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2022-04-01

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IWA Publishing

https://doi.org/10.2166/ws.2022.002

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Water Supply

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Water Supply Vol 22 No 4, 3588 doi: 10.2166/ws.2022.002

Assessment of contamination level of a Tanzanian river system with respect to trace metallic elements and their fate in the environment

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ABSTRACT

The quality of water and sediments from a marginally-studied river was investigated with respect to As, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn including their fractionation behavior and environmental risk. Samples were collected along the Kou River that flows across two districts in the Manyara region of Tanzania. The leaching behavior of Fe was studied using sequential extraction fractionation and kinetics approach. The Kou water failed to meet the irrigation, aquatic, and biological life standards with respect to one of more trace metallic elements (TMEs). Fe concentration in the river water ranged from 4.1 to 5.38 mg/L, exceeding all the three standards. Six pollution indices were applied to assess the contamination and ecological risks of the nine trace metallic elements in the sediments. Overall, the metals were found to moderately contaminate the sediments. Cr, Fe, and Mn fell under the '*severely polluted*' sediment quality class. Fe was the only metal that was found to significantly pollute both the river water and sediments. The Fe fractions in the sediments were in the order of residuals>Fe-Mn bound>organic bound>carbonate bound>water soluble>ion exchangeable; 7.8% of the total Fe content was bioavailable with a low potential to leach from the sediments. Under natural conditions, the sharpest release of the non-residual mobile fractions of Fe were identified to occur within the first 24 hours with the maximum Fe leached being 0.14% on the 12th day. None of the metals in the sediments were found with a potential to pose ecological risk.

Key words: ecological risk assessment, kinetics, pollution indices, sequential extraction, trace metallic elements, water and sediment quality

HIGHLIGHTS

- Water and sediment quality were obtained from a marginally-researched river.
- Water temperature, DO, pH, EC, and turbidity were acceptable by selected standards.
- One or more TME in water exceeded irrigation, aquatic and biological life standard limits.
- Sediment risk assessment and USEPA standard indicated that Cr pollution is 'very high'.

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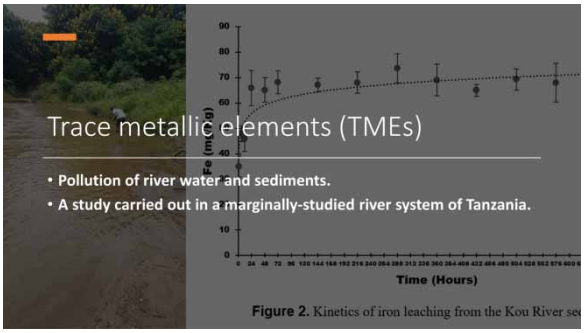
GRAPHICAL ABSTRACT



INTRODUCTION

One of the most notable factors that influence healthy environments is TMEs pollution. Sediments and water are major components of the riverine systems vulnerable to TMEs contamination, which promote environmental toxicity whose consequences present a real danger to aquatic life and human health. TMEs can bioaccumulate in body tissues and organs when they are introduced into the food chain through polluted water and sediments (Chaturvedi *et al.* 2018).

The Kou River is one of the Tanzanian rivers that flows through two districts, namely Mbulu and Babati, in the Manyara region. The water and sediment quality status of the Kou River has never been investigated with respect to TMEs pollution despite the fact that the water is largely utilized for irrigation, forestry, agriculture, and domestic consumption. In addition, this river is located close to Lake Manyara and Tarangire National Parks, two major tourist sites in the country. The river originates from Mbulu, a district characterized by large settlements with activities such as farming, livestock keeping, small-scale industries and mining of precious minerals (Raphael 2018). The literature indicate that pollution of different rivers have been exacerbated due to natural and anthropogenic activities. Industrial drainage pollution, landfill leachate, irrigation, horticulture, and livestock keeping are among the possible anthropogenic sources of TMEs pollution in natural waters (Holt 2000).

TMEs may enter the river and alter the quality of the water and sediment, which promote environmental toxicity whose consequences present a real danger to aquatic life and human health (Chaturvedi *et al.* 2018). In view of the significance of Kou River, it was deemed essential to assess the extent of water and sediment pollution to understand the leaching characteristics of the TMEs for environmental protection (Huang *et al.* 2020).

Whilst some TMEs such as Cr, Co, Cu, Fe, Mn, Ni, and Zn are vital nutrients for body development at low concentration, they may cause chronic and acute health defects when ingested in high doses by human and aquatic organisms (Singh & Kalamdhad 2011; Gautam *et al.* 2014; Nkinda *et al.* 2021; Wongsasuluk *et al.* 2021). As and Pb are among the TMEs that impair the functions of organisms even at low concentrations (Jaishankar *et al.* 2014).

Because water and sediments are good indicators of environmental pollution, regulatory organizations at both national and international levels have established standard guideline values for several parameters that are applied in quality assessment (Palma *et al.* 2014). Furthermore, a deep understanding of the bottom deposits of aquatic environments provides vital information on the main sources of pollution (Namieśnik & Rabajczyk 2010). To evaluate TMEs pollution in sediments, various pollution indices have been developed (Kowalska *et al.* 2018). The geo-accumulation index, enrichment factor, degree of contamination, and potential ecological risk index are commonly applied tools to appraise the risk of the existing metals to the environment. Additionally, they provide clues to understanding the intensity at which anthropogenic activities may impact metal levels in sediments (Kowalska *et al.* 2018). TMEs pollution depends on the individual metallic ion mobility and biological availability (Namieśnik & Rabajczyk 2010). Although total metal content can provide general information on some aspects, it does not particularly inform their bioavailability and actual risk (Alhadrami *et al.* 2016). Therefore, identifying the different fractions of metals in sediments is important for the determination of mobility and toxicity to living organisms. These fractions can be identified using the Community Bureau of Reference (BCR) and Tessier Sequential extraction methods, which are commonly used tools to speciate metals into four and five fractions, respectively (Tessier 1979; Delil & Köleli 2018).

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Leaching kinetics of adsorbed and inherent metals from sediments is one of the factors for TMEs remobilization in rivers (Ho *et al.* 2012). Conducting a study on the leaching kinetics of metals could provide information on their rate and degree of release during variations in natural conditions which adds more understanding on the mobility and toxicity of the metals (Gismera *et al.* 2004).

This study evaluated the level of water and sediment pollution with respect to TMEs and the associated risk of a 'neglected' riverine system. The presence, bioavailability, risk, and leaching patterns of the TMEs in the Kou River were compared using standard guidelines, pollution indices, sequential extraction, and leaching kinetics experiments.

