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Heavy Metal Pollution And Associated Health Implications Of The Yangtze River In Zhenjiang City, China.

Peter Kaba[1], Wanzhen Xu[1], Eric Gyimah[1], Weihong Huang [1,]*, Yunfei Cao[2], Xiaoni Ni[2,]*, Mansuur Husein[1]Samuel Atingabili[3]

[1] School of the Environment and Safety Engineering, Jiangsu University, Zhenjiang 212013, China
[2] Zhenjiang Food and Drug Supervision and Inspection Center, Zhenjiang 212004, China
[3]School of Management, Jiangsu University, Zhenjiang 212013, China
**Corresponding author*
Postal address: 301, Xuefu Road, Zhenjiang, Jiangsu Province, China

Abstract: *Water is a key factor of social and economic development, and therefore requires adequate policies for its sustainable use. Rapid industrialization, urbanization and agricultural advancements have led to contamination of precious resources with various contaminants such as heavy metals, which could pose several health problems in human beings. Anthropogenic activities are most likely to alter the natural composition of waters.Long-term exposure to heavy metals, even at low concentration, via different routes such as dermal and oral exposure of water may be detrimental to human health. Two pollution index assessment methods: Single-factor pollution index (Pi) and Nemerow' multi-factor Pollution Index (NPI) was employed to estimate the level of heavy metal pollution in the Yangtze river in Zhenjiang city. Dissolved and total metal pollution were analyzed, and the possible non-carcinogenic and carcinogenic health risks posed to a child and adult exposure. The results indicated that the non-carcinogenic health risk to humans by dermal and oral exposure to polluted water was relatively high as Pb and Cd recorded HQoral values of 1.27E+00 and 1.54E+00 for child and 1.09E+00 and 1.32E+00 for adult respectively which exceeds 1. Cancer risks of 2.30×10^{-2} and 3.57×10^{-6} were respectively recorded for a child and an adult oral exposure to dissolved Pb, suggesting a significant cancer effect observed in a child via oral exposure to dissolved Pb.*

Keywords: *Heavy metal, Water quality, Risk assessment, Hazard index, Single pollution Index, Nemerow multi pollution index*

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I. Introduction

Water is an essential element in human survival, ecological conservation and the growth of society [1, 2].Increased pollutant loads on surface areone of the topical problems of worldwide concern and this has led to about 1.2 billion people living in areas without adequate water supply, and it is estimated that a child dies of water-related diseases every minute[3]. Rapid urbanization, industrialization, and agricultural development have resulted in the pollution of essential water resources with various pollutants, such as heavy metals, pesticides, and detergents, etc. that are accountable for multiple human health issues [4]. Accumulation of heavy metals in aquatic biota has been observed over the past decades, posing a serious concern due to their adverse effects on human and wildlife health, especially in industrialized countries such as China.

Heavy metals such as cadmium (Cd) and lead (Pb) are considered systemic toxicants that are known to induce multiple organ damage even at trace levels (parts per billion, ppb) and can bioaccumulate in the main human body systems [5-7]; whereas chromium (Cr), nickel (Ni), copper (Cu), zinc (Zn), and manganese (Mn) are biologically significant metals under the WHO/FAO guidelines. Heavy metal pollution is covert, persistent and irreversible [8].Heavy metals and metalloids in groundwater and surface water are closely related to human healthand have been extensively studied worldwide in the past few decades [9-13]. Naturally, heavy metals exist in the environment through lithogenic processes including weathering and atmospheric deposition [14, 15]; however, anthropogenic activities such as land development, agriculture wastewater discharges, mining, manufacturing, and metal smelting are known to be potential sources of metal pollutionin surface water[16].

The human body can tolerate trace quantities of metals under normal conditions without having serious health issues. However, long-term exposure to heavy metals and metalloids at comparatively low levels can trigger elevated rates of accumulation of metals in the body, leading to body systems failure and ultimately death[17-19].An example isan excessive exposure to Pb, which is a nonessential element to the human bodythat could lead to damage ofthe nervous and immune systems [20].

The exploitation and utilization of these mineral resources have aidedChina in its socio-economic development. Notwithstanding the importance of mineral resources, mineral extraction has caused serious environmental damage, especially in relation to heavy metal pollution [21-23]. The Yangtze River is heavily disturbed by anthropogenic activities, with theconstruction of the world's largest hydroelectric project (Three Gorges Dam, TGD) at the west of the city of Yichang in Hubei province, as a typical example [24]. Furthermore, the Yangtze River plays a critical role in the economic development of China, supporting a population of 107million, irrigating approximately 15% of the agricultural land, and contributing 20% to China's gross domestic product[25]. The development of industry and agriculture has led to large amounts of pollutants discharged into the Yangtze River. The accelerated industrialization and urbanization coupled with economic reforms and population increases around the Yangtze river have greatly affected its water quality.The rate ofsewerage dischargeinto the Yangtze river is slowing down, because the government has increased energy saving and reduced emissions in the region, lessening the sewerage discharge in the basin[26].

Despite strict measures imposed by the Chinese government with regards to sewage discharge into the Yangtze river, the lack of sewage disposal equipment and effective management, water pollution has become more severe in midsized and small cities like Zhenjiang along the river. Zang Xiaopingthe Vice-director of the Yangtze River Water Resources Protection Bureau stated that "Water quality in Yangtze River is good, so please feel free to use or drink from it." [26].For this reason,the river serves as both drinking water and domestic use without proper treatment for people residing close to the river.

A lot of effort has been made toward thetreatment of natural river water by removing heavy metals for drinking purposesin the past decades.Variousmethods, such as flocculation, filtration, adsorption, flotation, phytoremediation,electrochemical treatment, membrane filtration, and chemicalprecipitation[27-29], have been used for heavy metal removal inriver waterfor drinking. Even though there is limited research on how heavy metals are removed from riverbodies, effective and efficient removal ofheavy metals using the above-mentioned treatment techniques in riverbodies is sparsely investigated.The objective of this studyis to assess thequality of waterby comparing it with the Chinese water quality standards and WHO standards since most of the people living close to the river use the river directly for their domestic needs and also serving as drinking water. Theestimation of metal levels(Cd, Cr, Cu, Ni, Pb, Zn, and Mn) from the Zhenjiang part of the Yantze River. Furthermore, the carcinogenic and non-carcinogenic health risks posed to both children and adults through ingestion and dermalexposure to analyzed total and dissolved metals from the Yangtze riverwere assessed.

