three locations represent ecologically sensitive hotspots. In contrast, none of the sediment samples collected from the Mun River exceeded either the national standard or the PEC threshold.

When considered together with the high-risk level MRAC according to Table 13, Cr, Ni, and Cu are the top three heavy metals requiring priority attention in risk assessments due to their high mobility under current physicochemical conditions. Since these results are based on a single seasonal snapshot (the dry season), the risk of mobility may increase further during the wet season, although other studies indicate that hydrogeological characteristics remain stable across seasons [49].

4.1.2. Short-Term Threats

Should there be changes in the pH conditions, such as those caused by hydrological fluctuations, sediment resuspension, or organic matter degradation, Mn, Co, and Zn are considered the second group of potentially toxic heavy metals that need attention, since they are at very high risk of mobilizing, as can be surmised from Table 12. Within this group, Zn, particularly at MK01, should be a priority since it presents as a dominant ICF (Figure 9).

4.1.3. Long-Term Threats Under the Influence of Clay Minerals

The positive correlation observed between montmorillonite abundance and Fe and Zn concentrations in riverbed sediments is consistent with findings from other major river systems, including the Yangtze and Ganges, confirming that clay mineral–metal associations are a primary control on PTE mobility and downstream transport in large fluvial systems [46]. Although both Fe and Zn show positive correlations with montmorillonite, their mechanisms of association differ fundamentally. Fe mobility is primarily governed by redox dynamics, with montmorillonite serving as a surface for Fe-oxyhydroxide precipitation and subsequent reductive dissolution, whereas Zn mobility is more directly controlled by clay mineral surface chemistry—particularly interlayer exchange capacity and edge hydroxyl group availability—and is strongly pH-dependent, with maximum adsorption occurring between pH 6.5–7.5, broadly consistent with the near-neutral pH conditions recorded in the lower Mekong during the dry season.

The present study was conducted during the dry season, when low discharge favors bedload transport over suspended particulate transport, which may explain the lower clay mineral content observed in riverbed sediments relative to suspended sediments. However, during the wet season, the increase in monsoon-driven discharge would mobilize clay-rich fine sediments, including montmorillonite-bound Fe and Zn, facilitating downstream transport and potential deposition in floodplain areas, where reducing conditions may trigger metal release [66–68].

This preferential association of Fe and Zn with montmorillonite-rich sediments has critical implications for transboundary metal transport. Clay-bound Fe and Zn transported

downstream into Cambodia, Laos, and Vietnam represent a latent geochemical reservoir susceptible to release during salinity intrusion in the Mekong Delta, estuarine mixing, and anoxic diagenesis in deltaic sediments [69]. These processes collectively pose a long-term diffuse contamination risk that necessitates coordinated sediment quality monitoring under the Mekong River Commission (MRC) framework [70].

4.2. Influence of Mun River

The results indicate that water from the Mun River has no substantial effect on the hydrochemistry of the Mekong River, likely because the Mun River discharge (20,000 million m^3) [71] is relatively small compared with the Mekong River, whose discharge is approximately 20 times greater. It is based solely on the hydrochemical facies (major ions) of MK17, which exhibits the same characteristics as those of MK01 to MK16 located upstream. The Mun River may be a possible source of chromium and nickel, but it does not change the water type.

At site MK17, downstream of the Mun River confluence, Cr concentrations exceed the national standard (Table 9). The source of Cr at this site may therefore be either the upstream Mekong River or the Mun River. Table 13 shows that Cr exhibits high MRAC risk at two Mekong sites (MK09 and MK13) and very high risk at one Mun site (MU06), indicating that Cr may be readily transported from either river.

Similarly, Ni concentrations downstream of the confluence also exceed the national threshold. Ni may likewise originate from either the Mekong River (MK12) or the Mun River (MU04), as both sites show high risk of MRAC values for Ni.

4.3. Source of the Heavy Metals

Both the riverbed and the suspended sediments do not comprise any minerals that may be the source for the metals present in the extracted fractions except for Fe. Rivers carry persistent heavy metals bound to sediments over hundreds of kilometers. These heavy metals settle into riverbeds and accumulate in aquatic life and local food chains. Seasonal shifts, such as heavy rains and increased runoff, regularly stir up contaminated river sediments, temporarily spiking heavy metal concentrations (like arsenic, cadmium, and manganese) detected in water.

