Determination of Heavy Metals in Irrigation Water, Soil, Paddy, and Produced Rice of Some Paddy Fields of Iraq

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Abstract
Iraq is a developing country with a high population. In Iraq, heavy metal and metalloid contamination has resulted from both industrialisation and environmental sources, providing serious health risks to the local population. We conducted one of the most comprehensive analyses on the current state of Iraq’s heavy metal and metalloid pollution in this paper, which included water, soil, paddy, and rice. A study was carried out to determine the concentration of heavy metals including Lead (Pb), Cadmium (Cd), Iron (Fe), manganese (Mn), Cobalt (Co), Magnesium (Mg), Aluminum (Al), and Copper (Cu) of 39 irrigation water samples, 75 soil samples, 75 paddy samples, and 75 rice samples in two Iraqi governorates (Diyala, and Salah al-Din). Samples were taken from three fields in each province. Atomic Absorption Spectrophotometer was used to determine heavy metals concentrations. Iraqi Quality Standardization (IQS) and World Health Organization (WHO) were considered as the permissible limits. The results showed that all irrigation water samples were exceeded the permissible limit for Pb, Cd, Fe, and Mn metals, while all soil samples were exceeded for Mn and Mg metals. Paddy and rice samples were exceeded for only Pb metal permissible limit, which was high, for example, Pb metal concentrations of rice and paddy ranged from 1.805-4.776 mg/kg, 0.642-3.481 mg/kg respectively, while the permissible limit was 0.2 mg/kg. Consequently, rice samples were deemed unfit for human consumption, with the contamination coming from irrigation water. therefore, this paper has suggested that the Irrigation water treatment should be strongly advised and evaluated.

Keywords: Heavy metals, Irrigation water, Soil, Paddy, Rice, Atomic Absorption Spectrophotometer.

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Einheit Schieß, und 75 Einheit Riz in beiden von Präfenzen der Provinzen den Wissens der Einheit. In der Untersuchung Magnet Nanosauer die Konzentration der schweren Metalle und die Grenzwerte der internationalen Standards IQS und WHO.

Es zeigt die Ergebnisse dass alle Proben des Schleischen und Riz überschritten die Grenze der zulässigen Werte für Mn, Fe, Cd, Pb. Die Proben des Schleischen und Riz überschritten die Grenze des Bleis. Die Konzentration des Bleis in Schleischen und Riz lag zwischen 2,6 und 9,1 Milligramm pro Kilogramm, während die zulässige Konzentration 2,2 Milligramm pro Kilogramm ist. Die Proben der Riz sind nicht sicher für menschlichen Verzehr.

1. Introduction

Heavy metals are metals with densities greater than 5 g/cm³ [1]. Heavy metals are carcinogenic and mutagenic compounds in nature [2], and because of their non-biodegradable property, they are highly persistent in the atmosphere, allowing dangerous quantities to accumulate quickly. [3]. Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Mercury (Hg), Nickel (Ni), and Lead (Pb) are some examples of heavy metals [4]. For examples, cadmium causes organs toxicity such as liver and kidney, pulmonary, osteoporosis, carcinoma [5]; while lead causes headaches, nausea, vomiting, decreasing hemoglobin synthesis, impaired renal function, deafness, blindness, and retardation [6]. Some metals such as calcium, iron, magnesium, and zinc are essential nutrients that become harmful and toxic when their concentrations exceed recommended standards [7]. Whereas the increase of iron intake on the required limit might be caused by Alzheimer's disease, Parkinson's disease, Huntington disease, and amyotrophic lateral sclerosis [8].

One of the most important foods on the planet is rice (Oryza sativa L). [9], and it is the second most widely consumed grain after wheat. [10]. It’s the second most popular grain. Rice is an important crop for Iraq because it is a staple diet for the majority of Iraqis and the second most often consumed grain after wheat. [11]. Amber is the most important local Iraqi rice variety, and it is characterized by high quality in terms of its aromatic character [12]. The production quantity of rice in Iraq for 2015, 2016, and 2017 were 200, 43, and 100 thousand tons respectively [13].

