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# Elemental Analysis of River, Marshes and Ground Water in Thi Qar Region, Iraq

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**Abstract** The elemental analysis of the samples collected from marshes water and river water in Thi Qar region of Iraq are done using the X-ray fluorescence technique (XRF). The water samples are collected from Euphrates River, Al- Hammar marshes, ground water and drinking water. The elements observed in various samples are $_{20}Ca$, $_{26}Fe$, $_{29}Cu$, $_{30}Zn$, $_{33}As$, $_{35}Br$ and $_{38}Sr$. The $_{20}Ca$ concentration in Euphrates river water constitutes ~ 2.3% of the left over residue, a value similar to that observed in water from the marshes. The $_{38}Sr$ concentrations in the Euphrates river water is in the range 2519-5691$\mu$g/L. The $_{38}Sr$ concentrations in Euphrates River are similar to that observed in the marshes water. In Al-Hammar marshes, the concentration of $_{34}As$ is estimated to be in general below 5 $\mu$g/L. The $_{35}Br$ concentration in various samples collected from Al-Hammar marshes are in the average value =1108 $\mu$g/L. The $_{35}Br$ concentration in various samples collected from Euphrates river are in the average value =676$\mu$g/L. The water from Euphrates river is not safe for use for drinking water supply due to high bromine content and the water from the drinking water schemes from the river needs to be monitored for the presence of bromate ions.

**Keywords** X-ray fluorescence, River and Marshes water, Elemental Analysis, Drinking water contamination

## 1. Introduction

The Tigris and Euphrates rivers supply majority of the water into the marshes. The Euphrates traverses a distance of 2700 km, of which some 40% is in Turkey, 25% in Syria, and 35% in Iraq. The width of the Euphrates river ranges from 100-200 m, and the Tigris river from 150-350 m in the area of the marshes [1, 2]. The flow depths of the rivers are generally 5-15 m. The Euphrates river collects 84% of its flow in Turkey and 13% in Syria. It obtains no flow inputs within Iraq. Euphrates river water within Iraq is used for agricultural irrigation and municipal water supply. The core of the marshes in Thi Qar is centered in the area around the confluence of the Tigris and Euphrates rivers. It is typically divided into the two major areas: the Al-Hammar marshes, south of the Euphrates and the Central marshes between the twin rivers. Al-Hammar marshes are situated south of the Euphrates, extending from near Nassiriyah in the west to the outskirts of Basra on Shatt al-Arab in the east. Al-Hammar marsh area comprises 2800 km$^2$ of permanent marsh and lake, expanding to over 4500 km$^2$ during periods of seasonal and temporary inundation. Al-Hammar Lake, which dominates the marshes, is the largest water body in the lower Euphrates. It is approximately 120 km long and 25 km wide. Maximum water depth in the lake ranges from 2-3 m. Al-Hammar marshes are fed primarily by flooding and tributaries of the Euphrates river. Groundwater recharge is another source of replenishment. Local rainfall supplies very little water to the marshlands. The Iraqi marshes are largest wetland of unique ecosystem. The biotic community of marshes mostly includes plants and animals, which inhabit this rich environment. It is, therefore, very important that the remaining marshes be protected and that their health enhanced wherever possible. This is important for the surrounding environment and for the people who share this part of Iraq. In the last twenty years, Iraq has undergone two wars in 1991 and 2003, which have probably adverse repercussions on the Iraqi environment. These wars involved extensive burning, heavy bombing and shelling [3]. Also these wars took place in and around the study area under the present investigation, and caused considerable damage and pollution. To the best of our knowledge, no data are available in the scientific literature regarding the water contamination in south of Iraq after the recent Gulf war. The present study includes elemental analysis of the water sample collected from numbers of locations in the marshes and rivers in Thi Qar province in Southern Iraq. The elemental analysis has been performed using the X-ray Fluorescence (XRF) technique. The XRF technique is capable of detecting many elements simultaneously and has the advantage of low detection limit, which is further improved by analyzing the residue obtained after drying the water sample.

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# 2. Materials and Methods

## 2.1. The Study Area

The present study area is within Thi Qar (Nassiriyah) province and located in southern Iraq between the provinces of Waset to the north, Basra to the south, Maysan (Amarah) to the east and Muthanna to the west. It is located 350 km south of the capital Baghdad. The area of Thi Qar is 12900 km² with a population of 1.85 million. Thi Qar governorate has five districts: Nassiriyah, Suq Al-Shuyukh, Chibayish, Shatrah and Rafai. The water sample collection regions are shown in Fig. 1.