MATERIALS AND METHODS

Study site description

The Kou River is located in Manyara region which is found in the northern part of Tanzania. It originates from Nou Hills in Mbulu district and flows through Darakuta ranch in Babati district (Figure 1). According to the Babati Urban Water Supply and Sanitation Authority (BAWASA), the river has a length of about 40 km, an average width of 3.7 km, an average annual depth of 2.5 m, a maximum depth of 3 m and a flow rate of about 1.32 m^3/s. The river, together with other streams, support lives of diverse habitats in the ranch that covers about 7000 ha. Ranching, artisanal and small-scale mining, wildlife, small-scale industrial activities and agricultural activities were found to take place in the study area. At the upstream of the Kou River, in the ranch area, there was a mini-hydropower plant with a capacity of 300 KW/h. In addition, the river served as an important domestic water source. BAWASA is one of the municipal utilities in Babati district that supply water for drinking and domestic purposes for Magugu, a township with more than 26,000 residents.

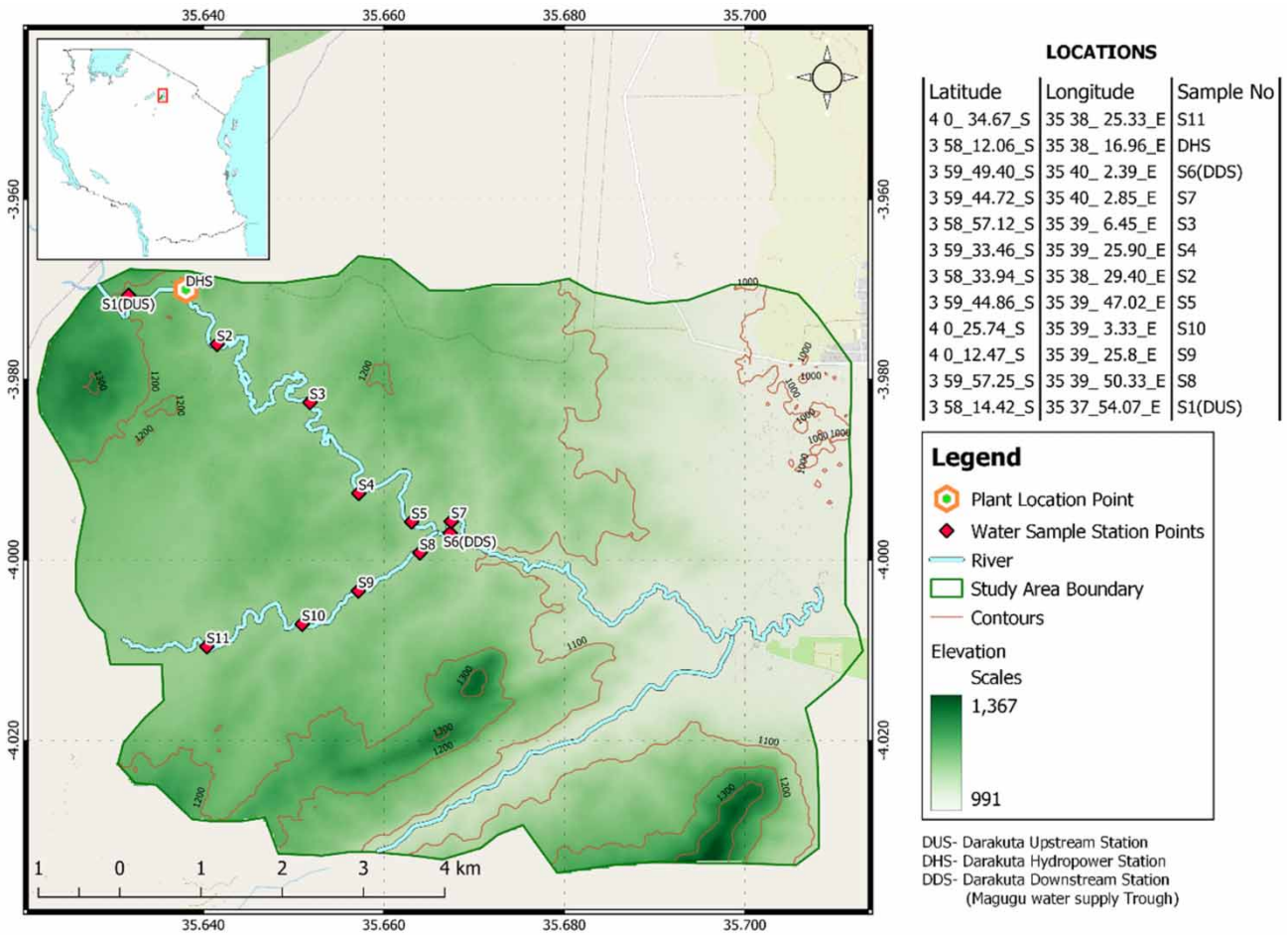

Figure 1 | Map of Tanzania (top left inset) indicating the Kou River and sampling points (right).

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Sample collection

The water samples and sediments were collected from seven sampling stations in the Kou River and four stations in an unnamed tributary in the Darakuta ranch. The sample collection was carried out during the early rainy season in the month of March in 2021. The water sampling was carried out in triplicate and the compound sampling method was used to sample sediments from the same sampling points in the river. Samples were taken from low flow regions where sediments deposited in large quantities. Water samples were collected using acid-rinsed polyethylene plastic bottles, filtered with conical membrane filtration assembly (0.45 micron), preserved with concentrated nitric acid (pH<2), kept in a ice cold box, transported to the laboratory, and stored at 4 °C until further analysis. A surface sediment sampler was used to collect surface river sediments at a depth of 7 cm from the surface of the sediment. A plastic spatula was used to prevent further sediment contamination. The samples were placed in polyethylene bags and stored in an ice-cold box for transport to the laboratory. The sediments were then dried in an oven at 105 °C and prepared for analysis.

Analysis of physicochemical properties

Parameters such as dissolved oxygen (DO), electrical conductivity (EC), pH, total dissolved solids (TDS), and turbidity of river water were measured *in situ* for 11 sampling sites using the Hanna Instrument Multiparameter (HI-9829). Hardness was analyzed in the laboratory using the EDTA Titrimetric method using the DIT 50 Behrotest device (APHA 2017).

Analysis of TMEs in water

Dissolved metal analysis was conducted for As, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in the Kou River upstream and downstream stations. Among these, Co, Cr, Mn, Ni, Pb, and Zn in water samples were analyzed using the WFX-210 atomic absorption spectrometer (AAS) using the EPA Method 1620 (Telliard *et al.* 1994). Five calibration standards for each element were used to calibrate the machine. The operating conditions such as wavelength, spectral bandwidth, lamp current, air pressure and flow, acetylene pressure and height of burner were customized, and samples were analyzed following the procedures listed in the USEPA procedures manual. A DR 2800 spectrophotometer device was used to analyze Cu (Method 8506 and 8026) and Fe (Method 8008) calorimetrically following the procedure as stipulated in the provided procedures manual (APHA 2017). Analysis for As was conducted using Palintest Arsenator (PT981) digital As test kit according to the provided digital Arsenator procedures manual.

