Health risk assessment of potentially toxic elements in Maros karst groundwater: a Monte Carlo simulation approach

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ABSTRACT
This study investigated potentially toxic elements (PTEs) pollution in groundwater across the Maros karst area. The groundwater quality was evaluated using three indexing methods, the heavy metal pollution index (HPI), the heavy metal evaluation index (HMEI) and the contamination index (Cd). The levels of PTEs were calculated to determine the noncancer and cancer risks to the residents through ingestion and dermal adsorption. To obtain high-level accuracy in cancer risk estimation, a Monte Carlo simulation model and sensitivity analysis were performed. The mean values of PTEs in rainy and summer season were followed the order of Cr > Pb > Zn > Cu and Cr > Zn > Pb > Cu, respectively. The high level of Pb and Cr were exceeded the permissible limit of the World Health Organization (WHO) and Indonesian Standards. However, TDS, pH, EC and temperature were still in accordance with WHO guidelines. The geostatistical interpolation of HPI, HMEI and Cd revealed that the groundwater quality around Maros karst is low, particularly in Tukamasea and Leang-Leang village. Hazard index values were lower than one, implying no possibility of noncancer risk. The Monte Carlo simulation results with 95% confidence demonstrated children and adults are at risk for developing cancer due to PTE exposure.

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1. Introduction

Groundwater supplies drinking water, provides half of the global population with freshwater, and plays critical roles for industrial water demand and sustaining healthy ecosystems. The quality of groundwater depends on geological factors, meteorological conditions, industrial discharge, urban activities and agricultural activities (Doyi et al. 2018; Haghnazari et al. 2021). This type of water is found underground or in rock structures called aquifers. The World Health Organization (WHO) has reported that the drinking water of hundreds of millions people is dangerously contaminated and chemically polluted (World Health Organization 2021). Rapid urbanization and industrialization have led to a considerable increase in the pollution load of groundwater. Among many pollutants, potentially toxic elements (PTEs) are pollutants derived from soil, rocks, anthropogenic factors and human activities. Their toxicity, high bioaccumulation and carcinogenicity can be fatal if exposed to ecological environments and humans (Briffa et al. 2020; Shang et al. 2020). Massive industrialization, poor wastewater management and lack of public awareness are critical factors of PTEs in groundwater.

The contamination of groundwater by PTEs has raised global concern and increased environmental and pollution research in recent years (Papazotos 2021). This group of elements consist of metals and nonmetals that are associated with contamination and high potential toxicity. Metals such as Cu, Ni and Zn are known as micronutrients, but they may be toxic to living organisms in excessive concentration and exposure levels. Among the toxic elements commonly found at contaminated sites are As, Cd, Cr, Cu, Hg, Ni, Pb and Zn. These pollutants usually occur due to natural processes in the environment and are associated with human activities (Dermatas et al. 2015; Pourret and Hursthouse 2019). In developing countries, the increasing number of industries with weak control pollution strategies and management can cause large-scale ecological destruction, resulting in the discharge of PTEs into the environment (Anyanwu et al. 2018). Several studies found that groundwater quality was influenced by agricultural fertilizers (Kubier et al. 2019; Papazotos et al. 2019). The R’mel region in Morocco and Sarigkiol basin in Greece experienced a serious threat to groundwater quality and,
therefore, to its rural inhabitants due to the metal accumulation from irrigated agriculture (Vasileiou et al. 2019; Sarti et al. 2021).

Maros karst is a growing region and has become the site of various industries that utilize its natural resources. As the second largest karst in the world, the Maros karst ecosystem is facing ecological problems through the industrial activities that possibly release harmful contaminants in the form of PTEs into the groundwater. Groundwater availability in this area is dependent on the hydrogeological situation and weather conditions. Unfortunately, the understanding of the groundwater system in the region is still lacking due to sparse groundwater observations. Moreover, the influence of topography on the groundwater has still not been evaluated and remains unclear. Investigating the source and pollution states of geological-related pollutants in the groundwater of this site are crucial. The fragility of karst environments and industrialization mean the groundwater around Maros karst is under serious threat.

The karst area is naturally vulnerable; water sources are affected by leaching conditions, rainfall, tectonic factors, lithology compound, expansion and thickness of karst topography (Zaree et al. 2019). Karst consists of limestone and alluvial that are easily weathered (abrasion and erosion) and highly soluble in natural surface waters (Astuti et al. 2021a; Malmir et al. 2021; Onac and van Beynen 2021). In Yunnan, 60% of metal and carbonated-host deposits occur in karst aquifers (Huang et al. 2019). These geological conditions cause the release of metal ions into the water bodies. It can be even worse if mining activities are established around karst areas. The mining waste in the form of acid mining drainage (AMD) with high levels of PTEs and sulphate affect the hydrochemistry of the groundwater (Zhu et al. 2020). A previous study confirmed that severe metal contamination of Zn, Mn, Ni and Cd was detected in mine drainage water, whereas Pb was found in tailing deposits and carbonate dissolution (Qin et al. 2019).

In this study, 16 representative sites were selected in rainy and summer seasons. The selection of metals was based on the level of toxicity and the possibility of its presence in the groundwater. Pb, Cr, Cu and Zn were included in the substance priority list of ATSDR, which were determined to be the most significant elements posing a potential threat to human health. From these measurements, the seasonal variation of PTEs was analyzed and the health risk of PTE exposure was evaluated in adults and children. Moreover, the water quality was evaluated by the heavy metal pollution index (HPI), the heavy metal evaluation index (HMEI) and the contamination index \( C_d \), due to the presence of PTEs. Some studies state the health risk as a single number and overlook the uncertainty. Previous results have relied on input variables (body weight, ingestion rate, etc.) without knowing the level of correlation and contribution of each assumption. Hence, this article uses probabilistic risk assessment, which is more developed and accurate than the health risk assessment model used in the past few decades. The Monte Carlo model investigates the distribution of a selected variable by simulating random numbers. Site specific data from questionnaires and interviews show the actual conditions and appropriate results from the perspective of risk analysis. Thus, this study aimed to (1) investigate the groundwater quality in Maros karst, (2) estimate the health risk of PTE exposure in groundwater through ingestion and dermal adsorption and (3) determine the probability of cancer.
risk and the most influential factors using Monte Carlo simulation. This study provides important information to improve water protection policies and estimate the presence of major cancer- and noncancer-related health risks.