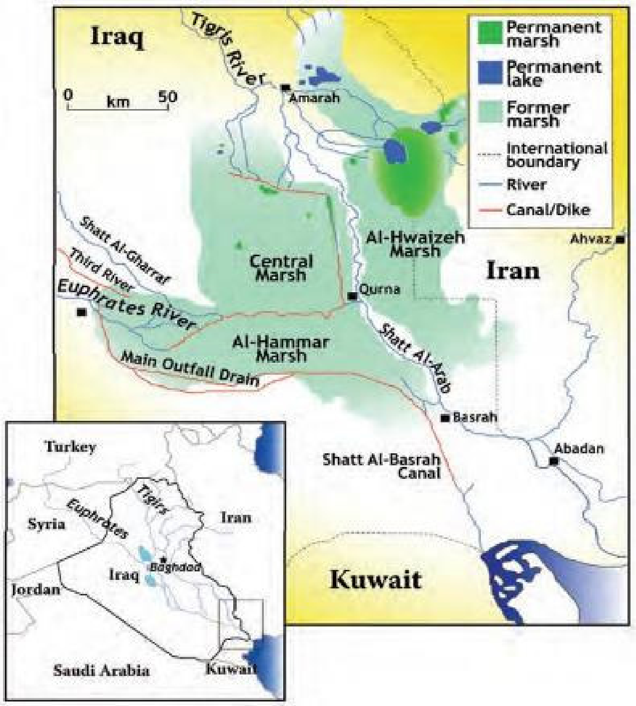


**Figure 1.** Iraqi marshlands location map [4]

The climate of southern Iraq is that of a tropical arid region. Temperature usually varies from 4 - 43 °C and annual precipitation from 10 - 170 mm. The combination of rain shortage and extreme heat makes much of Iraq a desert. The annual evaporation is up to 3000 mm [2]. Because of very high rates of evaporation, soil and plants rapidly lose the little moisture obtained from the rain, and vegetation could not survive without extensive irrigation. The Euphrates river crosses the city of Nassiriyah and passes through most of its southern towns, viz., Al-Islah, Sayyed Dikheel, Suq-Al-Shuyukh and Al-Chibayish. In order to achieve aim of the present study, water samples were collected from water resources in Thi Qar province, which lies between the Latitude 31° 14′ 0″ N and the Longitude 46° 19′ 0″ E. Water samples were collected from different regions of Thi Qar province of Iraq, *viz.,* Al-Hammar marshes and Euphrates river.

## 2.2. Experimental Measurements and Evaluation Procedure

The present study involved 26 locations from the Al-Hammar marshes, Euphrates rivers, drinking water and ground water from other locations. From each resource the water samples were taken in sterile plastic bottles under the surface of the water whenever possible. The bottles were labeled according to their sites and closed tightly. The water samples were filtered using normal filter paper (150 mm qualitative filter paper, whatman company, UK) and water samples were dried in disposable glass containers at ~ 70°C in an electric oven. About 100 *ml* of each of the water samples was used to obtain the residue. The residue was carefully scratched from the glass container and the remain sticking to the glass was removed using citric acid. The water residue samples were weighed and pressed into pellets of thickness 40-150 mg/cm$^2$. The elemental analysis of the samples was performed using the XRF spectrometer shown in Fig. 2. The exciter source consisted of a 3 kW long-fine-focus $_{42}$Mo-anode X-ray diffraction tube along with a 4 kW X-ray generator procured from Pan Analytic, the Netherlands.

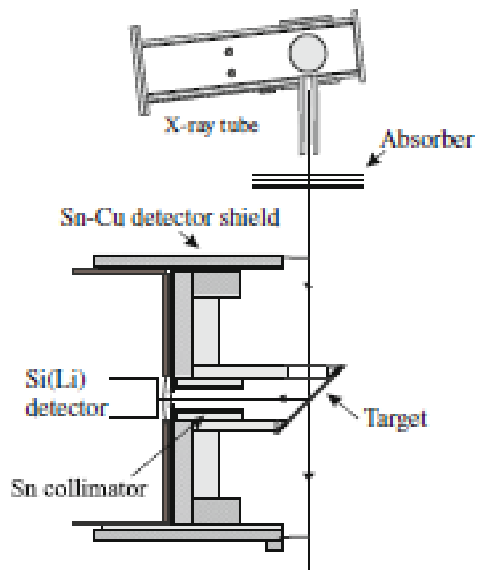


**Figure 2.** The XRF set up used in the present work

The sample targets were excited using the incident beam from the X-ray tube after passing through a combination of the selective absorbers consisting of the Zn, Y and Sr elements. The fluorescent X-ray spectra from the targets were taken for 2000 s using an Si (Li) detector (100 mm$^2$ x 5 mm, 8-$\mu$m Be window, FWHM = 180 eV at the Mn $K\alpha$ X ray energy, Canberra, US). The spectra for both the sides of each pellet were collected.