Analysis TMEs in sediments

TMEs in the sediment samples were analyzed using a Spectro Xepos™ Energy-Dispersive X-Ray Fluorescence (ED-XRF) machine following the SPECTRO XEPOS user manual. For each sample analysis, 4 g (dry weight) was weighed and put in a bowl together with 0.9 g cellulose binder and four spherical balls of 3-millimeter radius. The mixture was then ground and homogenized using a Fritsch Pulverisette™ pulverizer device (Industriiesstrasse, 8-55743 Idar-Okerstein, Germany) for 15 minutes at 150 rpm. The homogenized mixture was added to the lapped thrust piece and pressed with 12 tons using hydraulic Retsch™ to form pellets. For each sample, four replicate pellets were prepared. The pellets were measured using EDXRF machine and analysed using X–Lab Pro™ software for quantification of elements of interest.

Quality control

The quality of the reagents used throughout the experiments were of analytical grade. The DR 2800 machine and the reagents were used as prescribed in the provided user manuals. For the AAS, laboratory-prepared standards were used for calibration. The method quantification limit for both calorimetry and mass spectrometry was established using the equation (MDL=3.14S) where MDL is method detection limit, S is standard deviation from seven replicates of a selected standard and 3.14 is a t value for six degrees of freedom (7-1), at 99% confidence level, from a table of one-sided t distribution. The method detection limit (MDL) for Cr, Co, Pb, Zn, Mn, Ni, Fe, Cu, and As was 10.5, 8.75, 17.5, 1.75, 3.5, 17.5, 35, 70, and 3.5 μg/L respectively. As pre-determined by a standard addition method, the matrix effect was avoided by diluting the samples prior to analysis. The sediment analysis method was validated using certified reference material (Basalt Columbia River, BCR-2) (USGS 1998) (Table 1). Four batches were analyzed and the percent recovery was in the range of 90–110%.

Water and sediment contamination assessment

Because Kou is a multipurpose river, its water and sediment quality was assessed using different purpose-specific raw water and sediment quality standards established by regulatory organizations to specify its acceptability. The standards used for the

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Table 1 | Comparison of measured data with analytical results of certified reference materials (BCR-2)

Metal	Measured value	Certified value	Recovery (%)
Al (%)	7.79 ± 0.43	7.14 ± 0.1	109.10
Co (mg/kg)	39.98 ± 1.5	37 ± 3	108.05
Cr (mg/kg)	18.61 ± 0.7	17 ± 2	109.47
Cu (mg/kg)	17.59 ± 0.75	19 ± 2	92.58
Fe (%)	9.27 ± 0.05	9.65 ± 0.15	96.06
Mn (mg/kg)	1,482 ± 16.5	1,520 ± 60	97.5
Pb (mg/kg)	12.09 ± 1.7	11 ± 2	109.9
Zn (mg/kg)	121.62 ± 3.42	127 ± 9	95.76

evaluation of water quality were: irrigation water quality standards (Fipps 2003), aquatic life quality standards (USEPA 2014), the French system for the evaluation of the quality of water streams (SEQ-Eau) recommended by the water agencies for fresh waters, and the circular of 7 May 2007 DCE/23 defining 'standards of provisional environmental quality (NQEp)' for surface fresh waters as obtained from Soumia (Khaled-Khodja *et al.* 2018). The quality of sediments was evaluated using the SEQ-Eau standard for biological life and the USEPA sediment quality criteria (Dasar *et al.* 2009; Zoynab *et al.* 2013), which determine sediment contamination levels based on their impact on the quality of the overlying water and the health of the ecosystem (Lyman *et al.* 1987).

To inspect the risk of heavy metals in sediments, six pollution indices were calculated, namely the geo-accumulation index (*Igeo*), the enrichment factor (*EF*), the contamination factor (*CF*), the modified degree of contamination (*m*Cd), the ecological risk (*Eri*) and the potential ecological risk index (*RI*). Their detailed explanations and interpretations are described in Hakanson's and other research papers (Table S1 in the Supplementary Material) (Hakanson 1980; Kowalska *et al.* 2018; Shilla & Shilla 2021).

Iron fractionation using sequential extraction procedure

A step-by-step Tessier and modified BCR sequential extraction methods were applied for the fractionation of the potential bioavailable forms of Fe in the sediments (Tessier 1979; Pueyo *et al.* 2008; Sutherland 2010; Hossain *et al.* 2019). Metal fractions were extracted by thoroughly mixing 1 g of oven-dried sediments in 12.5 mL of leaching solution. This was done in triplicate for more concise results. After each step, the leachates were extracted in a centrifuge tube at 4000 rpm, filtered through a 0.45-micron membrane, and analyzed for Fe using the DR 2800 spectrophotometer following the procedures manual (Method 8008) (APHA 2017).

Leaching kinetics experiment

To study the leaching kinetics of Fe, 1 g of sediments was mixed with 12.5 mL of natural rainwater for each experiment. Fifteen experiments were carried out by continuously shaking separate samples at room temperature with 30 rounds per minute. The extraction time varied between 1, 6, 12, 24, 48, 72 h, up to one month with a 3-day interval. Leachates were filtered and Fe was analyzed immediately using the spectrophotometer. Each experiment was performed in triplicate. This experiment was carried out exclusively for Fe as it was the only metal found at appreciably high levels in both water and sediments. The kinetic study is known for its ability to provide clear understanding on the rate and extent of release of metals from the sediments during slight variations in environmental conditions.

RESULTS AND DISCUSSION

Kou River water quality

Water quality results for Kou River, and the recommended limits of various application-specific standards for each quality parameter tested, are presented in Tables 2 and 3. The Kou River was found to meet the minimum requirements of SEQ-Eau with respect to DO, EC, pH, temperature, and turbidity for biological life (Table 2). However, as with the other standards used, some TMEs in the Kou River water were found to be in a higher concentration than the recommended levels (Table 3).

