Original Research Article

Assessing Trace Metal Contamination and Associated Risks in the Kossan River Ecosystem, southern Côte d'Ivoire

ABSTRACT

Trace metals accumulate in aquatic systems and can pose a threat to human health and wildlife. In recent decades, human activity has become the main source of metals in the environment. In order to gain a better understanding of metal contamination in Ivorian rivers impacted by human activity, and to help set up a database, we studied the distribution of arsenics (As), cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) in the Kossan River.

A total of 21 surface water and sediment samples were taken at 7 stations along the River Kossan between March 2019 and July 2020. Total concentrations of the metals were analyzed by atomic absorption spectroscopy (AAS). Carcinogenic and non-carcinogenic risks were assessed in surface water. Contamination indices such as EF, CF; Igeo and PLI were calculated to determine the level of sediment contamination. Ecological risk indices Er and RI were used to assess the potential risks associated with metals.

The concentrations ofAs, Pb, Cd, Cu and Zn found in surface water samples fell within the following ranges: 2.03 - 17.19, 1.752 - 13.264, 0.067 - 0.774, 17.44 - 2369.11 and 136.72 - 3669.37 µg/L, respectively and in sediment: 0.69 - 4.60, 2.10 - 11.30, 0.13 - 5.00, 1.70 - 28.20 and 4.10 - 90.30 µg/g, respectively. The results showed high levels of As, Cu, Pb and Zn contamination in places, above WHO limits. The calculation of non-carcinogenic and carcinogenic risk indices revealed that arsenic and copper can present major health risks for humans through the consumption of water. Cd concentrations exceeded geochemical background values. The results suggest moderate to very severe Cd contamination of the sedimentsby anthropogenic origin at certain sampling points. In general, the results of the ecological risk indices revealed low to moderate levels of contamination for metals, with the exception of heavy cadmium contamination in the river.The highest concentrations of trace metals were observed in water and sediment samples collected from stations with high anthropogenic pressure.

The continuing intensification of human activity may in the long term present a major risk to man and his environment, hence the need to set up a system for monitoring river watercourses and to develop a system for remediating trace metals in river water such as phytoremediation.

Keywords: Trace metals, water, sediment, pollution, ecological risk, health risk

1. INTRODUCTION

Human activities such as urbanization, agriculture, mining and industry exert considerable pressure on aquatic environments. These pressures lead to a deterioration in the quality of aquatic ecosystems through the injection of pollutants into these environments [1]. Among these pollutants, trace metals are a major problem because of their resistance to biodegradation, their toxicity and their capacity to be incorporated into food chains [2,3]. Trace metals are introduced into the environment through natural phenomena and anthropogenic activities such as mining, agriculture, industry and domestic effluents [4–8]. Increased pollution of aquatic environments by trace metals can have harmful effects on humans and their environment [5]. Environmental pollution by trace metals is increasing with the intensification of industrial activities and increased urbanization.

Once in the aquatic environment, trace metals bind mainly to sedimentary particles and can accumulate in sediments through sedimentation [9]. Sediments are therefore natural reservoirs and secondary sources of trace metals in the environment. When physico-chemical changes occur, trace metals trapped in sediments are likely to be released into the water column [1] and contaminate water and aquatic organisms [3,9]. Sediment is therefore used as an indicator of the level of pollution in the environment. Assessing the level of trace metal contamination in sediments therefore helps us to understand the impact of human activities on aquatic environments[10–12].

In rural areas, the massive use of fertilisers and pesticides and charcoal are the main sources of trace metal contamination in aquatic environments [13]. The waters of the River Kossan are not to be outdone. The catchment area of the River Kossan is an area of high agricultural potential. It is vital to study the metal contamination of the water in this catchment area, as it is often used for multiple purposes (drinking, washing clothes, etc.) by rural populations without prior treatment.

The impact of human activities on metal contamination of rivers is not well established in agricultural rivers in Côte d'Ivoire. The aim of our work is to study the impact of human activities on the level of contamination of the trace metals arsenic, cadmium, copper, lead and zinc in the waters of the Kossan River. To achieve this objective, the study will focus on determining the total concentration of trace metals in the water column, determining the degree of accumulation of metals in sediments on the basis of contamination indices and the health risks associated with metals in the waters of the river.

2. MATERIAL AND METHODS

2.1. Sampling sites

The Kossan River is the main right bank tributary of the Comoé whose confluence is in the town of Alépé. The area of the river studied is located in the south of the catchment area in the Mé region, specifically in the department of Alépé. This area lies between the town and the Mabi-Yaya nature reserve (**Figure 1**). Samples were taken at seven stations along the study area.

