Profiling of seasonal variation in and cancer risk assessment of benzo(a)pyrene and heavy metals in drinking water from Kirkuk city, Iraq

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Abstract
Water samples at 13 sites were analyzed to evaluate heavy metals (cobalt, lead, manganese, copper) and benzo(a)pyrene using 2 methods of analysis (high-performance liquid chromatography (HPLC) and enzyme-linked immunosorbent assay (ELISA) kits). The Lesser Zap River is the main tributary of the Tigris and is used as a main source of drinking water in Kirkuk city through the General Kirkuk project. Risk evaluation for benzo(a)pyrene and lead in water samples was accomplished by Monte Carlo simulation. The highest concentrations of B(a)P were recorded at sites S7 and S5, with levels of 0.192 and 0.122 µg L⁻¹ detected by HPLC and ELISA, respectively. The WHO guidelines for benzo[a]pyrene in drinking water recommend 0.7 µg L⁻¹, and none of the samples surpassed this level; moreover, B(a)P levels exceeded EPA standards in 2014 (0.01 µg L⁻¹), particularly when the liquid–liquid extraction method with HPLC was used. Carcinogenic risks for human adults and children exist and are highest during the rainy season as compared with the carcinogenic risk during the dry season and risks for children exceed those of adults. This indicates that the 2nd round of sampling (winter season) harbors more carcinogenic risk than the 1st round of sampling (dry season).

Keywords Benzo(a)pyrene · Heavy metals · Drinking water · Cancer risk · Monte Carlo simulation

Introduction
Aquatic pollutants mainly consist of trace metals, fertilizers, microscopic organisms, and toxic organic substances (World Health Organization (WHO), 2011; Nambatingar et al. 2017). Heavy metals are important environmental toxic pollutants, and their toxicity is becoming more of concern for ecological, evolutionary, nutritional, and environmental reasons (Nagajyoti et al. 2010).

Water pollution has direct effects on human health, while sewage and industrial effluents exert indirect effects on human health through intake of foods irrigated with contaminated water (Aziz et al. 2014). According to the World Health Organization 2011, more than 80% of human diseases have origins in water. Heavy metals in surface and ground water containing Mn, Cr, Fe, Cu, Ni, Cd, and Zn have negative effects on human physiology (Singh et al. 2011). Heavy metals can be present in trace amounts in water and are still harmful to humans and other ecosystems, depending on factors such as the organisms exposed to an element, its composition, its biological function, and the length of time the organisms are exposed to the element. The relationships between organisms are described by food chains and food webs. Therefore, contamination of water by heavy metals affects all organisms, particularly those feeding at the highest level (Lee et al. 2002). These metals bind to protein sites by displacing original metals from their natural binding sites, causing cell malfunction and ultimately, toxicity. The binding of heavy metals to DNA and nuclear proteins is thought to be the primary cause of oxidative degradation of biological macromolecules, according to previous
studies (Flora et al. 2008). Ionic oxidation stress is caused by lead toxicity in living cells. Many studies such as Wadhwa et al. (2012), Tan et al. (2018), and Mehdi et al. (2020) have shown that oxidative stress in living cells is caused by an imbalance between the production of antioxidants to detoxify or restore reactive intermediates and the production of free radicals. The ability of lead metal ions to substitute for other divalent cations such as Fe$^{2+}$, Ca$^{2+}$, and Mg$^{2+}$, and the monovalent cation Na$,^+$ ultimately disturbs the biological metabolism of the cell (Jaishankar et al. 2014). Lead can substitute for calcium even at picomolar concentrations, affecting protein kinase C, which regulates neural excitation and memory storage (Jaishankar et al. 2014).

Polycyclic aromatic hydrocarbons (PAHs) in the environment consist of parent compounds and alkylated homologs. Such compounds (PAHs) are of great environmental concern due to their persistence, bioaccumulation, and toxic effects (Badawy and Emababy 2010). The health effects of single polycyclic aromatic hydrocarbons (PAHs) may be apparent under circumstances of high exposure. Long-term exposure (weeks or months) may be more important in terms of overall public health (Carpenter et al. 2002).

Among the sixteen PAH compounds, benzo(a)pyrene has sparked widespread interest due to its carcinogenic potential and pentachlorophenol-high-molecular-weight PAH structure. Benzo(a)pyrene and other polycyclic aromatic hydrocarbons (PAHs) are widespread environmental contaminants formed by incomplete combustion of organic material (IARC 2010). B(a)P has been classified by the US EPA as a probable human carcinogen. There is an increase in the risk of developing cancer even at low levels, and long-term exposure through drinking water is considered to represent a probable human carcinogenic risk according to the WHO (2011). B(a)P should not be present at concentrations above 0.2 μg L$^{-1}$, the maximum contaminant level (MCL). Water storage tanks and distribution lines may be the major sources of B(a)P in drinking water. B(a)P in tap water primarily results from the presence of PAH-containing materials in water storage and distribution systems (ATSDR 1990), and the presence of PAH-containing coal tar coatings on drinking water distribution pipes and storage tanks may be the primary source of B(a)P in drinking water (OEHHA 2010).

