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ORIGINAL ARTICLE

Exploring Health Risks Associated with Heavy Metal Contamination in Groundwater from Industrial Zones in Samut Prakan Province, Thailand

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KEYWORDS

Health risk assessment; Contamination; Heavy metals; Groundwater **ABSTRACT:** Groundwater in industrial zones is often contaminated with heavy metals, posing significant health risks. This study investigates the contamination of arsenic, nickel, lead, and zinc in groundwater from the Bangkok, Phra Pradaeng, Nakhon Luang, and Nonthaburi aquifers and assesses the health risks associated with heavy metal contamination in groundwater within Samut Prakan Province. Groundwater samples were collected from observation wells (n=16) and analyzed for dissolved heavy metals using USEPA 200.7 and 6010D standard methods. Health risks were assessed for both non-carcinogenic and carcinogenic effects using USEPA models. The results showed that arsenic levels exceeded USEPA and WHO standards in the Nakhon Luang and Nonthaburi aquifers. Nickel and lead levels surpassed the permissible limits of USEPA, WHO, and NOAA in all aquifers. Exposure assessments indicated that children had higher levels of heavy metals, with ingestion as the main route of exposure. Non-carcinogenic health risks from arsenic, nickel, lead, and zinc through ingestion and dermal contact were found to be significant for both children and adults (HI > 1) in all groundwater aquifers. The carcinogenic health risk assessment revealed unacceptable cancer risks from the ingestion of arsenic, nickel, and lead, and dermal exposure to arsenic and nickel (TCR > 10⁻⁴) in all groundwater aquifers. These findings indicate the need for close monitoring and management of industrial activities to prevent further heavy metal contamination in groundwater, thereby reducing health risks for individuals relying on this resource.

INTRODUCTION

Heavy metals are chemical substances that can significantly impact environmental quality [1] and are often toxic to living organisms. Poor environmental quality due to heavy metal contamination can result in harmful effects on humans, animals, and plants [2]. For example, mercury exposure can cause Minamata disease in humans, arsenic exposure can lead to neurological disorders, nickel contamination can impair blood circulation and slow plant growth [3], while lead exposure can cause disorders in both the human excretory system and the process of photosynthesis in plants [4]. In addition to toxic heavy metals, there is

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another group of heavy metals that are essential for living organisms. These metals are necessary for various physiological processes in the body to prevent disease. However, excessive intake of these metals can cause health issues and diseases if consumed in excessive quantities [5]. For instance, excessive zinc intake can negatively affect the nervous and immune systems [6]. This demonstrates that both toxic metals and those necessary for life can have harmful effects on living organisms when accumulated in amounts the body cannot eliminate, leading to the onset of diseases.

Environmental media such as soil, water, and air [7] are commonly impacted by heavy metal contamination. Sources of heavy metals can be both natural and anthropogenic [8], including industrial activities that use heavy metals, such as those in the paint, metal, and battery industries. According to the Department of Industrial Works in Thailand [9], there were 73,232 factories in the country in 2022, many of which are associated with the use of heavy metals. These include chemical manufacturing, pesticide production, plastic manufacturing, metal sheet, electrical appliances, and automobile and vehicle part manufacturing. Typically, these factories are located within various industrial estates across Thailand, with 6,958 factories situated in Samut Prakan province. As a result, Samut Prakan is one of the provinces at high risk of heavy metal contamination from industrial activities. One major environmental concern in this area is groundwater contamination with heavy metals. This contamination can spread to various regions and poses significant challenges in treatment before the water is used by humans.

In Samut Prakan industrial area, the primary causes of heavy metal contamination in groundwater are industrial activities that lead to the leakage of heavy metals and the leaching of contaminated soil into the groundwater [10-12]. Heavy metal leaching into groundwater may result from rainfall or activities involving significant water leakage into the environment, such as the use of water [11-13] and foam for firefighting in the severe fire at the Mingti chemical plant. This event involved 18 hours of water and foam usage, which may have contributed to heavy metal contamination in the groundwater through the leaching of metals from the soil into the aquifer [14]. Factories in Samut Prakan industrial zones that use heavy metals include battery plants, automobile parts factories, chemical manufacturing plants, metal parts factories, electroplating facilities, and pesticide manufacturing plants [15]. The heavy metals commonly used in industrial processes include arsenic, nickel, lead, and zinc. Therefore, industrial areas in these zones are at risk of heavy metal leakage, which could affect the quality of groundwater.

Studies on heavy metal contamination in groundwater and its effects on human health have shown significant concerns in industrial zones, such as Peenya in Bengaluru, India, and Lahore in Pakistan. In these areas, heavy metal contamination has led to substantial health risks for individuals who rely on groundwater for daily use [16]. In Pakistan, the contamination has resulted in severe health issues, with an approximate 30% death rate among those affected by water-borne diseases and heavy metals [17].

The spread of heavy metals in groundwater varies by region and is influenced by several factors, including hydrogeological processes, bedrock composition [18], the adsorption of heavy metals in aquifers [19], sedimentation, and the amount of metal leakage from sources. Additionally, the mobility of heavy metals in groundwater may be affected by chemical reactions with dissolved substances, such as high salt concentrations. If groundwater contains high levels of salts, heavy metals can form soluble compounds that spread more easily [20]. In the Samut Prakan industrial area, the presence of both heavy metal sources and high salt concentrations in groundwater, due to seawater intrusion, further exacerbates the spread of contamination. Thus, if industrial activities in this area lead to heavy metal leakage, the spread of contamination in the groundwater will intensify, potentially affecting human health even in areas distant from the original contamination sources. Therefore, due to the aforementioned reasons, the analysis of heavy metal contamination in groundwater remains a critical issue for further investigation. Additionally, this study primarily aims to assess the health risks associated with the exploitation of heavy metal-contaminated groundwater, a topic that has not been previously explored in this study area. The findings will provide valuable guidance for government agencies

responsible for pollution control, as well as for the public engaged in groundwater exploitation, ensuring its proper management to mitigate potential health risks in the future.