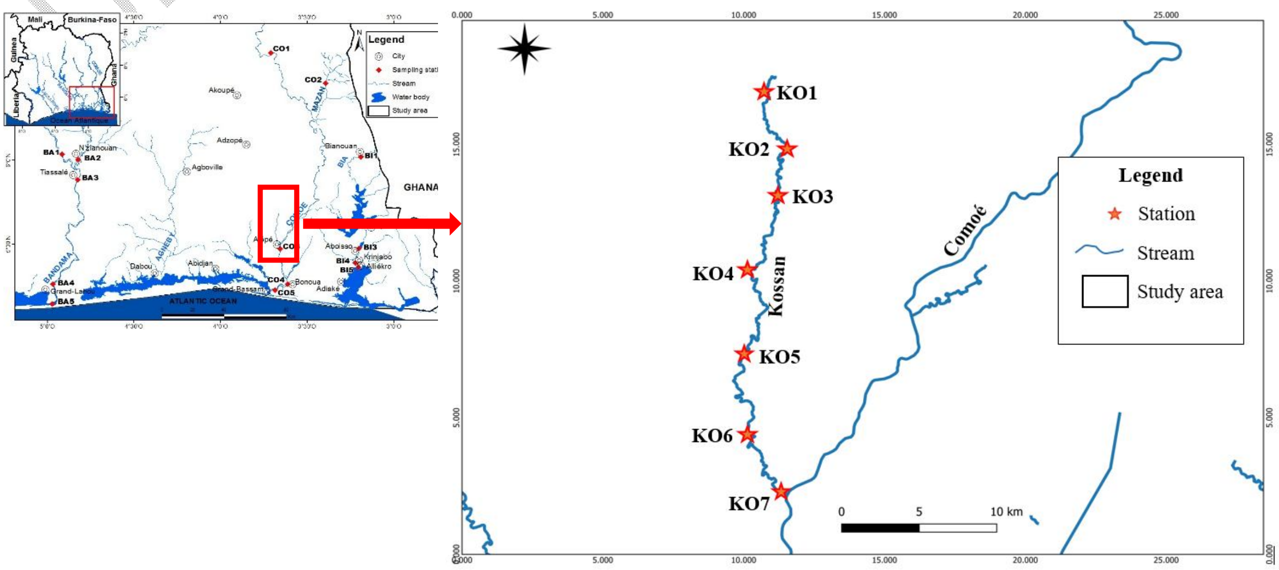


Fig. 1. Location of sampling sites on the Kossan River

2.2. Sampling

Surface water samples were collected from seven stations in the river (KO) (**Figure 1**). Surface water samples were collected at a depth of 25 cm using a 5 L Niskin bottle. The method used to process the samples was that described by [1]. The samples were stored at 4°C until analysis. To account for local variability, two replicate samples were taken at each station.

Sediment samples were collected using a small Van-Veen type bucket and placed in polyethylene bottles, then placed in the dark in a cooler (4°C). In the laboratory, the sediments were dried in an oven (30°C) for 24 hours, sieved to 2 mm, then stored in a dark cabinet (20°C) for analysis. All glasses and containers were thoroughly rinsed with Milli-Q water, cleaned with 30% nitric acid (65%, E. Merck, Darmstadt, Germany) for one week and rinsed five times with Milli-Q water before use.

2.3. Total sediment digestion

To determine the total concentration of metals Fe, As Cu, Cd, Pb and Zn in the sediments, the sediments were digested by total decomposition using the reference methods for marine pollution studies [1,6].

Total trace metal concentrations were measured directly by hydride generation atomic absorption spectroscopy (HG-AAS) for As and by graphite furnace atomic absorption spectroscopy (SpectrAA100 Varian spectrometer, Japan) for Pb, Cd, Cu and Zn. The detection limits were 0.05 µg / L for Pb, 0.02 µg / L for Cu and Zn, 0.13 µg / L for As and 0.01 µg / L for Cd. Repeated measurements showed errors of less than 6%.

2.4. Health risk assessment

Humans are exposed to trace metals by two main routes: orally and dermally. Two parameters have been used to assess non-carcinogenic and carcinogenic risks: the Hazard Quotient and the Carcinogenic Risk.

Chronic daily intake (CDI)

In order to assess the non-carcinogenic and carcinogenic risks to which humans are exposed through the consumption of water contaminated by trace metals, chronic daily intake (CDI) was calculated on the basis of the following relationships:

$$CDI_i = \frac{C \times IngR \times EF \times ED}{BW \times AT} \qquad \textbf{(1)}$$

$$CDI_d = \frac{C \times SA \times K_p \times ET \times EF \times ED \times CF}{BW \times AT} \qquad \textbf{(2)}$$

where: CDIi is the chronic daily dose by ingestion (oral) and CDId, the chronic daily dose by dermal route (skin) [14,15].
This parameter defines the dose ingested through water consumption by mouth or the dose absorbed through the skin by bathing in water. **Table 1** gives the values of parameters characterising CDI.

Table 1: Parameters characterising chronic daily intake (CDI) values.

Parameters	Units	Values	Source
Concentration of trace metal in water (C)	µg/L	-	[1]
Ingestion rate (IR)	L/day	2	[16]
Exposure frequency (EF)	day/year	365	[17]
Exposure duration (ED)	year	51	[3]
Body weight (BW)	kg	60.7	[3]
Average time (AT)	day	18615	[3,16,18]
Skin-surface area (SA)	cm^2	18	
Exposure time (ET)	h/day	0.6	
Conversion factor (CF)	L/cm^3	0.001	
Permeability coefficient (Kp)	cm/h		
Zn		0.0006	
Cu		0.001	
As		0.001	
Cd		0.001	
Pb		0.004	

Non-carcinogenic risk

The Hazard Quotient (HQ) is used to assess the non-cancer diseases to which humans are exposed by using water contaminated with trace metals. The hazard quotient is calculated from the following relationship:

$$HQ = \frac{CDI}{RfD} \quad (\mathbf{3})$$

where CDI is the chronic daily dose (µg.kg-1.day-1) and RfD is the reference dose of metals in a given condition (µg.kg^{-1}.day^{-1}). The reference dose by ingestion of water (RfD in) was obtained from the [13]. RfD by dermal absorption (RfD dermal) was obtained from RfDin multiplied by a gastrointestinal absorption factor [10,13].
If the HQ value is close to or equal to unity, this indicates potentially harmful effects on human health or the need for further investigation. HQ values > 1 suggest even higher probabilities of adverse health effects.

Hazardous index (HI)

In the environment, each metal can expose humans to health risks. However, metals can have adverse effects on human health by association or combination. These adverse effects by combination of metals are assessed by calculating the hazard index using the following relationship:

$$\mathrm{HI} = \sum_{i=1}^{n} \mathrm{HQ_i} \quad (\mathbf{4})$$

HDi is the exposure quotient for element i. When HI < 1, it would have no adverse effects while for HI > 1 adverse effects could occur [19,20].