Health effects from overexposure to heavy metals and other chemical components in water are dependent on the amount of drinking water, chemical form, age at exposure, nutritional status, and lifestyle (U.S. Environmental Protection Agency 2010). Copper is an essential element in human life, but chronic exposure to copper from drinking water can result in health problems such as anemia and liver and kidney damage. Even in small doses, lead can affect the central nervous system, brain, and kidneys, resulting in death or permanent damage. Manganese is an essential element for organisms and occurs naturally in many food sources. Adverse effects can result from both deficiency and overexposure (WHO 2003).

Main objectives for current study are the comparison between 2 methods of analysis for Benzo (a) pyrene in water samples (HPLC and ELISA) and determining the best method through the statistical analysis for results of current study and to provide insight into the profiles of heavy metals and benzo(a)pyrene in drinking water of Kirkuk city to government and researchers to produce a probabilistic cancer risk simulation with respect to human health.

Description of the study area

The Lesser Zab River originates in the Islamic Republic of Iran and is home to the Dokan Dam (6.8 km$^3$). The river basin of 21,475 km$^2$ (of which 74% is in Iraqi territory) generates approximately 7.17 km$^3$, with an annual safe yield of 5.07 km$^3$ after construction of the Dokan Dam (OXFAM 2017). The Kirkuk drinking water treatment plant is located on the border of the Lesser Zab River at coordinates 35.67943°, 44.08357°. Figure 1 shows map of Iraq and Kirkuk (a) and studied sampling sites for current study (b). Kirkuk, the location for which this study was carried out, with an estimated population density of 950,000, is one of the vital cities within northern Iraq (longitude 44° 24′ and latitude 35° 28′). Kirkuk city drains its water for drinking from the Lesser Zab River (one of the longest tributaries of the Tigris River) and groundwater in some areas that have not been linked with the Kirkuk unified treatment plant. The water treatment plant in Kirkuk city includes six units: receiving well, flash mixture, clariflocculator, filters, ground tanks and high lift pumping station. After treatment, water is stored in the main storage tank (ST1) and four other storage tanks (ST2, ST3, ST4, and ST5) that feed all areas within Kirkuk city (Kirkuk Water Directorate) (OXFAM 2017). Thirteen sites within Kirkuk city were selected (According to distance away from the source after treatment) for collection of water samples (Fig. 1b) (using clean acid-washed polyethylene bottles during June 2017 and December 2018) and to prevent any problems regarding distribution networks or pipelines that transfer water to the houses (Baird et al. 2017) (Table S1).

Material and methods

Chemicals

Solvents used for extraction and analysis, such as acetonitrile, toluene, hexane, etc., were of HPLC grade and were Merck and Rankem products. Standards from Sigma-Aldrich (ERS 009) for 16 PAH compounds were used. Silica gel with
particle size 0.063 to 0.200 mm, 100 to 200 mesh ASTM from Merck was used for the current work.

Extraction and analysis of benzo(a)pyrene in water samples

The liquid–liquid extraction method described by UNEP, 1989, was used to extract B(a)P from two liters of water sample with 60 mL of CCl₄. This step was performed twice, and the combined extracts were transferred into a flask for further preparation. Organic extracts were then evaporated to dryness by a rotary evaporator (50 °C for bath and 10 °C temperature for water refrigerator circulator). After evaporation, the residue was dissolved in 5 mL acetonitrile and then concentrated to 1 mL under gentle N₂ treatment. The extract was then stored at –20 °C until analysis by high-performance liquid chromatography (YL9100 HPLC system) at the Ministry of Sciences and Technology, Baghdad, Iraq.
 Approximately 12 μL of extract was injected into a capillary column (flow rate is 2.00 mL/min) of stationary phase with dimensions of 15 cm x 4.6 mm and then determined using a UV detector at 254 nm wavelength. Column used is C18 reversed phase with a column temperature of 30 °C. Detection limit for BaP was 0.003 µg/L and recovery rate is 87%. Water was the mobile phase, and the flow rate of acetonitrile was 1.5 mL/min. Peaks on the chromatogram were identified and compared with control retention time and spectra. B(a)P standard with a purity of >96% (HPLC) from Sigma-Aldrich with certified reference material, TraceCERT®, 1000 µg/mL in acetone were used.