The most dangerous sources of rice contamination are heavy metals [14]. Rice is contaminated by the water that comes into the soil and eventually contaminates the field crops [15]. As a consequence, consumers health is protected by monitoring their exposure to these dangerous elements [16]. Because of their availability, industrial and municipal wastewaters are increasingly being employed for irrigation in urban and peri-urban agriculture [17]. Long-term irrigation water creates heavy metal deposition in soils [18]. Heavy metals can also accumulate in soils as a result of pollution from quickly increasing industrial regions, mining tailings, high-metal waste disposal, leaded gasoline, paints, fertilizer land application, and other sources [19]. Consequently, high levels of heavy metals can impair soil function causing plant toxicity and contaminate the food chain by compromising the quality and safety of food [20]. Since plants can uptake toxic compounds from soils via their roots, the soil is a source of many contaminants for plants [21]. Heavy metal pollution is one of the significant concerns in agricultural soils due to the adverse influences on human health through the consumption of agricultural products [22]. Heavy metals have the potential to pollute rice. [23], and they classified as major chemical toxic due to their high potential risk to the ecosystem and human health [22]. Therefore, chemical analyses are the most used method for determining the safety
of cereal crops around the world [24]. In Iraq, the Quality Control Department/ Grain Board of Iraq conducts routinely chemical and microbiological analyses on imported rice [25]. Domestic rice, on the other hand, is not subjected to such chemical analyses by farmers.. Therefore, this study aimed to determine the safety of the paddy and rice from fields in terms of its heavy metals content. Also, determining the source of the contamination is an important step, therefore, the study included analyses to detect heavy metals of soils and irrigation water.

2. Materials and Methods

2.1 Description of the two study areas

Diyala governorate is one of the eighteen governorates of Iraq. Diyala governorate constitutes 4.1% of the area of Iraq, and its area is estimated to be 17,685 km$^2$. Between lines 22.44° - 56.45° east of the Greenwich line [26].

Salah Al-Din governorate is one of the Iraqi provinces. Salah Al-Din governorate constitutes 5.6% of the area of Iraq, and its area is estimated to be 24,363 km$^2$. It is located between 33.3° to 35.6° North latitude and 42.4° to 45° East longitude [27].

2.2 Sample collection

All irrigation water, soil, and paddy samples were collected from Diyala and Salah al-Din governorates during October 2020. Three fields of each province were used to gather the samples.

2.2.1 Irrigation water samples

A total of 39 irrigation water samples were taken from Diyala and Salah al-Din, each with a volume of 60 ml. For each field, eight Diyala water samples were collected. The first field was well water, the second was river water, and the third was pooled water, or irrigation water that came from fields that were overflowing with water. Salah al-Din provided five irrigation water samples for each field, with the first and third fields being pools and the second field being a river. The samples were placed in clean, dry containers and stored in an ice bath until subsequent analysis. [28].

2.2.2 Soil samples

Seventy-five soil samples were hand gathered using a shovel from Diyala and Salah al-Din, fifteen samples for each Diyala field and ten samples for each Salah al-Din field. Samples were taken using a random sampling method, as shown in Figure 1, which can be used in fields of any size, whether equal or unequal. Samples were taken from the surface of the soil to a depth of 20 cm below it. Plastic bags were used to store soil samples (polyethylene). The grass, leaves, roots, and stones were removed by hand once the samples arrived in the lab, and the soil samples were air-dried at room temperature. Air-dried soil samples were mashed with a pestle and mortar before being analyzed through a 2 mm mesh sieve. [7].

![Figure 1: Points of take paddy and soil samples, the random method for collecting soil samples](image_url)
2.2.3 Paddy samples

Seventy-five samples were collected from rice fields from Diyala and Salah al-Din, fifteen samples from each field of Diyala, and ten samples from each field of Salah al-Din. Samples were collected from the same soil samples locations. They were stored in plastic bags (polyethylene) then paddy was peeled to obtain rice by using Aljaon (its machine was used for the peeling cereal in past) [29].

2.3 Preparation of samples for heavy metals measurement

Irrigation water samples were filtered using a Whatman filter paper No. 1. Then a few drops of strong nitric acid were added to samples (60 mL) to inhibit metal precipitation and biological growth, and then the concentrations of the heavy metals were measured using Atomic Absorption Spectrophotometer (AAS) [30].

While the soil samples, 15 mL of 30% HCL and 70% HNO₃ (3:1 ratio) was added to one gram of dried soil and leftover a day. The mixture was placed on a hot plate for 45 minutes in a fume hood (chamber), then the solution was quantitatively transferred to a volumetric flask and the volume was completed to 100 mL by the addition of deionized water. After that, they were filtered by filter papers and heavy metals were measured by AAS [31].