Carcinogenic risk (CR)

Carcinogenic risks (CR) for metals have been estimated to assess the likelihood of an individual developing cancer during their lifetime following exposure to a potential carcinogen [21–23]. The CR is obtained using the Cancer Slope Factor (CSF) for the metal established by the [18][17,24]. The carcinogenic risk is determined by the following relationship:

$$CR = CDI \times SF \quad \textbf{(5)}$$

where SF is the carcinogenic slope factor (µg.kg^{-1}.day^{-1}); the SF by water ingestion (SFin) was provided by the US EPA [18] and SF by skin absorption was calculated by SFd = SFin / ABSg.

The slope factor (SF) is a toxicity value that quantitatively defines the relationship between dose and response. The probabilities of potential carcinogenic effects that an individual will develop cancer over a lifetime of exposure are estimated from the projected intakes and the slope factor. Table 2 gives the values of the slope factor and RfD.

Table 2: Reference doses (RfD) and carcinogenicity factors (CSF)[3]**.**

Elements	As	Cd	Pb
SF (mg/kg/j)	1.5	260	8.5
RfD (µg/kg/j)	0.3	0.5	1.4

The different levels of risk according to the values of carcinogenic risk are shown in **table 3.**

Table 3: Risk according to cancer risk level[17]**.**

Cancer risk level	**Risk**
< 1.00E-06	Very low
1.00E-06 to 1.00E-05	Low
1.00E-05 to 1.00E-04	Medium
1.00E-04 to 1.00E-03	High
>1.00E-03	Very high

2.5. Assessment of sediment contamination

Geo-Accumulation Index (Igeo)

The geo-accumulation index (Igeo) is calculated using the following formula:

$$I = \log_2\left(\frac{C_n}{1.5 \times B_n}\right) \quad \textbf{(6)}$$

where, C_n is the measured concentration of the metal (n) in the sediment and B_n is the geochemical background of the metal (n). The factor 1.5 is used for the possible variations of the background data due to lithological variations. Seven classes of the geochemical index have been distinguished (**Table 4**).

Table 4: Level of contamination according to Igeo values[6,25]

Igeo Value	Contamination
Igeo ≤ 0	unpolluted
0 <Igeo< 1	unpolluted to moderately polluted
1 <Igeo< 2	moderately polluted

2 <Igeo< 3	moderately to heavily polluted
3 <Igeo< 4	heavily polluted
4 <Igeo< 5	heavily to extremely polluted
Igeo> 5	extremely polluted

Contamination Factor (CF)

The contamination factor CF is used to determine the level of metallic contamination in sediments. It is calculated using the relationship:

$$CF = \frac{C_{metal}}{C_{metal\ background}} \qquad (\mathbf{7})$$

With:

C_{metal}: concentration of the metal in the sediment; $C_{metal\ background}$: value of the geochemical background for the metal [4,6].

The different levels of contamination according to CF values are shown in table 5.

Table 5: Level of contamination according to CF values

CF Value	Contamination
CF < 1	Low contamination
1 ≤ CF < 3	moderate contamination
3 ≤ CF < 6	Considerable contamination
CF ≥ 6	High contamination

Pollution Load Index (PLI)

The Pollution Load Index (PLI) is used to estimate the overall degree of contamination of the sediments in the study area, based on the total concentration of all the metals studied. The following equation was developed by Tomlinson et al [26] to calculate the Pollution Load Index (PLI):

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n} \qquad (\mathbf{8})$$

Where: CFi: contamination factor for metal i.

The metal pollution index gives cumulative information on metal pollution in sediments. For PLI = 0, there is no deterioration; for PLI = 1, only reference levels of pollutants are present, and the value of PLI > 1 indicates progressive deterioration of the estuary.

Enrichment Factors

The EF has been proposed as a means of distinguishing anthropogenic inputs from natural sources. The enrichment factor is calculated from the following relationship:

$$EF = \frac{([X]/[R])sample}{([X]/[R])reference\ material} \qquad (\mathbf{9})$$

Where:

X: element studied; R: normalizing element.

In our study, iron was chosen as the normalizing element because of the following reasons: (1) Fe is associated with fine solid surfaces; (2) its geochemistry is similar to that of many trace metals, and (3) its natural concentration tends to be uniform. EF values were interpreted as suggested by Sakan et al., [27] in table 6.

Table 6: Level of enrichment according to EF values[27]

EF Value	Enrichment level
EF < 1	no enrichment
1< EF< 3	minor enrichment
3< EF< 5	moderate enrichment
5 < EF < 10	moderately severe enrichment

10 <EF< 25	severe enrichment
25 < EF <50	very severe enrichment
EF >50	extremely severe enrichment

2.6. Risk assessment in sediment

The ecological risk index (E_r^i) (**10**) was calculated to evaluate ecological risks of an individual metal [27]. The comprehensive potential ecological risk index (RI) (**11**) was calculated to evaluate harmful effects of all the measured trace metals and metalloids in the environment.

$$E_r^i = T_r^i \times \left(\frac{C_i}{C_0}\right) \qquad (\mathbf{10})$$

Following equation was used to calculate the risk index (RI) of sampling sites:

$$RI = \sum_{i=1}^{n} \left(T_r^i \times \frac{C_i}{C_0}\right) \qquad (\mathbf{11})$$

C_i is the concentration of metal *i* in the sediment, C_0 is the background concentration of metal *i* in the UCC given by Wedepohl (1995) [6]; T_r^i is the biological toxicity factor of an individual element, referring to [25]. T_r^i values for As = 10, Cu = Pb = 5, Zn = 1 and Cd = 30. RI is defined as the sum of E_r^i for all trace metals.[25]categorisedE_r^i and RI values into five and four potential ecological risk levels, respectively (Table 7).