The aim of this study is to assess the levels of heavy metal contamination —specifically arsenic, nickel, lead, and zinc— in groundwater from the Samut Prakan industrial area. The study focuses on contamination of heavy metals in the Bangkok, Phra Pradaeng, Nakhon Luang, and Nonthaburi aquifers. Additionally, this study aims to evaluate the associated health risks from exposure to these metals within the Samut Prakan industrial area.

MATERIALS AND METHODS

Study area and groundwater sampling

The groundwater sampling area is located within a 30kilometer radius around the Samut Prakan industrial area, as shown in Figure 1. The coordinates of the sampling locations are provided in Table 1. Samples were collected from observation wells across four aquifers: Bangkok (3 wells, n=3), Phra Pradaeng (3 wells, n=3), Nakhon Luang (6 wells, n=6), and Nonthaburi (4 wells, n=4), at average depths of 50, 100, 150, and 200 m. [21], respectively. Groundwater sampling was conducted in collaboration with the Department of Groundwater Resources, Thailand, in August 2021, about one month after the severe fire at Mingti Chemical. Groundwater was pumped from the observation wells using a pump system, in accordance with the Department's standard procedure. At each observation well, three samples were collected. The volume of each sample was 2 L. To preserve the samples, concentrated nitric acid (QReC, Newzealand) was added to lower the pH to below 2 during transport. The samples were stored at 4°C [22] in a light-free environment until reaching the laboratory.



Groundwater sampling point Figure 1. Map of groundwater sampling locations generated using QGIS.

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Aquifer	Sampla No	GPS coor	dination	Donth (m)	Location	
		East	North	Deptii (iii)	Location	
	GW01	100°39'06.5"E	13°36'28.8"N	54	Theparak local park	
Bangkok	GW02	100°38'06.1"E	13°41'27.3"N	50	Wat wachiratham sathit	
	GW03	100°41'48.4"E	13°45'26.0"N	53	Wat lad bua khao	
	GW04	100°38'06.1"E	13°41'27.3"N	87	Wat wachiratham sathit	
Phra Pradaeng	GW05	100°41'48.4"E	13°45'26.0"N	99	Wat lad bua khao	
	GW06	100°42'38.1"E	13°39'34.5"N	116	Wat khlong chuat lak khao	
	GW07	100°41'22.9"E	13°38'41.7"N	140	Bang phli telephone exchange	
	GW08	100°42'17.3"E	13°36'31.4"N	163	Bang phli yai klang temple	
Nakhan luang	GW09	100°39'06.5"E	13°36'28.8"N	130	Theparak local park	
Naknon luang	GW10	100°38'06.1"E	13°41'27.3"N	181	Wat wachiratham sathit	
	GW11	100°41'48.4"E	13°45'26.0"N	160	Wat lad bua khao	
	GW12	100°47'57.5"E	13°40'10.5"N	146	Wat sriwaree noi	
	GW13	100°42'17.3"E	13°36'31.4"N	211	Bang phli yai klang temple	
	GW14	100°38'06.1"E	13°41'27.3"N	217	Wat wachiratham sathit	
Nonthaburi	GW15	100°41'48.4"E	13°45'26.0"N	204	Wat lad bua khao	
	GW16	100°47'57.5"E	13°40'10.5"N	203	Wat sriwaree noi	

Table 1. Geographic coordinates of the groundwater sampling points, groundwater depth levels, and sampling locations

Sample preparation and heavy metal analysis

Sample preparation for the analysis of dissolved heavy metals in contaminated groundwater was carried out in accordance with USEPA standard Method 200.7 [23,24]. A 50 ml. of groundwater sample was filtered using a filter paper (Whatman, USA) with a porosity of 0.45 μ m. The filtrate was then analyzed for heavy metals using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) (PerkinElmer model 8300, USA) following USEPA Standard Method 6010D [25]. The wavelengths used for the analysis of arsenic (As), nickel (Ni), lead (Pb), and zinc (Zn) were 193.693, 231.604, 220.353, and 213.856 nm., respectively.

Health risk assessment

Exposure assessment

The health risk assessment from heavy metal exposure through ingestion and dermal contact was conducted following the USEPA guidelines [26], as outlined in Equations (1-2).

EDIing (mg kg⁻¹ day⁻¹) = (C × IngR × EF × ED)/(BW × AT) (1)

EDIder (mg kg⁻¹ day⁻¹) = (C × SA × Kp × ET × EF × ED × CF)/(BW × AT) (2)

Where, EDI represents the amount of heavy metals entering the body via ingestion (EDIing) and dermal contact (EDIder); C is the concentration of heavy metals in groundwater (mg L^{-1}); IngR is the ingestion rate of groundwater (1.8 L per day for children, 2.2 L per day for adults) [27]; EF is the exposure frequency (365 days per year) [27]; ED is the exposure duration (6 years for children, 70 years for adults) [28]; BW is body weight (15 kg for children, 70 kg for adults) [28]; AT is the average exposure time (AT = ED \times 365 days) [29]; Kp is the dermal permeability coefficient in water (0.001 cm hr⁻¹ for As, 2×10^{-4} cm hr⁻¹ for Ni, 4×10^{-3} cm hr⁻¹ for Pb, 6×10^{-4} cm hr⁻¹ for Zn) [27, 30]; SA is the skin surface area (6,600 cm² for children, 18,000 cm² for adults) [27]; ET is the exposure time per day (1 hour per day for children, 0.58 hour per day for adults) [27]; and CF is the conversion factor $(10^{-3} \text{ L cm}^{-3})$ [31].