2. Methods

2.1. Study area

Maros karst is located in the northern part of South Sulawesi Province. Karst, alluvial soils and carbonate rocks surround this area. It is located between longitude 119° 34’ 19.19” E and latitude –5° 00’ 4.80” S. The geographic region is about 161,911 km². The lowest temperature in this area was 23°C in July and the highest was 34°C in October. This karst ecosystem is one of the largest karst areas in the world (Astuti et al. 2021b). According to the Deharveng classification, this area combines a series of exceptional features such as karst hills with unusual geological formations, several caves, an abundance of prehistoric artefacts, exotic fauna and the oldest rock painting on earth (Deharveng et al. 2021; Huntley et al. 2021). The various textures that make up the land consist of clay, silt, sand, mud, gravel, with high soil fertility. Limestone is easily found in Bantimurung subdistrict, which is the source of cement raw materials, marble and ceramics. The large limestone plateaus are dissected by a few deep valleys, up to an elevation of 700 m on the slopes of the extinct Bulusaraung volcano. In the last few decades, the sustainability of groundwater in this region has been increasingly disturbed due to industrial activities concentrated in the area.

2.2. Geological and hydrological condition

Maros Regency lies in South Sulawesi province, which is structurally part of East Indonesia. The geological formations of this area consist of three main landscapes, namely the Bantimala Mélange complex, the Spermonde archipelago and tower karst. The Bantimala Mélange was formed by the tectonic complex, which comprised ultramafic rock (chert, schist, mélange, quartzite and eclogite) and oceanic crust that aged 60–350 million years ago. This area is connected with the karstic area and limestone lithology, which is a part of the Tonasa Formation. Ultramafic rocks are interbedded with layers of limestone. These rocks are usually dark in color with a high color index (>90) based on the presence of mafic minerals of olivine and pyroxene, which consist of <45 wt% of SiO₂ in their bulk chemical composition (Downes 2020). Pyroxene (XY(Si,Al)₂O₆) is a rock forming mineral, where X represents the cations of intermediate to larger size, calcium (Ca), sodium (Na), iron (Fe II) or magnesium (Mg) and more rarely zinc, manganese or lithium and Y represents the cations of intermediate to smaller size, consisting of chromium (Cr), aluminum (Al), magnesium (Mg), cobalt (Co), manganese (Mn), scandium (Sc), titanium (Ti), vanadium (V) or even iron (Fe II) or (Fe III) (Nespolo 2020).

The Maros karst landscape covers an area of 450 km² between 4°7’S and 5°1’S (Huntley et al. 2021). The karst hills complex has a high topography and some steep hill sides called Polje. The elevation of Maros karst hills ranges from 100 to 1000 meters. Moreover, plain karst with flat topography covers 30.29% of the total karst area and is utilized as agricultural land (Setiadi et al. 2021). The karst hills were enriched by alluvial
plain, silica sand/quartz, basalt, coal, propylite, calcite, marble, clay and slate (Astuti et al. 2021a). These rocks are often associated with the mineralization process. Fault and fold form the geological structure of this area. Faults play a crucial role in the recharge and discharge of water into and from the aquifers (Rahmani et al. 2019). A previous study detected a fold around Leang-Leang village (Setiadi et al. 2021). If the rock layer experienced horizontal pressure, peaks and valleys would be formed. Meanwhile, the fault is widely distributed around the study area, particularly Mattoangin, Kalabbirang, Mengeloreng, Tukamasea and Baruga villages. The tensile stress from the fault results in more open fractures and is a groundwater exploration area. The rock weathering due to the presence of faults in the karst region is higher because the material is more susceptible than other rocks. This geochemical weathering of parent rocks are the natural sources of PTEs in groundwater. Water–rock interaction is the main factor in the accumulation of PTEs around karst aquifers (Ma et al. 2020).

The hydrological condition of the Maros karst area depends on the materials connected to the groundwater, which is the rock transported by a nearly horizontal underground pipeline flow. In the rainy season, for the lower alluvial plains, ions migrate and undercut the hillslopes. The ingress of rainwater through the fractures then percolates and forms subsurface channels. The residue pores are often filled with propylite mudstone and clastic carbonate which affects reservoir quality. This may influence the high aquifer productivity of the study area. A previous study detected high SiO₂ and Cr(VI) contents in wells used by residents (Rauf et al. 2021a), which means the monitoring of karst groundwater quality should be a major concern, as the groundwater wells are the source of water for daily use in this area. The wells are hand dug with only a small portion of the community using borehole wells. Figure 1 shows the geological map and rock compositions of the study area.
2.3. Sample collection

Sixteen well water samples were collected in the summer and rainy seasons, respectively. Samples were collected during the months of November 2020 and August 2021. Containers were washed three times with the well water before sample collection. The depth of the wells at the study site varied from 10 to 25 m. Samples were stored in 500 mL high-density polyethylene (HDPE) bottles and labelled for easy identification. In situ measurements, including temperature, pH, electrical conductivity (EC) and total dissolved solids (TDS) were determined in the field. For chemical analysis, samples were fixed with concentrated HNO₃ until pH < 2 and preserved in an ice box at low temperature approximately 4 °C before being sent to the laboratory to prevent the appearance of mineral salts and precipitation of metal. Mixed concentrated acids of 5 mL H₂SO₄ (97%), 2 mL HClO₄ (70%) and 10 mL HNO₃ (70%) were introduced into 100 mL of each water sample and heated for 10 min at 95 °C. The digested sample was filtered and diluted with 50 mL distilled water. A total of five potentially toxic elements (Cr, Pb, Zn, Cu and Cd) was determined; among them, the Cd concentration was below the detection limit of the instrument.

The concentrations of Cr, Pb, Cu and Zn were measured using flame atomic absorption spectrometry (AAS) PinAAcle 900 Perkin Elmer. All the equipment was cleaned properly before analysis. One blank sample and seven standards were prepared. The blank contained only distilled water, whereas standards of 0.01, 0.02, 0.05, 0.10, 0.20, 0.50 and 0.75 were used. A calibration curve for the target elements was established, where good linearity was obtained for Cr (0.9992), Pb (0.9947), Zn (0.9985) and Cu (0.9956). The standard reference material of NIST 1643b was employed to determine the accuracy of the analysis.