Table 7: Level of ecological risk according to $E_r^i$and RI values[27]

E_r^i values	ecological risk level	RI value
$E_r^i < 40$	Low	RI<150
$40 \leq E_r^i < 80$	Moderate	150≤ RI < 300
$80 \leq E_r^i < 160$	Considerable	300 ≤ RI < 600
$160 \leq E_r^i < 320$	High	
$E_r^i \geq 320$	Very high	RI ≥ 600

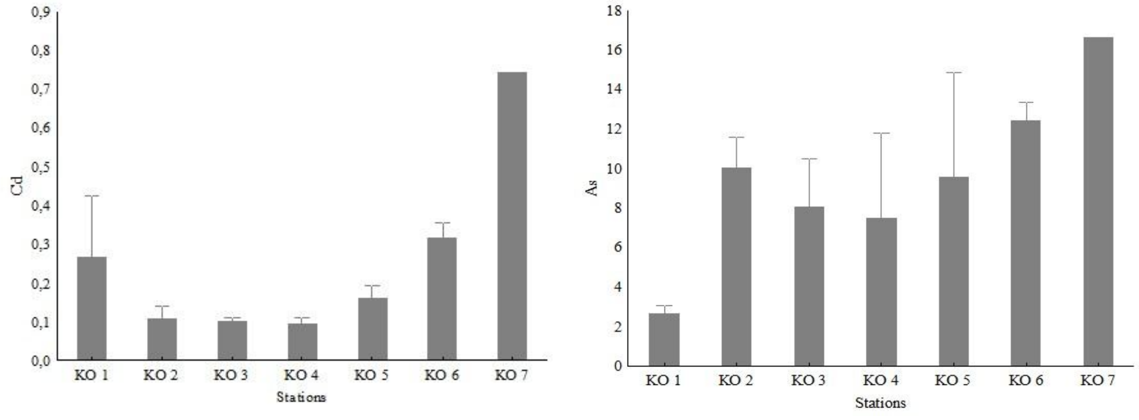
2.7. Statistical analyses

The One Way Analysis of variance (ANOVA) was performed to examine differences among the sites and the activity types. The pairwise multiple comparison procedures were performed using the Tukey Test when the tests of normality and equal variance were positive. The Kruskal-Wallis One Way Analysis of Variance on Ranks was performed when the equal variance test failed. The difference was considered statistically significant at $p < 0.05$. Statistical analyses were performed with Statistica 7.1 Software.

3. RESULTS AND DISCUSSION

3.1. Concentration of metals As, Cd, Cu, Pb and Zn in water

The variation of the total concentrations of the trace metals arsenic, cadmium, copper, lead and zinc (µg / L) in the Kossan River are presented in figure 2.



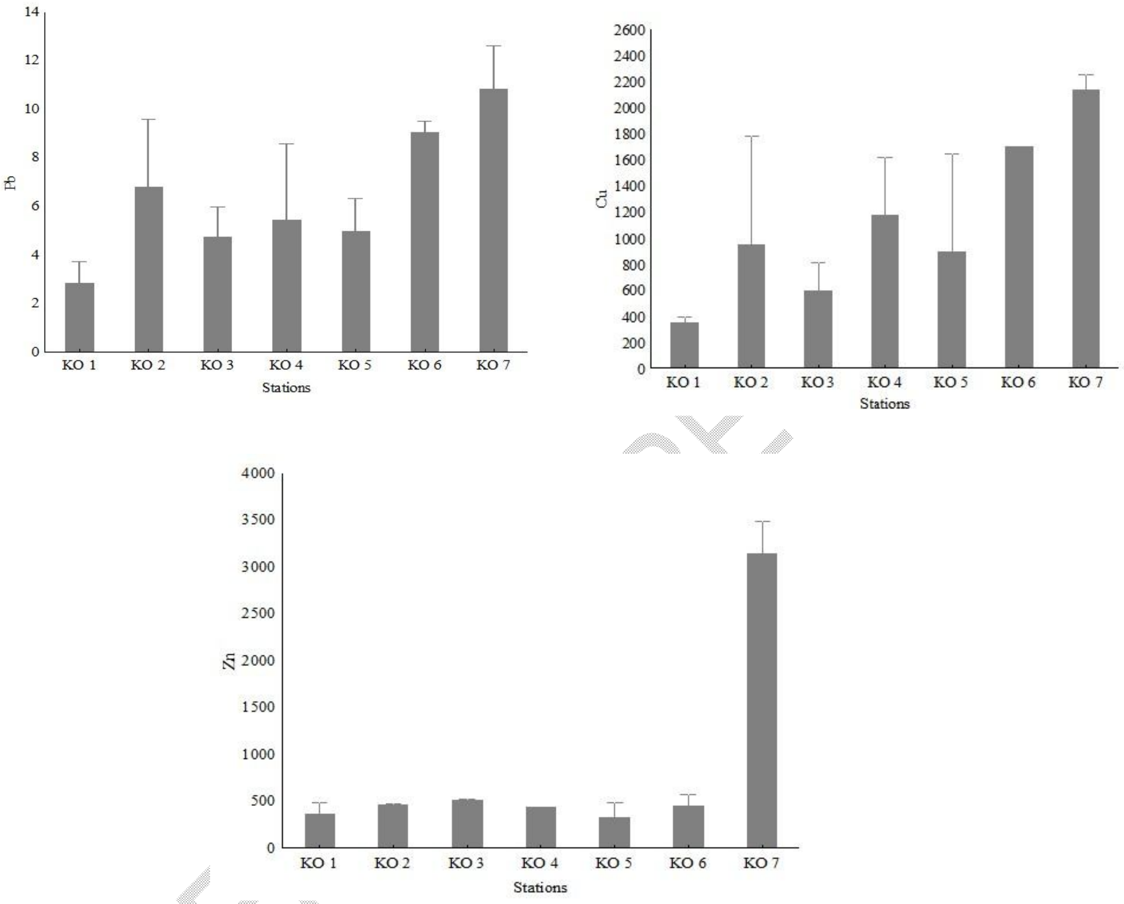


Figure 2. Location of sampling sites on the Kossan River

The results showed that the metals As, Cd, Cu, Pb and Zn were detected in the water samples taken.

