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# Assessment of heavy metal contamination of underground water sources Gorgan, Iran with HEI, HPI, Cd and MI indices and hazard risk assessment (Monte Carlo simulation)

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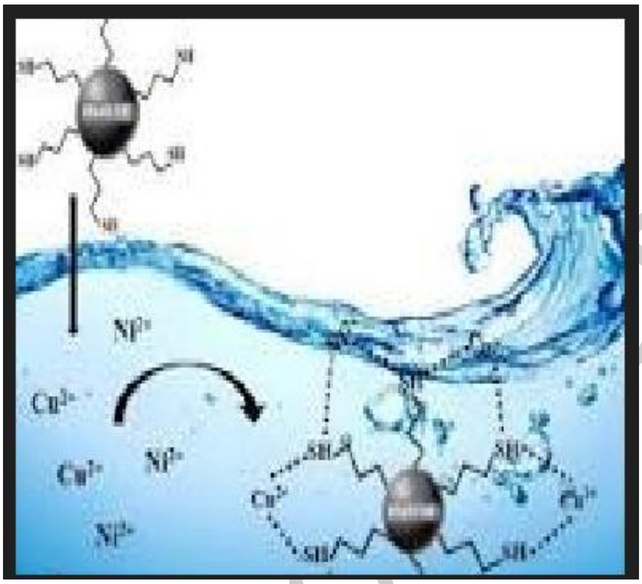
**Graphical abstract**



**Abstract**

Heavy metals are among the most harmful pollutants found in drinking water sources, causing serious damage to the body's metabolic, physiological, and structural systems. This study aimed to assess the concentrations of lead, cadmium, chromium, copper, zinc, iron and manganese in 50 groundwater samples from 25 water supply wells during wet and dry seasons. Water quality was comprehensively assessed using the Heavy Metal Evaluation Index (HEI), Heavy Metal Pollution Index (HPI), Contamination Degree (CD) and Metal Index (MI). Carcinogenic and non-carcinogenic risk assessments were performed using deterministic and probabilistic approaches for at-risk populations. Based on the results, zinc showed the highest concentration followed by chromium in both wet and dry seasons. Based on the non-carcinogenic risk assessment, the highest level of heavy metal contamination showed the highest concentration in children and adults. chromium had the highest carcinogenic risk in adults and cadmium had the lowest in children. In terms of sensitivity, the concentration and amount of heavy metal consumption significantly affect the carcinogenic and non-carcinogenic risks.

**Keywords:** Heavy metal, Contamination indices, Risk assessment, Monte Carlo simulation

## 1. Introduction

Today, heavy metal pollution is very important because of its toxicity, stability, wide distribution and non-biodegradability in the food chain as a threat to the environment and humans (Zaynab *et al*. 2022). Heavy metals enter water sources through domestic, urban, and industrial sewage as well as surface runoff (Saha *et al*. 2018; Raveena *et al*. 2024). Heavy metals enter the human body through eating contaminated water, air, and food and are gradually accumulated in fat tissues, muscles, bones, and human joints (Adekanmi *et al*. 2021). Among the effects of heavy metals entering the human body are diseases such as nervous disorders, types of cancer, and in severe cases, death (Mahurpawar *et al*. 2015). Heavy metals such as lead (Pb), chromium (Cr) and cadmium (Cd) have been found to be carcinogenic and dangerous. Even in low concentrations, they disrupt the normal functioning of the body (Renu *et al*. 2021). The main source of lead in water is from its dissolution in old pipes. Lead poisoning is more common in children due to their greater vulnerability (Levallois *et al*. 2018; Sannasi *et al*. 2025). Cr enters the environment as a result of chrome plating, industrial textiles, printing industry, potography and tanning (Coetzee *et al*. 2022). Cd enters the water through soil erosion, sewage from polluted areas and fertilizers in agriculture (Khan *et al*. 2017). Also, some rare metals such as Copper (Cu), Zinc (Zn), Iron (Fe), and Manganese (Mn) are needed in small amounts for the body's metabolic activities (Silva *et al*. 2019). Cu poisoning causes abdominal pain, nausea, diarrhea, vomiting liver damage, kidney disease and cancer (Engwa *et al*. 2019). Zn poisoning leads to diarrhea, Mn inhibits the intellectual development of children, and Fe causes genetic and metabolic diseases (Hussain *et al*. 2022; Mezzaroba *et al*. 2019). To evaluate the degree of water pollution by heavy metals for drinking purposes, indicators such as heavy metal evaluation index (HEI), heavy metal pollution index (HPI), metal index (MI) and pollution degree (Cd) can be used (Ahirvar *et al*. 2023; Gupta *et al*. 2017). The HPI is used based on the concentration of heavy metals in order to know the overall quality of underground water resources (Şener *et al*. 2023). The MI index is used to determine the potability of water sources and the Cd index is used to determine the combined effects of a number of quality parameters (Şener *et al*. 2023). Health risk assessment has four basic steps, which include risk identification, exposure assessment and determination, dose-response relationship assessment, and risk characteristics description (Ji *et al*. 2020). Health risk assessment is one of the useful tools in determining the level of human risk of cancerous and non-cancerous diseases (Alidadi *et al*. 2019). In cancer risk assessment, even the smallest amount of human contact with pollutants increases the risk of cancer. If the amount of human exposure to the pollutant does not exceed the threshold limit, the probability of non-cancerous health complications will not exist or the probability will be weak (Varol *et al*. 2023). A study conducted by Alidadi et al.in the drinking water of northeastern Iran in 2019. The HQ values of arsenic and heavy metals for the combined routes were below the safety level (HQ < 1) for adults, while the HI for children was above the safety level at some stations. Cr showed the highest mean share of HI total elements (55 to 71.2%) for adult and pediatric population. The average values of total carcinogenic risk (TCR) through drinking water exposure for children and adults were $1.33 \times 10^{-4}$ and $7.38 \times 10^{-5}$, respectively (Alidadi *et al*. 2019). but there has been no study on water pollution by heavy metals using the mentioned indicators, nor has there been any risk assessment. Therefore, the purpose of this study is to evaluate the quality of drinking water with HPL HEI, MI and Cd pollution indicators and to evaluate the risk of non-cancerous diseases (risk index) and the risk of cancer caused by drinking water consumption in a definitive way and simulation with Monte Carlo was done.