Ten grams of well-ground paddy or rice were placed in a ceramic crucible and burned in a muffle furnace at a temperature of 600 °C for 6 hours. Then 5 mL of HCl (5.5M) were added and placed on a hot plate, and 20 mL of HNO₃ (0.2M) was added and left for 90 min. Then they were filtered by filter papers for measuring heavy metals using AAS [32].

2.4 Statistical Analysis

One-way analysis of variance (ANOVA) was performed for statistical analysis of data. Tukey’s test of means was implemented by using IBM SPSS Statistics –Version 23.0.

3. Results

Table 1 shows lead metal concentrations in irrigation water, soil, paddy, and rice from the Diyala and Salah al-Din areas. The content of Pb in all irrigation water samples in the governorates of Diyala and Salah al-Din was substantially greater than the IQS and WHO permitted level. The lowest concentration of Pb was found in field 1 of Diyala, which the source of the irrigation water was well, while the highest concentration of lead was found in the pooled source of irrigation water. The average concentration of Pb in Diyala fields was 62, 97, and 133 times higher than the permissible limit for the first, second, and third fields respectively, and it was higher than by 104, 111, and 132 times for the first, second, and third fields of Salah al-Din fields respectively. The amounts of Pb in irrigation water varied significantly between fields. The concentration of Pb for all soil samples in Diyala and Salah al-Din governorates was less than the permissible limits of the WHO. Furthermore, there were no significant changes in soil Pb concentrations between farms. The concentration of Pb in paddy for all samples was much higher than the permissible limit of the WHO (Table 1). Pb concentration in Diyala was 9, 10, and 10 times higher than the permissible limit for the first, second, and third fields, respectively, and it was higher by 10, 10, and 11 times for the first, second, and third fields of Salah al-Din fields respectively. There were no significant changes in soil Pb concentrations between farms. Furthermore, there were no significant changes in soil Pb concentrations between farms. Also, all the concentration of Pb in rice was higher than the permissible limit of the IQS and WHO. Pb concentration was approximately 15 times higher than the permissible limits. There were no significant differences between Pb concentrations of rice among fields.
Table 1: concentration of Pb mg/L, or mg/kg in irrigation water, agricultural soils, paddy, and rice

| Sample       | Diyala          | Salah al-Din   | Limit          |
|--------------|-----------------|----------------|----------------|
| Water        |                 |                |                |
| Field 1      | 0.62±0.3        | 0.97±0.489     | 0.01           |
|              | 29<sup>b</sup>  | 1<sup>st</sup> | 0.0             |
| Field 2      | 1.32±0.40       | 1.047±0.34     | 1              |
|              | 1<sup>st</sup>  | 2<sup>nd</sup> |                |
| Field 3      | 1.111±0.35      | 1.332±0.40     | 3              |
|              | 9<sup>th</sup>  | 2<sup>nd</sup> |                |
| Soil         | 32.301±1.11     | 31.431±0.7     | 85             |
| Field 1      | 31.966±1.11     | 31.643±1.1     |                |
|              | 5<sup>s</sup>   | 57<sup>s</sup> |                |
| Field 2      | 31.431±0.7      | 31.188±3.0     |                |
|              | 89<sup>a</sup>  | 33<sup>s</sup> |                |
| Field 3      | 1.332±0.40      | 1.111±0.35     |                |
|              | 2<sup>nd</sup>  | 9<sup>th</sup> |                |
| Paddy        | 1.810±0.8       | 2.059±0.662    | 0.2            |
| Field 1      | 2.059±0.662     | 2.257±0.55     |                |
|              | 1.047±0.34      | 2.464±0.61     |                |
| Field 2      | 1.111±0.35      | 2.257±0.55     |                |
|              | 9<sup>th</sup>  | 3<sup>rd</sup> |                |
| Field 3      | 1.332±0.40      | 0.01           |                |
|              | 2<sup>nd</sup>  | 0.0            |                |
| Rice         | 3.071±0.8       | 3.168±0.795    | 0.2            |
| Field 1      | 3.168±0.795     | 3.586±0.82     |                |
|              | 7<sup>th</sup>  | 9<sup>th</sup> |                |
| Field 2      | 3.273±0.68      | 3.358±0.77     |                |
|              | 0<sup>st</sup>  | 1<sup>st</sup> |                |
| Field 3      | 3.183±0.80      | 3.358±0.77     |                |

WHO/ FAO = World Health Organization, Food and Agriculture Organization [33]. IQS = Iraqi Quality Standardization [34]. *overpassed WHO/IQS acceptable limit. Values in rows with different superscript letters refers to statistical significance at p < 0.05.