Total arsenic concentrations in surface water ranged from 2.03 to 17.19 µg/L, with an average of 9.59 ± 5.50 µg/L. The order of contamination was as follows: KO1 < KO3 < KO4 < KO5 < KO2 < KO6 < KO7.

The spatial average of the total lead concentration in surface water ranged from 1.75 to 13.26 µg/L, with an average of 6.38 ± 3.55 µg/L. The order of contamination was as follows: KO1 < KO3 < KO5 < KO4 < KO2 < KO6 < KO7.

Total cadmium concentrations were not detected at all stations and ranged from nd to 0.77 µg/L with an average of 0.26 ± 0.24 µg/L. The order of contamination was as follows: KO4 < KO3 < KO2 < KO5 < KO1 < KO6 < KO7. The concentration of Cd varied significantly between station KO7 and stations KO1, KO2, KO3, KO4 and KO5 ($p = .05$).

The total spatial concentration of copper in surface waters ranged from 17.44 to 2369 µg/L with an average of 1111.68 ± 814.05 µg/L. The order of contamination was as follows: KO1 < KO3 < KO2 < KO5 < KO4 < KO6 < KO7.

The total spatial concentration of zinc in surface water ranged from 136.72 to 3669.37 µg/L, with an average of 813.57 ± 1014.91 µg/L. The order of contamination was as follows:
KO5 < KO1 < KO4 < KO6 < KO2 < KO3 < KO7. The concentration of Zn varied significantly between station KO7 and others stations (p = .05).

Overall, no trends were observed along the river, but the highest total concentrations were observed at stations KO6 near cocoa, coffee and rubber plantations and KO7 in the town of Alépé, a densely populated area. The concentrations measured may therefore be due to discharges from agricultural land via rainwater run-off [20,28]and domestic discharges. The study area has a high agricultural potential. Farmers, most of whom are illiterate, make excessive use of agricultural inputs such as pesticides and fertilizers to treat their plantations in order to obtain good yields. However, these inputs contain low concentrations of trace metals that end up in the environment. In urban areas, the riverbanks are used as dumping grounds by the local population, and the river also receives domestic wastewater directly. To these sources we must also add mining activities. Since the 2010s, illegal gold panning has expanded rapidly in the study area [6]. The wastewater from these mining activities contains cyanide and trace metals and is discharged directly into the river.

As most local communities use the river water for drinking, washing and cooking without any prior treatment, total concentrations were compared with [29] health standards. The results show that 41%, 29%, 0.07% and 0.07% of the samples taken had concentrations above the [29] limits for As, Pb, Cu and Zn respectively.

In general, the average concentrations of arsenic, cadmium, copper, lead and zinc measured in the surface water of the Kossan River were lower than the average concentrations observed in three main rivers in Côte d'Ivoire [6,30]. This can be explained by the fact that the Kossan River is a small river that drains a smaller area than the catchment areas of the major rivers, and the human activities carried out in its catchment area, although significant, are still less important than those carried out in the major rivers.As the Kossan River is a tributary of the Comoé River, the results show that this river is a major contributor to the pollution of the Comoé River.The state of contamination observed in the Kossan River and the health risks associated with trace metals highlight the urgent need for a river monitoring plan and research into the remediation of trace metals in Côte d'Ivoire's rivers. These remediation systems must be inexpensive and take into account the level of local populations.

The values measured in the waters of the Kossan River were lower than those found in the Ojo, Badagry, Gbaji and Challawa Rivers in Nigeria, in the Winongo river in Indonesia, but higher than those found in the Tafna river in Algeria [5,9,16,31].

3.2 Health risk assessment in water

The chronic daily intake (CDI)

The chronic daily intake calculated for all metals are showed in table 8.

Table 8:Chronic daily intake (CDI) for individual metals from consumption of water of Kossan River

Stations	CDI-ing					CDI-dermal				
	As	Pb	Cd	Cu	Zn	As	Pb	Cd	Cu	Zn
KO 1	0.09	0.09	0.01	11.57	11.84	4.5E-04	1.9E-03	4.6E-05	6.0E-02	3.7E-02
KO 2	0.33	0.22	0.00	31.24	15.19	1.7E-03	4.7E-03	1.8E-05	1.6E-01	4.8E-02
KO 3	0.26	0.16	0.00	19.39	17.01	1.4E-03	3.3E-03	1.7E-05	1.0E-01	5.3E-02
KO 4	0.25	0.18	0.00	38.77	14.49	1.3E-03	3.7E-03	1.6E-05	2.0E-01	4.5E-02
KO 5	0.32	0.16	0.01	29.25	10.69	1.6E-03	3.4E-03	2.8E-05	1.5E-01	3.3E-02
KO 6	0.41	0.30	0.01	55.99	15.02	2.1E-03	6.2E-03	5.5E-05	2.9E-01	4.7E-02
KO 7	0.51	0.35	0.02	67.15	70.40	2.7E-03	7.3E-03	8.9E-05	3.5E-01	2.2E-01

CDI values of metals in the three rivers varied between 0.00 and 70.40 µg/kg.day. The highest CDI values were obtained for Cu and Zn at station KO7. The mean values of CDI of trace metals concentrations were found in the order of Zn > Cu > As >Pb> Cd in River and CDI (Ing) > CDI (dermal). The values obtained show that the local population is exposed to trace metal contamination through ingestion and absorption.