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Table 2 | Physico-chemical properties of Kou River water compared to the SEQ-Eau guidelines

Stations	DO (mg/L)	Temperature (°C)	pH	EC (μS/cm)	Turbidity (NTU)	TDS (mg/L)	Hardness (mg/L)
Main river							
S6 (DDS)	6.91 ± 0.19	24.4 ± 0.18	6.3 ± 0.03	64.9 ± 0.01	13.67 ± 0.92	41.5 ± 0.46	21.07 ± 1.6
S7	6.95 ± 0.28	23.2 ± 0.018	6.72 ± 0.18	62.6 ± 0.00	13 ± 0.93	40.1 ± 1.11	21.8 ± 1.1
S5	7.12 ± 0.29	22.8 ± 0.03	6.9 ± 0.03	60 ± 0.05	18.3 ± 1.84	38.4 ± 1.39	21.07 ± 1.6
S4	7.32 ± 0.18	22.3 ± 0.37	6.98 ± 0.1	63.5 ± 0.00	16 ± 0.46	40.6 ± 2.05	19.1 ± 0.1
S3	7.13 ± 0.32	22.6 ± 0.09	7.32 ± 0.06	58 ± 0.18	10.7 ± 1.2	37.1 ± 2.49	19.1 ± 0.2
S2	7.49 ± 0.16	23.8 ± 0.06	6.81 ± 0.05	58.9 ± 0.28	14 ± 0.8	37.7 ± 0.55	17.87 ± 1.7
S1(DUS)	7.21 ± 0.08	22.3 ± 0.23	6.8 ± 0.2	59.4 ± 0.00	16 ± 0.23	38 ± 1.85	15.48 ± 1.5
Average	7.16 ± 0.14	23.06 ± 0.55	6.83 ± 0.21	61.04 ± 1.79	14.52 ± 1.69	39.06 ± 1.14	19.07 ± 1.42
Tributary							
S8	7.12 ± 0.33	23.2 ± 0.4	7.37 ± 00	119 ± 0.00	5 ± 0.92	76.1 ± 0.62	48.37 ± 1.6
S9	6.79 ± 0.16	21.5 ± 0.18	6.85 ± 0.09	95.8 ± 0.22	18.33 ± 1.85	61.3 ± 0.49	41.77 ± 1.5
S10	6.77 ± 0.09	21.8 ± 0.32	6.81 ± 0.1	82.2 ± 0.32	16.7 ± 1.39	52.6 ± 1.18	40.63 ± 1.5
S11	6.70 ± 0.1	22.7 ± 0.46	6.89 ± 0.11	96.9 ± 0.00	13 ± 1.22	62 ± 1.85	36.15 ± 1.5
Average	6.85 ± 0.16	22.3 ± 0.67	6.98 ± 0.22	98.48 ± 12.92	13.26 ± 5.04	63 ± 8.25	41.72 ± 4.28
SEQ-Eau	>6	21.5–25.5	6–9	3,000	35	–	–

Table 3 | Concentrations of TMEs (mg/L) in the Kou River water and their respective guidelines

TME	S6 (DDS)	S1 (DUS)	SEQ-Eau (Khaled-Khodja *et al.* 2018)	NQEp	Aquatic life (USEPA 2014)	Irrigation (Fipps 2003)
As	0.008 ± 0.00	0.008 ± 0.00	0.010	0.004	0.150	0.100
Co	0.46 ± 0.04	0.57 ± 0.05	N.I.[a]	N.I.	0.004	0.050
Cr	0.0043 ± 0.00	0.006 ± 0.00	0.002	0.003	0.050	0.100
Cu	0.29 ± 0.02	0.91 ± 0.02	0.001	0.001	<2	0.2–1
Fe	4.12 ± 0.48	5.09 ± 0.37	N.I.	0.200	1.000	5.000
Mn	0.28 ± 0.009	0.27 ± 0.009	N.I.	0.050	0.100	2.000
Ni	0.04 ± 0.001	0.1 ± 0.00	0.003	0.002	0.052	0.200
Pb	BDL[b]	BDL	0.005	0.0004	0.025	5.000
Zn	0.56 ± 0.00	0.56 ± 0.05	0.002	0.008	0.120	2.000

[a]N.1.=guideline not indicated.
[b]BDL=Below detection level.

In both the Darakuta upstream station (DUS) and the Darakuta downstream station (DDS), eight TMEs, that is, As, Co, Cr, Cu, Fe, Mn, Ni, and Zn, were detected with concentrations between 0.0043 and 5.48 mg/L (Table 3). All TMEs except Co exceeded the NQEp standard limits for biological life. The concentrations of Cu (0.29 and 0.91 mg/L), Fe (4.12 and 5.09 mg/L), Mn (0.28 and 0.27 mg/L), Ni (0.04 and 0.1 mg/L) and Zn (0.56 mg/L) were far beyond the NQEp criteria (Table 3). Among the detected TMEs, Cu, Ni, and Zn indicated a significant increase in biological life suitability in comparison to the SEQ-Eau limit (Table 3).

With respect to the USEPA standard, As, Cr, Cu, and Pb at the two stations of the Kou River were acceptable for aquatic life, but Co, Fe, Ni, Mn, and Zn were above their recommended limits (Table 3). Regarding the utilization of the river water for irrigation purpose, Co (0.46 and 0.57 mg/L) and Fe (5.09) were the only metals that exceeded the permissible limits, showing that the water could be acceptable for irrigation with respect to the analyzed TMEs except for the two metals (Table 3).

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Of all the TMEs analyzed, Fe was the only metal that exceeded all the three standard limits for irrigation water, biological life, and aquatic life (Table 3). In addition, it was one of the three TMEs (Cu, Fe, and Zn) that surpassed their recommended biological life limits by more than 25-fold. The Fe level along the main river ranged between 4.1 and 5.38 mg/L, and that of the unnamed tributary ranged between 2.12 and 3.44 mg/L (Table 3). This was relatively higher than the limits recommended by the NQEp surface water quality (0.2 mg/L), the USEPA aquatic life standard (1 mg/L), and the irrigation water standards (5 mg/L). Therefore, the river water was observed to be unsuitable due to Fe, especially as it relates to the support of aquatic and biological life.

The significant alteration in the quality of the Kou River water with Fe could be derived from the natural geological formation of the area or was probably due to anthropogenic activities. Fe levels above permissible limits have been reported elsewhere, and it was stipulated that probably the TMEs had their source either in geological depositions or from domestic waste, industrial, and agricultural activities (Wogu & Okaka 2011; Kumar *et al.* 2017; Akhtar *et al.* 2021). A detailed study on sediments could determine TMEs pollution in rivers and indicate their main sources, as sediments may work as an adsorbent phase for various substances, including metals, giving a clue on the hydrochemical activities behind the water characteristics under investigation (Namieśnik & Rabajczyk 2010). Therefore, in the present study, the main TMEs in the river and their possible sources were determined through an in-depth sedimentological investigation.