2.4. Human data

The human data was collected through individual interviews in each respondents house. We took the anthropometric measurements data from 317 respondents. This study was obtained a permission from the local authority, respondents and Health Research Ethics Committee of Hasanuddin University with protocol number 28920093022. All respondents are the residents who had been living in the vicinity of measuring site for at least one year. The questionnaires in this study was presented as Supporting Information file 1.

2.5. Water quality assessment

2.5.1. Heavy metal pollution index

The evaluation of drinking water quality based on PTEs concentration was introduced by Mohan, et al. (1996). Four metals were considered for calculation of HPI in this study since Cd was not detected. The level of contamination was calculated based on weighted arithmetic quality mean method by two steps, (1) establish the rating scale (Qᵢ) for each PTE following the equation in the next step of Water Quality Index (WQI), (2) the unit of weightage (Wi) considered as a value inversely proportional to the recommended standard (Si) of the corresponding parameter. The maximum desired concentration of each element is 0. This level of contamination are
categorized into three groups, low (HPI value < 15); medium (HPI value = 15–30); high (HPI value > 30) (Edet and Offiong 2002). HPI model (Mohan et al. 1996) is calculated using Equation (1).

\[
HPI = \frac{\sum_{i=1}^{n} W_i Q_i}{\sum_{i=1}^{n} W_i}
\]  

(1)

where \(Q_i\) is the subindex of the ith parameter, \(W_i\) is the weightage of the ith parameter and \(n\) is the number of parameters considered. The subindex, \(Q_i\), is determined by using Equation (2).

\[
Q_i = \sum_{i=1}^{n} \frac{M_i(\frac{S_i}{I_i})}{C_0} \times 100
\]  

(2)

where \(M_i\) is the monitored elements, \(S_i\) is the standard value of ith parameter and \(I_i\) is the ideal value of ith parameter in ppb (\(\mu g/L\)). The ideal values \((I_i)\) represented as zero for all elements, since the Indonesian guideline does not have the desirable (ideal) value for drinking water in Indonesia. Permissible or critical pollution index of drinking water in this study set as 100 (Mohan et al. 1996).

2.5.2. Heavy metal evaluation index

This method represented the quality of groundwater concerning the presence of PTEs (Afonne et al. 2020; Astuti et al. 2021a).

\[
HMEI = \sum_{i=1}^{n} \frac{H_c}{H_{mac}}
\]  

(3)

where \(H_c\) is the average concentration of one metal, while the \(H_{mac}\) is the maximum allowable concentration of a specific metal concentration. To classify the quality of heavy metal evaluation index, HMEI < 1 is categorized as low and safe, if HMEI value > 1, groundwater quality considered unfit for consumption (Singh et al. 2017; Zakir et al. 2020).

2.5.3. The degree of contamination \((C_d)\)

This index represent the combined effects of several quality parameters considered harmful in drinking water (Backman et al. 1998). \(C_d\) was introduced by Rapant et.al (Singha et al. 2020). It is determined using Equation (4).

\[
C_d = \sum_{i=1}^{n} C_{fi}
\]  

(4)

where \(C_{fi}\) is the contamination factor for the ith component, and then, is calculated in Equation (5).

\[
C_{fi} = \frac{C_{Ai}}{C_{Ni}} - 1
\]  

(5)
where \( CAi \) is the analytical value of the \( i \)th component and \( CNi \) is the permissible concentration of the \( i \)th component. For \( CNi \), the value is similar with maximum admissible concentration (MAC) for drinking water guideline for every metal due to the less available data for upper permissible limit for chemical parameter (Afonne et al. 2020).

### 2.6. Human health risk assessment

The health risk assessment of this study is using The United States Environmental Protection Agency (USEPA) guideline. Exposure pathways are routes of contaminants enter into human body. The potentially harmful agents may be natural in origin and possibly from an anthropogenic activities. Average Daily Dose (ADD) is calculated separately for each exposure pathways (USEPA 1989). In this study, the human health assessment involve questionnaires to collect personal intake, home characteristics, time-activity patterns, exposure factors, environmental (or area) monitoring (Berglund et al. 2001). The ADD of both exposure routes were defined in Equations (6) and (7).

\[
ADD_{ing} = \frac{C \times IR \times ABS_g \times EF \times ED}{AT \times BW}
\]

(6)

\[
ADD_{derm} = \frac{C \times SA \times K_p \times ABS_d \times EF \times ED \times CF}{AT \times BW}
\]

(7)

Hazard Quotient (HQ) is determined by calculated the ratio between ADD of potentially toxic elements in well water to the reference dose (RfD). This ratio used to assess the noncarcinogenic risk. In this present study, RfD of various metal and parameters were taken into account (Table 1). If the HQ is greater than 1, the possibility of adverse health effect might be experienced by the residents. However, if

| Exposure variables | Ingestion | Dermal | Unit |
|-------------------|-----------|--------|------|
| Concentration of potentially toxic element. | Based on laboratory results | mg/L |
| Ingestion rate (IR) | adult: 2, children: 1 | L/day |
| Exposed skin surface area (SA) | adult: 5700, children: 2800 | cm² |
| Permeability constant (K_p) | Pb (0.0001), Zn (0.006), Cr (0.002), Cu (0.0001) | cm/h |
| Dermal absorption factor \((ABS_g)\) | 0.001 | 0.001 |
| Exposure frequency (EF) | 356 | day/year |
| Exposure time (ET) | 2.6 | hours/event |
| Exposure duration (ED) | Adult: 30 | years |
| Children: 6 | |
| Conversion factor (CF) | 0.001 | L/cm³ |
| Average time (AT) | ED x 365 | site-specific |
| Ingestion rate (IR) | ED x 365 | site-specific |
| Average body weight (BW) | Pb: 3.50 \times 10^{-3}, Zn: 3.00 \times 10^{-3}, Cr: 3.00 \times 10^{-3}, Cu: 4.00 \times 10^{-2}, | kg |
| Reference dose (RfD) | Pb: 5.25 \times 10^{-4}, Zn: 6.00 \times 10^{-2}, Cu: 1.20 \times 10^{-2}, | mg/kg/day |
| Cancer slope factor (CSF) | Pb: 8.50 \times 10^{-3}, Zn: -Cr: 0.5, Cu: - | (mg/kg/day)^{-1} |

Table 1. Exposure variables used in calculating human health risk (USEPA 1997, 2002, 2018).
THQ value is less than 1 then there is no likelihood of adverse health effect. The THQ can be calculated using Equation (8).

\[
HQ = \frac{ADD}{RfD}
\]  

(8)

where HQ is the hazard quotient caused by a single element in a specific route. The RfD is a reference dose for the same metal.