II. Materials And Methods

Study Area

The Yangtze river, shown in Fig 1 is situated inJiangsu Province of China and serves as a source of potable water to proximate inhabitants as well as China at large. Also, water from the river is immensely used for irrigation and other agricultural purposes. Zhenjiang City is located in the southwestern part of Jiangsu Province, on the south bank of the lower reaches of the Yangtze River, 31°37′-32°19′ North Latitude, and 118°58′-119°58′ Longitude East[30]. The maximum straight-line distance from east to west is 95.5 kilometers, and the maximum straight-line distance from north to south is 76.9 kilometers.

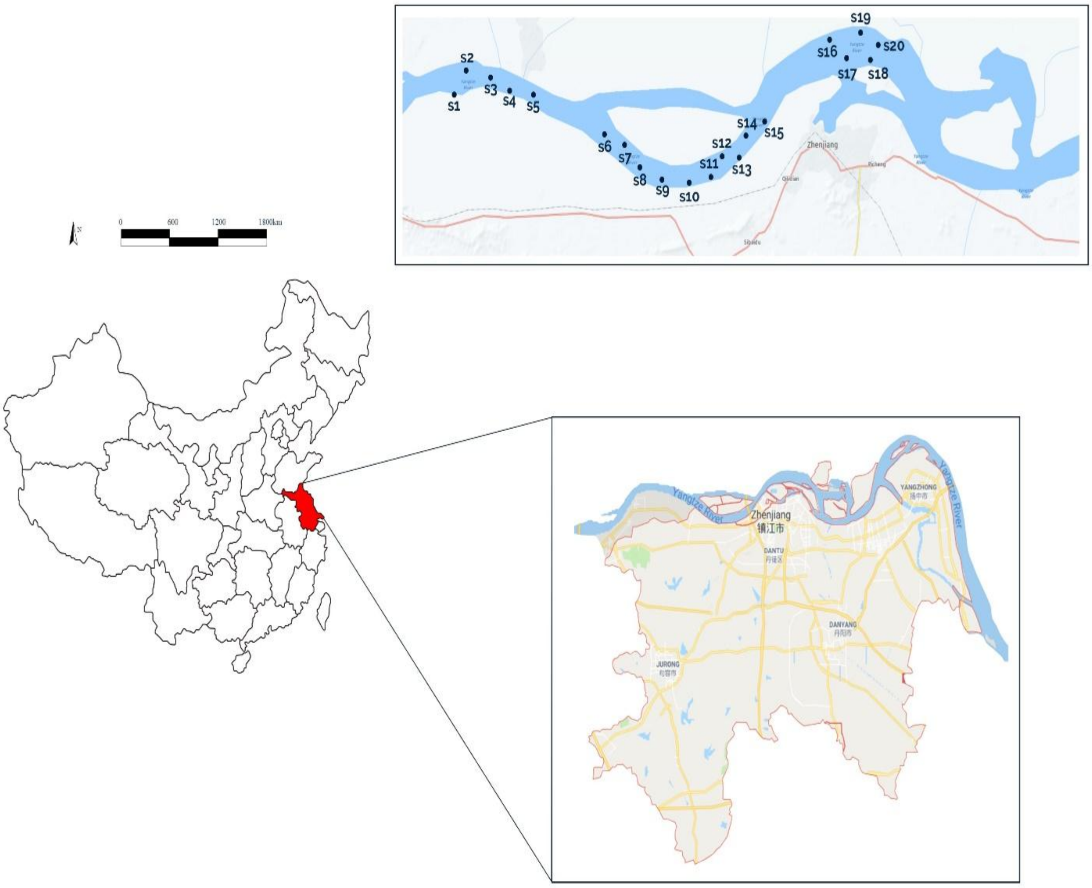

Fig. 1. Map showing the study area

The city's total land area is 3,847 square kilometers, accounting for 3.7% of the province [30]. There are high polluting industries (e.g. coal-fired plants, steel plants, electroplating factories, cement plants, and refineries) along the Yangtze River of Jiangsu province [31], which most of them discharge their wastewater into the river without proper treatment. This indicates that the Yangtze River has been suffering severe heavy metals pollution via anthropogenic activities.

Sampling and Sample Preparation

Field observations and water sample collection were conducted at the Yangtze river across the Zhenjiang city during the period from May 29^{th} to June12^{th}, 2019. Forty (40) water samples for heavy metal analysis were collected in 250ml acid-washed polyethylene bottles from three different sites of the Yangtze riverusing speed boat. The position of the sampling points was located using the geographical position system (GPS). The reason for the various sampling site is to have a water sample that represents the study area. Prior to sample collection, all bottles were soakedin20% $HNO_3$and then rinsed with distilled water. On the field, the bottles were rinsed three times with the river water and 200ml of water sample was then collected at about 10cm below the water surface. The water sample was divided into two portions for dissolved and total metal analysis. To the portion of total metal analysis,water sampleswere acidified with a concentration of 2ml of68% HNO_3solution to protect water samples from any fungal and other pathogenic attack and also to adjust the pH < 2 for estimation of contents of different metal ions[32]. Acidification also guaranteed that heavy metals did not get attached to the surface of the container during transportation [33]. For dissolved metal analysis, the water sampleswere filtered to remove suspended particles for acidification.Un-acidified portions of water samples were used for the determination of different Physico-chemical parameters. Water samples collected in a bottle were labeled separately with a unique identification number and were carefully transported in an ice chest to the laboratory of Environmental Science and Engineering at Jiangsu University, Zhenjiang for heavy metal analysis.