Kou River sediment quality

Similar to surface water analysis, the following metals were analyzed in the sediment samples: As, Cu, Co, Cr, Fe, Mn, Ni, Pb, and Zn for sediment quality and risk assessment purposes. According to the SEQ-Eau standard (Table 4), the river sediments had acceptable quality for biological life with respect to As, Cu, Pb and Zn, but the quality was poor with respect to Cr (213.6 and 176.6 mg/kg) and Ni (38.32 and 39.72 mg/kg) at the upstream and downstream stations, respectively. The concentrations of Fe (51,698 and 52,950 mg/kg) and Mn (896.6 and 915 mg/kg) were considerably high; however, the SEQ-Eau system did not have a standard limit for these elements (Khaled-Khodja *et al.* 2018). On the other hand, the USEPA sediment quality standard categorized the Kou River sediments as 'not polluted' with respect to Cu, Pb, and Zn, and 'slightly polluted' with respect to Ni. According to this guideline, the sediments were grouped into the 'severely polluted' class with respect to Cr, Fe and Mn (Table 5). Therefore, based on the two standards on TMEs that could degrade sediment quality, the Kou River sediments were polluted with metals, especially with Cr, Fe, Mn, and Ni. It should be borne in mind that, among the four

Table 4 | Concentrations of TMEs in the Kou River sediments (mg/kg) with recommended limits

	As	Cu	Co	Cr	Fe	Mn	Ni	Pb	Zn
DUS	1.42	24.66	29.78	213.6	51698	896.6	38.32	23.4	65.96
DDS	1.4	23.06	32.88	176.6	52950	915	39.72	23.3	71.72
SEQ-Eau	9.8	32	–	43	–	–	22	35	120

Table 5 | Concentrations of TMEs in the Kou River sediments (mg/kg) compared to the USEPA sediment quality classification

Heavy metal	Not polluted	Slightly polluted	Severely polluted	DUS levels	DDS levels
Cu	<25	25–50	>50	24.66	23.06
Cr	<25	25–75	>75	213.6	176.6
Fe	<17,000	17,000–25,000	>25,000	51,698	52,950
Mn	<300	–	>500	896.6	915
Ni	<20	20–50	>50	38.32	39.72
Pb	<40	40–60	>60	23.4	23.3
Zn	<90	90–200	>200	65.96	71.72

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TMEs, Fe was also observed in river water to be in concentrations that exceeded all the limits, possibly indicating a common source.

Assessment of the pollution in sediments using various pollution indices may provide a better understanding of the major sources of TMEs and their associated environmental risk. Thus, the pollution and the possible ecological risk of TMEs in the Kou River sediments were assessed using six pollution indices. Interpretation of pollution indices has been provided in the literature (Hakanson 1980; Kowalska *et al.* 2018; Shilla & Shilla 2021). Based on Table 6, the following sections discuss the analytical results for the six pollution indices:

Geo-accumulation index

The geo-accumulation index (I_{geo}), an indicator of sediment pollution with TME, groups the sediment contamination status into seven classes ranging from uncontaminated to extremely contaminated based on numerical values (Shilla & Shilla 2021). The sediments from both DUS and DDS were found to be in the categories of uncontaminated to moderately contaminated ($0 \leq I_{geo} < 1$) with respect to Co (0.78 and 0.92), Ni (0.46 and 0.51), Mn (0.18 and 0.21), Cu (0.2 and 0.1), and Fe (0.16 and 0.19) (Table 5). The I_{geo} values for Zn, Pb, and As were below zero, which could be indicative of no pollution with respect to the three TEMs. On the other hand, moderate to heavy contamination with respect to Cr, was determined in the DUS and DDS sediments.

Contamination factor

The contamination factor (*CF*) is a tool to monitor single metal contamination by comparing its level with background values (Kowalska *et al.* 2018). Moderate *CF* ($1 \leq CF < 3$) for Cu, Co, Fe, Mn, Ni, Pb, and Zn was observed at the DUS and DDS stations of the Kou River. The metals were in the following order: Co>Ni>Mn>Cu>Fe>Pb>Zn at DUS and Co>Ni>Mn>Cu>Fe>Zn>Pb at DDS. However, the *CF* for Cr was exceptional. Among the TMEs, Cr had the highest *CF* values. For the DUS sediments, Cr had a *CF* value of 6.1 which is categorized as very high degree of contamination ($CF > 6$), whereas the degree of Cr contamination was considerable ($3 \leq CF < 6$) at DDS ($CF = 5.05$). The lowest *CF* values ($CF < 1$) were observed for As at both DUS ($CF = 0.71$) and DDS ($CF = 0.7$). It was notable that the pollution class given for the metals using *CF* was higher than the category assigned by the geo-accumulation index. This observation supports previous

Table 6 | Results of metals content in Kou River sediments (mg/kg) and respective contamination indices at upstream (DUS) and downstream (DDS) stations

	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Pb	As
DUS	80,146	213.6	896.6	51,698	29.78	38.32	24.66	65.96	23.4	1.42
DDS	74,168	176.6	915	52,950	32.88	39.72	23.06	71.72	23.3	1.4
UCC[a]	77,440	35	527	30,890	11.6	18.6	14.3	52	17	2
$EF_{(DUS)}$		5.9	1.64	1.62	2.48	1.99	1.67	1.23	1.33	0.69
$EF_{(DDS)}$		5.27	1.81	1.79	2.96	2.23	1.68	1.44	1.43	0.73
$I_{geo(DUS)}$		2.02	0.18	0.16	0.78	0.46	0.2	−0.24	−0.12	−1.08
$I_{geo(DDS)}$		1.75	0.21	0.19	0.92	0.51	0.104	−0.12	−0.13	−1.1
$CF_{(DUS)}$		6.1	1.7	1.67	2.57	2.06	1.72	1.27	1.38	0.71
$CF_{(DDS)}$		5.05	1.74	1.71	2.83	2.14	1.61	1.38	1.37	0.7
$E^i_{r(DUS)}$		12.2	1.7	–	12.83	10.3	8.62	1.27	6.88	7.1
$E^i_{r(DDS)}$		10.09	1.74	–	14.17	10.68	8.06	1.38	6.85	7
$m\mathrm{Cd}_{(DUS)}$	2.13									
$m\mathrm{Cd}_{(DDS)}$	2.06									
$RI_{(DUS)}$	60.92									
$RI_{(DDS)}$	59.97									

UCC values were obtained from Wedepohl (1995).

[a]UCC is background value of metals taken from the upper continental crust.

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research findings that suggested that the *CF* values usually indicate a higher degree of contamination than their I_{geo} counterparts (Hołtra & Zamorska-Wojdyła 2020).