Non-Carcinogenic health risk assessment

The non-carcinogenic health risk assessment was conducted by calculating the Hazard Quotient (HQ), which is a numerical evaluation of the ratio between the amount of each heavy metal entering the body and its reference dose, as expressed in the Equation (3). Additionally, the Hazard Index (HI) was calculated to evaluate the risk from multi-element exposure via multiple pathways, as shown in Equations (4).

HQ = EDI/RefD(3)

HI = $\sum_{i=1}^{n} HQi$ (4)

Where, HQ represents the hazard quotient (unitless); HI represents the hazard index (unitless); RefD denotes the reference dose; and i refers to the metal species evaluated, including As, Ni, Pb, and Zn. The reference dose values for As, Ni, Pb, and Zn from dermal exposure are 1.23×10^{-4} , 5.4×10^{-3} , 5.24×10^{-4} , and 6×10^{-2} [32], respectively. The reference dose values for As, Ni, Pb, and Zn from ingestion are 3×10^{-4} , 2×10^{-2} , 1.4×10^{-3} , and 3×10^{-1} [32], respectively.

For the non-carcinogenic health risk assessment based on the HQ and HI values, as outlined by the USEPA, if the calculated HQ or HI values exceed 1, it indicates a potential health risk from heavy metal exposure. Conversely, if the HQ or HI values are less than 1, it implies there is no significant risk of non-carcinogenic health effects from the exposure to heavy metals.

Carcinogenic health risk assessment

The carcinogenic health risk assessment is a numerical evaluation method used to estimate the probability of cancer development following exposure to carcinogenic substances through various pathways. In this study, the health risks associated with exposure to As, Ni, and Pb through ingestion and As and Ni through dermal contact were assessed. The individual health risk from each heavy metal was calculated using the Cancer Risk (CR) as shown in Equation (5), while the health risk from multi-element exposure via multiple exposure pathways was determined by calculating the Total Cancer Risk (TCR) as shown in Equation (6).

$$CR = EDI \times SF(5)$$

TCR =
$$\sum_{i=1}^{n} CRi$$
 (6)

Where, CR is carcinogenic risk (unitless); TCR is total carcinogenic risk (unitless); SF is the slope factor; and i refers to the metal species evaluated, including As, Ni and Pb. The slope factors for As, Ni, and Pb for ingestion are 1.5, 1.7, and 0.0085 [32], respectively, while the slope factors for As and Ni for dermal exposure are 3.66 and 42.5 [32], respectively.

The health risk assessment for cancer development from exposure to heavy metals, based on the CR and TCR values provided by the USEPA [26], indicates that if the CR or TCR value is less than 10^{-6} , there is no risk of cancer from heavy metal exposure. However, if the CR or TCR value exceeds 10^{-6} , there is a risk of cancer development. If the CR or TCR value falls between 10^{-6} and 10^{-4} , the risk is considered acceptable, but if the CR or TCR value exceeds 10^{-4} , the risk is deemed unacceptable [33, 34].

Statistical analysis

The statistical analysis was conducted using SPSS software. Descriptive statistics were presented as means and standard deviations (SD), while inferential statistics were derived from two-way ANOVA and Pearson's correlation coefficient. A two-way ANOVA was conducted to analyze the variations in heavy metal concentrations across different groundwater aquifer levels. The analysis considered three factors: metal species (F1), groundwater aquifer levels (F2), and the interaction between these two factors (F1 \times F2), with a significance level set at 0.05. Pearson's correlation coefficient was used to analyze the sources of heavy metal contamination in groundwater, with a significance level of 0.05 [35-37].

Quality control and quality assurance

Quality control throughout the analysis process was carried out from sample collection, sample preservation, sample extraction, to sample analysis according to standard procedures. The chemicals used were AR grade. Glassware used for sample extraction was decontaminated by soaking in 10% nitric acid for 48 hours, followed by cleaning with DI water and drying at 120°C for 4 hours [38] before analysis. A standard curve was prepared at concentrations of 0, 0.5, 1, 2, and 5 mg L^{-1} . The results showed that the correlation coefficient (r²) was greater than 0.995, which is within the acceptable range (r² > 0.995) [39]. Additionally, quality control was performed by determining the % recovery using standard reference material (PerkinElmer, Lot: 3-18mkby1, USA), which ranged from 97.17-108.74%, within the acceptable range of 80-120% [40,41]. Sample analysis was performed with triplicate measurements [42], and the results had to show a %RSD < 20% [43].

RESULTS AND DISCUSSION

Contamination of heavy metals in groundwater

The contamination of heavy metals in groundwater (in mg L^{-1}) is presented in Table 2. The ranges of contamination for As, Ni, Pb, and Zn in groundwater are ND-0.041, 0.646-1.931, 0.026-0.107, and 0.027-6.450 mg L^{-1} , respectively. The average concentrations of As (0.015), Ni (1.496), Pb (0.087), and Zn (1.431) were highest in the groundwater aquifers from Nonthaburi, Phra Pradaeng, Bangkok, and Nakhon Luang, respectively. Meanwhile, the groundwater aquifers in Bangkok showed the lowest average concentrations of As (ND) and Zn (0.063), while Ni (0.976) and Pb (0.055) were lowest in the Nonthaburi aquifers. The factor that significantly influenced the levels of heavy metal contamination in the groundwater aquifers was the type of heavy metal (Factor 1) at a significance level of 0.01 (Table 1). On the other hand, the factor of groundwater aquifer (Factor 2) and the interaction between Factor 1 and Factor 2 had no effect on the heavy metal concentrations in the groundwater aquifers.

The differences in concentrations of heavy metals in the various groundwater aquifers can be attributed to the specific characteristics of the metals themselves, such as principal hadrochemical processes, interactions of heavy metals with soil and rock, and various geological formations. In addition, external factors affecting the dissolution of heavy metals in groundwater, such as pH value, temperature, groundwater flow rate, oxidation reactions [10], geological conditions [44], and the effect of parent rock and bedrock [44], can lead to varying dissolution capacities of the heavy metals.