Digestion of Water Samples

In the laboratory, the bottles were kept in a clean, cool and dry place at 4ºC. A 50mL aliquot of a well-mixed acidified water sample was transferred into 100 mL Pyrex beakers for total metal analysis. 1 mL of concentrated HCl and 2 mL of concentrated HNO_3 werethen added to the aliquot in the beakers. The water samples were heated on a hot plate for evaporation until the volume reduced to about 30 mL. The digests wereallowed to cool to room temperature and then filtrated through acid-washed glass fiber filter (0.45mm, Whatman GF/C) using vacuum[34], to remove suspended particles, into 50 mL volumetric flasks. The solution was topped up with double distilled water to the mark. The digested samples were labeled and stored at 4°C for total metal analysis.

To the portion for the dissolved metals, 2mL HNO_3 was added to the filtered water samples to keep the metals in solution until analysis[32]. "A reagent blank was prepared following the same procedure. Measurements of concentrations Mn, Cd, Cr, Ni, Cu, Zn and Pb in water samples were determined using Atomic Absorption Spectrometer (ZEEnit 700 P Zeeman graphite tube furnace).

Heavy Metal

Atomic Absorption Spectrometer (ZEEnit 700 P Zeeman graphite tube furnace) was used to quantitatively examine the metal levels in the water samples. Blank and drift standards were run after every 20 determinations to maintain instrument calibration. Cathode lamps were set at wavelengths of 279.50 nm, 240.70 nm, 357.9 nm, 324.70 nm, 228.80 nm, 283.30 nm, and 213.90nm, respectively for Mn, Cr, Cu, Cd, Pb, Zn, and Ni estimations. Cd, Cr, Cu, Fe, Mn, Pband Zn lamp currents were set at 3.00mA, 4.00mA, 3.00mA, 4.00 mA, 2.00mA, 2.00mA, 4.00mA and 3.00 mA respectively.

Quality Assurance/ Quality Control

Taking into consideration the quality assurance, double distilled water was prepared to run through the instrument at regular intervals to clean the instrument to prevent any analyte from being trapped in the instrument[35]. Detection limits (DL) were determinedusing elemental standards in dilute aqueous solution. Each sample was measured three times.The detection limits (µg/g) ofPb, Cr, Cu, Mn, Cd, Zn and Ni were 0.001, 0.007, 0.004, 0.001, 0.001, 0.046, 0.004, respectively. Furthermore, ISE 999, certified reference material (CRM), for Pb, Cr, Cu, Mn, Cd, Zn and Ni concentrations was used for method validation.A good accuracy with relative standard deviation of ≤ 4% and a recoveryrate ranged from 85 to 105% was observed upon triplicate analysis of CRM. The regression coefficients for the calibration curves were approximately 1.0. All chemicals used in this study were of analytical reagent grade or higher purity ≥ 99%; Sigma–Aldrich Co. LLC, Shanghai, China, and all solutions were prepared using Milli-Q deionized water.

Statistical Analysis

Microsoft Office Excel 2019, Origin 2018 and SPSS Ver. 20.0 (SPSS Inc., Chicago, IL, USA) were all used for analyzing the data by applying different statistical methods. Descriptive analysis of various physicochemical parameters and contents of heavy metals in surface water samples (studied in triplicates) were performed to study central tendency (Mean) and standard error in the data. One-way analysis of variance (ANOVA) was used to study the variation among different variables site at $p \leq 0.05$.

Water Quality Assessment

The level of contamination of drinking water with heavy metal base on the Chinese surface water quality standard was determined using single factor and Nemerous multi-factor pollution indices. According to (GB 3838-2002) standards of Environmental Quality Standard for Surface Water China (China 2002), surface water bodies are classified from Class I to Class V, applicable to all usable surface waters within the territory of China. The indices estimate the quality of water from pollution by employing a contamination degree which ranges from clean to seriously polluted. The water quality parameters for WHO and Chinese surface water standards for heavy metals are clearly defined in table 2 with their respective values.

Table. 1 Standard surface water quality classification criteria for single factor pollution index and Nemerow Multi-factor Pollution Index.

Water quality grade	Clean	Slightly Polluted	Moderately polluted	Heavily polluted	Seriously polluted	Reference
GB (3838-2002)	Class 1	Class II	Class III	Class IV	Class V	[36]
Single Pollution Index	$P_i \leq 1$	$1 < P_i \leq 2$	$2 < P_i \leq 3$	$P_i > 3$		
Multi factor index	Pij≤0.7	0.7<Pij≤1	1<Pij≤2	2<Pij≤3	Pij>3	

Single-Factor Pollution Index

The single-factor assessment method is based on the principle of maximum membership grade. The model is relatively simple and can be used clearly to understand the relationship between the state of water quality and criteria for assessment [37, 38]. The single-factor index is defined as:

$P_i = \frac{C_i}{S_i}$….. Eq. 8

where P_i is the pollution index of a pollutant "i" according to [36], C_i is the measured concentration of the pollutant (mg/l) and S_i is the evaluation standard of i. The water quality factor Pi is classified into four grades, as listed in table1.

Nemerow Multi-factor Pollution Index

The Nemerow multi-factor index reflects the effect of each pollutant on sampled water and also highlights the influence of the high concentration pollutants on water environmental quality. The Nemerow multi-factor index distinguishes pollution degrees [39].

$$P_{ij} = \left\{\left[\left(\frac{MaxC_i}{S_{ij}}\right)^2 + \left(\frac{1}{n}\sum\frac{C_i}{S_{ij}}\right)^2\right] \times 0.5\right\}^{0.5} \text{ ….. Eq. 9}$$

Where *j* is the number of functional area, *i*, the kinds of heavy metal elements, *Ci* is measured concentration of *i*, S_{ij}, Chinese water quality standard value, and *n* is the total number of kinds of heavy (n=7). The Nemerow multi-factor index is divided into 5 levels, to indicate the pollution degree from none to heavy pollution [39] as shown in table 1.