## 2. Materials and methods

### *2.1. Characteristics of the studied area*

This descriptive-cross-sectional study was conducted in 2022 on drinking water sources in Gorgan province. Gorgan city is located at 36.8418° N, 54.4334° E. Gorgan city has an area of 1615 km$^2$ at an altitude of 160 meters and the climate of Gorgan is moderate to slightly dry with an average rainfall of 148 mm per year. According to the 2006 statistics of the Water and Sewerage Organization, a total of 50 water samples were taken from 25 wells in the form of a census in two dry and wet seasons to measure the concentration of heavy metals. In this study, ARC GIS 9.3 software was used to prepare maps and quality assessment was used. According to the UTM geographic coordinates, the density map of the wells was prepared (**Figure 1**).

### *2.2. Water sampling and heavy metal analysis*

The method of sampling and storage of samples was based on the standard methods for the examination of water and wastewater (1998). First, polyethylene containers are washed twice with 1% nitric acid and distilled water. Samples were taken from polypropylene containers with a volume of 500 ml from 25 stations in dry and wet seasons. The samples were transported to the laboratory with a flask containing ice. After preparing a special standard solution for each of the heavy elements, the concentration of Pb, Cd, Cr, Cu, Zn, Fe and Mn was read in µg/ml using polarographic system (Model 797 VA, Metrohm, Switzerland) (Hifi et al. 2020).

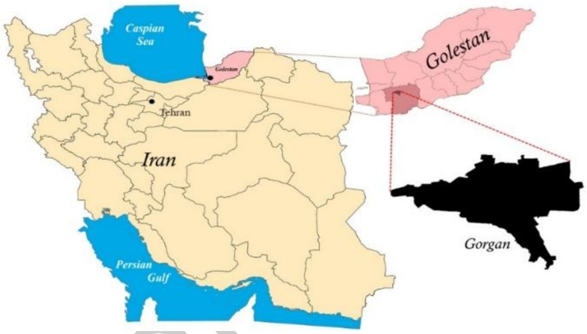



**Figure 1.** The location of the Gorgan Plain study area

### *2.3. Hazard risk assessment*

The assessment of human health risk (carcinogenic and non-carcinogenic risk) caused by heavy metals in water has been measured using the standards of the Environmental Protection Agency EPA (ASSESSment ERPR. Guidance for Superfund et al. 1989). The health risk of exposure to heavy metals through drinking water based on the results of measuring the concentration of metals in water by calculating the hazard ratio (HQ) to indicate non-carcinogenic effects and lifetime cancer risk based on the relationships provided by the EPA, respectively from the relationship 1 to 4 were determined (Bamuwamye et al. 2017; Shokoohi et al. 2021). According to Eq. 1, to calculate the risk ratio of non-carcinogenic diseases (HQ), Chronic Daily Intake (CDI) and pollutant reference dose (RFD) are required (Khan et al. 2013). CDI is the average daily dose of each metal by via pathways of drinking water, and food (mg/kg.day), According to the (USEPA), Eq. 2 and Eq. 3 are used to determine the chronic daily intake (CDI) through the routes of ingestion and dermal absorption (Mohammadi et al. 2019). C is the concentration of heavy metal in water (µg/ml), IR is the amount of daily water consumption, EF is the frequency of exposure, ED is the duration of exposure, BW is body weight, and AT is the average time in days. **Table 1** shows the default numbers for the parameters of this Eqs.

$$\text{HQ} = \frac{CDI_i}{RFD_i} \qquad (1)$$

$$\text{CDD ingestion} = \frac{C \times IR \times EF \times ED}{BW \times AT} \qquad (2)$$

The unit of RfD is (mg/kg.day) which and its amount for Cd= 0.0005, for Cr = 0.003, 0.0035 for Pb, 0.3 for Zn, 0.14 for Mn, 0.4 for Cu, and 0.7 for Fe were considered.

**Table 1.** Variables used to calculate health risk assessment

| | | amount | | | |
|---|---|---|---|---|---|
| **Parameter** | **Unite** | **Non-carcinogenic for men** | **Non-carcinogenic for women** | **Non-cancer for children** | **cancer** |
| Water consumption | liters / day | 2 | 2 | 1 | 2 |
| Frequency of exposure | Day/ year | 365 | 365 | 326 | 362 |
| Exposure time | year | 30 | 30 | 6 | 70 |
| Body weight | Kg | 70 | 60 | 15 | 70 |
| Average time | Day | 1095 | 1095 | 2190 | 25550 |

$$ADD_{Dermal} = \frac{C \times SA \times AF \times ABF \times EF \times ED \times 10^{-6}}{BW \times AT} \quad (3)$$

The hazard index (HI), which is used to estimate the total potential non-carcinogenic effects of exposure to a mixture of heavy metals in water, was calculated using HI according to the EPA guidelines for health risk assessment (Lei et al. 2015; Bamuwamye et al. 2015). From the following Eq. 4.

$$HI = \sum_{1}^{n} HQ = HQ_{Pb} + HQ_{Cd} + HQ_{Cr} + HQ_{Cd} + HQ_{Zn} + HQ_{Cu} + HQ_{Fe} + HQ_{Mn} \quad (4)$$

Total non-carcinogenic risk or total risk index in Eq. 4 is the sum of HQs caused by various pollutants (pollutants in this study are metals Cd, Cr, Pb, Mn, Zn, Cu and Fe) through ingestion and skin absorption. 1 means a certain degree of harmful effects on human health, and HI ≤ 1 means the absence of risk (Wang et al. 2020).

### *2.4. Assessment of carcinogenic risk*

Carcinogenic risk assessment (ELCR) can be calculated using Eq. 5, The ILCR is defined as the lifetime probability of developing cancer as a result of daily exposure to a given amount of any carcinogenic chemical for seventy years (Kamarehie et al. 2019). The following equation (Eq. 5). SF is the cancer slope factor of the metal with mg/ kg/day which is 0.38 for Cd and 0.19 for Cr (Gržetić et al. 2008).

The calculated ELCR is the probability of developing cancer during the lifetime of the general population exposed to any type of carcinogenic chemical (EPA U 2018).

$$\mathrm{ELCR} = ADD \times SF \quad (5)$$

According to the USEPA guidelines, the range of acceptable or tolerable carcinogenic risk for a single carcinogen and multi-element carcinogens is considered to be $10^{-6}$ and $<10^{-4}$ (Zaynab et al. 2022).