Enrichment factor

The level of anthropogenic impact on the abundance of TMEs in sediments was determined by calculation of the enrichment factor (*EF*) (Kowalska *et al.* 2018). In reference to Table 6, a minimum anthropogenic enrichment of Mn, Fe, and Cu was observed in DUS and DDS sediments. The *EF* values for Zn, Pb, and As were less than 1.5, which may indicate that their occurrence in the study area could be the result of natural processes (Barbieri 2016). At DUS and DDS stations, the *EF* of Co is 2.48 and 2.96, respectively, where an *EF* between 2 and 5 is regarded as moderate. Ni showed moderate enrichment at DDS (EF=2.23) and only minimum enrichment at DUS (EF=1.99). Significant effects that may be related to anthropogenic activities ($5 \leq EF \leq 20$) were observed only for Cr with an *EF* of 5.27 and 5.9 in the two stations. Mining activities, ashes from coal or municipal waste combustion, and the tanning industry are typical anthropogenic sources of Cr in rivers (Tumolo *et al.* 2020).

Modified degree of contamination

The modified degree of contamination (*m*Cd) is a generalized tool for determining the overall degree of contamination of a particular site based on the contamination factor (*CF)* of each TME with in the sediment (Rezaei *et al.* 2019). Taking the average *CF* of all the analyzed TMEs for each station, i.e. As (0.71 and 0.7), Cr (6.1 and 5.05), Co (2.57 and 2.83), Cu (1.72 and 1.61), Fe (1.67 and 1.71), Mn (1.7 and 1.74), Ni (2.06 and 2.14), Pb (1.38 and 1.37) and Zn (1.27 and 1.38), the *mCd* values for DUS and DDS stations are 2.13 and 2.06, respectively. This indicated that the sediments of the Kou River were moderately contaminated with heavy metals ($2 \leq mCd < 4$) with respect to the nine TMEs. Similar to values from *CF* and I_{geo}, Co, Cr, Cu, Fe, Mn, and Ni were the main TMEs responsible for the moderate overall contamination of the sediments.

Potential ecological risk

The ecological risk (E_r^i) of each TME in sediments was calculated from a single ecological risk factor of each metal based on their established toxicity response coefficients (T_r^i) (Hakanson 1980). The E_r^i groups the TMEs ecological risk as low ($E_r^i < 40$), moderate ($40 \leq E_r^i < 80$), considerable ($80 \leq E_r^i < 160$), high ($160 \leq E_r^i < 320$), and very high ($RI \geq 600$). The results from the present study (Table 6) revealed that all the individual TMEs used in the calculation were classified to have a low ecological risk ($E_r^i < 40$). The degree to which ecological risk was posed by the presence of the overall TMEs in sediments was determined by the potential ecological risk (*RI*) index, taking the total E_r^i values of all the TMEs. This index categorizes the risk levels of the overall TMEs into four classes: low ($RI < 150$), moderate ($150 \leq RI < 300$), considerable ($300 \leq RI < 600$) and high ($RI \geq 600$) (Nkinda *et al.* 2020). The *RI* of both DUS (60.92) and DDS (59.7) sediments indicated that the existing TMEs (excluding Fe) had low potential ecological risk.

Except Fe and Mn, the calculated pollution indices and the USEPA sediment quality standard were in agreement in that they classified the Kou River sediments into non- and moderately-contaminated classes with respect to As, Co, Cu, Ni, and Zn, and considerably to severely polluted with respect to Cr. While the pollution indices suggested only none to moderate pollution status with Fe and Mn, the USEPA standard grouped the sediments as severely polluted with the two TMEs in addition to Cr. Despite these metals being significantly high in the sediments of the Kou River, only Fe was found in the overlying water at concentrations extremely higher than all the standard limits used for water quality assessment. Despite significantly polluting the sediments, the concentration of CR in the river water was only marginal, possibly due to being in its insoluble trivalent form.

With regards to ecological risk posed by the metals, the standard guidelines contradicted the ecological risk (E_r^i) index. Although the USEPA and SEQ-Eau guidelines would delineate the Kou River sediments to be unsuitable for supporting biological life with respect to Cr, Mn, and Ni, the computed E_r^i values showed that the three TMEs had very low potential to pose an ecological risk. The USEPA guidelines also suggested a severe pollution status with respect to Fe, whereas neither the E_r^i index nor the SEQ-Eau standard had set ecological risk levels for the metal. It is worth noting that one of the USEPA criteria for classifying sediment pollution levels is their potential to alter the quality of the overlying water (Lyman *et al.* 1987). Hence, sediments classified as severely polluted with respect to Fe could be a significant contributor to Fe pollution of the overlying water that exceeded all the irrigation, aquatic, and biological life standards. To have a deeper understanding of the potential ecological risk of Fe in the sediments, further experiments were conducted to determine its leachability and bioavailability.

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Fe enrichment and impacts

Bioavailable fractions of Fe

Analysis of the total amount of metals cannot be regarded as a reliable indicator of their toxic effects. Distinguishing the various fractions of elements with respect to their physiochemical mobility and potential bioavailability provides information on the state of the pollution and their actual impact on the environment (Devi & Bhattacharyya 2018). Fe in the sediments was sequentially extracted and fractionated into six categories with separate remobilization regimes in varying environments. The categories used in the present study were as follows: water soluble (F1), ion-exchangeable (F2), carbonate bound (F3), Fe-Mn bound/reducible (F4), organics and sulfide bound/oxidizable (F5), and residual fractions (F6).

Two stations upstream (Station 1) and downstream (Station 6), at which water was being collected for domestic consumption, were chosen to study Fe fractionation in river sediments. The different fractions of Fe in the DUS and DDS sediments are presented in Table 7.

(a) Water-soluble fraction (F1)

The water-soluble fractions are the dissolved portions of the metal and reported as part of the exchangeable fractions in most of the literature. In the present study, they occupied only about 0.03% of the total Fe content in river sediment (Table 7). These results were consistent with Osakwe's study (Osakwe 2013) indicating that the percentage of Fe in the water-soluble species was negligible, probably due to the metal being easily absorbed by the aquatic biota.

(b) Ion exchangeable fraction (F2)

These are weakly-bound metal species on sediment grains that can be separated by electrostatic interactions by varying the ionic configuration of water. The ionic composition of the metal controls the sorption-desorption processes. Those forms sorbed on the surface of the sediments are easily removed by this process, and mostly by exchange of ions. Where acidic condition predominates, the release of these fractions would promote a harmful effect on the environment (Bakircioglu *et al.* 2011). River sediments of the present study comprised only 0.01% Fe in exchangeable forms, which was less than all other fractions (Table 7).

(c) Carbonate bound (F3)

Carbonate bound fractions are usually considered to be weakly absorbed. Metals in this fraction are bound to carbonates, phosphates, and sulfates. While the F1 and F2 fractions are to a large extent readily mobile and bioavailable, the F3 fractions are more affected by certain environmental changes, often acidic conditions (Bożym 2017). In the present study, F3 fractions of 0.22 and 0.01% were recorded at the DDS and DUS stations, respectively.