Table. 2. Water Quality Parameters Standards

Metals	Chinese Standards	WHO Standards
Pb	10	10
Ni	20	70
Cd	1	3
Zn	50	100
Mn	100	500
Cr	10	50
Cu	10	2000

Surface water quality standard (GB3838-2002) class I in China[36]
Guidelines for drinking-water quality, 2011. World Health Organization (WHO)[40]

Health Risk Assessment

In this study risk assessment was estimated for both dissolved and total metals concentrations via oral and dermal exposure. Exposure assessments of analyzed metals to human health through oral and dermal routes were estimated for children and adults according to guidelines proposed by the Environmental Protection Agency, United States, (USEPA, 2004)[41, 42]. For risk characterization, non-carcinogenic and carcinogenic models were applied to estimate the possible health effect on humans via oral and dermal exposure.

$$ADD_{ingest} = \frac{C \times IR \times ABS_{GI} \times ED \times EF}{BW \times AT} \text{…...Eq. 1}$$

$$ADD_{dermal} = \frac{C \times SA \times K_P \times EF \times ED \times ET \times 10^{-3}}{BW \times AT} \text{……Eq. 2}$$

Where Average daily dose (ADD) provides the average of exposure or doses by dermal and oral over the exposure time estimated in µg/g/day; C, the average concentration of heavy metals in water samples (µg/L) from the Yangtze river; IR is drinking water intake rate or water ingestion rate (L/day); BW is the average body weight of both Child and Adult (Kg); ED, exposure duration; EF, exposure frequency; ET, exposure time; ABS_{GI}, gastrointestinal absorption factor (unitless); SA, Skin surface area; Kp, dermal permeability coefficient in water;Their respective parameter values are clearly defined in table 3.

Table 3 Parameter values for health risk assessment.

Parameter	Unit	Child	Adult
Ingestion rate (IR)	L/day	1	2
Body weight (BW)	kg	15	70
Skin surface area (SA)	cm^2	6,600	18,000
Exposure time (ET)	h/day	1	0.58
Exposure frequency (EF)	days/years	6	30
Exposure duration (ED)	years		
Average time (AT):			
For carcinogenic		365×70	365×70
For Non carcinogenic		365×ED	365×ED

Non-carcinogenic Effect

The non-carcinogenic risks were determined by evaluating the hazard quotients (HQ) and the hazard index (HI) in Eqn. 3 and Eq. 4. HQ is a dimensionless quantity, expresses the probability of an individual suffering a non-cancer effect upon exposure to the metal. HQ is defined as the ratio of exposure levels or ADD of analyzed metals in a sample to the reference dose (RfD). RfD is considered to be a safe level of exposure over a lifetime.

$HQ = \frac{ADD}{RfD}$…Eq. 3

$HI = \sum_{i=1}^{n} HQi$…Eq. 4

The estimation of HQ of dermal exposure (HQderm), was done by converting RfDo into dermal reference dose (RfDderm) following the equation proposed by [43] as shown in equation 5.

$RfD_{dermal} = RfD_{oral} \times ABS_{GI}$….Eq. 5

Where RfDo is the oral reference dose (µg/g/day) of the metal. The risk is unacceptable if HQ > 1 while it is acceptable for HQ < 1. This implies that the estimated ADD is greater than the recommended reference dose, hence might be of significant concern to non-carcinogenic effect to consumers [44]. If the HQ of metal exceeds 1, it implies its estimated ADD is greater than the recommendedreference dose, hence might be of significant concern to non-carcinogenic effect to consumers. For more than one possible route of exposure to a metal, the resultant potential non-cancerouseffect posed could be estimated using the hazard index (HI) which sums the HQs of metal from all applicable pathways as shown in the equation 4.

HQi represents the hazard quotient for the ith metal for an exposure route; “n”, the number of possible routes. HI > 1 denotes that the non-carcinogenic adverse effect of the contaminant should be investigated further whereas HI ≤ 1 denotes that the chemical can be screened out without further investigation for its adverse effect of the exposed population.

Table 4 Oral and dermal exposure used for health risk assessment.

	RfD dermal	**Kp (cm/hr)**	**RfD oral**	**Carcinogen**	**ABS_{Gi}**
Pb	1.40E-04	1.00E-04	1.40E-03	0.0085	0.1
Ni	8.00E-04	2.00E-04	2.00E-02	1.7	0.04
Cd	2.50E-05	1.00E-03	5.00E-04		0.05
Zn	3.00E-01	6.00E-04	3.00E-01		1
Mn	5.60E-03	1.00E-03	1.40E-01		0.04
Cr	7.50E-05	1.00E-03	3.00E-03	0.5	0.025
Cu	2.85E-03	1.00E-03	5.00E-03		0.57

RfD(dermal) were estimated values. ABSGI, gastrointestinal absorption factor; KP, dermal permeability coefficient in water; RfD (oral) were values according to [43, 45];

Carcinogenic Effect

Carcinogenic risk assessment estimates the incremental probability of an individual developing an effect of cancer over a lifetime due to exposure to a potential carcinogen [46] in water. Cancer risks indicate the probability of a population developing any type of cancer due to the intake of the carcinogens.Cancer risks were calculated based on the USEPA human risk assessment model.

In this assessment, a cancer slope factor (*CSF*) according to the USEPA (2004) was used to convert the estimated ADD of the metal over a lifetime exposure to the risk of individual developing cancer as shown in table 4. The USEPA equation for cancer risk assessment used in the study is shown in Equation 6.

$CR = ADD \times CSF$…...Eq. 6

Where CR is the cancer risk factor, ADD (µg/g/day) is the average daily dose and CSF (µg/g/day) is the oral cancer slope factor. For dermal cancer risk, the CSF was derived according to the USEPA (2004) equation given for the absorbed slope factor.