### *2.5. Monte Carlo simulation and uncertainty analysis*

In the usual methods of risk assessment, the amount of risk is estimated and reported as a point estimate. Risk point estimation provides quantitative information about the degree of uncertainty and variability around the estimated risk point. To achieve more accurate information of the Monte EPA simulation method, the risk or risk ratio (MCS) of Carlo is proposed has done Monte Carlo simulation is based on mathematical statistics and probability theory to achieve the uncertainty model by means of random sampling and probability distribution for each input variable (Seifi et al. 2020).

**Table 2.** Description of input parameters to Monte Carlo simulation software

| **Input parameter** | **Unite** | **Children** | **Adult** |
|---|---|---|---|
| Cadmium concentration (fw), $C_{tCd}$ | mg/kg | Mean= 0376/0, SD= 0606/0 | |
| Lead concentration (fw), $C_{tPb}$ | mg/kg | Mean= 346/0, SD= 428/0 | |
| EF | days/year | 350 | 350 |
| ED | year | 10 | 70 |
| IngR | mg/day | Mean=0/232, SD=0/0232 | Mean=0/345, SD=0/0345 |
| BW | kg | Mean=32/7, SD=3/27 | Mean=70, SD=7 |
| AT | day | 25550 | 25550 |

**Table 2** describes the input parameters to the Monte Carlo simulation software. In this study, the Monte Carlo simulation was performed using the Cristal Ball software (version 11.1.2.4, Oracle, Inc., USA) that It is activated as an add-on in MS-Excel software. Description of input parameters to the Monte Carlo simulation software is given in **Table 2**.

### *2.6. Pollution assessment indicators and toxic quality parameters of underground water resources*

Special pollution indicators are usually used for different purposes, which are mentioned below.

#### *2.6.1. Heavy Metal Pollution Index (HPI)*

The HPI index is a method for evaluating the concentration of heavy metals in water, which is calculated based on the weighted average quality and includes two main steps. Creating a rating scale and a weight for each parameter and determining the pollution parameters on which the index should be calculated. Its value is calculated using Eqs 6 and

7. The numerical value of 100 has been introduced as the critical limit of this index, and If HPI > 100, the water quality is considered unacceptable and polluted (Sarhat *et al*. 2023; Grema *et al*. 2022)

$$\mathrm{HPI} = \frac{\sum_{i=1}^{n} \mathrm{Wi\ Qi}}{\sum_{i=1}^{n} \mathrm{Wi}} \tag{6}$$

Based on Eq. 6, Wi is the weight ratio of the i-th component and is inversely standardized, and Qi is the sub-index of the evaluated element. which is calculated from Eq. 7. where Qi is the sub-index, Mi is the measured concentration of the element, Ii is the ideal concentration assessed metal and Si are the permissible limits for assessed metals in µg/L (Anyanwu *et al*. 2022).

$$\mathrm{Qi} = \sum_{i=1}^{n} \frac{\{Mi(-)li\}}{(si - li)} \times 100 \tag{7}$$

*2.6.2. Heavy Metal Evaluation Index (HEI)*

The HEI, calculates the overall water quality according to the presence of heavy metals. that is calculated based on Eq. 8 (Rajkumar *et al*. 2020).

$$HEI = \sum_{i=1}^{n} \frac{H_i}{H_{max}} \tag{8}$$

where $H_c$ and $H_{max}$ are respectively the measured values and the maximum allowed concentration of each metal. According to the existing classification, if HEI<400, indicates low pollution, 400<HEI<800 indicates moderate pollution and HEI≥800 indicates high pollution (Herath *et al*. 2022).

*2.6.3. Metal Index (MI)*

The metal index is used to determine the amount of water pollution in terms of heavy metals and to evaluate the potability.

$$\mathrm{MI} = \frac{\mathrm{C}}{(\mathrm{MAC})} \tag{9}$$

In Eq. 9, C is the concentration of each element in the MAC solution, the highest limit for a metal element in the standard state, and i is the number of the element. If the values obtained for MI are less than one, the water is potable, and if it is more than one, the water is not potable, and it is at the threshold of danger (Gueddari *et al*. 2022).

*2.6.4. Pollution Degree Index (Cd)*

The Cd index is a tool for evaluating water pollution with heavy metals and the relative pollution of different metals and then the combined effect of metals calculates separately, in such a way that the parameters with concentration exceeding the permissible limits are entered into the equation (Ghobadi *et al*. 2022). If Cd < 1, 1 >Cd> 3, and Cd> 3 indicate low, medium, and high levels of pollution, respectively. Eqs 10 and 11 show how to calculate this index: in which $C_{fi}$, $C_{Ai}$ and $C_{Ni}$ respectively are pollution factor, concentration was measured and the maximum allowed metal concentration was checked (Kumar *et al*. 2021).

$$\mathrm{Cd} = \sum_{i=1}^{n} Cfi \tag{10}$$

$$\mathrm{CFi} = \frac{CAi}{CNi} - 1 \tag{11}$$

In calculating these indices, the highest concentration of Zn= 5000, Cd= 3, Cr= 50, Cu= 1000 and Pb 10 µg/l are considered. The ideal concentration for Zn, Pb, Cd, Cr, and Cu is 10, 3000, 10, 3, 50, and 2,000 µg/l, respectively, and the World Health Organization guideline values for Zn are 5,000 and Pb is 100 (Ghobadi *et al*. 2021).

*2.7. Statistical analysis*

Descriptive statistical analysis was performed by SPSS 16.0. To prepare a zoning map using ArcGIS 10.3 software and to assess possible risk, Monte Carlo simulation was performed using Cristal Balle software (version 11.1.2.4, Oracle, Inc., United States) was used (Hilfi *et al*. 2020; Seifi *et al*. 2020).