The Hazard Index (HI) is a cumulative metric that considers the combined contribution of all metals in this study. This ratio calculate the potential of noncarcinogenic health risk caused by PTEs. HI < 1 is an acceptable risk and negligible, while HI > 1 means an unacceptable level of risk. Both pathways was calculated using Equations (9) and (10).

\[
HI_{\text{ingestion/dermal}} = \sum HQ_{\text{ingestion/dermal}}
\]  

(9)

\[
HI = HI_{\text{ingestion}} + HI_{\text{dermal}}
\]  

(10)

The carcinogenic risk (CR) is an assessment that used to determine the estimation of developing cancer after exposure to carcinogen. In this study, only Pb and Cr were classified as potential carcinogenic contaminants. According to EPA, the range risks borderline is \(1 \times 10^{-4}\) to \(1 \times 10^{-6}\), means the risk are acceptable. If the risk value < \(1 \times 10^{-6}\) represent no carcinogenic threats from PTEs exposure. Whereas if the risk value > \(1 \times 10^{-4}\) is unacceptable and poses health hazards.

\[
CR = ADD \times SF
\]  

(11)

Total Cancer Risk (TCR) is estimated as a probability of an individual to develop cancer over a period of time. TCR is associated with the combined cancer risk of all PTEs. The value of TCR is calculated using Equation (12).

\[
TCR = \sum CR
\]  

(12)

2.7. Monte Carlo simulation

A health risk analysis is commonly expressed in a single numeric. However, the EPA recommends the use of multiple risk descriptors in addition to protective single-point risk estimates (USEPA 1994). The Monte Carlo simulation is a statistical technique that is an effective source of multiple risk descriptors. This approach is able to minimize uncertainty. Previous studies in health risk prediction showed the probability that chemical exposure can effect human health (Shalyari et al. 2019; Orosun et al. 2020). A number of issues were identified related to the use of MCS to identify the risk and decision making related to environmental problems (Tong et al. 2019; Yang et al. 2019; Sayadi et al. 2020). This study was carried out by the Monte Carlo simulation technique using the software Oracle Crystal Ball version 11.1.2.
Table 2. Drinking water quality result at present study.

| Site          | Village       | Pb (mg/L) | Zn (mg/L) | Cr (mg/L) | Cu (mg/L) | pH | TDS (mg/L) | Temperature (°C) | Conductivity (μS/cm) |
|---------------|---------------|-----------|-----------|-----------|-----------|----|------------|-------------------|----------------------|
|               |               | I         | II        | I         | II        | I  | II         | I                  | I                    |
| 1             | Salenrang     | 2.03      | 0.06      | 0.64      | nd        | 3.48| 1.78       | 0.59               | 8.59                 | 6.10                 |
| 2             | Salenrang     | 3.24      | 0.03      | 0.31      | nd        | 2.28| 1.74       | 0.8                | 6.96                 | 7.08                 |
| 3             | Baruga        | 3.86      | 0.03      | 1.16      | nd        | 2.86| 1.77       | 0.59               | 6.83                 | 7.30                 |
| 4             | Baruga        | 2.42      | 0.12      | 1.04      | 0.31      | 3.47| 1.75       | 0.8                | 7.61                 | 7.44                 |
| 5             | Ammasangeng   | 2.64      | 0.16      | 1.02      | 0.01      | 2.88| 1.87       | 0.61               | 7.23                 | 6.68                 |
| 6             | Tukamasea     | 3.06      | 0.19      | 0.71      | 2.25      | 4.47| 1.87       | 0.79               | 8.73                 | 7.33                 |
| 7             | Tukamasea     | 2.23      | 0.16      | 0.9       | 0.38      | 3.16| 1.91       | 0.56               | 5.98                 | 7.96                 |
| 8             | Tukamasea     | 2.45      | 0.22      | 0.62      | 0.38      | 2.96| 1.91       | 0.66               | 7.77                 | 7.50                 |
| 9             | Bungaeja      | 9.28      | 0.19      | 0.77      | nd        | 3.46| 1.83       | 0.4                | 7.42                 | 6.66                 |
| 10            | Leang-Leang   | 4.15      | 0.19      | 0.94      | 0.53      | 4.32| 1.91       | 0.57               | 8.26                 | 7.16                 |
| 11            | Mattoangin    | 0.22      | 0.16      | 7.02      | 0.07      | 1.69| 1.95       | nd                 | 7.29                 | 7.65                 |
| 12            | Mattoangin    | 0.32      | 0.25      | nd        | nd        | 1.63| 2.12       | nd                 | 6.98                 | 7.45                 |
| 13            | Mattoangin    | 0.32      | 0.19      | nd        | nd        | 1.54| 1.82       | nd                 | 7.12                 | 8.54                 |
| 14            | Mattiro Deceng| 0.35      | 0.22      | 3.68      | nd        | 1.61| 2.08       | nd                 | 6.34                 | 7.15                 |
| 15            | Mattiro Deceng| 0.34      | 0.19      | 0.26      | nd        | 1.58| 2.08       | nd                 | 6.37                 | 7.35                 |
| 16            | Maccini Baji  | 0.34      | 0.28      | 0.22      | nd        | 1.56| 1.95       | nd                 | 7.14                 | 6.72                 |

Min–Max: 0.22–9.28, 0.03–0.28, 0.22–7.02, 0.01–2.25, 1.54–4.47, 174–212, 0.4–0.8, 0.02–0.08, 5.98–8.73, 6.10–8.54, 98–417, 109–891, 25.7–31.7, 28.3–37.2, 48–193, 114–903
Mean: 2.33, 0.16, 1.21, 0.25, 2.68, 1.89, 0.40, 0.29, 7.29, 7.25, 272, 332.9, 27.5, 32.5, 110.4, 521.8