$CSF_{ABS} = \frac{CSF_O}{ABS_{GI}}$…Eq. 7

Where CSF_{ABS} is the absorbed slope factor $(mg/kg\text{-}day)^{-1}$; CSF_O is the oral slope factor $(mg/kg\text{-}day)^{-1}$; ABSGI is the fraction of contaminant absorbed in the gastrointestinaltract (unitless) with their respective clearly shown in table 4. The USEPA (2012) provides the oral slope factor for Pb, Cd, and Ni only of all the metals analyzed in this study. Therefore, the dermal carcinogenic risks were estimated for these metals(metalloids) for both children and adults’ exposures. The recommended value based on USEPA (2004) for a tolerable range of carcinogenic risks is 10^{-4} to 10^{-6}.

III. Result And Discussion

Concentration of Heavy Metal in Yangtze River

The fig. 2 shows the average concentrations of dissolved and total metal concentration in water samples collected from the 3 sampling sites of the Yangtze river in Zhenjiang city. The mean concentrations of Total metal in water samples were in decreasing order of Ni>Zn>Mn>Cu>Pb>Cd>Cr, whereas dissolve metal levels recorded were in decreasing order of Ni>Zn>Mn>Cu>Cd>Pb>Cr. For all analyzed samples, the levels of total metal did not differ significantly from the dissolved metal concentrations, except for that recorded for Pb (F = 5.187, p = 0.028) using the independent sample test. Inference from our results is that, the sediment of the Yangtze River could be enriched with Pb.[47] recorded an average concentration of 51.01mg/kg of Pb in surface sediment in Yangtze river, which exceeds the background value of 25.00mg/kg. According to the safe water standards defined by the World Health Organization (WHO) and China's surface water quality standard (GB3838-2002), the concentration of heavy metals, both for the dissolve and total,recorded for the Yangtze River was generally below the maximum contaminant limit set by these institutions[36, 48].

In respect of the studied heavy metals in water samples, Ni recorded the maximum concentration of 12.95µg/L, whereas0.057 µg/L was also estimated for Pb as the minimum concentration among the 20 sites for total metal analysis.The average concentration of total Pb in the Yangtze river was found to be 0.53µg/L, whereas the average dissolve concentration was 0.34 µg/L.The maximum concentration recorded for Pb was (1.087µg/L) for total metal and the lowest concentration was found (0.034µg/L) at S3 for dissolved metal in the study area.However, levels of Pb in the water samples in this study were found to be significantly lower than that recorded by [49] in water from Kilimambogo, Kenya and similar to what was recorded by [50]for dissolved Pb of 0.47µg/L on the surface layer of the Yellow River. Pb is a nonessential metal and it can affect the gastrointestinal tracts, kidney, and central nervous system via the exposure routes. Again, it breaks the blood-brain barrier and interferes with the normal development of the brain in an infant [51].

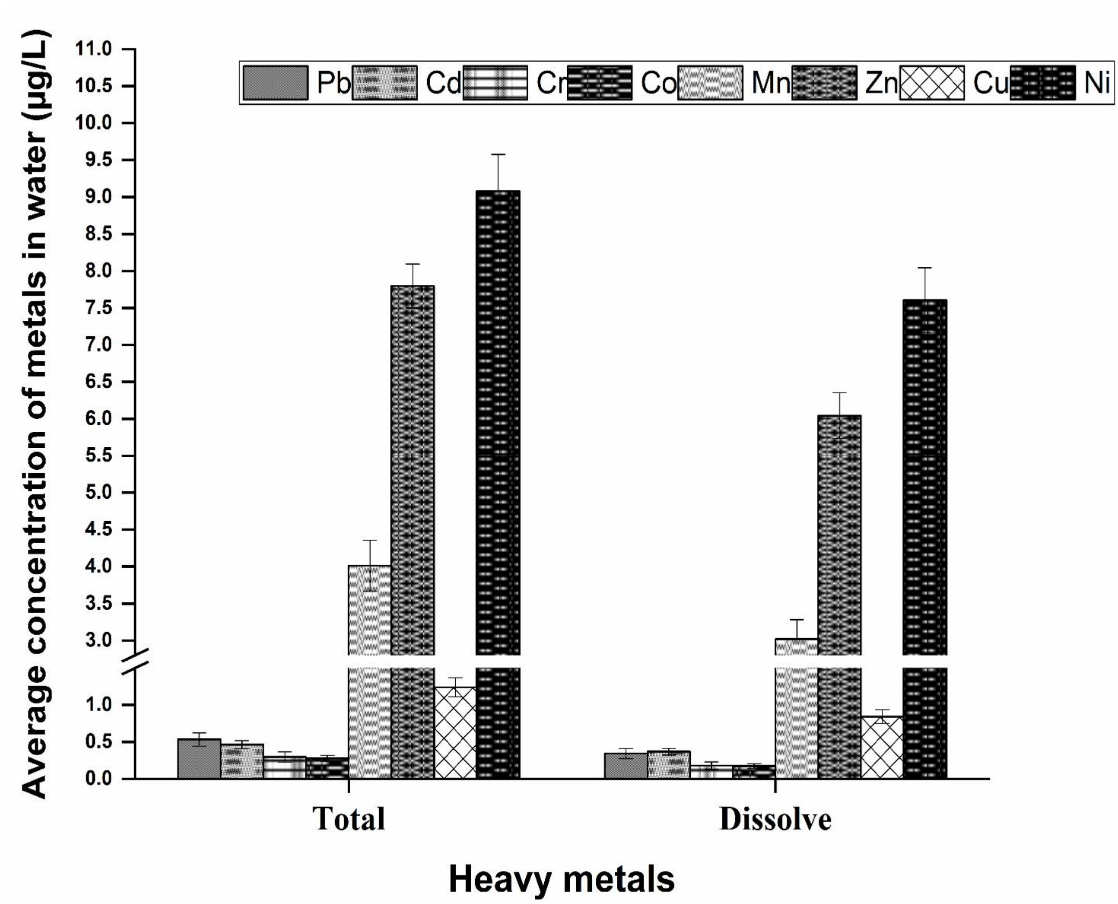

Fig. 2 The average concentration of heavy metal in both Total and Dissolved state.