*2.8. Statistical analysis of metals in underground water sources*

The statistical description of the concentration of metals (Cd, Cr, Pb, Mn, Zn, Cu and Fe) in the underground water sources of Gorgan city in the dry and wet season and the related water standards are presented in **Tables 3 and 4**. Among the measured metals, Zn and Cr have the highest concentration among heavy metals in water with an average concentration of 149.71, 49.87 µg/l in the dry season and 220.85, 62.08 µg/l in the high rainfall season. The highest average concentrations presented in water respectively include Zn= 513.08, Cr= 94.52, Cu= 57.60, Pb= 5.44, Fe= 0.94, Cd= 0.13 and Mn= 0.013 µg/l in the dry season and Zn= 1458.88, Cr= 120. 89, Cu= 120.89, Pb= 11.39, Fe= 0.6, Cd= 0.28 and Mn= 0.013 µg/l in the wet season. The findings showed that except for Zn and Cr, the concentration of all heavy metals measured was lower than the national standard of Iran 1053, WHO and EPA. The concentration of all metals in the high wet season was higher than the concentration of metals in the dry season. The concentration of metals in water sources was obtained in the order of Zn > Cr > Cu > Pb > Fe > Cd > Mn.

*2.9. Zoning of heavy metals in Gorgan Plain drinking water sources*

**Figure 2** shows the distribution of heavy metals Cd ($A_1$), Pb ($A_2$), Cr ($A_3$), Cu ($A_4$), Zn ($A_5$), Mn ($A_6$) and Fe ($A_7$) in the dry season Cd ($B_1$), Pb ($B_2$), Cr ($B_3$), Cu ($B_4$), Zn ($B_5$), Mn ($B_6$) and Fe ($B_7$) and in the wet season. **Figure $A_1$** shows the concentration of Cd in the dry season and $B_1$ shows the concentration of Cd in the wet season. The lowest Cd concentration in the dry season corresponds to well 23 and the highest amount of Cd in the wet season corresponds to well 8 with concentrations of 0.05 and 0.28 µg/l, respectively. In general, the average Cd in the water of Gorgan Plain is 0.13 ± 0.02 µg/l, which is not statistically difference between the dry and wet seasons. The Cd concentration of the water in the surrounding wells is within the permissible range for all the stated standards.

**Table 3.** The results of the heavy metal concentration in drinking water sources of Gorgan city in the dry season and standards related to drinking water

| Heavy metal | The lowest concentration (μg/l) | The highest concentration (μg/l) | Average concentration (μg/l) | Maximum allowed (standard 1053 of Iran) (mg/l) | Maximum allowed (WHO 2017 standard) (mg/l) | Maximum allowed (2018 EPA standard) (mg/l) |
|---|---|---|---|---|---|---|
| Cd | 0.05 | 0.13 | 0.09 | 0.003 | 0.003 | 0.005 |
| Cr | 25.36 | 94.52 | 49.87 | 0.05 | 0.05 | 0.1 |
| Pb | 0.03 | 5.44 | 3.62 | 0.01 | 0.01 | 0.015 |
| Mn | 0.006 | 0.013 | 0.008 | 0.4 | 0.4 | 0.05 |
| Zn | 47.01 | 513.08 | 149.71 | - | - | 5 |
| Cu | 0.01 | 57.60 | 35.88 | 2 | 2 | 1.3 |
| Fe | 0.02 | 0.94 | 0.33 | - | - | 0.3 |

**Table 4.** The results of the concentration of heavy metals in the drinking water sources of Gorgan city in the wet season and the standards related to drinking water

| Heavy metal | The lowest concentration (μg/l) | The highest concentration (μg/l) | Average concentration (μg/l) | Maximum allowed (standard 1053 of Iran) (mg/l) | Maximum allowed (WHO 2017 standard) (mg/l) | Maximum allowed (2018 EPA standard) (mg/l) |
|---|---|---|---|---|---|---|
| Cd | 0.06 | 0.28 | 0.13 | 0.003 | 0.003 | 0.005 |
| Cr | 16 | 129 | 62.08 | 0.05 | 0.05 | 0.1 |
| Pb | 1.17 | 11.43 | 4.63 | 0.01 | 0.01 | 0.015 |
| Mn | 0.006 | 0.013 | 0.008 | 0.4 | 0.4 | 0.05 |
| Zn | 88.26 | 1458.88 | 220.85 | - | - | 5 |
| Cu | 11.67 | 120.89 | 58.10 | 2 | 2 | 1.3 |
| Fe | 0.07 | 0.6 | 0.28 | - | - | 0.3 |

**Figure $A_2$** shows the concentration of Pb in the dry season and $B_2$ shows the concentration of Pb in the wet season. The highest amount of Pb is related to well 18 in the dry season and the lowest is related to well 8 in the wet season, with values of 2.73 and 11.43 μg/l respectively. there is a difference between the dry season and the wet season. According to Iranian standard 1053, the standard amount of Pb for drinking water is 10 μg/l, and the concentration of Pb in Gorgan water is within the permissible range. **Figure $A_3$** shows the concentration of Cu in the dry season and $B_3$ shows the concentration of Cu in the wet season. The lowest Cu concentration corresponds to well 7 in the dry season and the highest Cu concentration corresponds to well 12 in the wet season with the values of 11.67 and 121.89 μg/l, respectively. Statistically, there is no difference between spring and summer. Therefore, the amount of Pb in the surrounding wells is within the permissible range. **Figure $A_4$** shows the concentration of Zn in the dry season and $B_4$ shows the concentration of Zn in the wet season. The highest amount of Zn is related to well No. 22 in the wet season and the lowest is related to well No. 16 in the dry season, with values of 1458.88 and 86.5 μg/l, respectively. In general, statistically there is a difference between the dry season and the wet season. In map number 4, the highest amount of Mn in the wet season is related to well 12 and the lowest is related to well 18 with optimal values of 13.04 and 5.66 μg/l. With this calculation, the concentration of Mn in Gorgan Plain is within the permissible range. According to map 3, the highest amount of Fe is related to well number 19 in the wet season and the lowest is related to well number 9 in the spring season with the best values of 940.04 and 21.85 μg/l. Also, statistically, there is no difference between spring and summer. According to Iran standard 1053, the maximum allowed amount of Fe for drinking water is 3 μg/l. The average concentration of heavy metals in underground water samples of Gorgan during the wet season is as follows:

Fe >Pb>Zn>Cd>Mn>Cr>Cu

And the average concentration of heavy metals in underground water samples of Gorgan during the dry period is as follows:

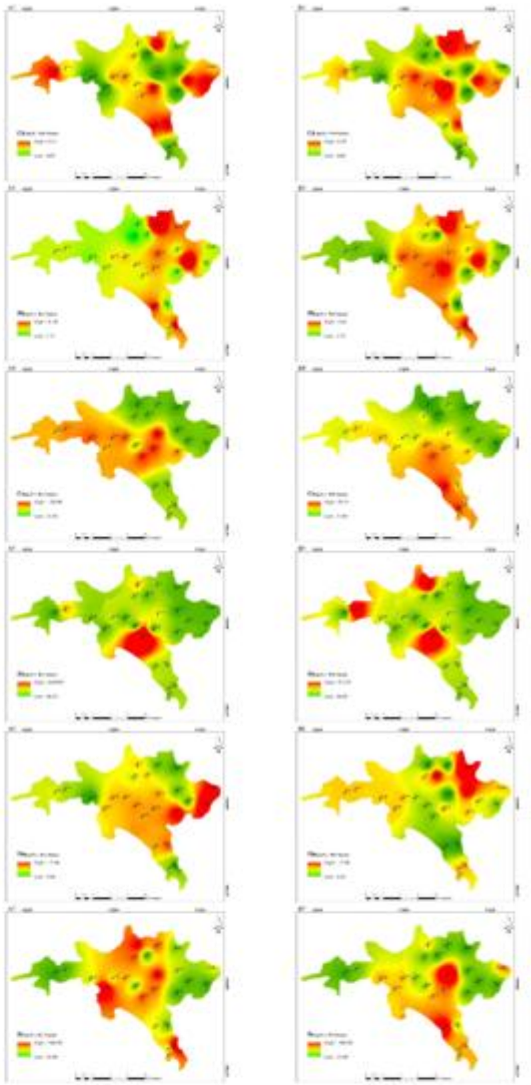
Fe >Zn>Mn>Pb>Cd>Cr>Cu

*2.10. The results of evaluation of pollution indicators and toxic parameters of water resources quality in Gorgan Plain*

In order to calculate the (Cd), (MI), (HPI), and (HEI) to determine the degree of pollution (Cd) of water sources in terms of heavy metals, the concentrations obtained from metals were compared with the maximum permissible limit of a metal element in the standard state. According to the obtained results and based on **Figure 3**, the degree of Cd pollution in the dry season ($A_1$) and wet season ($B_1$) is low in all the wells of the Gorgan Plain. According to the results of the heavy metal evaluation index (HEI) in the dry ($A_2$) and wet ($B_2$) seasons, it shows that the degree of pollution in the dry season ($A_2$) is only in (W22) and in the wet season (B2). Well number W22 had a high level of pollution. The results of calculating the heavy metal pollution index (HPI) in the dry season ($A_3$) and wet season

($B_3$) showed that all the wells had a low level of pollution in the dry season. In the dry season, W28 and W22 wells had an average degree of pollution. According to the results of the evaluation index of heavy metals (MI) in the dry season ($A_4$) and wet season ($B_4$) in all stations, it shows that the degree of pollution in the dry season ($A_4$) in W11 has a low degree of pollution and in well W22 it has a moderate degree of pollution and in the wet season ($B_4$) in wells No. W19, W17 it has a severe degree of pollution and in W22 it has a high degree of pollution. The point is that in this index, if the amount of only one of the metals is more than the highest limit, the amount of the index will be more than one and it will be placed in the non-drinkable category in terms of drinking.

**Figure 2.** Spatial distributions of pollutants during wet and dry season samples



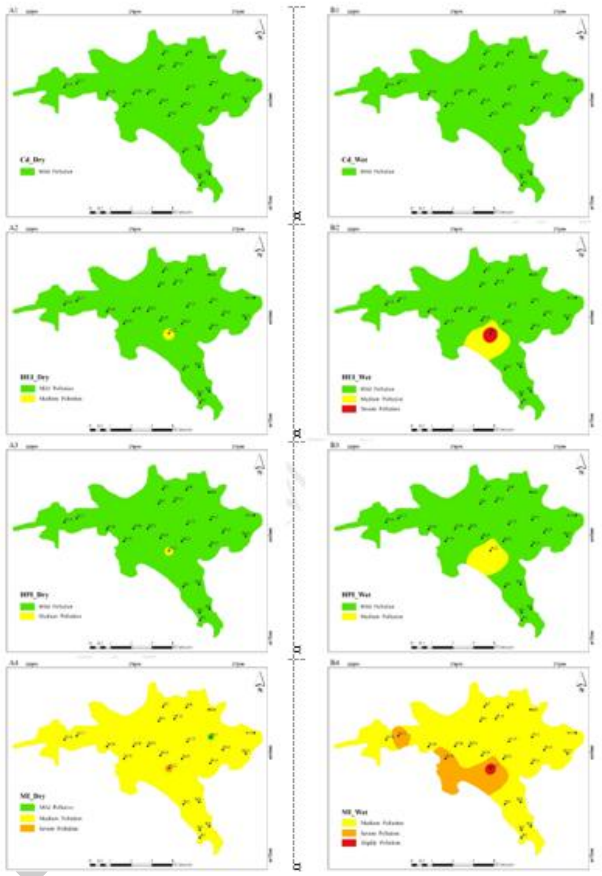


**Figure 3.** Classification of MI, HPI, HEI and pollution degree index (Cd) in (A) dry season and (B) wet season

*2.11. Non-carcinogenic risk assessment*

Based on **Table 5**, The level of non-carcinogenic risk of HQ in the wet and dry season from the ingestion route in the order >Cu> Pb> Zn> Cd> Fe> Mn > Cr and Cr> Pb>Cu> Zn > Cd> Fe>Mn in both age groups of adults and children were obtained. From the route of skin absorption (**Table 6**), the HQ index calculated in the age group of adults and children in both high and dry seasons was obtained in the order of Zn>Cr>Pb>Cd>Cu>Fe>Mn. According to the results of the HQ calculation, it can be said that the non-carcinogenic risk of the studied metals from both ingestion and skin absorption routes in both age groups, except Cr metal, which is from the ingestion route in the age group of children in both dry and wet seasons. And nitrate, which is more than 1 in the wet season, was calculated to be less than 1 in all samples.