**Enzyme-linked immunosorbent assay test kit method**

B(a)P exists at very low levels in drinking water: to achieve high recovery, high sensitivity, and high reproducibility, a B(a)P enzyme-linked immunosorbent assay (ELISA) test kit (MaxSignal® Benzo(a)pyrene (B(a)P) ELISA Test Kit) was used as another method for measuring levels of B(a)P and then compared with HPLC. It is a competitive enzyme immunoassay method. A 1.5 mL water sample was taken at a pH range between 6.5 and 7.5 and adjusted by 0.1 M HCl or NaOH. A B(a)P conjugate coating was applied in the plate wells. If the target is present in the sample, it will compete for antibody binding by preventing the antibody from binding to the B(a)P attached to the wells. After adding substrate, the color of the secondary antibody tagged with a peroxide enzyme strengthened, and the target primary antibody associated with the B(a)P coating the plate wells, resulting in an inverse relationship with the target concentration in the sample. According to the Max Signal Benzo(a)pyrene ELISA test manufactured by Bio Scientific, the detection limit (sensitivity) is 0.3 µg L⁻¹.

**Extraction and analysis of heavy metals**

For heavy metals, polyethylene containers were used for sample collection. Sampling tools and containers were contamination free. Containers were washed with 10% v/v nitric acid, rinsed several times with deionized water and then collected and acidified using HNO₃. Acid digestion with HNO₃ was performed as recommended by Baird et al. (2017).

One hundred milliliters of well-mixed acid-preserved sample was transferred to a flask. Five milliliters of concentrated HNO₃ to a hood. To slow boiling and evaporation on a hot plate to the smallest volume possible (approximately 10 to 20 mL) before precipitation, a reflux temperature of approximately 95 °C was achieved. Heating was maintained, with concentrated HNO₃ added as required, until a light-colored, transparent solution emerged. Digested samples were filtered using glass fiber filters and then transferred to a 100-mL volumetric flask. Samples were cooled, diluted to the correct mark, and mixed thoroughly. Standard solutions with different concentrations of each heavy metal were prepared to obtain a standard curve according to the linear regression method to obtain $R^2=0.997$. The curve with the related parameters was plotted automatically. An AAS9000 Flame/Graphite Furnace Integrated Atomic Absorption Spectrophotometer of Skyray Company was employed. IONEX Reference Standards from CHEM-LAB Company were used, which are certified under our ISO90001 Quality System and under the principles of GUM: 1995; ISO Guide 31:2000; ISO/IEC 17,025. The certified value for each analyzed heavy metal was 1000 ± 4 µg/mL, and the density was ±0.0002 g/mL. The detection limit for the analyzed parameters was 0.001 mg/L. Major pollutants such as lead, manganese, copper, and cobalt were analyzed in collected water samples.

**Data analysis and mapping**

Data were statistically analyzed for correlation coefficients and coefficient of variation (CV) with SPSS (Version 24) with respect to means of water parameters in the study area. Surfer program V16 was used to represent the results of the current study between sampling sites as a surface contour map for analyzed parameters. Contouring map facilitate calculation of geographical data in more accurate visualization.

**Cancer risk assessment**

PAHs are natural environmental contaminants that are thought to play a role in the development of human cancers. PAH compounds are metabolized enzymatically, and some of them are reactive. The CYP1A1, CYP1A2, CYP1B1, and CYP3A4 cytochrome P450 enzymes are important in the metabolism of polycyclic aromatic hydrocarbons (PAHs) (Walsh et al. 2013). PAHs undergo metabolic activation to diol-epoxides, which bind covalently to DNA. The DNA binding of activated PAHs is essential for the carcinogenic effect (Tarantini et al. 2011) and has been discovered in a variety of human tissues. A strong association between epidemiological studies has found a connection between PAH exposure and the number of PAH-DNA adducts (Jedrychowski et al. 2013).

For human exposure to chemicals (PAHs and heavy metals) in drinking water by way of overt ingestion and dermal absorption, the exposure dose through the ingestion pathway was measured and calculated by Eq. 1, adapted from Exhibits 1–3, United States Environment Protection Agency (2001):
where CDI stands for chronic daily ingestion of chemicals (mg kg$^{-1}$ day$^{-1}$), C$_w$ stands for chemical concentration in water (mg/L), IR stands for ingestion rate of water (L/day$^{-1}$), EF stands for exposure frequency, 350 days year$^{-1}$, ED stands for exposure period (year), CF stands for conversion factor (1106 kg mg$^{-1}$), BW stands for body weight in (kg), and AT stands for average time (day), 25,550 da.

The exposure dose of B(a)P through the dermal uptake pathway during bathing was calculated through Eqs. 2 and 3, which were obtained from ‘Dermal Absorbed Dose per event for Organic Compounds—Water Contact,’ US EPA (2004):

$$D_{\text{A event}} = 2FA \times K_p \times C_w \sqrt{\frac{6t_{\text{event}} \times t_{\text{event}}}{\pi}} \{\text{provided } t_{\text{event}} \leq t^*\}$$

$$DAD = \frac{D_{\text{A event}} \times SA \times EV \times EF \times ED \times CF}{BW \times AT}$$

DA denotes daily chemical exposure via the dermal absorption pathway (mg kg$^{-1}$ day$^{-1}$), SA denotes exposed skin region in cm$^2$, and EV denotes event frequency (1 bath per day; event day$^{-1}$).

