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# Trace Element Analysis Using ICP-MS in the Shallow Aquifers of The Haier Region, Saudi Arabia

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**Abstract:** This work focuses in the monitoring of trace elements using inductively coupled plasma mass spectrometry (ICP-MS) in the shallow water aquifers of Haier, near the capital of Riyadh Saudi Arabia. Considering that the Haier Basin is one of the main sources of irrigation at the city outskirts. Therefore this work mainly aims to identify possible risks to humans considering the relative concentration of trace elements identified. Water samples were collected from the main three groundwater wells serving the largest established farming area in the Haier region. Results showed that the concentration of S, Na, Mg, K, Si, Sr, Br, B, I, Zn, P, Li, Se, Mo, Al, Cu, U, Cr, Co, Pb, Mn, As, Cd, Hg and F were all lie within the permissible limits for irrigation purposes and drinking purposes. However, we detected elevated levels of iron (Fe) in 100% of the samples. In particular iron (Fe) showed a presence of almost 140% higher than the maximum permitted levels according to EPA and WHO for all collected water samples. On the other hand, although concentration of calcium (Ca) was found to be within permissible levels, it still showed elevated values indicating a persistence of hardness in the water quality. The observed results are important for selecting the proper purification methods in order the water to be acceptable for drinking and irrigation purposes.

**Key words:** ICP-MS · Groundwater · Trace elements · Heavy metals · Irrigation

## INTRODUCTION

Trace elements occur at different concentrations within the hydrosphere and many are essential for various metabolicand physiological processes of organisms [1]. They are part of enzymes, hormones and cells in the body and insufficient intake of such micro minerals can cause symptoms of nutritional deficiency. Nevertheless high concentration of trace metals, especially as a result of contamination [2-5] can also pose serious concerns for humans and the ecosystem.

Groundwater, under most conditions, is safer and more reliable for use than surface water, partially due to its reduced exposure to pollutants compared to surface waters. Nevertheless it is still vulnerable to contamination [6-8]. Groundwater can get contaminated by materials moving through the soil from the land's surface. For example, pesticides, fertilizers, toxic substances from mining sites and used motor oil can find their way into groundwater supplies over time. Additionally, it is possible for untreated waste from septic tanks and toxic chemicals from underground storage tanks and leaky landfills to contaminate groundwater. Another issue that is also of concern when assessing groundwater is also the possibility of containing elevated levels of naturally occurring heavy metals and radionuclide, which in all cases should be examined.

In arid regions such as Saudi Arabia [9, 10], the need for reliable, clean water resources is paramount both as drinking water, but also for irrigation purposes.

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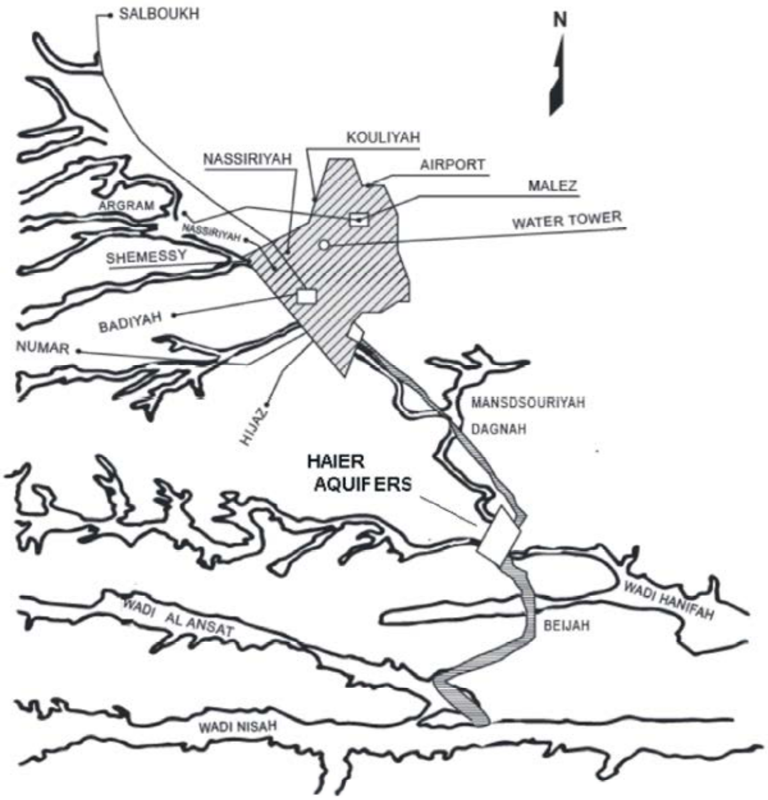