**Table 5.** The results of calculating the risk ratio of non-carcinogenic diseases of the studied metals from the ingestion route

| Heavymetals | RfD | HQ men | | HQ women | | HQ child | |
|---|---|---|---|---|---|---|---|
| | | dry | wet | dry | wet | dry | wet |
| Cd | 0.025 | 0.0074 | 0.0053 | 0.00863 | 0.00619 | 0.01725 | 0.01238 |
| Cr | 0.075 | 0.4623 | 0.5912 | 0.6898 | 0.5542 | 1.3795 | 1.1083 |
| Pb | 0.525 | 0.0378 | 0.02951 | 0.04406 | 0.03443 | 0.08811 | 0.06886 |
| Mn | 4.8 | 0.00001 | 0 | 0.00001 | 0.00001 | 0.00002 | 0.00002 |
| Zn | 0.06 | 0.02103 | 0.01428 | 0.02454 | 0.01666 | 0.04908 | 0.03327 |
| Cu | 22.8 | 0.04150 | 0.02563 | 0.04842 | 0.02989 | 0.09683 | 0.05979 |
| Fe | 140 | 0.00001 | 0.00001 | 0.00001 | 0.00001 | 0.00002 | 0.00003 |

**Table 6.** The results of the risk ratio calculations of non-carcinogenic diseases of the studied metals from the skin absorption route

| Heavy metals | RfD | HQ men | | HQ women | | HQ child | |
|---|---|---|---|---|---|---|---|
| | | dry | wet | dry | wet | dry | wet |
| Cd | 0.025 | 0.00078 | 0.00054 | 0.0009 | 0.00063 | 0.00228 | 0.0016 |
| Cr | 0.075 | 0.2469 | 0.1984 | 0.2880 | 0.2314 | 0.7284 | 0.5851 |
| Pb | 0.525 | 0.005257 | 0.0041 | 0.0061 | 0.0048 | 0.0155 | 0.0155 |
| Mn | 4.8 | 0 | 0 | 0 | 0 | 0 | 0 |
| Zn | 0.06 | 0.3294 | 0.2233 | 0.3843 | 0.2605 | 0.9717 | 0.6587 |
| Cu | 22.8 | 0.0004 | 0.00024 | 0.0004 | 0.00027 | 0.001121 | 0.00069 |
| Fe | 140 | 0 | 0 | 0 | 0 | 0 | 0 |

**Table 7.** The results of the carcinogenic risk assessment of the studied metals from the ingestion route in the dry season

| Heavy metal | ELCR | | | Degree of risk | DF | Reception |
|---|---|---|---|---|---|---|
| | Men | Women | Children | | | |
| Cd | 0.01565 | 0.01826 | 0.3652 | too high | 6.1 | The risk is not acceptable and action must be taken to eliminate the risk |
| Cr | 0.2707 | 0.3159 | 0.05414 | too high | 0.19 | The risk is not acceptable and action must be taken to eliminate the risk |
| Pb | 0.0009 | 0.002 | 0.002 | high | 0.0085 | The risk is not acceptable and action must be taken to eliminate the risk |

**Table 8.** The results of the carcinogenic risk assessment of the studied metals from the ingestion route in the wet season

| Heavy metal | ELCR | | | Degree of risk | DF | Reception |
|---|---|---|---|---|---|---|
| | Men | Women | Children | | | |
| d | 0.01565 | 0.01826 | 0.03652 | too high | 6.1 | The risk is not acceptable and action must be taken to eliminate the risk |
| Cr | 0.2707 | 0.3159 | 0.05415 | too high | 0.19 | The risk is not acceptable and action must be taken to eliminate the risk |
| Pb | 00009 | 0.001 | 0.002 | high | 0.0085 | The risk is not acceptable and action must be taken to eliminate the risk |

**Table 9.** The results of the carcinogenic risk assessment of the studied metals from the route of skin absorption in the dry season

| Heavy metal | ELCR | | | Degree of risk | DF | Reception |
|---|---|---|---|---|---|---|
| | Men | Women | Children | | | |
| Cd | 0.001634 | 0.0019 | 0.004821 | High | 122 | The risk is not acceptable and action must be taken to eliminate the risk |
| Cr | 0.112 | 0.1319 | 0.00055 | too high | 7.6 | The risk is not acceptable and action must be taken to eliminate the risk |
| Pb | 0.00013 | 0.00015 | 0.00038 | medium | 0.056 | There is no problem |

**Table 10.** The results of the carcinogenic risk assessment of the studied metals from the route of skin absorption in the wet season

| Heavy metal | ELCR | | | Degree of risk | DF | Reception |
|---|---|---|---|---|---|---|
| | Men | Women | Children | | | |
| Cd | 0.00275 | 0.00275 | 0.0695 | High | 122 | The risk is not acceptable and action must be taken to eliminate the risk |
| Cr | 0.1642 | 0.1642 | 0.415 | too high | 7.6 | The risk is not acceptable and action must be taken to eliminate the risk |
| Pb | 0.0002 | 0.0002 | 0.0005 | medium | 0.056 | There is no problem |

**Table 7, 8** shows the results of the carcinogenic risk assessment of the studied metals from the consumption route during the dry and wet season respectively. The calculated carcinogenic risk in both age groups and from both routes of ingestion and skin absorption was obtained in the order of Cr > Cd > Pb. The amount of ELCR calculated for all three metals from the route of ingestion and skin absorption, except lead metal, which is in the medium range from the route of skin absorption, was calculated to be more than 4-10 in both age groups, which indicates the high risk of carcinogenicity of metals in this region.

*2.12. The results related to the evaluation of the risk of carcinogenesis and infertility (Monte Carlo simulation)*

According to **Figure 4**, it shows the distribution of carcinogenic risk caused by heavy metals in the studied drinking water in three groups of children, women and men based on Monte Carlo uncertainty algorithm. The highest average THQ of heavy metals in water is in the children group 1.52 and the lowest amount of these metals in the water in the male group is 0.73. According to the results of **Figure 4**, the average carcinogenicity of heavy metals in men and women is higher than in children. Also, the carcinogenic risk of 95% of drinking water in relation to heavy metals was 2. 95 in children, 1.16 in men and 1.33 in woman, higher than the limit recommended by the EPA. Also, in order to evaluate the influencing factors on the risk assessment, including the target concentration of each metal (C), Daily water consumption rate per day (IR), body weight (BW), duration of exposure (ED), average exposure time (AT), frequency of exposure days (EF) according to chart 4, sensitivity analysis has been performed. The results showed that the concentration of Pb and Cd and IR in the two exposed groups had the greatest impact on the assessment of the carcinogenic risk of metals. AT and BW had a negative effect on risk assessment. The effects of other variables included ED, (EF), and BW, respectively.