The total carcinogenic risk for B(a)P present in consumed water for drinking is calculated by Eq. 4:

$$R_c = (C_DI \times SF_i) + (DAD \times SF_d)$$

where $R_c$ is the probability of developing cancer over a lifetime because of exposure to B(a)P. $SF_i$ is the ingestion cancer slope factor of B(a)P (mg kg$^{-1}$ day$^{-1}$), which is expressed as the oral administrative dose, and $SF_d$ is the dermal cancer slope factor for B(a)P (mg kg$^{-1}$ day$^{-1}$). All parameter values collected from citations are provided in Supplementary Table S2.

In the case of heavy metals, we used the ‘Dermal Absorbed Dose Per Event for Inorganic Compounds—Water Contact’ formula from the US EPA (2004). In this case:

$$DA_{\text{event}} = K_p \times C_w \times t_{\text{event}}$$

The rest of the formulation for heavy metals is the same as that for B(a)P. The cancer slope factor for lead is $8.5 \times 10^{-3}$ mg kg$^{-1}$ day$^{-1}$ for ingestion and 0.073 mg kg$^{-1}$ day$^{-1}$ for dermal absorption (Mukherjee et al. 2020). $K_p$ of lead is 0.13 m h$^{-1}$ (USEPA 2004). The rest of the detected heavy metals are not immediately carcinogenic and do not have well-defined cancer slope factor values (IRIS and USEPA 1988; MDH 2020; USEPA 2008).

To assess which probability density functions have the greatest impact on the risk estimates, a sensitivity analysis was performed using Spearman rank order correlations. Oracle’s Crystal Ball (11.1.2.4.600) program was used to complete the evaluation and sensitivity analysis. The same software created the 90% certainty dimension of risk evaluation. To ensure numerical stability, a total of 50,000 iterations were considered (Tarafdar et al. 2020). While the simulation is running, Crystal Ball determines sensitivity by calculating rank connection coefficients between each assumption and each prediction. Correlation coefficients show how often expectations and predictions are altered when they are combined.

A sensitivity analysis was performed to discover which input parameters (or their probability distributions) have the greatest effect on the final risk distribution. Monte Carlo simulation is a technique for simulating events. The normalized rank correlation coefficients were generated during the simulation to analyze each parameter’s sensitivity in relation to the others. It is important to remember, however, that health risk assessment is intrinsically fraught with ambiguity due to a lack of information about the elements that influence it. Therefore, other uncertainties remain in the cancer risk assessment procedure, which can affect the final risk estimate.

Results and discussion

B(a)P in drinking water

The levels of B(a)P in the studied water samples were analyzed and showed seasonal fluctuations during the summer and winter seasons (Table 1, Fig. 2 and Fig. 3a, b). B(a)P, a carcinogenic PAH listed as a priority pollutant by the US EPA, was detected and ranged from 0.001 to 0.192 µg L$^{-1}$ and 0.001 to 0.162 µg L$^{-1}$ as measured by HPLC and ELISA methods, respectively. A significant correlation ($P \leq 0.01$) was found between the two methods for B(a)P levels in drinking water samples; moreover, a significant correlation coefficient ($P \leq 0.01$) was found between B(a)P measured by HPLC with Cu, Co, Pb, and between B(a)P measured by ELISA kit with Co only, which indicates that HPLC is more sensitive for B(a)P measurement in drinking water due to the coefficient variations (CV) between both methods.
B(a)P levels were found to be high during the winter season compared with the summer season due to inhibition of the biotransformation of B(a)P under ambient nutrient conditions and increase rate of biodegradation under higher water temperature and the presence of adapted microorganisms (Aamand et al. 1989 and Boonchan et al. 2013). Total means of 0.012µg L⁻¹ and 0.0469µg L⁻¹ were measured during the summer and winter seasons, respectively, when the ELISA method was used, while mean values of 0.01914µg L⁻¹ and 0.08585µg L⁻¹ were recorded during the summer and winter (Aamand et al. 1989 and Boonchan et al. 2013). Total means of 0.012µg L⁻¹ and 0.0469µg L⁻¹ were measured during the summer and winter seasons, respectively, when the ELISA method was used, while mean values of 0.01914µg L⁻¹ and 0.08585µg L⁻¹ were recorded during the summer and winter seasons, respectively, when the ELISA method was used.