Cadmium concentrations in irrigation water, soil, paddy, and rice from Diyala and Salah al-Din fields was placed in Table 2. The concentration of Cd for all irrigation water samples in Diyala and Salah al-Din governorates was higher than the permissible limit of IQS and WHO. There was no significant difference between Cd concentrations of different fields. The concentration of Cd for all soil, paddy, and rice samples in Diyala and Salah al-Din governorates were less than the permissible limits of the IQS and WHO. There were no significant differences among the fields in soil and rice but there was a significant difference in paddy concentration of different fields.

Table 2: concentration of Cd mg/L, or mg/kg in irrigation water, agricultural soils, paddy, and rice

| Sample       | Diyala          | Salah al-Din   | Limit          |
|--------------|-----------------|----------------|----------------|
| Water        |                 |                |                |
| Field 1      | 0.006±0.0       | 0.007±0.000    | 0.003          |
|              | 02<sup>s</sup>  | 2<sup>nd</sup> | 0.003          |
| Field 2      | 0.005±0.000     | 0.007±0.000    | 0.003          |
|              | 2<sup>nd</sup>  | 2<sup>nd</sup> | 0.003          |
| Field 3      | 0.007±0.000     | 0.007±0.000    | 0.003          |
|              | 2<sup>nd</sup>  | 2<sup>nd</sup> | 0.003          |
| Soil         | 1.128±0.492<sup>a</sup> | 1.089±0.520<sup>a</sup> | 1.172±0.483<sup>a</sup> | 1.614±0.28<sup>a</sup> | 1.270±0.372<sup>a</sup> | 1.276±0.45<sup>a</sup> | 3 | – |
| Field 1      | 1.089±0.520<sup>a</sup> | 1.089±0.520<sup>a</sup> | 1.172±0.483<sup>a</sup> | 1.614±0.28<sup>a</sup> | 1.270±0.372<sup>a</sup> | 1.276±0.45<sup>a</sup> | 3 | – |
| Field 2      | 1.089±0.520<sup>a</sup> | 1.089±0.520<sup>a</sup> | 1.172±0.483<sup>a</sup> | 1.614±0.28<sup>a</sup> | 1.270±0.372<sup>a</sup> | 1.276±0.45<sup>a</sup> | 3 | – |
| Field 3      | 1.089±0.520<sup>a</sup> | 1.089±0.520<sup>a</sup> | 1.172±0.483<sup>a</sup> | 1.614±0.28<sup>a</sup> | 1.270±0.372<sup>a</sup> | 1.276±0.45<sup>a</sup> | 3 | – |
| Paddy        | 0.054±0.0       | 0.072±0.014<sup>b</sup> | 0.055±0.002<sup>a</sup> | 0.055±0.002<sup>a</sup> | 0.057±0.002<sup>a</sup> | 0.042±0.019<sup>b</sup> | 0.4 | – |
| Field 1      | 0.072±0.014<sup>b</sup> | 0.055±0.002<sup>a</sup> | 0.055±0.002<sup>a</sup> | 0.057±0.002<sup>a</sup> | 0.042±0.019<sup>b</sup> | 0.4 | – |
| Field 2      | 0.072±0.014<sup>b</sup> | 0.055±0.002<sup>a</sup> | 0.055±0.002<sup>a</sup> | 0.057±0.002<sup>a</sup> | 0.042±0.019<sup>b</sup> | 0.4 | – |
| Field 3      | 0.072±0.014<sup>b</sup> | 0.055±0.002<sup>a</sup> | 0.055±0.002<sup>a</sup> | 0.057±0.002<sup>a</sup> | 0.042±0.019<sup>b</sup> | 0.4 | – |
| Rice         | 0.030±0.0       | 0.065±0.02     | 0.054±0.033<sup>a</sup> | 0.050±0.01<sup>a</sup> | 0.065±0.02<sup>a</sup> | 0.4 | 0.4 |
| Field 1      | 0.065±0.02     | 0.065±0.02     | 0.054±0.033<sup>a</sup> | 0.050±0.01<sup>a</sup> | 0.065±0.02<sup>a</sup> | 0.4 | 0.4 |
| Field 2      | 0.065±0.02     | 0.065±0.02     | 0.054±0.033<sup>a</sup> | 0.050±0.01<sup>a</sup> | 0.065±0.02<sup>a</sup> | 0.4 | 0.4 |
| Field 3      | 0.065±0.02     | 0.065±0.02     | 0.054±0.033<sup>a</sup> | 0.050±0.01<sup>a</sup> | 0.065±0.02<sup>a</sup> | 0.4 | 0.4 |