I: rainy season, II: summer season, nd: not detected (below the instrument limitations).
3. Result and discussion

3.1. Concentration of PTEs in groundwater

The mean concentrations of the PTEs for all samples in the rainy and summer seasons were found to be in the order Cr > Pb > Zn > Cu and Cr > Zn > Pb > Cu, respectively. The study showed that Cr is the major pollutant in the groundwater wells of the residents. According to Table 2, the mean value of Cr in both seasons was above the critical limit proposed for drinking water by the WHO, USEPA and the Indonesian Government. These results were similar to the high levels of Cr in groundwater from Sais plain, Morocco (Lotfi et al. 2020) and China (Wang et al. 2018), as those studies were located near tannery and agricultural activities. In addition, other factors such as an ultramafic-dominated environment and the weathering of natural rocks are also strongly related to the presence of Cr in the environment (Vasileiou et al. 2019). This occurs at the research site where the weathering process from karst rocks may influence the enrichment of water bodies with Cr and other PTEs. Moreover, at location nine, a very high concentration of Pb was found (9.28 mg/L). This well is located next to agricultural land and a cement plant site, and it may be affected by particulates carried by the wind and accumulated in soil from the loading process of the transport vehicles. A previous study confirmed that road transport activities increased Pb concentration in the groundwater (Wang et al. 2018). However, Cu levels in the rainy and summer seasons were found to be the lowest in all samples.

The pH value measured the acidity and alkalinity of groundwater. As shown in Table 2, pH values in the present study ranged from 5.19 to 8.73 across both seasons. Most locations had a pH in accordance with the WHO permissible limit of 6.5–8.5 (Astuti et al. 2021b). Effluent discharge from industries (cement plants, mines and chemical industries) might influence the acidity of the groundwater. The pH should be measured because it affects the characteristics of PTEs in groundwater. There was a strong correlation of Cr in groundwater with acidity (p < .01), whereas Zn and Cu were not related to the pH conditions (Supporting Information file 2). Chromium (Cr) is weakly mobile in low pH and becomes stable if the pH increases (ATSDR 2008). The stability and solubility of Cr(VI) are high in neutral or alkaline pH (Mani Tripathi and Chaurasia 2020). This is due to the natural rapid interconversion of different forms of Cr in water, which is the oxidation of Cr(III) to Cr(VI). In natural groundwater, the pH is typically 6 to 8 and CrO_4^{2-} is the predominant species of chromium in the hexavalent oxidation state (ATSDR 2008).

The mean values of total dissolved solids (TDS) in the rainy and summer seasons were 272 mg/L and 332.9 mg/L, respectively, indicating that TDS in the summer season was slightly higher than the rainy season. This may be due to the topographic condition and temperature of the study area. Groundwater at higher temperatures can dissolve more minerals from the surrounding rocks. TDS was classified as low TDS (<1000 mg/L) at high topography and high TDS (>2000 mg/L) at low topography. The result followed topographic conditions and water flow paths (Rao et al. 2012). High TDS is also associated with agricultural and industrial pollution (Rao et al. 2012; Javadi et al. 2020). The presence of TDS in groundwater will be related to
hardness and several health effects as shown by several studies (Gawle et al. 2021; Khan et al. 2021). Hardness occurs with the dissolved polyvalent metallic ions, predominantly calcium (Ca\(^{2+}\)) and magnesium (Mg\(^{2+}\)) cations. This parameter is not

Figure 2. Potentially toxic elements levels in rainy and summer season.
the main indicator of drinking water quality but is an easy indicator on physical tests for odor, appearance and color of water (Amarasooriya and Kawakami 2019).

Temperature is an important parameter because of its influence on water chemistry. The average value of groundwater in the rainy and summer season was 27.5°C and 32.5°C, respectively. Most of the groundwater temperature in this study was in accordance with the standards set by WHO, 30–32°C (WHO 2011; Astuti et al. 2021b). Higher air temperatures existing in summer might affect the groundwater temperatures. A study from Li et al. reported that the release rates of Zn, Cu, Pb, Cr and Cd in low and high temperature experiments were greater at high temperature than low temperature (Li et al. 2013). Some metals could exhibit some degree of stability with temperature variations (Adekunle 2009). For example, in five years, the temperature rose to 15.92°C and affected the condition of the aquifer, input and quality of groundwater in the Najafabad area, where industrial activities, expansion of the cultivated area and domestic use put high pressure on groundwater in this region (Malmir et al. 2021).

Conductivity is an indicator of total salinity or the total amount of dissolved solids (Elumalai et al. 2017). Conductivity values were highly associated with the temperature of groundwater in the study area. The warmer the water was, the higher the conductivity. In Table 2, the average value of conductivity in all groundwater samples for the rainy and summer seasons was 110.4 μS/cm and 521.8 μS/cm, respectively. In this study, Pb and Cr were negatively correlated with electrical conductivity ($p < .01$). This condition might be influenced by the organic matter released from the karst environment, which plays a higher role than thermal conductivity (Brown 2017). The majority of groundwater samples had a high EC value (>600 μS/cm) in the summer season, except for sites 15 and 16. These results are in line with a previous study in Ethiopia (Meride and Ayenew 2016) and slightly lower than a study in Bangladesh (Islam et al. 2015).

Repeated and long-term exposure to PTEs can cause metabolic and digestive problems. According to the water quality standard for drinking water, all samples exceeded the WHO, USEPA and Indonesian National Standard for Pb and Cr (Table 2). This condition is of great concern due to the adverse effects and nonbiodegradable characteristics of PTEs, particularly Pb and Cr that are also classified as heavy metals (Nordberg et al. 2015; Briffa et al. 2020). In the present study, the highest concentration of Cr was recorded in Tukamasea Village. This area was nearest to agricultural land and a cement industrial complex. The fly ash and particulate matter, which bonded to toxic elements from the cement plant may spread to the nearest village (Khan et al. 2020; Rauf et al. 2021b). Figure 2 shows the seasonal variation of PTEs in the study area.