The highest levels of benzo(a)pyrene were recorded at the border sampling sites of Kirkuk city in comparison with the center in both methods used and seasons at which samples were collected (Figs. 2 and 3). Because of its close association with soil, there is little knowledge regarding B(a)P concentrations in groundwater, and B(a)P is not supposed to leach into groundwater. Between 2002 and 2012, 97.6% of the 6678 samples collected in distribution networks in Québec were below the detection level (range of 0.002–0.01 µg L⁻¹). The median value for the studied water was 0.004 µg L⁻¹, with 20 results above 0.01 µg L⁻¹. All results were below 0.01 µg L⁻¹ in Nova Scotia (MDL 0.009–0.01 µg L⁻¹) (FPTCDW 2015). According to results of current study, highest B(a)P levels by HPLC method exist in sites close to the border of Kirkuk city such as S4, S5, S7, and S9 and then pass to other sites toward center of Kirkuk (Figs. 2 and 3). Badawy and Emababy (2010) concluded that none of the drinking water samples of Egypt contain any B(a)P levels of significant value. Similar results were obtained by Mohamed et al. 2010 in drinking water of Ifraz water treatment plants of Erbil-Iraq.

High levels of benzo(a)pyrene can cause skin, lung, and bladder cancer in humans and animals, making it a likely cancer-causing agent (FPTC 2015). According to the International Agency for Research on Cancer (IARC), there is enough evidence to suggest that B(a)P is carcinogenic in laboratory animals and could be carcinogenic in humans, with the ability to cause cancer in experimental animals according to Rajendran et al. (2013, 2014), due to the capability of B(a)P to induce tumors (Rajendran et al. 2008).

### Risk analysis

The total B(a)P concentrations for each of the samples were calculated. The geometric mean concentration of B(a)P in drinking water is (0.014, 2.300) in summer and...
(0.073, 1.877) in winter (geomean, geostdev in μg L\(^{-1}\)), as determined by the liquid–liquid extraction method. For the ELISA extraction method, these concentrations were (0.008, 2.296) in summer and (0.034, 2.465) in winter (geomean, geostdev in μg L\(^{-1}\)). Bearing the different attributes of the two age groups, including ED, AF, BW, SA, EF, HR, and so forth, as a primary concern, the carcinogenic hazards for children and adults were determined based on Eqs. [1–5]. At a 90% confidence level, Monte Carlo simulation was used to evaluate risk estimation for children and adults, and the simulation results were published (for liquid–liquid extraction) and are depicted in Fig. 4. Risk simulations for ELISA extractions are depicted in Supplementary Data Figure S1.

Standard deviation for cancer risk assessment is with values of 6.95E-4, 3.86E-3, 3.85E-4, and 3.24E-4 for cancer risk predicted in winter season for children, adults (Fig. 4 a
and b) and in summer season for children and adults (Fig. 4 c and d) from B(a)P content of drinking water. Median levels for risk assessment in current project are fluctuated from 2.06E-6, 3.64E-6, 6.34E-8, and 1.07E-7 respectively for winter season for children, adults and in summer season for children and adults from B(a)P content of drinking water (Fig. 4).

According to Fig. 4b, the cancer risk from drinking water was 6.35E-08 with a mean of 6.45E-05 for children and ranged from 1.06E-07 to 1.13E-04 with a mean of 1.34E-04 for adults in the winter season, according to Monte Carlo simulation. For infants, the cancer risk from drinking water ranged from 8.09E-10 to 7.39E-06, with
a mean of 1.29E-05, and for adults, the risk ranged from 1.41E-09 to 7.39E-06, with a mean of 1.58E-05.

B(a)P was listed as carcinogenic to animals and humans by the Agency for Research on Cancer (1987) and the US Environmental Protection Agency (1984), which agreed with results obtained by Chen et al. (2020) (benzo(a) pyrene (B(a)P) > anthracene (Ant) > pyrene (Pye) > phenanthrene (Phe) > fluoranthene (Flua) >acenaphthene (Ace) >fluorene (Flu) > naphthalene (Nap)). The results of the total risk assessment in the current study had values of 4.27E-06 in children to 7.39E-06 in adults during the wet season (Fig. 4a and b) and 6.63E-05 and 1.13E-04 in children and adults during the dry season (for results obtained by the HPLC method) (Fig. 4c and d), with a total mean of 4.77E-05, which agreed with the results obtained by Yan et al. 2018 in southern China with a level of 2*10−5 and the results obtained by Karyab et al. (2016) in Tehran, Iran, with a mean value of 8.81*10−05, and were lower
The results of the total risk assessment in the current study include values of 4.27E-06 in children to 7.39E-06 in adults during the wet season and 6.63E-05 and 1.13E-04 in children and adults during the dry season (for results obtained by the HPLC method). Moreover, lower carcinogenic risks were obtained when an ELISA kit was used, and all results for total risks (oral and skin exposure) were lower, which supports our opinion that the HPLC method is more sensitive and accurate for B(a)P measurement between the summer and winter seasons. This was confirmed by variation of coefficient with values 9.08E-09 in summer (Supplementary data Figure S2). These results do not heavily contribute to the total risk calculated for B(a)P. However, follow-up studies are needed to determine concentrations of heavily carcinogenic heavy metals such as arsenic and cadmium.