WHO/ FAO = World Health Organization, Food and Agriculture Organization [33]. IQS = Iraqi Quality Standardization [34]. *overpassed WHO/IQS acceptable limit. Values in rows with different superscript letters refers to statistical significance at p < 0.05.

Table 3. demonstrated Cu metal concentrations in irrigation water, soil, paddy, and rice from Diyala and Salah al-Din fields. The concentration of Cu for all irrigation water, soil, paddy, and rice samples in Diyala and Salah al-Din governorates was less than the permissible limits of the IQS and WHO. There were significant differences in irrigation water, soil, and rice fields, but there was no significant difference for paddy samples of different fields.
Table 4 demonstrated Fe metal concentrations in irrigation water, soil, paddy, and rice from Diyala and Salah al-Din fields. The concentration of Fe for all irrigation water samples in Diyala and Salah al-Din governorates was higher than the permissible limit of IQS and WHO. There was no significant difference between Fe concentrations of different fields. The concentration of Fe for all soil, paddy, and rice samples in Diyala and Salah al-Din governorates was less than the permissible limits of the IQS and WHO. There were significant differences among the fields.

Table 3: concentration of Cu mg/L, or mg/kg in irrigation water, agricultural soils, paddy, and rice

| Sample | Diyala | Salah al-Din | Limit |
|--------|--------|--------------|-------|
| Water  | Field 1 | Field 2 | Field 3 | Field 1 | Field 2 | Field 3 | WH/O/FAO | IQS |
|        | 0.050±0.0 | 0.079±0.06 | 0.275±0.22 | 0.452±0.2 | 0.414±0.33 | 0.665±0.327 | 2 | 1 |
|        | 54° | 0° | 2° | 71° | 2° | 2° |
| Soil   | 5.507±1.2 | 3.993 ± 1.918 | 5.738±1.55 | 5.33±1.03 | 6.34±1.15 | 5.54±0.866 | 140 | – |
|        | 35° | 38° | 8° | 8° | 8° | 8° |
| Paddy  | 0.318±0.26 | 0.447±0.23 | 0.532±0.18 | 0.429±0.215 | 0.548±0.26 | 0.52±0.27 | 20 | – |
|        | ±0.26 | ±0.23 | ±0.18 | ±0.215 | ±0.26 | ±0.27 | |
| Rice   | 0.089±0.0 | 2.082±0.08 | 0.048±0.02 | 0.048±0.0 | 0.050±0.02 | 0.042±0.02 | 10 | – |
|        | 38° | 86° | 4° | 4° | 3° | 3° |

WHO/FAO =World Health Organization, Food and Agriculture Organization [33]. IQS = Iraqi Quality Standardization [34]. *overpassed WHO/IQS acceptable limit. Values in rows with different superscript letters refers to statistical significance at p < 0.05.

Table 4: concentration of Fe mg/L, or mg/kg in irrigation water, agricultural soils, paddy, and rice

| Sample | Diyala | Salah al-Din | Limit |
|--------|--------|--------------|-------|
| Water  | Field 1 | Field 2 | Field 3 | Field 1 | Field 2 | Field 3 | WH/O/FAO | IQS |
|        | 0.533±0.05 | 0.452±0.1 | 0.542±0.2 | 0.547±0.1 | 0.555±0.11 | 0.678±0.15 | 0.3 | 0.3 |
|        | 3° | 38° | 4° | 84° | 1° | 9° |
| Soil   | 32.59±1.1 | 34.38±2.4 | 31.696 ± 1.1 | 32.52 | 30.51±3.8 | 32.45±1.0 | 150 | – |
|        | 72° | 72° | 1° | 1° | 1° | 1° |
| Paddy  | 9.38±2.43 | 9.08±1.9 | 10.23±1.6 | 10.70±8.1 | 11.50±1.2 | 11.31±1.2 | – | – |
|        | 7° | 3° | 1° | 87° | 1° | 1° |
| Rice   | 2.39±1.27 | 8.00±4.47 | 2.63±0.74 | 2.59±0.6 | 2.58±0.88 | 2.64±0.87 | 15 | – |
|        | 5° | 3° | 2° | 85° | 8° | 8° |