Fig. 1: TheHaier Basin- a map of the Riyadh area

It is well known that for this purpose large-scale aquifers systems are being currently used, along with treated wastewater effluent and desalinated water for all domestic, agriculture and industrial uses [11, 12]. It is thus important that all such water resources are carefully analysed for their suitability for human consumption as well as providing a concise mineral profile for all samples. In particular, the Kingdom of Saudi Arabia with a population of approximately 28 million relies up to 55% on groundwater for domestic and agricultural use [13]. Such groundwater originating from wells is either used directly or in other cases it is treated to reduce the salt content and other impurities.

Our area of interest lies at the southern suburbs of Riyadh, namely the Haier region. It is an area with shallow aquifers from the Biyad formation consisting mainly of sandstone with subordinate shale and marine limestone of Tertiary age. Haier is one of the main agricultural areas [14] at the outskirts of Riyadh where groundwater is used directly and without previous treatment for farming purposes (Fig. 1).

In general groundwater tends to increase its mineral content while moving through the pores and fracture openings in rocks. As a results deeper and older waters are usually highly mineralized and such a tendency in accumulation should be studied for human consumption purposes in order to prevent toxicity [15]. When assessing the presence of trace elements we note that certain minerals are essential for human health [16], such as Zn, Se, Cu, I, Mo, Cr, Mn and Si. Thus both deficiency and excess intake of essential elements can be detrimental to human health. As an example a deficiency of Zn [17] will cause loss of appetite, growth retardation, skin changes and immunological abnormalities. Nevertheless, although Zn has biological significance, excessive consumption of these kinds of metals will affect the humans and lead to toxic exposure. Some heavy metals in groundwater such as Cd, Cr, Mo Pb and Hg can be toxic even at low concentrations [16], thus their potential presence in irrigation systems would lead to toxic build up in human bodies, leading to long term health threats.

Thus close monitoring of groundwater used for irrigation purposes [18] and its assessment are of prime importance in order suggest remedial measures. The most usual methods in analysing trace elements in effluents is usually carried out by conventional analytic techniques such as atomic absorption spectroscopy (AAS) [19, 20] and UV-Vis Spectrophotometry [21] or Inductively

Coupled Plasma Mass Spectrometry (ICP-MS). In our study we employ ICP-MS technology [22] as it offers many advantages over more traditional techniques for elemental analysis, including Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Atomic Absorption Spectroscopy (AAS). ICP-MS is a fast, multielemental technique and generally has the productivity of ICP-AES, but much lower detection capabilities. Previous efforts [23] to employ Laser Induced Breakdown Spectroscopy (LIBS) in liquid samples showed a high threshold in the identification of element concentrations

The objective of this study is to analyse the occurrence of different trace metals such as Ca, S, Na, Mg, K, Si, Sr, Fe, Br, B, I, Zn, P, Li, Se, Mo, Al, Cu, U, Cr, Co, Pb, Mn, As, Cd, Hg and F in groundwater samples from the Haier Basin at the outskirts of Riyadh in order to build a mineral profile as well as assessing its pollution and suitability for drinking and irrigation purposes.

## MATERIALS AND METHODS

In this work we analysed specimens from three main groundwater wells (Fig. 2) used for irrigation in the Haier farming area in order to build a mineral profile. Such groundwater wells are one of the main sources of irrigation as well as being used for drinking purposes particularly from the staff employed at such farming areas.