According to the IARC (International Agency for Research on Cancer), there is sufficient evidence to conclude that B(a)P is carcinogenic in laboratory animals and may be carcinogenic in humans, with the potential to cause lung cancer in experimental animals, as stated by Rajendran et al. in 2013 and 2014 (Rajendran et al. 2008). B(a)P is a carcinogenic product produced through a three-step metabolic activation process.

Uncertainty and sensitivity

To assess the variability and ambiguity of the parameters in the risk pathway with respect to the risk assessment, a quantitative analysis of the sensitivity of the risk parameters was performed. The results of the sensitivity analysis of cancer risk assessment are presented as tornado plots, which depict the Spearman rank order correlation coefficients on a rank scale (Fig. 5a and b).

Variations in B(a)P (Cw) concentrations in various sampling sites appear to contribute the most to variation in overall cancer risk, followed by exposure length (ED). The key cause for consistently higher cancer risks in adults is ED, which is 11 years for children and 52 years for adults (Fig. 5a and b). ED is followed by body weight (BW) for children and ingestion rate of water (IR) for adults. This result is consistent with previous studies (Tarafdar et al. 2018; Tarafdar and Sinha 2017a). The accuracy of the evaluation can be improved by using a more accurate and well-defined probability distribution of ED, IR, and BW.

Uncertainties/vulnerabilities in health hazard assessments are unavoidable due to a lack of appropriate knowledge regarding the investigation’s boundaries (Tarafdar and Sinha 2018a). However, we have utilized Monte Carlo simulation to limit vulnerability, although some of it still exists in the risk evaluation measure (Tarafdar and Sinha 2017b, 2018b). The probable exposure parameters for water ingestion rate (IR), skin surface area (SA), and body weight (BW) were directly calculated from US EPA suggested values. These probably will not be a precise match to the Iraqi situation, making their uncertain parameters of the investigation. Precise studies are also needed for more refined definitions of the parameters identified by sensitivity analysis.

Heavy metals in drinking water

Cobalt concentrations throughout the entire study period ranged between 0.01 and 0.28 mg/L, with a total mean value of 0.0817 mg/L. The lowest value of Co (0.01 mg/L) was recorded at site 2 during the winter season, while the maximum value (0.28 mg/L) was recorded at site 12 during the winter season (Table 2). The Co results indicated that there was a significant correlation between Co and Pb and B(a)P for the studied water samples in Kirkuk city. These similarities show that the geological structure, composition of rocks, and wastewater discharge from nearby villages to water systems represent the sources of heavy metals and govern chemical parameters in water samples (Issa and Alshatteri 2018). Results of the current study were higher than the results obtained by Malkani et al. 2019 for ground
Fig. 5  Sensitivity analysis of cancer risk parameters in two groups: children (a) and adults (b).

Table 2  Mean levels of heavy metals (Co, Pb, Cu, Mn) in water samples at studied sites during summer and winter (mg/L)

| Site | Cobalt (Co) | Lead (Pb) | Copper (Cu) | Manganese (Mn) |
|------|-------------|-----------|-------------|----------------|
|      | Summer      | Winter    | Summer      | Winter         | Summer      | Winter    |
| 1    | 0.061       | 0.054     | 0.047       | 0.060          | 0.004       | 0.006     |
| 2    | 0.031       | 0.040     | 0.037       | 0.080          | BDL         | 0.004     |
| 3    | 0.055       | 0.080     | 0.033       | 0.073          | BDL         | BDL       |
| 4    | 0.031       | 0.053     | BDL         | 0.023          | 0.350       | 0.133     |
| 5    | 0.027       | 0.093     | 0.037       | 0.043          | 0.087       | 0.102     |
| 6    | 0.038       | 0.067     | 0.070       | 0.100          | 0.460       | 0.647     |
| 7    | 0.054       | 0.070     | 0.003       | 0.030          | 0.143       | 0.100     |
| 8    | 0.109       | 0.103     | BDL         | 0.027          | BDL         | BDL       |
| 9    | 0.100       | 0.153     | 0.030       | 0.073          | 0.160       | 0.177     |
| 10   | 0.114       | 0.149     | 0.067       | 0.043          | 0.213       | 0.263     |
| 11   | 0.101       | 0.200     | 0.050       | 0.08           | 0.067       | 0.070     |
| 12   | 0.080       | 0.160     | 0.047       | 0.073          | BDL         | BDL       |
| 13   | 0.059       | 0.063     | BDL         | 0.030          | BDL         | BDL       |
| Mean | 0.0662      | 0.0988    | 0.0324      | 0.0565         | 0.1142      | 0.1155    |
| STD  | 0.0314      | 0.0504    | 0.0248      | 0.0251         | 0.1495      | 0.1800    |
| SEM  | 0.0087      | 0.0140    | 0.0069      | 0.0070         | 0.0415      | 0.0500    |

BDL Below detection limit
water systems in India, with levels ranging between 0.128 and 0.159 ppb.