A comparison of heavy metal contamination in groundwater with the maximum contamination levels in groundwater established by USEPA and NOAA and the drinking water standards defined by WHO, demonstrated that the concentrations of Ni and Pb in the groundwater samples (GW01–GW16) and the average concentrations of Ni and Pb in each groundwater aquifer exceeded the standards of WHO, USEPA, and NOAA. In contrast, the average concentrations of As and Zn from all groundwater aquifers were below the standards. However, the contamination levels of As and Zn in some groundwater samples exceeded the standards. Specifically, As concentrations exceeding the USEPA and WHO standards in the Nakhon Luang aquifer (GW07-GW09 and GW12) and Nonthaburi groundwater aquifer (GW14 and GW16). Additionally, Zn concentrations exceeded the NOAA, USEPA, and WHO standards in the Nakhon Luang aquifer (GW07). These findings suggest that the contamination of heavy metals in groundwater in the study area is not suitable for consumption due to the potential health risks posed by high levels of Ni and Pb.

Table 2. Concentration of heavy metals (mg L ⁻¹	¹) in groundwater in the presented study, with standard limits, statistical analysis results using two-way
	ANOVA, and comparisons with other previous studies

	a 1	Concentrati	Concentration of heavy metals (mg L ⁻¹) in groundwater (mean <u>+</u> SD)					
Aquifer	Sample No.		in presen	ted study		Reference		
	-	As	Ni	Pb	Zn			
	GW01	ND	1.480 <u>+</u> 0.48	0.107 <u>+</u> 0.03	0.093 <u>+</u> 0.02			
Dangkak	GW02	ND	1.783 <u>+</u> 0.02	0.046+0.02	0.041 ± 0.01			
Daligkok	GW03	ND	1.014 <u>+</u> 0.32	0.107 <u>+</u> 0.02	0.055 <u>+</u> 0.01			
	Average	ND	1.426	0.087	0.063			
	GW04	ND	1.698 <u>+</u> 0.01	0.078 <u>+</u> 0.01	0.027 <u>+</u> 0.01			
Phra Pradaana	GW05	0.003 <u>+</u> 0.03	1.724 <u>+</u> 0.01	0.066 <u>+</u> 0.02	2.969 <u>+</u> 0.10			
T IIT a T Tauacing	GW06	ND	1.065 <u>+</u> 0.44	0.080 <u>+</u> 0.03	0.378 <u>+</u> 0.03			
	Average	0.001	1.496	0.075	1.125			
	GW07	0.012 <u>+</u> 0.12	0.909 <u>+</u> 0.00	0.072 <u>+</u> 0.03	6.450 <u>+</u> 0.01			
	GW08	0.013 <u>+</u> 0.00	1.371 <u>+</u> 0.48	0.101 <u>+</u> 0.03	0.596 <u>+</u> 0.08			
Nakhon	GW01 GU012_0.02 GU012_0.00 GU012_0.03 GU012_0.01 GW08 0.013±0.00 1.371±0.48 0.101±0.03 0.596±0.08 GW09 0.023±0.02 1.522±0.52 0.079±0.03 0.118±0.01 GW10 ND 1.931±0.02 0.063±0.02 0.733±0.04 GW11 0.002±0.03 0.726±0.01 0.058±0.03 0.628±0.02 GW12 0.034±0.02 1.216±0.01 0.081±0.02 0.061±0.01 Average 0.014 1.279 0.076 1.431 GW13 ND 0.689±0.01 0.026±0.02 0.323±0.01 GW14 0.017±0.03 1.556±0.01 0.067±0.03 0.188±0.02 GW15 ND 0.646±0.28 0.071±0.02 0.394±0.01 GW16 0.041±0.01 1.014±0.32 0.055±0.02 0.138±0.01 Average 0.015 0.976 0.055 0.261 D 0.976 0.055 0.261 0.825 Standard limits for heavy metal concentrations (mg L ⁻¹) in groundwater. 0.01 0.							
Luang	GW10	ND	1.931 <u>+</u> 0.02	0.063 <u>+</u> 0.02	0.733 <u>+</u> 0.04			
Duang	GW11	0.002 <u>+</u> 0.03	0.726 <u>+</u> 0.01	0.058 <u>+</u> 0.03	0.628 <u>+</u> 0.02			
	GW12	0.034 <u>+</u> 0.02	1.216 <u>+</u> 0.01	0.081 <u>+</u> 0.02	0.061 <u>+</u> 0.01			
	Average	0.014	1.279	0.076	1.431			
	GW13	ND	0.689 <u>+</u> 0.01	0.026 <u>+</u> 0.02	0.323 <u>+</u> 0.01			
	GW14	0.017 <u>+</u> 0.03	1.556 <u>+</u> 0.01	0.067 <u>+</u> 0.03	0.188 <u>+</u> 0.02			
Nonthaburi	GW15	ND	0.646 <u>+</u> 0.28	0.071 <u>+</u> 0.02	0.394 <u>+</u> 0.01			
	GW16	0.041 <u>+</u> 0.01	1.014 <u>+</u> 0.32	0.055 <u>+</u> 0.02	0.138 <u>+</u> 0.01			
	Average	0.015	0.976	0.055	0.261			
Average concentratio study	n in present	0.009	1.272	0.072	0.825			
	Standard lin	nits for heavy metal co	oncentrations (mg L ⁻¹)	in groundwater.				
USEPA standard		0.01	0.1	0.015	5	[46,47]		
WHO standard		0.01	0.07	0.01	3	[48]		
NOAA standard		0.05	0.1	0.015	5	[49]		
Concer	trations of heavy	metals (mg L ⁻¹) in gr	oundwater from studi	es conducted in other	areas.			
Peenya Industrial	Area, India	0.012	0.014	0.009	0.126	[16]		
Pepper production	area, China		0.022		0.065	[50]		
Hayatabad Indust Pakista	rial Estate, n		4.49	5.86	44.9	[51]		
Dar es Salaam cit	y, Tanzania –	6.64		0.02	1.19	[52]		
Industrial zones, So	uthern India		0.4	0.8	0.54	[53]		
Industrial a Sheikhupura distri	rea in ict, Pakistan	38.49×10^{-3}	0.03×10^{-3}	0.05×10^{-3}	1.07×10^{-3}	[54]		
Meghna Ghat indu Banglade	istrial area, sh			0.1819		[55]		
		Two-way ANOVA test						
Source of variation		F-va	lue	P value				
Factor 1 (type of heav	vy metal)	7.5	90	0.00	00*			
Factor 2 (aquifer)		0.7	66	0.5	0.517			
Interaction		0.6	09	0.82	27			