The mean concentration of Cd was0.46µg/L and 0.37µg/L for both total and dissolved metal with an average concentration of 0.41485µg/Lwhich exceeded the range of 0.01 to 0.064µg/L forCd concentration reported by Koto, et al. [52] at Karavasta Lagoon in Albania.S14 recorded the maximum Cd concentration of 0.83µg/L for total metal, whereas S12 had a minimum Cd concentration of 0.106µg/L for dissolved metal.

Mn recorded an average concentration of 4.0128µg/L and 3.01935µg/L for total and dissolved metal respectively in the water samples.For total metal analysis, Mn recorded a range value of 1.523 µg/L -7.212µg/L, whereas a range value of 1.033µg/L - 4.822µg/Lwas also recorded for dissolved metal analysis, which is similar to the range values (4.3µg/L-8.8µg/L) reported by Wu, et al. [53] of heavy metal pollution in surface water from the Yangtze River in Nanjing section. The average concentration of Mn was within the regulatory limit set by USEPA, WHO, and Chinese surface water standards.

Furthermore, Zn recorded maximum value of 9.95µg/L and a minimum value of 5.341µg/L for total metal for total metal and also a maximum value of 7.954µg/L and a minimum value of3.883µg/L was estimated for dissolved metal.High levels of Ni and Zn reported in water in this study could be traced to the activities of the agricultural activities and citing of industries close to the study area.The concentration of these metals in the water sample calls for a critical evaluation of the most consumed fish samples in the Yangtze river due to the high possibility of bioaccumulation of these metals in their tissues and other parts.

Water Quality

Table 5shows the single factor pollution index (P_i) and the Numerous pollution index (P_{ij}) of the selected heavy metals of the studied sites in reference to Chinese surface water quality criteria [36]. Generally, it was observed that heavy metals of varying concentrations were detected in the various water samples in the study area, and all the measured metals including Pb, Cd, Cr, Mn, Zu, Cu, and Ni were all at a safe level based on the water quality classification in table 3. Also, there was generally no significant variation in the concentration of the parameters in all the studied sites. A comparison of the concentration of the heavy metals with the [48] guideline values for drinking water showed most of the metals were below acceptable limits.

The highest Pi value for the various site was, site A (0.5243), site B (0.4717) and site C (0.5172) for Ni, Cd, and Cd respectively using Eq. 6 as stated aboveand based on the water quality classification indicated in Table 2. Cr recorded the lowest Pi of 0.02546 at site A.Rivers are highly susceptible to contamination due to due to lithogenic and anthropogenic activities such as sewage and industrial discharge, and agricultural runoff among water bodies[54].

Table 5 The Single Factor Pollution Index (Pi) and The Nemerow' Pollution Index of the three selected Sites on the Zhenjiang part of the Yangtze River.

	SITE A				SITE B				SITE C			
METALS	Ci	S_i	P_i	Pollution grades	Ci	Si	P_i	Pollution grades	Ci	Si	P_i	Pollution grades
Pb	7.36E-01	1.00E+01	7.36E-02	1	4.82E-01	1.00E+01	4.82E-02	1	4.33E-01	1.00E+01	4.33E-02	1
Cd	3.89E-01	1.00E+00	3.89E-01	1	4.72E-01	1.00E+00	4.72E-01	1	5.17E-01	1.00E+00	5.17E-01	1
Cr	2.55E-01	1.00E+01	2.55E-02	1	2.99E-01	1.00E+01	2.99E-02	1	3.33E-01	1.00E+01	3.33E-02	1
Mn	2.74E+00	1.00E+02	2.74E-02	1	4.54E+00	1.00E+02	4.54E-02	1	4.23E+00	1.00E+02	4.23E-02	1
Zn	8.16E+00	5.00E+01	1.63E-01	1	7.30E+00	5.00E+01	1.46E-01	1	8.42E+00	5.00E+01	1.68E-01	1
Cu	1.09E+00	1.00E+01	1.09E-01	1	1.24E+00	1.00E+01	1.24E-01	1	1.38E+00	1.00E+01	1.38E-01	1
Ni	1.05E+01	2.00E+01	5.24E-01	1	7.80E+00	2.00E+01	3.90E-01	1	1.03E+01	2.00E+01	5.13E-01	1
NPI			0.39369	1			0.30340	1			0.39123	1

Health Risk Assessment

Non- carcinogenic Risk

The non-carcinogenic risks for Pb, Cd, Cr, Mn, Zu, Cu, and Ni exposure were determined by evaluating the hazard quotients and hazard indices for adults and children. The meanconcentration each for dissolved and total metal in water samples were also used to estimate the average daily dose (ADD) for both oral and dermal routes of exposure in children and adults. The oral reference dose (RfDo) of respective metalwas used to calculate the hazard quotients of ingestion exposure (HQoral) to which humans are constantly exposed over a lifetime without considerable risk of carcinogenic effects.

According to the results, ADD for adult's oral exposure to total metal wasbelow their respective RfDs, except forZn, Cu, and Ni which recorded2.60E-01, 2.35E-02,and 1.21E-02 (RfDs values of 3.00E-01, 5.00E-03 and 2.00E-02 respectively). However, the ADDfor a child dermal exposure to total metal (Cd, Cr, Mn, and Ni) exceeded the respective RfDs; except for Pb, Zn, and Cu which were estimated to be 2.34E-05, 2.06E-03, and 5.44E-04 respectively.The estimated ADD value of both adult and child exposure to dissolved metals were below their respective RfDs except for Cr (2.65E-05), Ni (2.27E-04) recorded for adults; Cd (1.62E-04), Mn (1.33E-03) and Ni (6.69E-04) recorded for a child upon dermal exposures. For oral exposure, Zn (2.23E-01), Cu (2.01E-02) and Ni (1.04E-02) for adults recorded ADD values above their RfDo value for total metal as shown in table 6. Whereas, adults ADD values were below their respective RfDo except for Cu (1.37E-02) which recorded ADD above its RfDo via oral exposure.

The estimated results of this study indicate potential non-carcinogenic health risksvia oral and dermal exposure ofthe average daily intake of these metals.