WHO/FAO =World Health Organization, Food and Agriculture Organization [33]. IQS = Iraqi Quality Standardization [34]. *overpassed WHO/IQS acceptable limit. Values in rows with different superscript letters refers to statistical significance at p < 0.05.

Table 5 demonstrated Mn metal concentrations in irrigation water, soil, paddy, and rice from Diyala and Salah al-Din fields. The concentration of Mn for all irrigation water samples in Diyala and Salah al-Din governorates was much higher than the permissible limits of the IQS and WHO. Manganese concentration of irrigation water of all fields was 10 times or more than the limit, and there was no significant difference among the fields. The
concentration of Mn for all soil samples in Diyala and Salah al-Din governorates was higher than the permissible limits of the WHO. There were no significant differences between Mn concentrations among fields. The concentration of Mn for all paddy and rice samples was less than the permissible limits of the IQS and WHO.

**Table 5:** concentration of Mn mg/L, or mg/kg in irrigation water, agricultural soils, paddy, and Rice

| Sample          | Field 1    | Field 2    | Field 3    | Field 1    | Field 2    | Field 3    | WHO/ FAO I QS |
|-----------------|------------|------------|------------|------------|------------|------------|---------------|
| Water           | 0.967±0.170 | 0.997±0.34 | 1.284±0.54 | 1.111±0.41 | 1.325±0.44 | 1.277±0.36 |               |
|                 | 30.51±3.18  | 34.02±4.7  | 30.83±1.4  | 30.51±3.18 | 31.32±4.6  | 31.34±1.2  |               |
| Soil            | 2.80±0.36   | 2.96±0.49  | 2.76±0.14  | 2.76±0.14  | 3.03±0.26  | 3.05±0.15  |               |
| Paddy           | 2.00±0.69   | 2.96±0.14  | 2.74±0.75  | 2.49±0.8  | 2.67±0.7  | 300±500     |               |
| Rice            | 2.00±0.69   | 2.96±0.14  | 2.74±0.75  | 2.49±0.8  | 2.67±0.7  | 300±500     |               |

WHO/ FAO = World Health Organization, Food and Agriculture Organization [33]. IQS = Iraqi Quality Standardization [34]. *overpassed WHO/IQS acceptable limit. Values in rows with different superscript letters refers to statistical significance at $p < 0.05$.

Table 6 demonstrated Mg metal concentrations in irrigation water, soil, paddy, and rice from Diyala and Salah al-Din fields. The concentration of Mg for all irrigation water, paddy and rice samples in Diyala and Salah al-Din governorates was much less than the permissible limits of the WHO. There was no significant difference between Mg concentrations in irrigation water and paddy samples but a significant difference in rice. The concentration of Mg for all soil samples was higher than the permissible limits of WHO. There was no significant difference between Mg concentrations of different fields.

**Table 6:** concentration of Mg mg/L, or mg/kg in irrigation water, agricultural soils, paddy, and Rice

| Sample          | Field 1    | Field 2    | Field 3    | Field 1    | Field 2    | Field 3    | WH O FA O I QS |
|-----------------|------------|------------|------------|------------|------------|------------|---------------|
| Water           | 11.00±0.6  | 11.01±0.5  | 11.18±0.5  | 10.99±0.6  | 11.10±0.6  | 11.08±0.5  | 50± -         |
| Soil            | 399.59±1.7 | 392.59±5.7 | 394.66±.7  | 396.862±1.1| 395.14±5.7 | 394.02±8.6 | 255± -        |
| Paddy           | 13.94±1.21 | 13.85±1.3  | 13.83±1.8  | 13.83±1.8  | 13.83±1.8  | 13.90±1.1  | - -           |
| Rice            | 13.83±1.21 | 13.85±1.3  | 13.83±1.8  | 13.83±1.8  | 13.83±1.8  | 13.90±1.1  | 143.5± -      |

WHO/ FAO = World Health Organization, Food and Agriculture Organization [33]. IQS = Iraqi Quality Standardization [34]. *overpassed WHO/IQS acceptable limit. Values in rows with different superscript letters refers to statistical significance at $p < 0.05$. 