Hazard Quotient (HQ)

The results of the non-carcinogenic risk of trace metals by the ingestion route (HQi) and by the dermatological route (HQd) in the waters of the River Kossan are presented in in table 9.

Table 9: Hazard quotients (HQ) for individual metals from consumption of water of Kossan River.

Stations	HQ-ing					HQ-dermal				
	As	Pb	Cd	Cu	Zn	As	Pb	Cd	Cu	Zn
KO 1	0.29	0.07	0.02	0.29	0.04	1.5E-03	1.4E-03	1.8E-03	7.5E-03	6.2E-04
KO 2	1.10	0.16	0.01	0.78	0.05	5.7E-03	3.3E-03	7.4E-04	2.0E-02	7.9E-04
KO 3	0.88	0.11	0.01	0.48	0.06	4.6E-03	2.3E-03	6.9E-04	1.3E-02	8.9E-04
KO 4	0.82	0.13	0.01	0.97	0.05	4.3E-03	2.7E-03	6.4E-04	2.5E-02	7.6E-04
KO 5	1.05	0.12	0.01	0.73	0.04	5.5E-03	2.4E-03	1.1E-03	1.9E-02	5.6E-04
KO 6	1.37	0.21	0.02	1.40	0.05	7.1E-03	4.4E-03	2.2E-03	3.7E-02	7.8E-04
KO 7	1.72	0.25	0.03	1.68	0.23	9.0E-03	5.2E-03	3.6E-03	4.4E-02	3.7E-03

The Hazard Quotient (HQ) index is used to assess the adverse effects on human health of exposure to trace metals other than cancer. HQ is used to understand the dangers posed by trace metals to various organs and systems in the human body, such as the respiratory system, liver, nervous system, kidneys, etc. Karki et al., (2024).

The HQi values for metals Cd, Pb and Zn are less than 1 in all samples for the three rivers.The HQ values obtained for Cu are greater than 1 in stations KO6 and KO7, close to 1 in stations KO2, KO4 and KO5 and less than 1 in stations KO1 and KO2. For arsenic, the HQi values obtained are greater than 1 in samples from stations KO2, KO5, KO6 and KO7, while they are close to 1 for stations KO3 and KO4. The HQd values calculated are all well below 1 for all elements.

The results obtained show that the consumption of untreated water from the river can expose the local population to illnesses caused by copper and arsenic. However, there is no health risk associated with dermatological exposure of the population for any of the metals studied [32–34].

Hazard Index (HI)

Figures 3 shows the HI values for oral intake and the dermal route of trace metals through the use of river water.

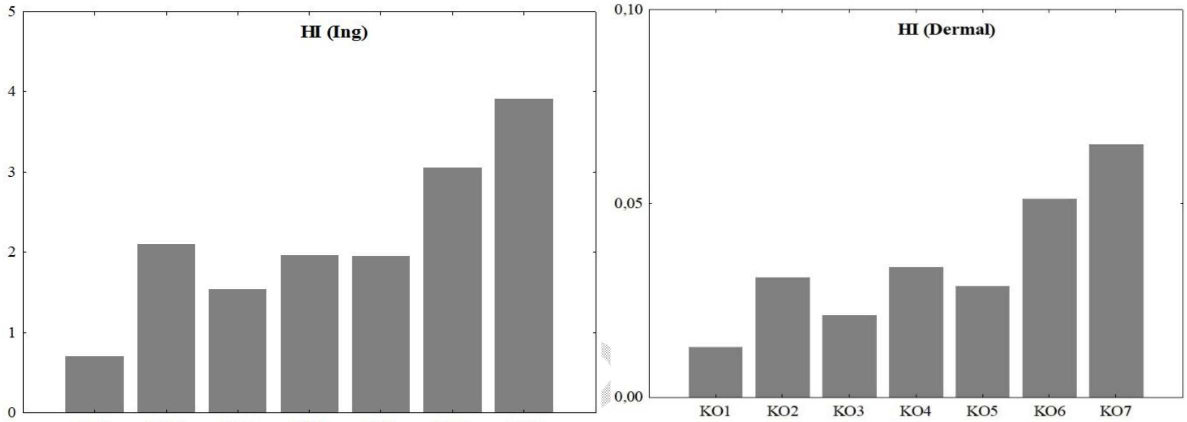


Figure 3. Hazard index ingestion (HI (Ing)) and dermal route (HI (Dermal)) in Kossan River

The HI values by ingestion found are higher than the limit suggested by USEPA [18] (HI = 1) for all samples except samples of station KO1. This suggests a risk of chronic contamination, and hence health problems for the population. Arsenic and copper are the major contributors to the non-carcinogenic risk of water ingestion by residents. While, the dermatological HI values for all trace metals are less than 1 in all station (Figure 3), indicating that there is no health risk to the population from prolonged skin contact with river water.

Taking into account their carcinogenic nature, we have assessed the carcinogenic risk associated with arsenic, lead and cadmium via the oral and cutaneous routes.

Carcinogenic risk assessment (CR)

The CR results are given in table 10.

Table 10. Carcinogenic risk of trace metals in Kossan River.