Most cement production in Indonesia still uses coal (Sagala et al. 2018). This is dangerous due to the fact that coal combustion at high temperatures releases heavy metal particulates in fly ash into the environment and water bodies, including wells and rivers (Darmono 2010). Fly ash contains trace elements and can cause pollution. For example, leached Cr(VI) can pass through a relatively thin (12–15 cm) layer of soil, even at low temperatures. This stabilization depends on the pozzolanic reactions (Tsioptias et al. 2020). The size of fly ash that has gone through the grinding process exhibits pozzolanic activity. The increase in fly ash increased the immobilization and acidity of Cr$^{6+}$ and Pb (Dermafas and Meng 2003). Quicklime-sulphate treatment
effectively immobilized Pb with a pH between 8 and 11. High concentration of PTEs in groundwater and other media were also reported in Morocco (Lotfi et al. 2020) and Nigeria (Adeyemi and Ojekunle 2021), where the PTEs were linked to industrial origins (Qin et al. 2019; Haghznazar et al. 2021).

The average level of Pb in groundwater revealed that the concentration was above the permissible limit by the WHO, USEPA and the Indonesian National Standard. As shown in Table 2, the levels of Pb were higher in the rainy season (2.33 mg/L) than summer season (0.16 mg/L). High levels of Pb in groundwater may be due to the leaching process from runoff and metal accumulation from soil (Doyi et al. 2018). In the environment, the accumulation of Pb is possibly the result of anthropogenic activity. Industrial byproducts, atmospheric fallout and fertilizers are dissolved when it rains and leak into groundwater (IARC 2006). Maros is the biggest rice producer in South Sulawesi where the use of fertilizers in agricultural area may increase the accumulation of toxic metals. Pb concentration in groundwater was also reportedly high in Ghana (Doyi et al. 2018), China (Qin et al. 2021) and Nigeria (Adeyemi and Ojekunle 2021). Improper effluent discharge from the industries and pollutant distribution from the nearest area could have contributed to the high Pb load in the groundwater.

The concentration of Zn in all groundwater samples in the rainy and summer seasons ranged from 0.01 to 7.02 mg/L with average values of 1.21 mg/L and 0.25 mg/L, respectively. The average concentration in the rainy season was higher than the summer season. These results were within the WHO maximum permissible limit of 3 mg/L (WHO 2011). In Table 2, the highest level was in station eleven (7.02 mg/L) during the rainy season, which was located in Mattoangin Village. This area is traversed by faults, which play a role in the displacement of deep fluids and act as a flow barrier. A prior study in the Mt. Vettore–Pian Grande plain area confirmed that SO$_4^2$ increased in the aquifer from the fault system during the seismic sequence (Fronzi et al. 2021). The main inorganic components such as Cl$^-$ and SO$_4^{2-}$ in karst aquifers (Shang et al. 2020) will bind PTEs in the form of cations, be stored in groundwater or carried away by mud puddles or water flows on the surface. Climate change, runoff and higher leaching rates also contributed to the high load of Zn in surface water (Wijngaard et al. 2017). In this study, there were no rooftop factories or mines that are commonly related to Zn. So, it can be assumed that the Zn appearance in groundwater came from the leaching process of rocks.

Chromium compounds are commonly found in water and highly reactive in biological systems (OEHHA 2011). The obtained concentration of Cr in this study from the rainy and summer seasons was 2.68 mg/L and 1.89 mg/L, respectively. These values were higher than permissible limit of the WHO, USEPA and the Indonesian standard (Table 2). Chromium levels in this area were higher than a study conducted by Kazakis (2015), where concentrations of Cr(VI) in groundwater varied from 5 to 70 g/L (Kazakis et al. 2015). Another study in Nigeria recorded the range of Cr concentration in groundwater from Ota and Sagamu between 0.012 and 0.020 mg/L and 0.010 and 0.022 mg/L, respectively (Adeyemi and Ojekunle 2021). Metal concentrations in borehole and hand dug wells are highly affected by industrial pollution, mineral dissolution from the weathering process and domestic waste (Sojobi 2016;
Adeyemi and Ojekunle (2021); Rauf et al. (2021a). In the rainy season, the location with the highest concentration of Cr was Tukamasea village, whereas the concentration of Cr in summer tended to decrease. This location is the closest to the large cement industry and agricultural area, which may affect the Cr content in residents’ wells. Leaching events during rainfall and the addition of fly ash from cement plants will contribute to the dissolution and mobility of Cr. In this study, the pH condition was strongly related to the Cr concentration ($p < .01$). Moreover, phosphorous-bearing fertilizers applied to agriculture may release PTEs which contain high Cr content. N and P anthropogenic inputs cause desorption of anionic Cr$^{6+}$ with simultaneous PO$_4^{3-}$ adsorption. A previous study found a link between elevated Cr$^{6+}$ in the Psachna basin from cultivated soils to groundwater, although the correlation was lower compared to the high Cr input from ultramafic rocks and soils (Nziguheba and Smolders 2007; Papazotos et al. 2019, 2020).

The average values of Cu in the rainy and summer seasons were 0.40 mg/L and 0.29 mg/L, respectively. These results are within the maximum permissible limit of the WHO, USEPA and Indonesian standard (Table 2). The range of Cu level in this study was lower compared to those recorded values in studies from Nigeria (Afone et al. 2020; Orosun et al. 2020), Morocco (Lotfi et al. 2020), Iran (Saleh et al. 2019) and North Carolina (Tomlinson et al. 2019). In the rainy season, the runoff containing ion of metals accumulates in the river floodplain. The impounded water in the floodplain then ultimately infiltrates into the groundwater (Aithani et al. 2020). The accumulation of Cu in the present study may occur from a natural enrichment of geochemical processes. After the heavy rains, the runoff water carries huge amount of Cu and other elements into water reservoirs where humans and animals consume the contaminated water (Cisneros 2011; Kumar et al. 2020).