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The concentration of Co and Al of all samples, irrigation water, soils, paddy and rice, was less than the detection limit, therefor the data has not been stated in tables.

The number of samples that exceeded the allowed limit was shown in Figure 2. Pb concentrations were found to be higher than the limit in all irrigation water, paddy, and rice samples (Figure 2A). While there was no soil sample had Pb concentration more than the permissible limit. Figure 2B stated all other samples that exceeded the limit, which was irrigation water samples for Cd, Fe, and Mn, in addition to soil samples for Mg and Mn.

**Figure 2:** number of samples exceeded the heavy metals limit to the total number of samples. A: Pb, B: Cd, Fe, Mn, and Mg.

### 4. Discussion

The acceptable levels for Pb, Cd, Fe, and Mn were exceeded in all irrigation water samples (Figure 2). Heavy metal concentrations were highest in pooled water, followed by river water, and finally well water, as expected. In comparison to the literature, the Tigris River had a Pb value of 0.05 mg/L [35], which was higher than the WHO standard of 0.01 mg/L. However, in this study, Pb values range was 0.286-1,801 mg/kg, which was much higher than Pb concentration of the Tigris River. Tigris River and Euphrates River are the main sources of water in Iraq. The range of Cd of irrigation water samples of this study was 0.0021-0.0096 mg/L, which was lower than the Cd concentration of a river in Cameron.
The concentration of Pb in the paddy samples in the two study areas was higher than the permissible limit of the WHO (Figure 2). The lead concentration for this study ranged from 2.0032 - 2.20 mg/L, which was higher than the observed range of this study 0.415-0.831 mg/L of Fe. Also, Fe concentration of southwest Baghdad, wells -Yusufiyah in Iraq was 0.1-0.63 mg/L [40]. Concentrations of Mg of irrigation water samples ranges 0.452-11.87 mg/L were less than those range 2-680 mg/L in India [41]. The reason for the high concentration of heavy metals in irrigation water is probably due to the disposal of waste from the stations in this area and the disposal of some household waste.

The concentrations of Pb, Cd, Cu, and Fe in the soil were less than the WHO limit for Diyala and Salah al-Din fields, while the concentration of Mn and Mg was higher than the WHO limit for both fields (Figure 2). The lead concentration for this study ranged from 30.15-33.63 mg/kg, which was higher than the concentration of lead in the soil of Kurdistan, Iraq. In their study, they found that Pb concentration was 14.67 mg/kg for soil depth 20 cm, while it was 6.5 mg/kg for the surface layer of the soil [42]. The Cd concentration of rice soil in Mishkhab Area, in Iraq was ranged from 0.21-0.33 mg/kg [43], which was lower than the Cd concentration of the two study areas of this study, 0.254-1.932 mg/kg. The concentration of cadmium of soil in Mogla Bazar in Sylhet, Bangladesh was 0.05 mg/kg, which was less than the permissible limit of the WHO and less than the Cd concentration of this study [44]. Copper concentrations of all soil samples ranged 1.92-8.28 mg/kg, which were less than those ranged 13.76 - 60.56 mg/kg of rice soil in Nepal. The soil contamination with Cu could be due to wastewater irrigation, chicken manure, and pesticides in the farmland [3]. The Cu concentration of soils in Bangladesh was below the permissible limits recommended by Indian Standard Awashthi and European Union [45]. Iron concentrations of all soil samples ranged from 30.2-40.32 mg/kg, which were within the range of a peri-urban area of Lahore district India, 8.89- 35.03 mg/kg [46]. Manganese concentrations of all soil samples ranged from 25.91-37.86 mg/kg, and this result was placed within the range of the Deepmala et al. [20] study 12.5 -53.9 mg/kg that was done in the Indian paddy soil. Also, a similar range was observed in Pakistan, 9.12- 30.08 mg/kg [47]. The concentration of Mg in the upper layers of the soil at a depth of 0-20 was higher than its concentration in the layers of soil at a depth of (20-40) [48]. Mg concentrations of paddy fields in 0–20 cm and 20–40 cm soil layers were averaged 282 and 243 mg/kg respectively, while Mg concentrations range of the two study areas was 383.08-448.32 mg/kg, which were more than the above-mentioned study.