ND, not detected: *, significant at 0.01 level

When comparing the heavy metal contamination in the study area's groundwater with other areas with similar

sources from industrial factories and human activities (Table 2), it was found that the average concentration of

As in groundwater in the Samut Prakan industrial area was higher than in the industrial area in Sheikhupura District (Pakistan). The concentrations of Ni and Zn in groundwater in Samut Prakan were higher than in the Peenya Industrial Area (India), the industrial zones in southern India, pepper production area in China and the industrial area in Sheikhupura District (Pakistan). The concentration of Pb in groundwater in Samut Prakan was also higher than in the Peenya Industrial Area (India), Dar es Salaam city (Tanzania), and the industrial area in Sheikhupura District (Pakistan). The higher concentrations of certain heavy metals in the study area compared to other areas may be due to the greater number of sources of heavy metals in the study area and the better prevention systems for heavy metal leakage in the other areas. To reduce the heavy metal contamination in the study area, improvements in the prevention systems for leakage should be made.

Aquifer	Element	Arsenic	Nickel	Lead	Zinc
	Arsenic	-	-	-	-
Danahah	Nickel		1	-0.799	-0.141
Dangkok	Lead			1	0.708
	Zinc				1
	Arsenic	1	0.530	-0.991	0.994
Dhua Duadaang	Nickel		1	-0.637	0.434
r iira r raueang	Lead			1	-0.971
	Zinc				1
	Arsenic	1	-0.033	0.517	-0.182
Nabban Luana	Nickel		1	0.171	-0.406
Naknon Luang	Lead			1	-0.149
	Zinc				1
	Arsenic	1	0.467	0.185	-0.911
	Nickel		1	0.390	-0.729
Nonthaburi	Lead			1	-0.076
	Zinc				1

Table 3. Pearson correlation coefficient values between heavy metal concentrations in groundwater from different aquifers

The analysis of the sources of heavy metal contamination in groundwater, based on correlation calculations shown in Table 3, found that the metals had no significant correlation at the 0.05 significance level. This indicates that the sources of heavy metals contributing to the contamination of groundwater in the study area are not correlated [56,57], meaning it is not possible to identify a single source for the heavy metals. Heavy metal contamination in the groundwater of the study area may be attributed to multiple sources or originate from distinct origins. This is consistent with the nature of the study area, as there are various types of industrial factories that can contribute to the contamination of heavy metals, such as chemical factories, metal wire manufacturing, electrical circuit board production, ZnCl₂, ZnSO₄, and ZnCO₃ chemical plants, can manufacturing factories, paint factories, pesticide and insecticide

factories, automotive parts factories, fertilizer factories, battery factories, hazardous waste disposal sites in industrial parks, industrial waste disposal and treatment factories, galvanizing and metal coating factories, and leather tanning factories. Furthermore, more than 350 factories are located in the surrounding industrial areas, some of which, both within the industrial parks and nearby areas, may use multiple types of heavy metals (As, Ni, Pb, and Zn) in their industrial processes, which could contribute to contamination if leakage occurs into the groundwater.

Exposure assessment

Health risk assessment, encompassing both noncarcinogenic and carcinogenic risks from heavy metal exposure through ingestion and dermal contact, involves calculating the quantity of substances entering the body by determining the EDI values for As, Ni, Pb, and Zn, as shown in Table 4.

The results of the metal intake calculations indicate that heavy metals primarily enter the body via ingestion (EDIing) rather than dermal contact (EDIder). The metal species in each aquifer show that As has the lowest intake compared to other metals across all exposure routes and population groups. In contrast, the highest metal intake via ingestion in both children and adults in the Bangkok, Phra Pradaeng, and Nonthaburi aquifers is Ni. The highest metal intake via dermal contact in the Bangkok and Nonthaburi aquifers is Pb, while in the Phra Pradaeng and Nakhon Luang aquifers, it is Zn. Key factors contributing to the varying levels of metal intake include the differing concentrations of heavy metals, leading to diverse intake levels, the higher ET value in children compared to adults, which results in greater metal intake in children, [46] and the higher absorption rate of the gastrointestinal system relative to dermal contact [58,59], making ingestion a more prominent route of exposure. Additionally, other factors influencing the differential intake include the skin barrier [60], which prevents absorption through the skin, and the distinct Kp values for each metal.