The fundamental parameter approach has been used to deduce elemental concentrations in the residue samples from the observed count rate ($Ni$) for the characteristic X-ray of i*th* element. The procedure is detailed elsewhere [5, 6].

## 3. Results and Discussion

Typical water residue spectra from water samples collected from various places are shown in Figs. 3-5. The spectra show peaks of the *K* X-rays of $_{20}Ca$, $_{26}Fe$, $_{29}Cu$, $_{30}Zn$, $_{33}As$, $_{35}Br$ and $_{38}Sr$.

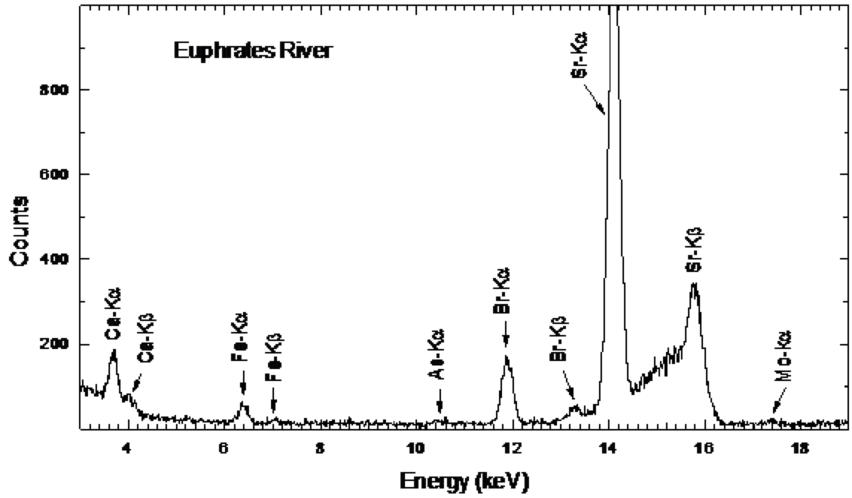


**Figure 3.** Typical spectra from residues of water samples taken from Euphrats River

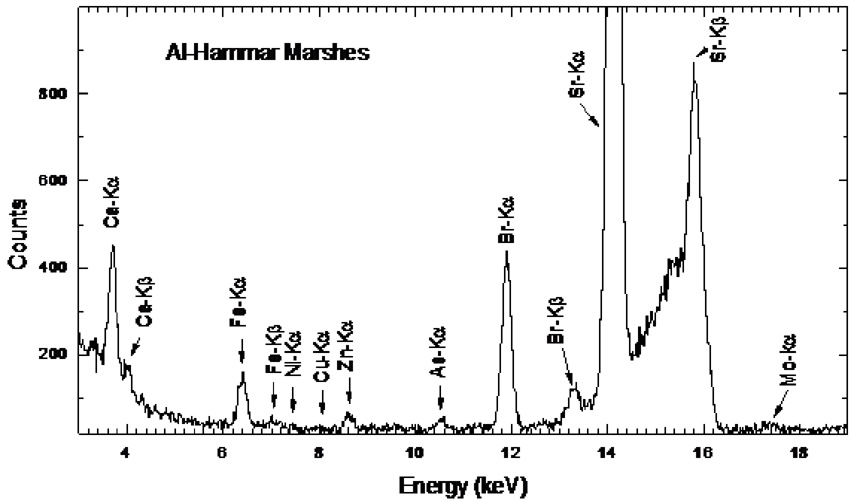


**Figure 4.** Typical spectra from residues of water samples taken from Al-Hammar Marshes

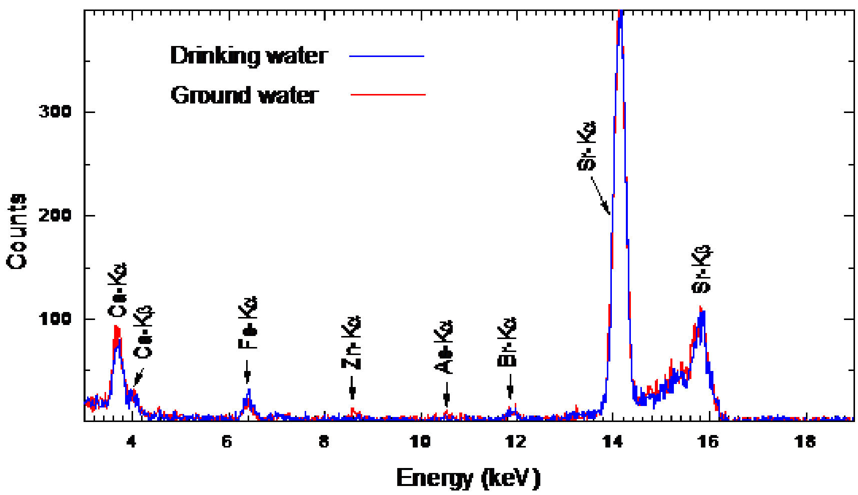


**Figure 5.** Typical spectra from residues of Ground water and drinking water samples taken from Thi qar region

**Table 1.** Elemental concentrations ($\mu$g/L) in water samples collected from the Al-Hammar marshes in Thi Qar region

| Location | Residue (mg/L) | Concentration ($\mu$g/L) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Ca (mg/L) | Fe | Zn | As | Br | Sr |
| North Al- Ekekah | 2720 | 51 | 1222 | 386 | < 6 | 685 | 3306 |
| Al-Jassim Marsh | 5318 | 168 | 6968 | 70 | < 5 | 1264 | 6398 |
| Al-khamisiyah Town | 7663 | 431 | 5228 | 1552 | 20 | 539 | 7434 |
| South Al-Ekekah | 3255 | 62 | 866 | 14 | < 4 | 794 | 3995 |
| Suq Al-Shuyukh | 4253 | 88 | 1047 | 225 | < 4 | 890 | 4219 |
| Garmah | 3275 | 74 | 916 | 154 | < 4 | 606 | 3741 |
| Al-khamisiyah Marsh | 4457 | 69 | 337 | 243 | - | 1302 | 3992 |
| Al-Ismail Marsh | 3310 | 71 | 2149 | 140 | - | 750 | 4119 |