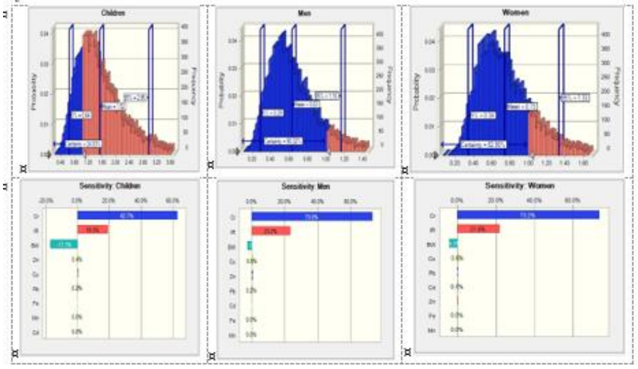


**Figure 4.** Histograms of the uncertainty analysis of nitrate HQ in heavy metals: children (1), men (2), and woman (3)

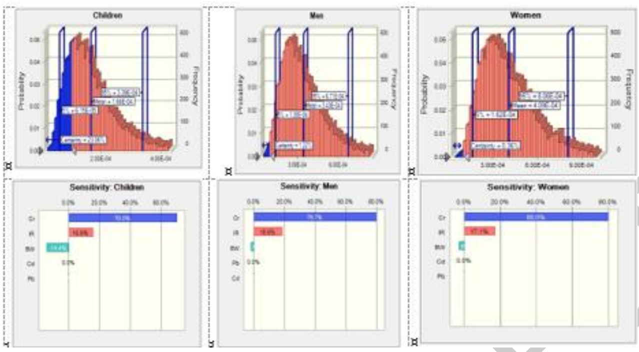


**Figure 5.** Monte Carlo sensitivity analysis of the output of heavy metals in drinking water (in three groups, women and men).

According to chart 5, the TCR of heavy metals is in adults $3.4\times10^{-4}$, in children $1.66\times10^{-4}$ and in $4.09\times10^{-4}$. Also, the carcinogenic risk of 95% of drinking water in relation to heavy metals with the amount in children ($3.39\times10^{-4}$) and in adults ($3.43\times10^{-4}$) was higher than recommended by the EPA. **Figure 5** shows the results of the sensitivity analysis that the concentration of Cr metal and the IR in the 3 exposure groups had the greatest effect on the assessment of the carcinogenic risk of metals. BW had a negative effect on risk assessment.

## 3. Discussion

In this study, in order to investigate the water pollution of Gorgan city with heavy metals, water sampling was done in two seasons of 2021 from 25 stations and the concentration of Cd, Pb, Cr, Cu, Zn, Fe, and Mn was measured. The results of investigating the concentration of heavy metals in underground water in wet and dry seasons in the drinking water sources of Gorgan city are shown in **Tables 3 and 4**. The results of comparing the concentration of heavy metals in drinking water with WHO and EPA standards and Iranian standard 1053 show that the concentration of heavy metals (Maleki *et al*. 2021), except for Zn and Cr, is lower than the permissible limit. which was consistent with the argument of Ravanipour et al. (2021) and Maleki et al (2021). Therefore, the sources of drinking water in the wells in the region are reliable sources in terms of heavy metals and due to various reasons such as the lack of industries in the region, the geological composition of the region, the lack or reduction of urban and rural sewage penetration into water sources, geographical conditions and the environment, Dominating the region, are not exposed to heavy metal contamination (Li *et al*. 2015). The concentration of heavy metals in the wet season was higher than the concentration of metals in the dry season. The reason for this can be the use of agricultural pesticides in the winter season and the penetration of metal materials into the soil, their washing and entering the underground water (Shokoohi *et al*. 2021). According to **Tables 3 and 4**, The average concentration of Cd is 0.09 and 0.13 µg/l in dry and wet season respectively. and it was less than the WHO value, higher than Iran's standards. The concentration range was between 0.09 and 0.23 µg/l, which shows that the concentration of Cd in some samples is lower than the national standard of 1053 (Mohammadi *et al*. 2019). According to **Tables 3 and 4**, the average metal of Fe, Mn, Cu, and Zn was below EPA and WHO, Iran's national standards 1053 (Ravanipour *et al*. 2021). The average concentration of Cr in groundwater is higher than EPA and WHO, Iran's national standards 1053.Therefore, it can be said that agricultural activities, the use of wastewater for irrigation, industrial activities and human sewage (Zaynab *et al*. 2022). According to **Tables 3 and 4**, the amount of lead in water is more than other places and above the permissible limit set by WHO (10 ppb) such that in wells 9 and 13 in Southwest of its area is 11.7 and 10.27 ppb respectively (Mohammadi *et al*. 2019). According to **tables 3 and 4** and the distribution map of Cu in underground water, this does not indicate any special changes and its amount is much lower than the permissible limit set by WHO (2000 ppb) (Saha *et al*. 2018).

According to **Tables 4 and 5**, changes in zinc in the studied range do not show any particular problem and its amount is much lower than the permissible limit set by WHO and the national standard of Iran (3000 ppb) (Zaynab *et al*. 2022). Based on **Tables 4 and 5** and the **Figure 2**, the concentration of Mn in the study area is lower than the limit set by WHO (500 ppb). According to the map, the concentration of Fe in the south and center of the plain is higher than the northern half of the plain, so that in wells 3, 4, 5, 8, 24 and 13, it is more than the permissible limit by WHO (300 ppb). The results of examining the spatial pattern of heavy metals (Map 2) in the western and southwestern parts of Gorgan Plain show that the amount of most heavy metals is higher than in other places. Esfahani et al.'s study showed that the concentration of heavy metals changes over time, and wells in the same location can have widely different levels of metals. In fact, the concentration of heavy metals in shallower wells has a higher concentration (Esfahani *et al*. 2023). According to **Figure 3**, the distribution results of HEI heavy metal evaluation indices showed that in all stations, this index was much lower than the risk threshold. Therefore, in all stations, except well (ASSESSment ERPR. Guidance for

Superfund *et al*. 1989) in the wet season, it was placed in the low pollution class. **Figure 3** shows the results of the HPI. Most of the underground water samples are below the pollution risk threshold. The HPI is also used to determine the effect of heavy metals on human health. In all stations, it showed a negative value for all metals, which was much lower than the danger threshold (100). In most of the stations, the level of pollution indices (HEI and HPI) of heavy metals assessment in the dry season is lower than in the wet season, which can be a result of the washing of polluting sources in the wet season which is consistent with Ghobadi study (Ghobadi *et al*. 2018). The evaluation results of the MI pollution index in **Figure 3** showed that the numerical value of this index in all stations was at the threshold of drinking risk. Therefore, there was no contamination with heavy metals in all the stations. Also, the Cd index showed that the obtained index values were lower than the negative value in all the stations and were much lower than the danger threshold. In this way, the Cd index in all stations was at a low degree of pollution for all heavy metals investigated which is consistent with study Bayati et al (2020) and Ghobadi et al. (2021).