Table 4. Estimated daily intake (mg kg ⁻¹ day ⁻¹) of heavy metals from ingestion and dermal exposure in children and adults across different ad	juifers.
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Aquifer	D (Exposure		Average daily inta	ge daily intake (mg kg ⁻¹ day ⁻¹)	
	Keceptor	pathway	As	Ni	Pb	Zn
	Children	Ingestion	0	1.711×10 ⁻¹	1.040×10 ⁻²	7.560×10 ⁻³
Bangkok	Children	Dermal	0	1.255×10 ⁻⁴	1.525×10 ⁻⁴	1.663×10 ⁻⁵
		Ingestion	0	4.481×10 ⁻²	2.724×10 ⁻³	1.980×10 ⁻³
	Adult	Dermal	0	Average daily int Ni 1.711×10 ⁻¹ 1.255×10 ⁻⁴ 4.481×10 ⁻² 4.399×10 ⁻⁵ 1.795×10 ⁻¹ 1.316×10 ⁻⁴ 4.702×10 ⁻² 4.615×10 ⁻⁵ 1.535×10 ⁻¹ 1.126×10 ⁻⁴ 4.020×10 ⁻² 3.947×10 ⁻⁵ 1.172×10 ⁻¹ 8.591×10 ⁻⁵ 3.068×10 ⁻² 3.012×10 ⁻⁵	5.349×10 ⁻⁵	5.832×10 ⁻⁶
-	Children	Ingestion	1.200×10 ⁻⁴	1.795×10 ⁻¹	8.960×10 ⁻³	1.350×10 ⁻¹
	Children	Dermal	4.400×10 ⁻⁷	1.316×10 ⁻⁴	1.314×10 ⁻⁴	2.969×10 ⁻⁴
Phra Pradaeng	Adult	Ingestion	3.143×10 ⁻⁵	4.702×10 ⁻²	2.347×10 ⁻³	3.535×10 ⁻²
		Dermal	1.543×10 ⁻⁷	4.615×10 ⁻⁵	4.608×10 ⁻⁵	1.041×10 ⁻⁴
-	Children	Ingestion	1.680×10 ⁻³	1.535×10 ⁻¹	9.080×10 ⁻³	1.717×10 ⁻¹
Nakhon		Dermal	6.160×10 ⁻⁶	1.126×10 ⁻⁴	1.332×10 ⁻⁴	3.778×10 ⁻⁴
Luang	Adult	Ingestion	4.400×10 ⁻⁴	4.020×10 ⁻²	2.378×10 ⁻³	4.497×10 ⁻²
		Dermal	2.160×10 ⁻⁶	3.947×10 ⁻⁵	4.670×10 ⁻⁵	1.325×10 ⁻⁴
-	Children	Ingestion	1.740×10 ⁻³	1.172×10 ⁻¹	6.570×10 ⁻³	3.129×10 ⁻²
Ni an tha hard	Children	Dermal	6.380×10 ⁻⁶	8.591×10 ⁻⁵	9.636×10 ⁻⁵	6.884×10 ⁻⁵
inontnaduri	۸ dult	Ingestion	4.557×10 ⁻⁴	3.068×10 ⁻²	1.721×10 ⁻³	8.195×10 ⁻³
	Adult	Dermal	2.237×10 ⁻⁶	3.012×10 ⁻⁵	3.379×10 ⁻⁵	2.414×10 ⁻⁵

Analysis of the trends in metal intake reveals that the trend for heavy metal intake via ingestion in the Bangkok aquifer for both children and adults is Ni > Pb > Zn > As, while via dermal contact, it follows the order Pb > Ni > Zn > As. The trend of dermal intake in the Bangkok aquifer is similar to that in Nonthaburi. In Nonthaburi, the trend of metal intake through ingestion mirrors that of Phra Pradaeng, with Ni > Zn > Pb > As, while the trend of ingestion through the gastrointestinal route in the

Nakhon Luang aquifer is Zn > Ni > Pb > As. The trend of dermal intake in the Phra Pradaeng aquifer is identical to that of ingestion in the Nakhon Luang aquifer, whereas the trend of dermal intake in the Nakhon Luang aquifer is Zn > Pb > Ni > As.

Non-carcinogenic health risk assessment

The non-carcinogenic health risk assessment from the calculation of HQ and HI is shown in Table 5.

Aquifer	Receptor	Exposure		Hazard quotient			Hazard index	
		path	pathway	As	Ni	Pb	Zn	
	Children	Ingestion	0	8.554	7.429	2.520×10 ⁻²	16.322	
		Dermal	0	2.323×10 ⁻²	2.911×10 ⁻¹	2.772×10 ⁻⁴		
Bangkok		Ingestion	0	2.240	1.946	6.600×10 ⁻³	4 202	
	Adult	Dermal	0	8.147×10 ⁻³	1.021×10 ⁻¹	9.720×10 ⁻⁵	4.303	
Phra Pradaeng	Children	Ingestion	4.000×10 ⁻¹	8.974	6.400	4.499×10 ⁻¹	16 500	
	Children	Dermal	3.577×10 ⁻³	2.437×10 ⁻²	2.508×10 ⁻¹	4.949×10 ⁻³	16.508	
	Adult	Ingestion	1.048×10 ⁻¹	2.350	1.676	1.178×10 ⁻¹	4.240	
		Dermal	1.254×10 ⁻³	8.547×10 ⁻³	8.794×10 ⁻²	1.735 x10 ⁻³	4.349	
-	Children	Ingestion	5.600	7.675	6.486	5.724×10 ⁻¹	20.664	
Nakhon		Dermal	5.008×10 ⁻²	2.085×10 ⁻²	2.541×10 ⁻¹	6.296×10 ⁻³	20.664	
Luang	Adult	Ingestion	1.467	2.010	1.699	1.499×10 ⁻¹	5.442	
		Dermal	1.756×10 ⁻²	7.310×10 ⁻³	8.912×10 ⁻²	2.208×10-3		
	Children	Ingestion	5.800	5.858	4.693	1.043×10 ⁻¹	16 202	
Nonthaburi		Dermal	5.187×10 ⁻²	1.591×10 ⁻²	1.839×10 ⁻¹	1.147×10 ⁻³	16./0/	
		Ingestion	1.519	1.534	1.229	2.732×10 ⁻²	1.000	
		Adult	Dermal	1.819×10 ⁻²	5.579×10 ⁻³	6.448×10 ⁻²	4.023×10 ⁻⁴	4.398

Table 5. The hazard quotient (HQ) and hazard index (HI) values of heavy metals from ingestion and dermal exposure in children and adults a	across
different aquifers.	