| Al-kirmashiya Marsh | 2760 | 71 | 1941 | 545 | < 5 | 715 | 4692 |
| North Al-Tar | 3308 | 61 | 1214 | 38 | - | 857 | 4406 |
| Al-Fuhood | 10448 | 208 | 2459 | 231 | - | 2671 | 10698 |
| Al-Chibayish | 1163 | 52 | 3955 | 304 | < 4 | 118 | 2486 |
| Al-Hammar Town | 902 | 189 | 548 | 83 | - | 367 | 2034 |
| Al-Tar Town | 15265 | 277 | 8204 | 323 | < 4 | 3963 | 13508 |
| Average | 4864 | 121 | 2646 | 308 | < 4 | 1108 | 5359 |

**Table 2.** Elemental concentrations ($\mu$g/L) in drinking and ground water samples collected from the Thi Qar region

| Location | Residue (mg/L) | Concentration ($\mu$g/L) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Ca (mg/L) | Fe | Zn | As | Br | Sr |
| DW1 | 855 | 45 | 1222 | 34 | 24 | 31 | 1668 |
| DW2 | 1023 | 48 | 628 | 7 | 14 | 43 | 1598 |
| GW1 | 805 | 52 | 501 | 12 | 16 | 43 | 1645 |
| GW2 | 668 | 36 | 391 | 154 | 15 | 56 | 1624 |
| *Average* | 838 | 45 | 686 | 52 | 17 | 43 | 1634 |

**Table 3.** Elemental concentrations ($\mu$g/L) in water samples collected from Euphrates river in Thi Qar region

| Location | Residue (mg/L) | Concentration ($\mu$g/L) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Ca (mg/L) | Fe | As | Br | Sr | Mo |
| South Nassrriya | 4432 | 109 | 1326 | < 5 | 939 | 5691 | 28 |
| North Nassrriya | 4900 | 124 | 960 | 8 | 806 | 5675 | 2 |
| Al-Fadhliyah | 1788 | 56 | 2467 | 4 | 432 | 2734 | 10 |
| Al-Ekekah | 1680 | 39 | 1284 | 11 | 523 | 2519 | 75 |
| Suq Al-Shuyukh | 1918 | 46 | 737 | 4 | 603 | 2934 | 8 |
| West Nassrriya | 4347 | 66 | 1293 | 5 | 910 | 5483 | 7 |
| East Nassrriya | 2040 | 55 | 1441 | 12 | 520 | 3262 | 15 |
| Average | 3015 | 71 | 1358 | 8 | 676 | 4042 | 12 |