	CR (Ing)			CR (Dermal)		
Stations	**As**	**Cd**	**Pb**	**As**	**Cd**	**Pb**
KO 1	5.8E-05	1.4E-09	1.1E-05	3.0E-07	1.8E-10	2.3E-07
KO 2	2.2E-04	5.4E-10	2.6E-05	1.1E-06	7.1E-11	5.5E-07
KO 3	1.8E-04	5.1E-10	1.8E-05	9.2E-07	6.7E-11	3.8E-07
KO 4	1.6E-04	4.7E-10	2.1E-05	8.5E-07	6.2E-11	4.4E-07

KO 5	2.1E-04	8.1E-10	1.9E-05	1.1E-06	1.1E-10	4.0E-07
KO 6	2.7E-04	1.6E-09	3.5E-05	1.4E-06	2.1E-10	7.3E-07
KO 7	3.4E-04	2.6E-09	4.1E-05	1.8E-06	3.4E-10	8.6E-07

The CR (Ing) values calculated for cadmium (CR < 1.00E-06) showed that there is no carcinogenic risk in all surface water samples. For lead, the values (10^{-5}< CR < 10^{-4}) found show low risks of contracting cancer. Whereas the values observed for arsenic are higher than 10^{-4} all station except station KO1 where the value is range between 10^{-5} and 10^{-4}. There is therefore a high probability that an individual will develop cancer by ingesting water after a certain length of time at these stations.

3.3. Distribution of metals As, Cd, Cu, Pb and Zn in sediments

The concentrations of the metals arsenic cadmium, copper, zinc and lead in the sediments of the stations are summarised in table 11.

Table 11: Concentrations of metals As, Cd, Cu, Pb, Zn and Fe in sediments from the stationsµg/g

Site	As	Cd	Cu	Pb	Zn	Fe
KO1	1.63 ± 0.32	1.30 ± 0.18	3.70 ± 1.64	11.3 ± 1.28	22.2 ± 7.20	15048.5 ± 2118.5
KO2	3.90 ± 0.25	0.70 ± 0.22	2.50 ± 1.49	2.50 ± 1.27	5.40 ± 3.74	7353.7 ± 1074.45
KO3	1.10 ± 0.15	0.30 ± 0.25	6.00 ± 2.11	3.80 ± 1.32	10.1 ± 6.71	2951.5 ± 881.36
KO4	0.83 ± 0.31	0.22 ± 0.11	2.90 ± 1.44	2.30 ± 1.22	4.60 ± 2.02	3194.2 ± 1317.68
KO5	0.69 ± 0.21	0.13 ± 0.05	1.70 ± 0.82	2.10 ± 1.04	4.10 ± 1.91	2705.7 ± 1479.63
KO6	1.30 ± 0.68	0.40 ± 0.08	11.6 ± 3.60	4.20 ± 2.29	15.2 ± 4.81	3812.9 ± 2439.22
KO7	4.60 ± 0.80	5.00 ± 1.03	28.2 ± 6.07	6.90 ± 1.97	90.3 ± 17.85	59082.9 ± 3853.28
UCC	**2**	**0.102**	**14.3**	**17**	**52**	**30890**

Cd concentrations were well above pre-industrial upper continental crust (UCC) values [4] (0.102 µg/g Cd) at all stations. As concentrations were well above pre-industrial upper continental crust (UCC) in sediments of stations KO2 and KO7. Cu and Zn concentrations were well above pre-industrial upper continental crust (UCC) values [4] (14.3 µg/g Cu; 52 µg/g Zn) in all sediments from station KO7 (Alépé). These results suggest anthropogenic contamination of these metals. This accumulation may be due to local activities such as the use of herbicides and fertilisers and charcoal. In fact, fertilisers and herbicides are commonly used in this area to treat rubber tree nurseries. On the other hand, Pb concentrations were found to be lower than pre-industrial global UCC values, indicating that the main source is natural.Concentrations measured in the sediments of the River Kossan were found to be lower than concentrations measured in three main rivers in Côte d'Ivoire[35]. However, concentrations in the sediments were higher than concentrations found in the sediments of the riversOjo, Badagry, Gbaji and Challawa Rivers in Nigeria, in the Winongo river in Indonesia and in the TafnaRiver in Algeria.

3.4. Pollution assessment in river sediment of As, Cd, Cu, Pb and Zn

The results of Igeo, CF and EF are shown in table 12. The results indicate low to moderate arsenic contamination of sediments at stations KO2 and KO7 (0 <Igeo<1; 1 ≤ CF < 3), low to moderate copper and zinc contamination of sediments at station KO7 (0 <Igeo<1; 1 ≤ CF < 3) and very low lead contamination of sediments at all stations (Igeo< 0; 1 ≤ CF < 3). River sediment samples range from unpolluted to extremely polluted with arsenic (0 <Igeo< 6; 1 ≤ CF < 50). Sediments from the KO7 station show the highest levels of contamination (Igeo = 5.03; CF = 49.02). The calculated EF values show a high level of anthropogenic cadmium enrichment in all samples 14 ≤ EF < 32, minor level of anthropogenic arsenic enrichment in the samples from the KO1 and KO7, moderate enrichment at station KO4 and KO5 stations and moderately severe enrichment in the samples from the KO3, KO3 and KO6 stations. For copper, the results indicate a minor enrichment in sediment of stations KO4, KO5 and KO7, moderately severe enrichment in the sediment of the KO6 and moderate enrichment at station KO3. While for lead and zinc the results indicate a no to minor enrichment in the sediments.

Table 12: Contamination factor (CF), enrichment factor (EF) and geo-accumulation index (Igeo) of the sediment of the river.