The cobalt concentration was found to be above the US EPA (2008) guideline (0.1 mg/L) at 3 sites during the summer season and 4 sites during the winter season, with mean values ranging from 0.027 to 0.114 and 0.04 to 0.2 mg/L, respectively. High levels of cobalt were measured at both seasons in sampling sites S8, S10, S11, S12 due to the low topographic features of the study areas particularly at southern part of the study area (Fig. 5a and b). Twenty-one percent and 28% of sampling sites during the summer and winter seasons, respectively, did not comply with the US EPA guidelines (0.1 mg/L) for the maximum admissible limits of cobalt in drinking water (Table 2) (Fig 6).

Data for lead concentration showed significant differences ($P \leq 0.05$) with Cu and Co and with B(a)P ($P \leq 0.01$) between the studied sampling sites and date of sampling, with an overall mean value of 0.04542 mg/L. Lead levels ranged between 0 to 0.08 and 0.01 to 0.11 mg/L during the summer and winter seasons, respectively. The results of the current study exceed the WHO guidelines (0.01 mg/L) for drinking water in most samples collected, although Pb levels at some sites are below detection limits and agree with results obtained by Mebrahtu and Zerabruk (2011), with values ranging between <0.005 and 1.347 mg/L. High levels of lead in drinking water can permanently damage the central nervous system, brain, and kidneys (Hanada et al. 2000).

During the winter season, the highest level of Pb (0.11 mg/L) was found in drinking water samples 2, 6, and 9, and the lowest level of BDL was found in drinking water samples 4, 8, and 13 (Table 2). More than 10% of the samples tested contained levels of lead that exceeded the WHO (2011) guidelines, and the maximum allowable level of lead in drinking water was 0.01 mg/L. Results of current study agreed with those obtained by Ehi-Eromosele and Okiei (2012), with levels ranging from 0.020 to 0.215 mg/L (Fig. 7a and b).

The unusually high level of lead in tap water of S2, S6, S9, S10, S11, S12 (Fig. 7a and b) might be due to fittings made from brass, runoff from domestic use, and industrial wastes (such as improper disposal of acid lead batteries and wind-blown dust), and agricultural waste might be the main source of Pb pollution in the lesser Zab River which was not removed by the Kirkuk water treatment plant or picked up by weathering and leaching of lead from waste rocks dumps particularly during rainy season (Rajkovic et al. 2008). The levels are affected by temperature, acidity, water hardness, the length of pipes, and the time that water is left to stand in the pipes (stagnation) before it is drawn off (Ehi-Eromosele and Okiei 2012); moreover, lower results were obtained by Alrakabi and Ramadan (2020) in drinking water of Baghdad city, with levels ranging from 0 to 0.04 mg/L, yet still higher than the WHO guideline. BDL results recorded by Issa and Alshatt (2018) from drinking water systems of the Garman area in the Kurdistan Region of Iraq were lower than the results of Ibrahim et al. 2018 for surface and groundwater of Samarra City, Central Iraq, with levels ranging from 0.176 to 1.133 mg/L, and those of Aleseyyed et al. (2018) on ground water systems in urban and rural areas of Hamadan Province in Iran, with levels ranging from 2.63 to 40.155 ppb. Lead and its compounds can be present in pipes that transport water, contaminating the water (Brochin et al. 2008). Ionic toxicity occurs mainly due to the ability of lead metal ions to replace other divalent cations, such as Ca$^{2+}$, Mg$^{2+}$, Fe$^{2+}$, and monovalent cations, such as Na$^+$, which ultimately disturbs the biological metabolism of the cell (Papanikolaou 2005).

The results clearly indicated that there was a significant correlation ($P \leq 0.01$) with Mn and HPLC-B(a)P and ($P \leq 0.05$) with Pb. These similarities show that the geological structure, composition of rocks and wastewater release to water systems from nearby villages represent the sources of heavy metals and determine chemical parameters in water samples (Issa and Alshatteri 2018). Significant differences were found with respect to the first round of sampling at sites S2, S3, S12, and S13. The results of the current study agreed with the WHO guideline of 2 mg/L and are higher than the results of Hussain et al. 2017 (0.00–0.01 mg L), Ehi-Eromosele and Okiei 2012 (0.020 to 0.120 mg/L) and Malkani et al. 2019 (0.027 to 0.053 mg/L) for copper in drinking water. Levels of Cu in the current study ranged from 0 to 0.88 mg/L, particularly at sites located in eastern part of Kirkuk toward western part (Fig. 8a and b). Copper poisoning will result in chronic anemia (Acharya et al. 2008) or death due to nervous system, liver, and kidney failure if large quantities of copper compounds are consumed (Sharma and Sharma 2020).