Within this frame sixty water well 24 hour composite samples from each collection point were collected daily between the months March 2014 to May 2014; using 250ml amber glass bottles for each sample they were carried using cooler boxes (to avoid degradation) to the analytical lab and were stored at 4°C according to the Standard Methods proposed by the American Public Health Association (APHA) [24], until analysis which was conducted. At first instance the parameters ofpH, electrical conductivity and total dissolved solids (TDS) were also measured using the Standard Methods [24].

**The ICP-MS Instrumentation:** The analytical determination of trace metals (Ca, S, Na, Mg, K, Si, Sr, Fe, Br, B, I, Zn, P, Li, Se, Mo, Al, Cu, U, Cr, Co, Pb, Mn, As, Cd, Hg, F) was carried out by a NexION 300 D (Perkin Elmer, USA) ICP-MS (Inductively Coupled Plasma-Mass Spectrometer). The system was equipped with an ultrasonic nebuliser model Cetec U 5000 AT, allowing an up to 50 fold improvement in the detection limits allowing for better reproducibility in determining the levels of the trace elements. The analysis was done in triplicate and average values were taken each time. The ICP was calibrated with the relevant Perkin Elmer Pe-Pure Spectroscopy grade standards. Additionally replicate analysis of blank, standard and samples was done to achieve high precision. Experiments were repeated until an accuracy of 95%-105% and precision of +/-5% were obtained. One standard with one set of samples was analysed routinely.

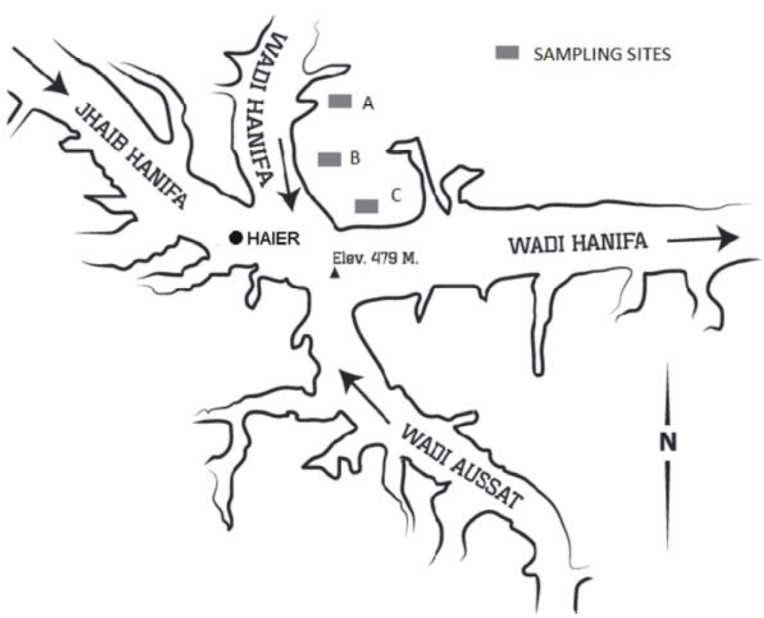


Fig. 2: The Haier Basin at the outskirts of Riyadh city, Najd and the sampling sites (wells)

## RESULTS AND DISCUSSION

The pH of all water samples for all three main sampling sites (wells) A, B and C ranged from 6.7 to 8.1. Additionally the electrical conductivity for all three sampling sites ( wells) A, B and C ranged between 402 μS/cm to 1387 μS/cm and the total dissolved solids (TDS) ranged between 240.0-871.0 mg/L.

Further analysis of the ICP-MS results from the wells A, B and C showed the presence of the following elements in 100% of our samples, namely: calcium (Ca), sulphur (S), sodium (Na), magnesium (Mg), potassium (K), silicon (Si), strontium (Sr), iron (Fe), bromine (Br), boron (B), iodine (I), zinc (Zn), phosphorus (P), lithium (Li), selenium (Se), molybdenum (Mo), aluminium (Al), copper (Cu), uranium (U), chromium (Cr), cobalt (Co), lead (Pb), Manganese (Mn), arsenic (As), cadmium (Cd), mercury (Hg) and fluorine (F). Their average concentration values in PPB are displayed in given Table 1.