Table 6 Average daily dose (ADD); µg/g/day of dissolved and total metals for carcinogenic and Non-carcinogenic risk assessment.

		Non-carcenogenic				Cancer risk			
		ADDoral (µg/g/day)		ADDderm (µg/g/day		ADDoral (µg/g/day)		ADDderm (µg/g/day)	
Total	Metal	Child	Adult	Child	Adult	Child	Adult	Child	Adult
	Pb	1.78E-03	1.52E-03	2.34E-05	7.95E-06	3.05E-04	6.53E-04	2.01E-06	3.41E-06
	Cd	7.71E-04	6.60E-04	2.03E-04*	6.89E-05	1.32E-04	2.83E-04	1.74E-05	2.95E-05
	Cr	2.47E-04	2.12E-04	1.30E-04*	4.42E-05*	4.23E-05	9.07E-05	1.12E-05	1.89E-05
	Mn	5.35E-03	4.59E-03	1.77E-03*	5.98E-04	9.17E-04	1.97E-03	1.51E-04	2.56E-04
	Zn	2.60E-01*	2.23E-01*	2.06E-03	6.98E-04	4.45E-02	9.55E-02	1.76E-04	2.99E-04
	Cu	2.35E-02*	2.01E-02*	5.44E-04	1.84E-04*	4.03E-03	8.63E-03	4.66E-05	7.91E-05
	Ni	1.21E-02*	1.04E-02*	7.99E-04*	2.71E-04	2.08E-03	4.45E-03	6.85E-05	1.16E-04
CR									
	Pb					3.58E-02	7.68E-02	2.36E-04	4.01E-04
	Cr					8.46E-05	1.81E-04	2.23E-05	3.79E-05
	Ni					1.22E-03	2.62E-03	4.03E-05	6.83E-05
Dissolve	Pb	1.14E-03*	9.79E-04	1.51E-05	5.11E-06	1.96E-04	4.19E-04	1.29E-06	2.19E-06
	Cd	6.12E-04	5.25E-04	1.62E-04*	5.48E-05	1.05E-04	2.25E-04	1.39E-05	2.35E-05
	Cr	1.48E-04	1.27E-04	7.80E-05	2.65E-05*	2.53E-05	5.43E-05	6.69E-06	1.13E-05
	Mn	4.03E-03	3.45E-03	1.33E-03*	4.50E-04	6.90E-04	1.48E-03	1.14E-04	1.93E-04
	Zn	2.01E-01*	1.73E-01*	1.60E-03	5.41E-04	3.45E-02	7.40E-02	1.37E-04	2.32E-04
	Cu	1.60E-02*	1.37E-02*	3.70E-04	1.26E-04	2.74E-03	5.88E-03	3.18E-05	5.38E-05
	Ni	1.01E-02*	8.69E-03	6.69E-04	2.27E-04*	1.74E-03	3.72E-03	5.74E-05	9.72E-05
CR									
	Pb					2.30E-02	3.57E-06	1.52E-04	2.58E-04
	Cr					5.07E-05	1.09E-04	1.34E-05	2.27E-05
	Ni					1.02E-03	2.19E-03	3.37E-05	5.72E-05

Among the non-carcinogenic risk, children recorded the highest HQ value through dermal exposure to total Cd. Figure 3 and 4 show the estimated hazard quotients (HQoral and HQderm) and hazard indices (HI) for child and adult exposures to both dissolve and total metal levels respectively.The HQderm values for adult and child exposure to both total and dissolved metals were all < 1 except Cd which had HQ value >1. Dermal exposure to total Cd estimated an HQ value of 8.14E+00 for child whereas an HQ value of 2.76E+00 was also estimated for adults through dermal exposure to total Cd in water from the Yangtze River. Dissolved Cd and Cu also recorded HQoral value of 1.22E+00 and 3.20E+00 fora child, and 1.05E+00 and 2.74E+00 for adults respectively, exceeding HQ value of 1. Zn and Mn HQ values did not exceed 1 for both exposure route and were similar to HQ values reported by [55]. The estimation of the individual HQs values was >1 indicating possible health risk from the consumption of water from the Yangtze River.

HI values were estimated for child and adult on the basis of dissolved and total metals/ metalloids. It is noteworthy mentioning that HI > 1 was recorded for child (1.98E+01), adult (1.17E+01) for total metal and child (1.46E+01), adult (7.98E+00) for dissolved metals respectively. This shows a probability of non-cancer risk to consumers as shown in figure 4.