Surprisingly, irrigation water had a significant heavy metal level, although soil had a low concentration. The insolubility of metals because of high pH of the soil in addition to soil worms and redox potential of soil might reduce minerals. Also, heavy metals were absorbed by the roots of the plant, where the highest percentage was in the root, then the stem, leaves, and finally the grain, and this was might be the reason for its decrease in rice [46], [49]. The concentration of Pb in the paddy samples in the two study areas was higher than the permissible limit of the WHO (Figure 2), in contrast to the concentrations of the rest of the heavy metals, Cd, Cu, Fe, Mn, and Mg, which were less than the limit. Pb concentrations in the two study areas was ranged from 0.642 to 3.481 mg/kg, which was similar to the results obtained in the Malaysia, 2.06 mg/kg. The concentrations of Cd and Cu in the fields of Diyala and Salah al-Din were 0.009-0.092 mg/kg and 0.064-0.962 mg/kg respectively were less than
those in Malaysia were 0.13 and 0.74 mg/kg [50]. The concentrations of Fe, Mn, and Mg were 6.062-14.37 mg/kg, 2.163-3.593 mg/kg, 12.435-15.890 mg/kg respectively lower than the limit and less than the concentrations of the study conducted in India and united states [51].

All rice samples were exceeded the IQS and WHO limit for Pb (Figure 2), while all other detected metals were within the limit. Lead concentration of rice was generally higher than the Pb concentration of paddy, and this result was probably because of the husk of paddy that works as a diluted factor. Pb concentration of the produced rice from Diyala and Salah al-Din was ranged from 1.805-4.776 mg/kg, which was much higher than Pb concentration of rice produced from Alnajaf and Aldiwaniaa provinces, Iraq that was ranged from 0.093 to 0.339 mg/kg [52]. Pb concentration of rice in Al-Mishkhab, in Iraq was 0.778mg/kg [43]. Pb concentration of wheat planted in several region of Iraq ranged from 0.017 to 0.191 mg/kg [13], which was significantly lower than the concentration of Pb in rice. The reason for the high concentration of lead in rice might be because of its high concentration in irrigation water, which is transferred from water to plant because the planting of rice needs soaking in water for a while [53]. Internationally, Pb concentrations in Bengal rice were 0.42-6.39 mg/kg and that exceeded 100 times the WHO limit, which is posing a significant threat to human health [54]. Cd concentration of rice produced at Najaf and Diwaniaa provinces, Iraq was 0.055 – 0.066 mg/kg [52], which was more than the concentration of the current study, 0.014-0.095 mg/kg. Almayahi and Aljarrah [54] mentioned that Cd concentration of Anber rice of Nasiriyah, Iraq was 0.0468 mg/kg. Internationally, Singh et al. [55] reported that Cd of Indian rice was 0.014 mg/ kg. Regarding other heavy metals concentrations of rice, which were within the limits of WHO, such as Cu, Fe, Mn, and Mg. These results agreed with the [56], and [57] studies that they mentioned the Cu concentrations in Tangail district of Bangladesh and Nigerian rice samples were within the limit of WHO. However, Fe concentration, 135.5 mg/kg, reported by Konda et al. [51] was higher than the range of this study, 0.668-3.719 mg/kg. Magnesium concentrations of all Rice samples were ranged 12.042-15.725 mg/kg, which were less than the concentration of Mg ranged 250 - 1127 mg/kg in Arkansas for long rice kernel [51].

Conclusions
The high content of heavy metals, Pb, Cd, Fe, and Mn in irrigation water from the two study provinces was unsatisfactory. The high concentration of heavy metals in the irrigation water might be because of the discharge of water from factories and hospitals that had a high concentration of heavy metals. Although irrigation water was exceeded most of the studied heavy metals, the soil was exceeded only for Mn and Mg, which might be referred to the recent increase of heavy metals in the irrigation water, and the fixing will be easier than if the soil was contaminated. Regarding the paddy and rice, which were the most important, Pb concentration was the only metal that exceeded the limit. However, the produced rice was considered non-safe for human consumption. Finally, the two provinces’ irrigation water is the principal source of heavy metals and must be closely monitored. In order to lower the concentration of contaminants, the source of contamination must also be treated.

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