(d) Fe-Mn bound/reducible fraction (F4)

Fe and Mn oxides are unstable in low oxidation reduction potential (Eh) of an environment, and are reduced during anaerobic conditions promoting metal adsorption as they decompose (Bożym 2017). Usually, Fe and Mn concentrations in the F4 fractions are high because the two TMEs are common constituents of rocks and sediments (Devi & Bhattacharyya 2018). Fe bound to Fe-Mn oxides was the most dominant fraction after the residual fraction in both sediments, that is, 4.96 and 6.59% at the DUS and DDS stations, respectively.

(e) Organics and sulfide bound/oxidizable fraction (F5)

These fractions are usually bound to organic matter and sulfide compounds. Oxic/anoxic conditions of an environment plays the greatest role on the oxidation state of sulfides which have a direct relationship with the mobility of metal fractions

Table 7 | Iron fractionation in river sediments

	Upstream (DUS)		Downstream (DDS)	
Fractions	**Amount of Fe (mg/kg)**	**Percentage**	**Amount of Fe (mg/kg)**	**Percentage**
Water soluble (F1)	16.46	0.03%	9.79	0.02%
Ion exchangeable (F2)	4.17	0.01%	2.92	0.01%
Carbonate bound (F3)	5.42	0.01%	118.96	0.22%
Reducible (F4)	2,562.5	4.96%	3,491.67	6.59%
Oxidizable (F5)	1,416.67	2.74%	458.33	0.87%
Residual (F6)	47,694.8	92.25%	48,868.3	92.29%
Total amount	51,698		52,950	

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bound to the oxidizable phase (Ouddane *et al.* 2018). Metals in this fraction tend to be released more in an oxidized condition as a result of mineralization, which later results in complexation and bioaccumulation. At the DUS and DDS, Fe in the F5 fraction made up 2.74 and 0.87% of the total metal content, respectively.

(f) Residual fraction (F6)

Residual fractions are the remaining metals that are bound through their crystalline structure, immobilized, and biologically inert, with no risk of harming the environment (Al-Mur 2020). A high percentage (>92%) of Fe was found in the residual fraction which indicates its strong immobile bonds in the sediment's lattice structures.

In general, the Fe fractions in the river sediments followed the trend: Residuals>Fe-Mn bound>organic bound followed by the three readily available species (carbonate bound, water-soluble, and ion-exchangeable). Fe in the first three labile fractions was almost negligible, while the reducible fractions were the dominant fractions following the residuals. The higher reducible fraction than the other weakly bonded fractions indicate that the solubility of Fe in the sediment was more associated with reducing conditions in the environment. These observations correspond well with some previous findings that Fe content is usually low in easily soluble and exchangeable species (Klink *et al.* 2019).

Bioavailability factor

The bioavailability factor (*BF*) is the ratio of the content of potential mobile fractions to total content of metallic elements (Bielicka-Giełdoń *et al.* 2013). This is given by Equation (1):

$$BF = \frac{C_{bio}}{C_{total}} \tag{1}$$

where C_{bio} and C_{total} represent the concentration of the potential bioavailable metals and the total concentration of metals in the studied sediment, respectively. In this respect, all the non-residual fractions are considered as bioavailable forms as they can be easily taken up by living organisms (Bielicka-Giełdoń *et al.* 2013). The calculated *BF* of the river sediments made up approximately 7.8%, which shows that about 92% of the total metal content had no potential to leach into the environment. This indicated that probably the sediments had no significant contribution for the excessive Fe presence in the overlying water.

Risk assessment code

The risk assessment code (RAC) is applied to assess the health risk of metals in sediments to living organisms. The classification is based on the percentage of metals in the first three fractions (water-soluble, ion-exchangeable, and carbonate bound). These fractions together are regarded as very weakly bonded fractions and readily available for biological uptake (Hossain *et al.* 2019). According to the criteria of the risk assessment code, a value below 1% is considered safe, whereas a very high risk to the environment is greater than 50%. The interpretation of the RAC and the results at the two stations is provided in Table 8.

As can be seen from Table 9, Fe in river sediments had an RAC value of less than 1%. Although Fe in sediments was determined to possibly affect the health of the ecosystem based on the USEPA sediment quality guideline, the RAC values suggested that Fe was not harmful to the environment.

Leaching kinetics of Fe

The mobility and toxicity of metals in sediments can be associated with the leaching kinetics that provide information on their rate and degree of release during variations in natural conditions (Gismera *et al.* 2004). Various leaching chemical solutions, including

Table 8 | Risk assessment code (RAC) for Fe in upstream and downstream sediment samples

RAC	Criteria (F1+F2+F3) (%)	DUS Fe (%)	DDS Fe (%)
No risk	<1	0.05	0.25
Low risk	1–10		
Medium risk	11–30		
High risk	31–50		
Very high risk	>50		

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Table 9 | Maximum TME concentrations of in water (mg/L) and sediments (mg/kg) of Kou River compared to other rivers

	Rivers	Kou (Tanzania)	Bartin (Turkey)	Buriganga (Bangladesh)	Mvudi (South Africa)	São Carlos, Urban (Brazil)	Voghji (Armenia)
As	Water	0.008	NA	0.22	–	–	0.004
	Sediment	1.42	6.17	26.4	–	–	29.7
Co	Water	0.57	NA	0.4	–	0.11	0.003
	Sediment	32.88	10.3	11.28	–	17.5	13.8
Cr	Water	0.006	0.003	0.18	0.593	0.049	0.001
	Sediment	213.6	25.6	60.5	175	76.88	11.8
Cu	Water	0.91	0.004	0.99	0.567	0.029	0.083
	Sediment	24.66	42	85.2	5,690	90.9	620
Fe	Water	5.38	0.48	2.2	5.07	3.04	0.376
	Sediment	52,950	29,600	80.2	7,460	2,508.23	20,018
Mn	Water	0.28	0.04	0.31	0.675	0.23	0.181
	Sediment	915	683	26.4	2,160	275.53	450
Ni	Water	0.1	0.008	0.4	–	0.069	0.003
	Sediment	39.72	31	59	–	43.04	18.8
Pb	Water	NA	NA	0.521	0.046	0.23	0.0005
	Sediment	23.4	21	80.2	7.95	28.29	40.5
Zn	Water	0.56	0.01	0.99	0.548	0.41	0.1
	Sediment	71.72	94	60.5	1,524	190.65	92.3
References		Present study	Gunes (2021)	Bhuiyan *et al.* (2014)	Edokpayi *et al.* (2016)	Chiba *et al.* (2011)	Gabrielyan *et al.* (2018)

acid rain, have been used in studies to estimate the leachability potential of elements from sediments as a function of time. The time required for equilibrium conditions to take place can be determined through kinetics experiments (Lee *et al.* 2012).