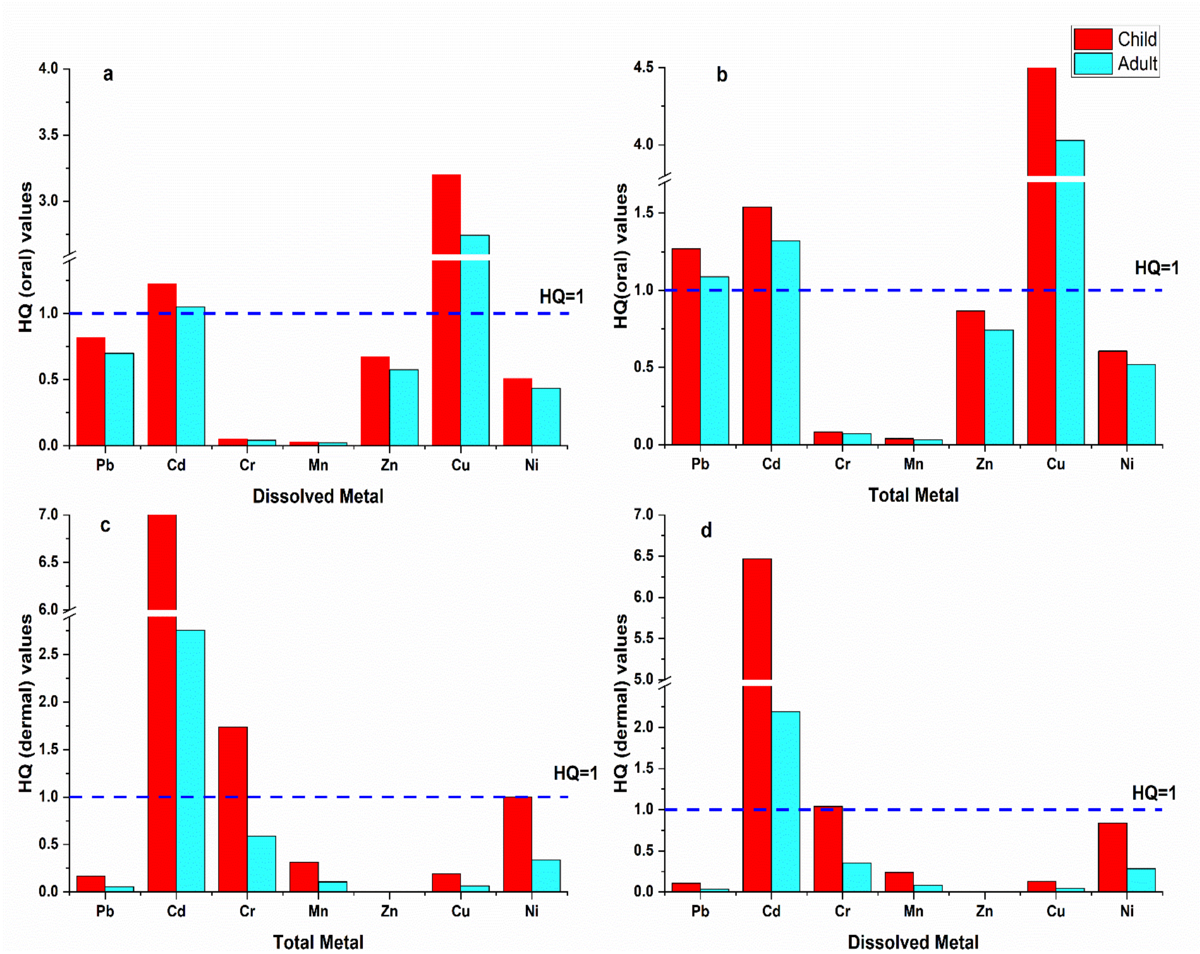

Fig. 3 Hazard quotient (HQ) values of dissolved and total metals to child and adult via their respective exposure route

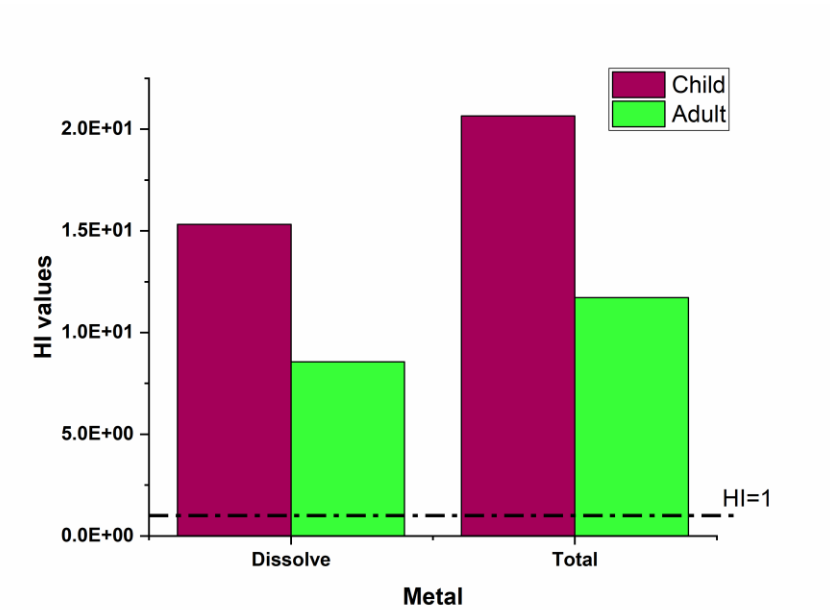

Fig. 4 HI values of studied metals for Child and Adult

Carcinogenic Risk

The average daily dose of child and adult for oral and dermal exposure to dissolved and total metals was calculated for both child and adult using the Average time for carcinogenicity as shown in Table 5.Carcinogenic risks were calculated for Pb, Cr and Ni in water from the Yangtze river using the cancer slope factor of 0.0085, 0.5 and 1.7 respectively as proposed by USEPA for both adult and child and the results are presented in Table 5. The cancer risks for childand adults via dermal exposures to total and dissolved Pb, Cr, and Ni in water from the Yangtze River were within the USEPA set range of 10^{-4} to 10^{-6} as reported in table 2.

Carcinogenic health risk for a child oral exposure to dissolve Pb and Ni are 0.023 and 0.00102 respectively and that for total Pb and Ni are 0.0358 and 0.00122 respectively. Moreover, the cancer health risk for adult oral exposure to dissolve Ni was 0.00219 and that for total Pb and Ni are 0.0768 and 0.0026 respectively. Thus, the carcinogenic health risk of Pb and Ni oral exposure for both child and adult were higher than the maximum acceptable level of 1.0×10^{-4} recommended by [56].

IV. Conclusion

Ultimately, in the current study, HQ values estimated for individual metals show non-cancer effects for children and adults exposure to both dissolved and total Mn and Zn via the possible routes for both oral and dermal. However, HI values, which were also estimated for total and dissolvedmetals for both dermal and oral exposure were all > 1 for both adult and child, which denotes that the non-carcinogenic adverse effect of the contaminant should be investigated. This research will provide an important reference for the management of the Yangtze River and its uses (Irrigational, industrial activities, potable water, etc.) in the Zhenjiang city. Government regulators must take pragmatic steps to address heavymetal pollution generated byanthropogenic activities as well as the related health risks associated with industrial development. We recommend that efficient control of pollution sources and strict enforcement of environmental regulations, especially in terms of waste discharge and application of pesticides in farms, as an effective approach of mitigating heavy metal pollution in the surface water.

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

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