### 3.2. Water quality index

The HPI, the metal evaluation index (HMEI) and the contamination index ($C_d$) were calculated for four metals. The values of HPI, HMEI and $C_d$ in groundwater varied from 12.38 to 306.9, 0.16 to 3.20 and 0.05 to 0.52, respectively. In previous studies
(Afonne et al. 2020; Lotfi et al. 2020; Haghnazar et al. 2021), HPI, HMEI and $C_d$
were used to determine the quality considering the influence of PTEs in groundwater.
The spatial distribution maps of the water quality assessment are illustrated in Figure 3. In this study, the Empirical Kriging method was used to present the spatial arrangement of the measured points and groundwater quality. This method is a sophisticated interpolation technique that uses semivariogram/covariance, which allows measurement error (Paramasivam and Venkatramanan 2019). Moreover, it can be employed by decision-making authorities as a tool for regional planning and groundwater quality management.

Overall, the riskiest location was in the northeast, next to the karst hills. The HPI index was calculated to show the comparison of pollution load and water quality of selected locations. The high values of HPI were recorded in location 2 (106), 3 (125.8), 6 (105.17), 9 (306.09) and 10 (140.38). These obtained results revealed all these locations were above the critical index value of 100 and exceeded the water quality standard for contamination. The location of all the highest values is surrounded by karst rocks with medium and high elevations that influence the possibility of metal accumulation caused by the lower inland water flow to the wells. The condition of five sites fell in the category of unsuitable water for drinking. Regular consumption of the groundwater in this area should be an area of concern and consideration for the local government. Only locations 11, 12, 13, 14, 15 and 16 were of excellent quality. Similar studies of HPI and $C_d$ showed distance and location also affected the load index of PTE pollution in groundwater (Wang et al. 2018).

The HMEI was calculated using the average concentration of four metals (Pb, Zn, Cr and Cu). The values of HMEI this present study ranged from 0.163 to 3.207 with an average value of 0.873. Similar to the HPI result, the high values of HMEI were found in location 2 (1.13), 3 (1.34), 6 (1.14), 9 (3.20) and 10 (1.50). All these locations were rated as unfit for domestic usage. Meanwhile, other locations tended to be safe for consumption (HMEI $< 1$) (Singh et al. 2017; Zakir et al. 2020). The presence of PTEs in these locations still needs to be considered because even at low concentrations, the presence of PTEs is a concern because of the long-term accumulation, biodegradability and toxicity of these metals can cause cancer (Briffa et al. 2020; Mallongi et al. 2020). The high values of HPI and HMEI may be due to the presence of industrial activities (Milivojević et al. 2016). Several karst rock processing industries such as cement, tile and lime factories have been established. The cement factory in this region is one of the largest in eastern Indonesia and has been in operation for almost 20 years. The use of coal in the cement production process will release PTEs particulates through fly ash into the environment (Darmono 2010; Nordberg et al. 2015; Uzma et al. 2018).

The contamination index ($C_d$) provides the contamination degree of combined PTEs and possible risk to humans. In this study, the levels of $C_d$ were below the desirable limit of 1 (Backman et al. 1998; Edet and Offiong 2002). The $C_d$ values in all locations were categorized as low ($<1$). This result was illustrated in Figure 3 and was consistent with the spatial distribution of HPI and HMEI. Unlike HPI and HMEI, the $C_d$ values were lower. This is due to the formula of $C_d$, which
Table 3. Hazard Quotient (HQ) and Hazard Index (HI) values on adult and children.

| PTEs | Rainy season | Summer season | | Rainy season | Summer season | |
|------|--------------|---------------|---|--------------|---------------|---|
|      | HQ Ingestion | HQ Dermal      |   | HQ Ingestion | HQ Dermal      |   |
|      | Adult        | Children      |   | Adult        | Children      |   |
| Pb   | $9.0 \times 10^{-3}$ | $1.7 \times 10^{-3}$ |   | $6.1 \times 10^{-4}$ | $1.2 \times 10^{-4}$ |   |
| Zn   | $4.4 \times 10^{-3}$ | $8.7 \times 10^{-4}$ |   | $9.2 \times 10^{-4}$ | $1.8 \times 10^{-4}$ |   |
| Cr   | $1.2 \times 10^{-2}$ | $2.3 \times 10^{-3}$ |   | $3.1 \times 10^{-5}$ | $9.9 \times 10^{-6}$ |   |
| Cu   | $3.1 \times 10^{-4}$ | $6.1 \times 10^{-5}$ |   | $3.1 \times 10^{-5}$ | $6.1 \times 10^{-6}$ |   |
| THI  | $3.0 \times 10^{-2}$ | $5.9 \times 10^{-3}$ |   | $9.8 \times 10^{-4}$ | $1.8 \times 10^{-4}$ |   |
incorporates the maximum allowable concentration of heavy metals to address the risk to humans (Fallah et al. 2019).

### 3.3. Health risk assessment

The hazard quotient (HQ) values from Pb, Zn, Cr and Cu were lower than one, which revealed that the noncarcinogenic risk to the residents was still negligible for adults and children. As shown in Table 3, the HQ value of ingestion in adults was slightly higher than in children. This is possible since adults have had a longer duration of exposure and have consumed more water than children. Similar results in Bangladesh and China also showed that adults were more susceptible than children to contaminated groundwater (Gao et al. 2019; Saha and Rahman 2020). The concentration of heavy metal in consumed water is the most important factor to determine HQs. The result was opposite to a study of Fallahzadeh et al. (2017), where the children’s condition was recorded to be more severe compared to adults from heavy metal exposures. HQ values of ingestion in adults and children contribute more risk than skin contact to the HI. This implies that oral ingestion is the major pathway of noncarcinogenic exposure to pollutants followed by dermal contact (Basu et al. 2011; Gao et al. 2019; Xiao et al. 2020). The sum of HQ was expressed as a Total Hazard Index (THI) value and was used to assess the overall estimation for noncarcinogenic risk posed by more than one chemical. The THI values for adults and children in the rainy and summer seasons were $3.0 \times 10^{-2}$, $5.9 \times 10^{-3}$, $4.8 \times 10^{-3}$ and $9.2 \times 10^{-4}$, respectively. The noncarcinogenic risk in the rainy season was slightly higher than the dry season. These results indicated that adults have a higher possibility of experiencing adverse health effects from PTE exposure than children, even though none of them exceeds the permissible limit set by the USEPA (THI < 1). It was observed that in both the rainy and summer seasons Pb, Cr, Cu and Zn metals had negligible risks.