In the present study, natural rainwater with pH of 6.2 ± 0.1 was used to investigate Fe leaching trends from Kou River sediments at different times ranging from 1 to 720 hours (1 month) with a 3-day interval after the third day (Figure 2). A sample from the DDS station whose total Fe concentration was 52,950 mg/kg was used to carry out the experiment.

In the first 1 hour, the average concentration of Fe that leached from the sediment was 35 mg/kg, equivalent to 0.07% of the total metal content (Figure 2). A steep increase was observed in the 6 hours leaching where 47.8 mg/kg (0.09%) Fe was extracted with pH dropping from 6.2 to 6.12. The 12 hours experiment had only a slight difference (45.85 mg/kg) from the 6 hours extraction. The sharpest rise occurred in the 24 hours where 65.9 mg/kg (0.12%) iron was released with pH dropping down to 6.09. After 24 hours, no significant differences were observed until 288 hours (12 days) extraction, where the maximum leaching was obtained (0.14%) with a final pH of 6. Fe that leached after the 12th day to one month did not indicate a significant increase (0.12–0.13%), when the pH was maintained in the range of 6.0–6.13. This indicated that in case of pH change in the river during heavy rains, most of the soluble phase of Fe will possibly be released from sediments within the first 24 hours and continue to be released slightly until 12 days of contact.

Comparing TME concentrations

The TME concentrations in the water and sediments of the Kou River and other rivers around the world are provided in Table 9 to help visualize the level of contamination of the Kou River in relation to other rivers.

CONCLUSIONS

The present study investigated the extent of TMEs pollution for Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb, and As in surface water and sediments of the Kou River in Tanzania. According to NQEp and SEQ-Eau standards, the water of the Kou River was not suitable to support biological life with respect to Cu, Fe, Mn, Ni, and Zn. The concentrations of Co, Fe, Mn, Ni, and Zn in the river water failed to meet the USEPA aquatic life requirements. The river water was suitable for irrigation purposes, except for its concentrations of Co and Fe. The overall TMEs contamination level of the Kou River sediments was moderate where Cr, Fe, Mn, and Ni were the major contaminants. According to pollution indices, the contamination level for Fe and

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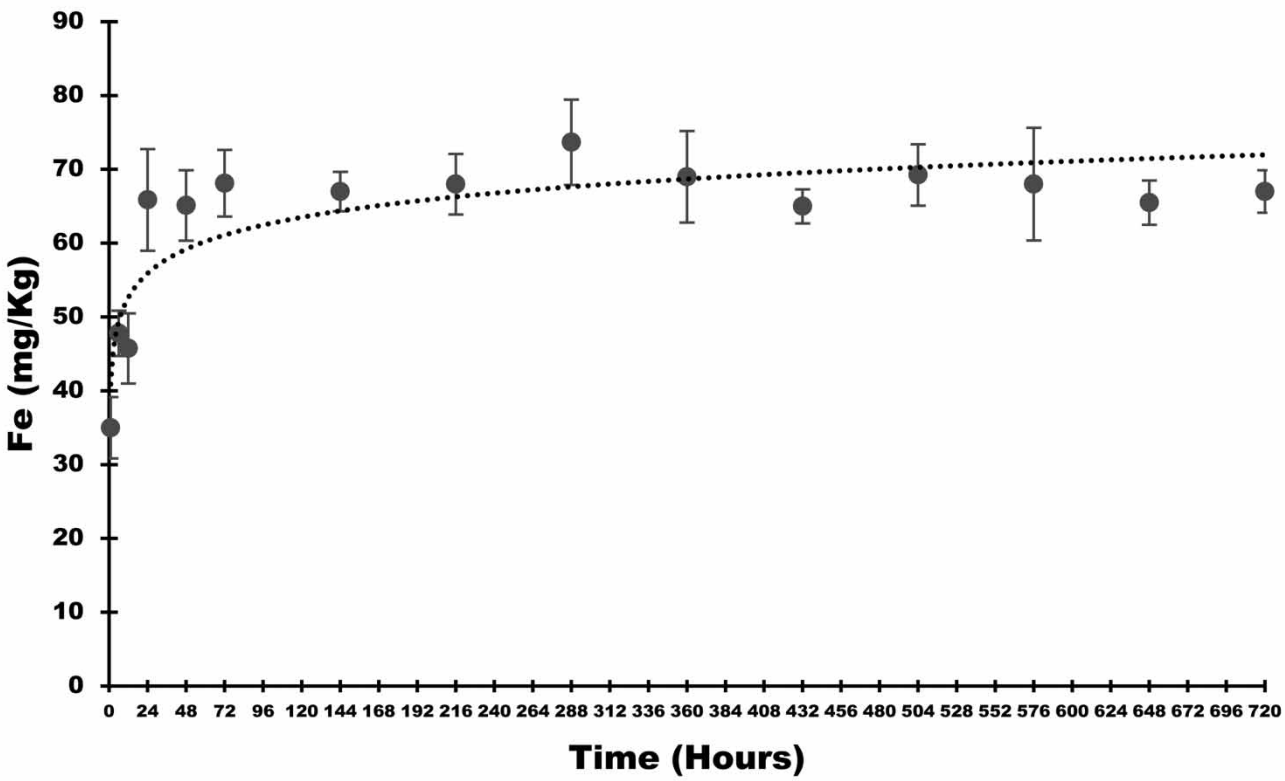

Figure 2 | Kinetics of iron leaching from the Kou River sediment.

Mn was none to moderate; however, the USEPA standards suggested a severe contamination status by the two metals. The TMEs in the sediments had no anthropogenic enrichment except Cr, which was probably significantly sourced from human activities. Only Fe was found to exceed all the standard limits of water irrigation, aquatic, and biological life. The level of bioavailable Fe in the sediments was very low, posing no ecological risk to the environment, and probably, the sediments were not the source of Fe pollution in the overlying water. Despite the unsuitability of the Kou River water for irrigation, aquatic, and biological life in relation to one or more metals, the nine TMEs in the sediments had very low potential to pose ecological risks. The present study recommends that suitable water treatment techniques should be applied to alleviate undesirable metallic contents in river water prior to application for a specific purpose.

ACKNOWLEDGEMENTS

This work was kindly supported by the Inter-University Council for East Africa (IUCEA). We thank the Nelson Mandela African Institution of Science and Technology (NM-AIST) for providing further support related to laboratory work, sampling, and analysis. The Arusha Technical College (ATC) for assistance in sample analysis, thank you. The authors would also like to thank the Babati Urban Water and Sanitation Authority (BAWASA) for permission to conduct research in their catchment area.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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First received 19 August 2021; accepted in revised form 19 December 2021. Available online 3 January 2022

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