**Tables 6 and 7** about the effect of heavy metals on non-carcinogenic diseases show that Cr has the highest effect and Mn has the least effect from the ingestion route in both groups in the dry and wet seasons. Also, from the route of skin absorption in both age groups in the dry and wet season, the metals Zn and Cr had the greatest effect and Fe and Mn had the least effect on non-carcinogenic diseases. Pb has the least effect and Cr has the most effect on the risk of carcinogenesis in people. According to **Tables 5 and 6**, the results obtained from the health risk assessment of heavy metals using the EPA index showed that Zn, Fe, Cu, Mn metals do not have carcinogenic properties, and among the three metals Cr, Cd, and Pb, according to their average concentration in water, The carcinogenic risk of Cr was higher than that of Cd and lead.

In the shams et al. study that assessed the health risk of heavy metals in Joghtai city, Total HI (Hazard Index) values in drinking water were higher for children than for adults. The total cancer risk values of metals (sum of As, Cd, and Cr) for children and adults in all villages were higher than the USEPA limit (Shams *et al*. 2022).

The findings of **Tables 6 and 7** showed the risk index for all heavy metals (HQ ingestion) for the three age groups of children, man and woman is 0.57005, 0.81547 and 1.63081 in dry season and 0.66593, 0.64139 and 1.28265 respectively. So, the risk index for all heavy metals (HQ dermal) for the three age groups of children, man and woman is 0.582737, 0.6797 and 1.719001 in dry season and 0.42658, 0.4976 and 1.26159 respectively. Which is above the threshold for the age group of children. The findings of **Tables 8 and 9** show The results of the cancer risk assessment of Cr metal showed that the excess risk of cancer ($ELCR_{ingestion}$) for the three age groups of children, man and woman is 0.2725, 0.33616 and 0.42134 in dry season and 0.28725, 0.33516 and 0.0926 respectively. So, The risk index for all heavy metals (HQ dermal) for the three age groups of children, man and woman is 0.11376, ,0.13395 and 0.005751in dry season and 0.16715 and 0.485 respectively. The results of the health risk assessment of heavy metals for non-carcinogenic diseases, similar to the present study, were reported in the safe range, which showed that there was no danger to the people of the region. The results of the study conducted on the drinking water of a number of villages in Hashtroud showed that the concentration of heavy metals in the drinking water of the study area was much lower than the national standards and the health risk caused by them was negligible (Sheikhi *et al*. 2021). According to **Figure 4**, the highest mean THQ of heavy metals in water in the children group was 1.52 and the lowest level of these metals in water in the men group was 0.73. According to the results of **Figure 4**, the mean carcinogenicity of heavy metals in men and women was higher than in children. Also, the carcinogenic risk of 95% of drinking water in relation to heavy metals in children was 2.95, in men 1.16 and in women 1.33 higher than the level recommended by EPA. According to **Figure 4**, the results showed that the concentration of Pb and Cd and IR in the two exposed groups had the greatest impact on the assessment of the carcinogenic risk of metals. AT and BW had a negative impact on the risk assessment. The effects of other variables included ED, (EF) and BW, respectively. According to **Figure 5**, the TCR of heavy metals in adults is $3.4\times10^{-4}$, in children $1.66\times10^{-4}$ and in $4.09\times10^{-4}$. Also, the carcinogenic risk of 95% of drinking water for heavy metals in children ($3.39\times10^{-4}$) and in adults ($3.43\times10^{-4}$) was higher than the EPA recommended level. **Figure 5** shows that the concentration of Cr and IR in the 3 exposure groups had the greatest impact on the assessment of the carcinogenic risk of metals. BW had a negative impact on the risk assessment.

## 4. conclusion

The results showed that in the wet season, the average concentration of all elements in the water samples was higher than in the warm season which can be due to agricultural activities and the use of agricultural fertilizers and pesticides in the wet season. The average values of HEI, Cd, HPI and MI indices to evaluate the pollution of the plains in the wet season respectively indicate "low pollution", "low pollution", "low pollution" and "moderate pollution" and in the wet season respectively Low pollution, "moderate pollution", "low pollution" and "severe pollution" were the water sources of Gorgan city. In most of the stations, the amount of heavy metal pollution indicators in the dry season is lower than in the wet season, which can be a result of the washing of polluting sources in the wet season. The results of the sensitivity analysis show that the concentration of metal and the amount of water consumed per person per day had the greatest effect on the assessment of the carcinogenic risk of metals. Effective measures should be taken for the effluent entering the plain. Also, due to the heavy consequences of any type of pollution in the aquifer on plant and animal ecosystems, it is necessary to create and maintain a suitable protection zone for urban and rural drinking water supply sources to prevent its pollution. To more accurately assess the efficiency of the indicators, a larger number of elements should be examined in a wider range of concentrations and their desirability should be assessed. It also seems necessary to further examine the indicators in different environments in order to eliminate their existing shortcomings, especially the pollution grading that leads to minor differences in the results. From this study, the level of carcinogenic and non-carcinogenic risk due to the presence of metals and their exposure through the digestive and inhalation routes at the time of the study was lower than the acceptable levels allowed for the groups of children and adults, but in the future, due to the characteristics of accumulation, non-degradability, toxicity and long-term persistence of heavy metals in the urban environment, it may lead to harmful effects on the health of citizens. Therefore, given the importance of the issue, periodic monitoring of water resources in terms of heavy metal content, which was not possible to examine in this study due to time constraints, financial resources, lack of sufficient laboratory equipment and lack of sufficient human resources (environmental health experts) for sampling, is recommended to protect the health of citizens.

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