The elemental concentrations of the $_{20}$Ca, $_{26}$Fe, $_{29}$Cu, $_{30}$Zn, $_{33}$As, $_{35}$Br and $_{38}$Sr elements along with the amount of total residue in the water samples collected from different locations of Thi Qar province of Iraq, viz., Al-Hammar marshes, Euphrates river, drinking and ground water are given in Tables 1- 3, respectively. The overall errors in the measured concentrations for the $_{20}$Ca, $_{26}$Fe, $_{35}$Br and $_{38}$Sr elements have been estimated to be in the range 8-10%. The error for the trace elements $_{29}$Cu, $_{30}$Zn and $_{33}$As concentration is estimated ~20%, which is mainly attributed to uncertainty associated with the photopeak area. The quoted errors in the concentration values are obtained by quadrature sum of the error associated with the photopeak area, the effective thickness $m\beta_i$ (~ 8%) and the $I_oG\varepsilon_i\sigma_i$ factor (~ 5%). The average value of leftover residue obtained after drying the water samples from Al-Hammar marshes is ~ 4.8 g/L. The $_{20}$Ca and $_{38}$Sr concentrations also exhibit similar trend and constitute ~2.5% of the leftover residue in the marshes water.

In Al-Hammar marshes, the concentration of $_{33}$As is estimated to be in general below 5$\mu$g/L. The $_{28}$Ni and $_{29}$Cu are not observed in Al-Hammer marshes. The $_{26}$Fe concentrations in the marshes waters are high with value ~ 25 mg/L. The average value of concentration of $_{30}$Zn in Al-Hammar marshes is 308 $\mu$g/L. The $_{35}$Br concentration in various samples collected from Al-Hammar marshes (average value = 1108$\mu$g/L) are in general higher compared to those from Euphrates river (average value = 676 $\mu$g/L). The average value of total residue obtained after drying the water samples from Euphrates river is ~ 3 g/L.

The $_{20}$Ca concentrations in the Euphrates river water is about half of the value in Al-Hammar marshes. The $_{20}$Ca concentration in the Euphrates river water constitutes ~2.3% of the total residue, a value similar to that observed in water from the marshes. These values are considered higher in some locations for the presence of calcium in the waters of the study area, ranging from (75 - 200) ppm [7]. The $_{38}$Sr concentrations in the Euphrates river water are in the range 2519-5691$\mu$g/L. The $_{38}$Sr concentration in Euphrates river is similar to that observed in the marshes water. The $_{33}$As element is observed with concentration of ~ 20$\mu$g/L in Euphrates river. The other elements $_{28}$Ni, $_{29}$Cu and$_{30}$Zn are found to be below the detection limits. The overall detection limit for the elements in water samples was in ppb .The $_{26}$Fe concentrations in the river water are lower by a factor of 2-3 as compared to that observed in the water from the marshes. The presence of significantly high Br concentration in the river water is a matter of concern in case it is used for drinking purpose after treatment. Normally, bromine is present in the bromide anion form. In case it is present in the form of bromate anions, which are highly toxic for humans and is a carcinogenic chemical. According to the WHO, 25 ppb of bromate ions is the maximum concentration permitted in the drinking water [8, 9]. The normally present bromide anions can generate bromate anions in the water purification based on ozonation or chlorination or ultraviolet radiation [8]. In case the $_{35}$Br concentration of water is very high, it is likely that bromate ions will also be formed to significant extent.

# 4. Conclusions

From the present study, it is concluded that water from Euphrates river not safe for use for drinking water supply due to high bromine content and the water from the drinking water schemes from the river needs to be monitored for the presence of bromate ions. The drinking water and ground water samples from Thi Qar region show similar concentrations of $_{20}Ca$, $_{35}Br$ and $_{38}Sr$. The drinking water samples have been collected from water supply schemes based on the river water. The concentration of $_{38}Sr$ is ~ 1650 µg/L, which is much higher than the permissible limit of 70 µg/L [10, 11] throughout the study area. Very few values above 1000 µg/L have been reported for waters, for instance, 2980 µg/L for an Australian river [12, 13]. The high $_{38}Sr$ contents in study area water samples were likely related to the dissolution of Calcium-sulphates such as gypsum. It is well known that $Sr^{2+}$ easily replaces $Ca^{2+}$ in the crystalline network of several mineral phases, so that these ions are usually well correlated. The samples of drinking water supply show higher concentration of $_{26}Fe$ and $_{30}Zn$, which are likely to be linked to the water pumps and pipes used in the system. Traces of $_{33}As$ have also been observed in the ground water. It is recommended that drinking water sources in the study area should be routinely monitored to ascertain its suitability for drinking and other purposes.

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