Cancer risk (CR) values were calculated from two metals, Pb and Cr. Both of these metals have a cancer slope value and are classified as dangerous heavy metals according to IARC (IARC 1990, 2006; Langård and Costa 2015). The values of CR for adults through ingestion from Cr accumulation in groundwater in the rainy and summer seasons were recorded as the highest with $1.8 \times 10^{-5}$ and $1.2 \times 10^{-5}$, while the CR values in children were $1.3 \times 10^{-6}$ and $2.4 \times 10^{-6}$. Moreover, the CR results from Pb exposure through ingestion and dermal contact were below the permissible limit and classified as acceptable risk. The combined sum values of CR were expressed in total cancer risk (TCR). The values for adults and children were above the USEPA permissible limit. The values showed the TCR values were slightly higher than the established standard of $1.0 \times 10^{-6}$ to $1.0 \times 10^{-4}$, indicating the possibility of cancer risk for humans in the future. In an animal study, liver damage was experienced by

### Table 4. Carcinogenic risk (CR) values on adult and children.

| PTEs | Rainy season | Summer season |
|------|--------------|---------------|
|      | CR Ingestion | CR Dermal     | CR Ingestion | CR Dermal     |
|      | Adult    | Children | Adult    | Children | Adult    | Children | Adult    | Children |
| Pb   | $2.6 \times 10^{-7}$ | $5.2 \times 10^{-8}$ | $1.9 \times 10^{-9}$ | $3.7 \times 10^{-10}$ | $1.8 \times 10^{-10}$ | $3.5 \times 10^{-9}$ | $1.3 \times 10^{-10}$ |
| Cr   | $1.8 \times 10^{-5}$ | $3.5 \times 10^{-6}$ | $1.3 \times 10^{-6}$ | $2.1 \times 10^{-8}$ | $1.2 \times 10^{-5}$ | $2.4 \times 10^{-6}$ | $7.9 \times 10^{-8}$ | $1.5 \times 10^{-8}$ |
rats after exposure to chromium in drinking water (liver weight, ALT, ALP) (Duan et al. 2019). As shown in Table 4, CR values through dermal adsorption were below the permissible level and indicated a negligible potential health risk. This is in accordance with research conducted by Basu et al. (2011); the frequency of metal exposure through showering/bathing for a short time will not be harmful to humans compared to the ingestion route. Dermal contact from Cr exposure was higher than Pb, although at moderate risk. Furthermore, the obtained values of CR for dermal contact can be considered as negligible. This result was in line with a previous study using a Monte Carlo simulation, which revealed the cancer risk estimation from dermal contact is not significant with less than 1% (Saha and Rahman 2020).

3.4. Monte Carlo simulation

The probability of cancer risk was estimated by using the Monte Carlo Simulation (MCS) from the combined pathways of ingestion and dermal contact. The simulation model ran for 10,000 trials. According to the simulation in Figure 4, the 95th percentile value of TCR for adults and children were $1.88 \times 10^{-5}$ and $3.48 \times 10^{-6}$, respectively.
respectively. From these results, the estimated cancer risk was above the acceptable range of the USEPA. The input parameters of the model that were most important in terms of cancer risk were identified through sensitivity analysis, as shown in Figure 5.

The sensitivity chart revealed the concentration of Cr in groundwater was the most significant factor for developing cancer in children (99.8%), followed by ED (0.1%). Whereas in adult, the highest contribution was EF (50.4%), followed by Cr concentration (49.5%). This results are in line with previous studies that confirmed the influence of toxic metals that had the highest impact in carcinogenic hazard calculation (Fallahzadeh et al. 2017; Hossain and Patra 2020). The most suitable scenarios focus on periodic monitoring of industrial waste, remediation and controlling the use of fertilizers in rice fields close to water sources. It is expected that hazardous metals such as Cr and Pb will not be present in the groundwater due to their toxicity levels, persistence in the environment and bioaccumulative nature. In children, EF was indicated as the most significant factor in cancer risk. The more often discrete exposure events occur, the higher the possibility that children will be at risk of cancer. Hence, children should reduce their consumption of drinking water that contains harmful metals. Children absorb more metal than adults due to their body ratio. Moreover, the contribution of Pb concentration, BW and SA were recorded below 0.01%, indicating a low effect, which can be ignored.

4. Conclusion

This study revealed that the groundwater of Maros karst contains potentially toxic elements such as Pb, Cr, Cu and Zn. The values of TDS, pH, temperature and EC were within the desired limits, whereas PTE concentrations were found above the WHO and Indonesian standards. This indicates that the levels of Pb, Cr, Cu and Zn can cause several health issues for the local residents. The water quality index using HPI and HMEI revealed heavy contamination of PTEs was possibly due to the influence of the cement plant, natural enrichment and agricultural activities, while $C_d$ showed a low to moderate level. Overall, the spatial distribution map shows a consistent result for all indexes, where the northeast area which is located in Tukamasea.
and Leang-Leang villages are the areas with the lowest drinking water quality. Therefore, prevailing reducing conditions in the aquifer of Maros karst may enhance the dissolution of trace metals and require careful monitoring of the groundwater. The Monte Carlo simulation model identified the probability that TCR in adults was slightly higher than children. The sensitivity analysis showed that the influence of Cr concentration was a significant contributor to the possibility of developing cancer in adults and children. Long-term action is required to reduce the intake of PTEs from directly drinking groundwater in this region where high levels of PTEs were found in the groundwater.

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**Animal research**

Not applicable.

**Author’s contribution**

Anwar Mallongi, created the ideas, planned the experiments and writing manuscript; Annisa Utami Rauf, writing the manuscript, data analysis and data collection; Anwar Daud, Muhammad Hatta and Wesam Al Madhoun, validation and supervision; Ridwan Amiruddin and Atjo Wahyu, data verification, design and methodology; Stang, Data Analysis; Ratna Dwi Puji Astuti, writing the manuscript and verified the numerical result.

**Consent to publish**

The authors grant the journal/publisher to publish the work and guarantees this work has not been previously published elsewhere. All involved participants in the study are aware of the planned publication and have given their consent.

**Data availability**

The data that support the findings of this study are available on request from the corresponding author.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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