The manganese results revealed a negative correlation with Cu and a positive correlation with Pb, with values of $-0.008$ and 0.02, respectively. At levels exceeding 0.1 mg/L, manganese in water manifests an undesirable taste in beverages and stains sanitary ware and laundry (Table 2 and Fig. 9a and b) and accumulates deposits in the distribution system specifically at the center of Kirkuk city (S8). Concentrations below 0.4 mg/L are usually acceptable to consumers according to WHO 2011; moreover, a concentration of 0.2 mg/L will form a black coating on pipes. Highest levels of heavy metals were recorded during winter season, whereas minimum values found during summer season (CPCB 2008). High Co (At S8, S9, S10, S11, S12), Pb (At S6), Mn (At S8),
and Cu (At S6) contents may be due to the discharge of considerable number of untreated effluents into river from small factories and domestic wastewater, same conclusions have been made by a Banerjee et al. 2016 and Goran 2014. The health-based value of 0.4 mg/L for manganese is lower than the acceptability threshold of 0.4 mg/L (WHO 2011). Manganese deficiency can cause serious health problems, including weak bones (osteoarthritis), muscle and joint pain, and sexual dysfunction (Zofkova et al. 2017). Human exposure to higher amounts
of manganese can result in severe disorders in the nervous system, and long-term exposure can cause permanent neurological effects (USEPA 2004). The maximum concentration of manganese (0.38 mg/L) was less than the WHO permissible limit. Zainulabdeen (2018) concluded that the water supplied to consumers is of good quality, but the periodic distribution of water may cause damage to the distribution network.
Conclusion

As for the risk calculated from heavy metal concentration (lead), it is almost negligible in comparison with the risk from B(a)P. B(a)P measurement is more accurate with HPLC than ELISA kits, and detected levels were higher during the wet season than during the dry season depending on statistical analysis (coefficient of variance) between both methods which showed more homogeneity for HPLC method for determination of B(a)P in studied water samples than ELISA method. Lower carcinogenic risks were obtained when an ELISA kit was used, and all results of total risks (oral and skin exposure) were lower than those of the HPLC method. Carcinogenic risks for both methods

Fig. 8 Seasonal variation in (a and b) Copper concentrations during wet and dry seasons.
were within acceptable ranges and did not surpass standards, with the highest levels found in children in comparison with adults. The most significant contributors to variation in overall cancer risk appear to be fluctuations in the concentration of B(a)P (Cw) in various sampling locations, followed by exposure length (ED).

High levels of lead were measured in the studied drinking water. The risk from heavy metal exposure (lead) is almost negligible in comparison with the risk from B(a)P. This study may open the gateway to future endeavors with respect to PAHs, and Iraqi drinking water is contaminated with heavy metals.
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Author contribution  We state that we are the authors of this work for the Environmental Science and Pollution Research Journal based on the following criteria:
1. Significant contributions to the work’s conception or design; or the work’s acquisition, analysis, or interpretation of data; AND
2. Drafting the work or critically revising it for important intellectual content; AND
3. Final approval of the version to be published; AND
4. Agreement to be accountable for all aspects of the work in ensuring that questions related to the accuracy or reliability of the work are addressed; AND
All listed authors (Awaz Bahroz Mohammed, Siraj Muhammed Abdulla Goran, and Abhrayjoti Tarafdar) met the Environmental Science and Pollution Journal criteria. We attest that all authors contributed significantly to the creation of this manuscript, each having fulfilled criteria as established by the Environmental Science and Pollution Journal. We confirm that all mentioned authors have read and accepted the manuscript. We confirm that all named authors have accepted the order of authors mentioned in the manuscript.

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Data availability  All data generated or analyzed during this study are included in this published article [and its supplementary information files].

Declarations

Ethics approval  Every element of the work discussed in this manuscript that does not include human patients or animals is presented within the manuscript.

Consent for publication  Not applicable.

Competing interest  We would like to confirm that this publication (profiling of seasonal variation in and cancer risk assessment of benzo(a)pyrene and heavy metals in drinking water from the Kirkuk region, Iraq) is free of any known conflicts of interest. This study has received no direct financial funding that could have affected its results.

Intellectual rights  We confirm that the protection of intellectual property associated with this work has been carefully considered and that there are no intellectual property impediments to publication, including publication timing. As a result, we confirm that we have complied with the intellectual property policies of our respective institutions.

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