Stations	EF					IGEO					CF				
	As	Cd	Cu	Pb	Zn	As	Cd	Cu	Pb	Zn	As	Cd	Cu	Pb	Zn
KO1	1.67	26.16	0.53	1.36	0.88	-0.88	3.09	-2.54	-1.17	-1.81	0.82	12.75	0.26	0.66	0.43
KO2	8.19	28.83	0.73	0.62	0.44	0.38	2.19	-3.10	-3.35	-3.85	1.95	6.86	0.17	0.15	0.10
KO3	5.76	30.78	4.39	2.34	2.03	-1.45	0.97	-1.84	-2.75	-2.95	0.55	2.94	0.42	0.22	0.19
KO4	4.01	20.86	1.96	1.31	0.86	-1.85	0.52	-2.89	-3.47	-4.08	0.42	2.16	0.20	0.14	0.09
KO5	3.94	14.55	1.36	1.41	0.90	-2.12	-0.24	-3.66	-3.60	-4.25	0.35	1.27	0.12	0.12	0.08
KO6	5.27	31.77	6.57	2.00	2.37	-1.21	1.39	-0.89	-2.60	-2.36	0.65	3.92	0.81	0.25	0.29
KO7	1.20	25.63	1.03	0.21	0.91	0.62	5.03	0.39	-1.89	0.21	2.30	49.02	1.97	0.41	1.74

From the spatial distribution on PLI in figure 4, the PLI values indicate gradual deterioration in sediment quality at station KO7.

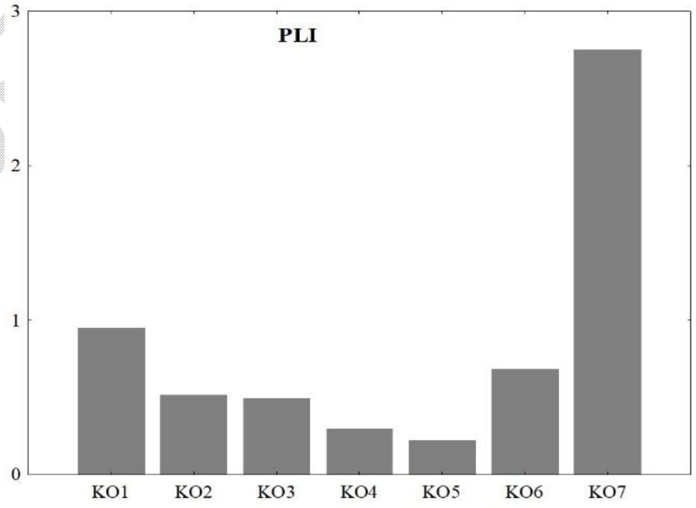


Figure 4. Pollution load index (PLI) of the sediment of the river

The values of the ecological risk index linked to sediments are presented in table 13. According to the results obtained, the degree of pollution of the Kossan River indicates a low ecological risk for all the metals studied except for cadmium. For cadmium, the Er values indicate very high ecological risks in the KO1 and KO7 stations, high risks in the KO2 station and moderate to considerable risks in the KO3, KO5 and KO6 stations.

Table 13: Potential ecological risk factor (E_r).

Stations	Er				
	As	Cd	Cu	Pb	Zn
KO1	8.15	382.35	1.29	3.32	0.43
KO2	19.50	205.88	0.87	0.74	0.10
KO3	5.50	88.24	2.10	1.12	0.19
KO4	4.15	64.71	1.01	0.68	0.09
KO5	3.45	38.24	0.59	0.62	0.08
KO6	6.50	117.65	4.06	1.24	0.29
KO7	23.00	1470.59	9.86	2.03	1.74

In addition, the results obtained from the Potential ecological risk index (RI) show a high ecological risk in the sediments of KO7, KO1 and KO2 (Figure 5). The RI values, ranked from highest to lowest, are as follows: KO7 > KO1 > KO2 > KO6 > KO3 > KO4 > KO5. The highest RI values were found at station KO4, located downstream near an area of intense mining, agricultural and charcoal-making activity.

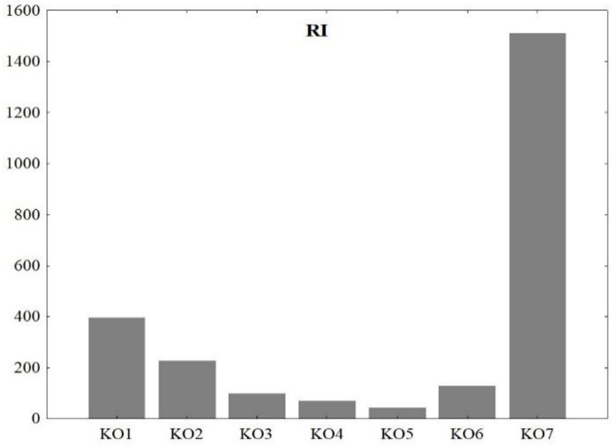


Figure 5. Potential ecological risk index (RI).

4. CONCLUSION

In this study, trace metal contamination in the water and sediment of the Kossan River was evaluated using spatial distribution, Hazard index (HI), cancer risk (CR), the enrichment factor (EF), the geo-accumulation index (Igeo), the contamination factor (CF), the loading pollution index (PLI), the ecological risk index (Er), and the potential risk index (RI). The results showed that trace metals As, Cu, Pb and Zn in the river water exceeded threshold values according to WHO at station KO7. The spatial distribution of trace metals in the water indicates that the concentrations in station located in the locality where domestic activities, illegal gold panning and farming are mixed together are higher than in the other locality. In sediments, the results of trace metal analysis and pollution assessment using EF, Igeo, CF, PLI and Er generally imply that the trace metal contamination from anthropogenic sources is very high for cadmium and low to moderate for all metal. The Er and the RI results indicate a low risk for all metal except for cadmium where the risk are high. Research into the risks associated with trace metals in Côte d'Ivoire, particularly in rural areas, has been limited, which is why this study has only limited information on the nature and age of the sediments. However, the sources of pollution of aquatic systems are generally similar, such as agricultural, domestic and mining activities. This study therefore completes a database on metal contamination of aquatic systems in Côte d'Ivoire.

Disclaimer (Artificial intelligence)

Option 1:

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc) and text-to-image generators have been used during writing or editing of manuscripts.

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