4.4. Factors Affecting the Geochemical Speciation of Toxic Heavy Metals

4.4.1. Water Soluble Fraction and Risk

For the Modified Risk Assessment Code (MRAC), elevated proportions in the water-soluble fraction (F1) do not necessarily mean these metals exhibited consistently elevated total concentrations across the sampling sites. In environmental chemistry, heavy metals can have a high water-soluble percentage even if their total bulk concentration is low, depending on their chemical speciation, pH, and soil/sediment characteristics. The MRAC integrates element-specific toxicity mobile in only water. However, the RAC treats all heavy metals equally, which is relative to total concentration. It assumes that if a metal is highly mobile, the risk is automatically high in several locations. The MRAC is conceptually advantageous because it alters how the water-soluble fraction is handled, which we then quantitatively demonstrate via the detection of toxic heavy metals as detailed in sequential extraction (F1).

4.4.2. Clay Minerals

Clay minerals naturally dominate the finest fraction of sediments. If the statistical analysis was performed on bulk sediment samples rather than the isolated clay fraction, the signature of sand and silt, which dilute metal concentrations, could weaken or obscure the statistical relationship. Changes in pH, salinity, or redox potential drastically alter metal

speciation and solubility. These dynamic factors can break down straightforward statistical relationships between total clay content and partitioned metals. The higher clay mineral content in the suspended sediments compared to the riverbed sediments is consistent with regional hydrodynamic sorting processes. In this catchment, turbulent river flow preferentially keeps fine-grained, low-density clay minerals in suspension, transporting them downstream. Conversely, coarser and denser tectosilicates (such as quartz and feldspar) selectively settle to form the bedload.

4.4.3. Spatial Distribution of Heavy Metals

The spatial variability within the study area obscures potentially significant correlations between suspended sediment mineralogy and heavy metal concentrations. Mineralogical composition and heavy metal inputs frequently operate on distinct spatial gradients driven by localized lithology, hydrodynamic sorting, and point-source anthropogenic discharges. Aggregating samples across spatially disparate zones introduces high variance.

4.4.4. Sediment Quality and Ecological Risk

The conclusions regarding the ecological risks of chromium (Cr), nickel (Ni), and copper (Cu) are based primarily on sediment quality guidelines (SQGs) and operationally defined geochemical fractions rather than direct, site-specific biological evidence like toxicity assays or bioaccumulation tests. Direct biological toxicity assessments should be conducted within the present study.

5. Conclusions

This study presents a comprehensive assessment to characterize the spatial distribution and geochemical speciation of toxic heavy metals in surface water and channel sediments along a 680 km reach of the lower Mekong River in Thailand, one of Southeast Asia's most ecologically and socioeconomically vital river systems. By employing a modified 4-stage sequential extraction protocol that incorporates a novel water-soluble fraction (F1)—absent in conventional Tessier and BCR schemes—this work advances geochemical fractionation methodology by capturing the most immediately bioavailable metal pool under ambient riverine conditions.

Based on the analysis of ten heavy metals in Mekong River sediments, As and Pb were below the detection limit in all analytical tests and no evidence of widespread acute sediment toxicity was found. Nevertheless, the spatial variability in metal concentrations and chemical fractions indicates that contamination is largely localized rather than basin-wide. Although the water quality of the Mekong River complies with the National Surface Water Quality Standard, localized sediment contamination remains a concern and can be categorized into five priority groups.

The first group, comprising Ni, Cr, and Cu, warrants the highest priority because concentrations exceeded the PEC at multiple sites, indicating a potential for adverse ecological effects, and these elements are also readily mobile under ambient conditions. The second group consists solely of Cd, which exceeds the PEC at one site but shows limited mobility. The third group includes Zn, which is highly susceptible to mobilization under changing pH conditions and is also a dominant contributor to the GCF. The fourth group comprises Mn and Co, which carry a moderately high risk of mobilizing under changes in pH. The final group consists of Fe, whose mobility is primarily governed by redox dynamics bound to montmorillonite in the riverbed.

Although the sources of all identified toxic heavy metals require further investigation, the Mun River may have contributed Cr and Ni to the Mekong River. These results carry direct implications for transboundary water resource management across the six Mekong

River nations and provide an evidence-based foundation for targeted remediation and monitoring strategies in the region.

Author Contributions: Conceptualization, K.T. and S.P.; methodology, S.P.; formal analysis, K.T.; investigation, S.P.; resources, S.P.; data curation, K.T.; writing—original draft preparation, S.P.; writing—review and editing, K.T.; funding acquisition, S.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Fundamental Fund of Khon Kaen University from National Science, Research and Innovation Fund or NSRF, Thailand, Project ID 203179.

Data Availability Statement: A georeferenced Google Earth (.kmz) file containing all sampling locations as well as all laboratory data (.xls) used the analysis are available via Mendeley [72] and can be downloaded at: https://data.mendeley.com/datasets/7j3wgnftyy/2, accessed on 17 July 2026.

Conflicts of Interest: The authors declare no conflicts of interest.

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