The assessment of the health impacts and risks from exposure to As, Ni, Pb, and Zn via a single exposure pathway reveals that the HQ values for As, Ni, Pb, and Zn via ingestion in children range from 0 to 5.800, 5.858 to 8.974, 4.693 to 7.429, and 2.520×10^{-2} to 5.725×10^{-1} , respectively, while in adults, the ranges are 0 to 1.519, 1.534 to 2.350, 1.229 to 1.946, and 6.600×10^{-3} to 1.499×10⁻¹, respectively. The trend in HQ values shows that children have higher HQ values than adults, indicating that children are at a higher health risk from heavy metals than adults.

The assessment of health risks from exposure to heavy metals via ingestion shows that the only metal with no health risk through ingestion is Zn (HQ<1), while As, Ni, and Pb have unacceptable HQ values (HQ>1). Specifically, the HQ value for As in children from groundwater in the Nakhon Luang aquifer (5.600) and Nonthaburi aquifer (5.800), and in adults from groundwater in Nakhon Luang aquifer (1.467) and Nonthaburi aquifer (1.519) are all higher than 1. Additionally, the HQ values for Ni and Pb in both children and adults across all aquifers indicate significant health risks. In particular, the HQ values for Ni in children are 8.554, 8.974, 7.675, and 5.858 for the

Bangkok, Phra Pradaeng, Nakhon Luang, and Nonthaburi aquifers, respectively. and in adults, the values are 2.240, 2.350, 2.010, and 1.534. Pb HQ values for children from groundwater in Bangkok, Phra Pradaeng, Nakhon Luang, and Nonthaburi aquifer are 7.429, 6.400, 6.486, and 4.693, and in adults, the values are 1.946, 1.674, 1.699, and 1.229, respectively. This indicates that in the Bangkok and Phra Pradaeng aquifers, the concentrations of Ni and Pb pose a health risk from ingestion.

The health risk assessment from exposure to As, Ni, Pb, and Zn via contact shows that there is no health risk from exposure to these metals through contact for either children or adults (HQ<1). The metal that poses the least risk for both children and adults is As, with an HQ value of 0. The highest risk metal is Pb in children (2.911×10^{-1}).

Furthermore, the study also shows that the EDI is not the only factor contributing to higher health risks. Another important factor is the RefD for each metal, which represents the amount of a metal that can be safely consumed over a lifetime without adverse health effects. A lower RefD results in a higher HQ when compared to cases where the same amount of metal is ingested. The analysis shows that Zn has the lowest RefD, which leads to lower HQ values for Zn, even though the intake of Zn via ingestion in the Nakhon Luang aquifer and via contact in the Phra Pradaeng and Nakhon Luang aquifer is high.

The health risk assessment from multiple exposure pathways shows that health risks are unacceptable (HI>1), with children's risk being 4 times higher than that of adults in all aquifers. The aquifer with the highest health risk is the Nakhon Luang aquifer, with an HI of 20.664 in children and 5.442 in adults. Other aquifers show similar trend in HI values for both children and adults as in the Nakhon Luang aquifer.

Based on the analysis, it can be concluded that diseases that could arise from health risks exceeding the acceptable level may result from exposure to As, Ni, and Pb with HQ values >1. The potential health impacts include: 1) Exposure to As could affect the digestive system, skin, nervous system, brain, and circulatory system [61]. 2) Exposure to Ni, although typically inhaled through industrial activities, can also pose risks when ingested from contaminated groundwater, leading to respiratory issues, heart disease, and, when in contact with the skin, inflammation [62]. Additionally, ingestion of Ni could affect the urinary system, especially the kidneys [63]. 3) Pb exposure in children poses a greater risk to the nervous system and brain than in adults, potentially lowering IQ and impairing memory. In adults, Pb exposure can lead to anemia, kidney disease, and disorders in the reproductive system, nervous system, and bones [64].

Carcinogenic health risk assessment

The health risk assessment for carcinogenic heavy metals, including As, Ni, and Pb, was calculated using CR and TCR values, as shown in Table 6.

 Table 6. The carcinogenic risk (CR) and total carcinogenic risk (TCR) values of heavy metals from ingestion and dermal exposure in children and adults across different aquifers.

Aquifer	Pagantar	Exposure		Total			
	Receptor	pathway	As	Ni	Pb	Zn	carcinogenic risk
	GL 11	Ingestion	0	2.910×10 ⁻¹	8.840×10 ⁻⁵	NC	
	Children	Dermal	0	5.332×10 ⁻³	NC	NC	2.963×10
Bangkok	A .]](Ingestion	0	7.617×10 ⁻²	2.315×10 ⁻⁵	NC	7.006 10-2
	Adult	Dermal	0	1.870×10 ⁻³	NC	NC	7.806×10 ⁻²
-	Children	Ingestion	1.800×10^{-4}	3.051×10 ⁻¹	7.616×10 ⁻⁵	NC	2 110, 10-1
	Children	Dermal	1.610×10 ⁻⁶	5.594×10 ⁻³	NC	NC	3.110×10
Phra Pradaeng	Adult	Ingestion	4.714×10 ⁻⁵	7.991×10 ⁻²	1.995×10 ⁻⁵	NC	0.104.102
		Dermal	5.647×10 ⁻⁷	1.961×10 ⁻³	NC	NC	8.194×10 ⁻
-	Children	Ingestion	2.520×10 ⁻³	2.610×10 ⁻¹	7.718×10 ⁻⁵	NC	2 (94, 10-1
		Dermal	2.255×10 ⁻⁵	4.784×10 ⁻³	NC	NC	2.684×10
Nakhon Luang	Adult	Ingestion	6.600×10 ⁻⁴	6.834×10 ⁻²	2.021×10 ⁻⁵	NC	7.071.10-2
		Dermal	7.906×10 ⁻⁶	1.678×10 ⁻³	NC	NC	/.0/1×10
		Ingestion	2.610×10 ⁻³	1.992×10 ⁻¹	5.585×10 ⁻⁵	NC	2.055.10-1
Nonthaburi	Children	Dermal	2.335×10 ⁻⁵	3.651×10 ⁻³	NC	NC	2.055×10
	Adult	Ingestion	6.836×10 ⁻⁴	5.216×10 ⁻²	1.463×10 ⁻⁵	NC	5 415 10-2
		Dermal	8.188×10 ⁻⁶	1.280×10 ⁻³	NC	NC	5.415×10 ⁻

NC, not calculated

The CR values for single-element exposure to As, Ni, and Pb via ingestion in children ranged from 0 to 2.601×10^{-3} , 1.992×10^{-1} to 3.051×10^{-1} , and 5.585×10^{-5} to 8.840×10^{-5} , respectively. In adults, the CR values ranged from 0 to 6.836×10^{-4} , 5.216×10^{-2} to 7.991×10^{-5}

², and 1.463×10^{-5} to 2.315×10^{-5} , respectively. For dermal exposure, the CR values for As and Ni in children were 0 to 2.335×10^{-5} and 3.651×10^{-3} to 5.594×10^{-3} , respectively. In adults, these values ranged from 0 to

 8.188×10^{-6} and 1.280×10^{-3} to 1.961×10^{-3} , respectively.

The CR results indicate that the intake of Ni through ingestion and dermal exposure in both children and adults across all aquifers, as well as the intake of As through ingestion in children across all aquifers (except the Bangkok aquifer) and in adults in the Nakhon Luang and Nonthaburi aquifers, poses unacceptable health risks $(CR > 10^{-4})$. In contrast, Pb intake via ingestion in both children and adults across all aquifers, As intake via dermal exposure in children in the Phra Pradaeng, Nakhon Luang, and Nonthaburi aquifers, and in adults in the Nakhon Luang and Nonthaburi aquifers, as well as As intake via ingestion in the Phra Pradaeng aquifer, fall within acceptable risk levels $(10^{-6} < CR < 10^{-4})$. On the other hand, As intake through dermal exposure in adults in the Phra Pradaeng aquifer and ingestion and dermal exposure in all population groups in the Bangkok aquifer present no significant health risks. Therefore, Ni represents the most significant health risk in all population groups and aquifers, while As presents a risk in the Phra Pradaeng, Nakhon Luang, and Nonthaburi aquifers for specific exposure pathways and population groups.

The results of the multi-element exposure assessment using multiple exposure pathways based on TCR values show that health risks for both children and adults in the aquifers exceed acceptable levels (TCR $> 10^{-4}$). The highest risks are found in the Phra Pradaeng aquifer, with TCR values of 3.110×10^{-1} for children and 8.194×10^{-2} for adults. The Nonthaburi aquifer also shows high risks, with TCR values of 2.055×10^{-1} for children and $5.415 \times$ 10⁻² for adults. Therefore, groundwater in these industrial areas should undergo quality improvement before use, as prolonged exposure could lead to cancer. Lead exposure could result in stomach, brain, and kidney cancers [65], while arsenic exposure could lead to stomach, skin, and lung cancers [66], and nickel exposure could cause lung and nasal cancers [67]. Methods for improving groundwater quality before use include chemical treatments, combined chemical and physical treatments, biosorption techniques [68]. and Additionally, development plans [69] and legislation to control and prevent heavy metal leakage from industrial processes into aquifers should be implemented to reduce health

risks associated with groundwater usage. In comparing the health risks from heavy metals in groundwater in this study with the risks from previous research conducted in the study area, this comparison revealed limitations due to the lack of data on health risk assessments from previous studies, particularly regarding contamination in deep aquifers. Sampling from these deep groundwater aquifers requires observation wells that reach significantly below the surface, and the number of such wells is limited, being under strict management by the responsible agencies. Furthermore, sampling from deep groundwater aquifers necessitates specialized tools and equipment, posing additional challenges in obtaining a sufficient amount of data.

CONCLUSIONS

The groundwater in the studied industrial area is contaminated with As, Ni, Pb, and Zn, which are heavy metals commonly used in local industries. The assessment of contamination levels reveals that Zn is the only metal that does not exceed the standard in all groundwater aquifers. However, the average concentration of As in the Nakhon Luang, and Nonthaburi aquifers exceeds the USEPA and WHO standards. The average concentration of Pb and Ni also exceed the standards when compared to the USEPA, WHO, and NOAA groundwater standards. When groundwater from these areas is used, heavy metals can enter the body. The highest metal intake in each aquifer occurs through ingestion in children. Ni is the metal with the highest intake in the Bangkok, Phra Pradaeng, and Nonthaburi aquifers, while Zn is the metal with the highest intake in the Nakhon Luang aquifer.

Health risk assessment for non-carcinogenic effects from single-element exposure pathways shows that the health risk from Pb and Ni through ingestion in both children and adults exceeds the acceptable threshold. Meanwhile, As poses a non-carcinogenic risk only for children and adults through ingestion in the Nakhon Luang and Nonthaburi aquifers. Zn is the only metal that remains within acceptable risk levels in all aquifers.

Health risk assessment from multi-element exposure pathways shows that the risk from heavy metals in both children and adults across all aquifers exceeds the acceptable threshold, which could lead to non-cancer diseases from groundwater utilization.

Regarding carcinogenic health risks from single-element exposure pathways, Ni poses an unacceptable health risk through ingestion and dermal contact across all aquifers for all population groups. As exposure through dermal contact and ingestion in both children and adults in the Bangkok aquifer, as well as through dermal contact in adults in the Phra Pradaeng aquifer, shows no significant risk, while other exposure pathways and population groups for As and ingestion in all population groups for Pb pose a risk. Based on the findings, it can be concluded that groundwater used in areas with heavy metal contamination will pose health risks. Therefore, groundwater should be treated before use to mitigate potential health risks from heavy metal exposure.

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Conflict of interest

The authors declares no conflict of interest.

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