In Figs. 3, 4 and 5 we show in declining concentration order the average values of the trace elements detected in sites A, B and C respectively compared to the maximum allowed values for eachtrace element according to the WHO [25] and the EPA [26].

We note that iron (Fe) shows the highest levels and in particular amongst all three sampling sites A, B and C it reaches 140% of the permitted levels according to the EPA and WHO as shown in Fig. 6.

We noted that elevated levels of iron (Fe) can be common when looking at groundwater quality issues. The reason lies in the fact that iron makes up 5% of earth underground formations (earth's crust) and is thus found in most aquifers in dissolved form ($Fe^{+2}$) [26].

Iron is a beneficiary nutrient in adult diets and currently there is no direct health threat identified directly to elevated iron (Fe) levels. Nevertheless such increased levels can be related to potentially unpleasant organoleptic qualities [26] related to the groundwater. Furthermore the presence of dissolved iron tends to encourage the growth of iron bacteria that leads to dark-coloured slime layers on the inner side of any pipes related to the system.In cases of elevated concentrations > 0.3 ppm it is recommended that iron is removed through oxidising the dissolved iron and then remove any small oxidised iron particles (rust) that become suspended in the water through filtration.

Another element that is elevated is calcium (Ca). Although within permissible levels its increased levels represent a persistent hardness [27] in the water quality.

Apart from calcium it is also evident that strontium also is in considerable amounts with an average concentration amongst all three wells of 40% of the maximum allowed levels. The strontium identified is non-radioactive and represents a stable naturally occurring strontium that can be found in groundwater. It is a mineral common in soil and bedrock and thus it can find its way dissolved within aquifers. In general any risk posed by strontium would require exposure of levels more than 4000 PPB daily [28]. Such effects would lead to an increase in bone density in adults as well as affecting bone and dental growth [29] during infancy and childhood.

Potassium on the other hand is present with an average concentration amongst all three wells of 35% of the maximum allowed levels. It is a chemical commonly found in soils and rocks, belonging to the alkali earth metals. Potassium is often associated with chloride and

Table 1: The average values of the trace elements as detected in wells A, B and C

| Elements | Well A (PPB) | Well B (PPB) | Well C (PPB) | Elements | Well A (PPB) | Well B (PPB) | Well C (PPB) |
|---|---|---|---|---|---|---|---|
| Ca | 53284.1100 | 68874.8910 | 56014.9820 | Se | 1.2980 | 2.4580 | 0.6530 |
| S | 25883.8780 | 26339.3480 | 28919.2970 | Mo | 0.6010 | 1.4290 | 2.3450 |
| Na | 8178.9470 | 9712.3340 | 8451.3610 | Al | 0.5340 | 2.3420 | 0.8620 |
| Mg | 5667.5500 | 6601.6790 | 5100.2200 | Cu | 0.6730 | 0.9830 | 1.8730 |
| K | 3315.5300 | 4248.8440 | 3902.9540 | U | 0.3160 | 1.4120 | 0.7650 |
| Si | 1584.2780 | 2144.0160 | 1756.5430 | Cr | 0.7720 | 0.8030 | 0.6730 |
| Sr | 410.4640 | 612.8420 | 742.6780 | Co | 0.1120 | 0.1980 | 0.3470 |
| Fe | 427.3870 | 433.9870 | 401.3210 | Pb | 0.1550 | 0.3140 | 0.1820 |
| Br | 60.4190 | 84.3280 | 73.9830 | Mn | 0.1240 | 0.1840 | 0.2900 |
| B | 43.5280 | 63.9810 | 49.9010 | As | 0.2290 | 0.0260 | 0.3420 |
| I | 22.6280 | 27.9320 | 31.4320 | Cd | 0.1440 | 0.0940 | 0.3480 |
| Zn | 14.5200 | 17.8740 | 26.4310 | Hg | 0.0480 | 0.0830 | 0.0590 |
| P | 6.9790 | 8.9430 | 4.1020 | F | 0.0001 | 0.0007 | 0.0043 |
| Li | 4.8840 | 7.6010 | 5.2350 | | | | |

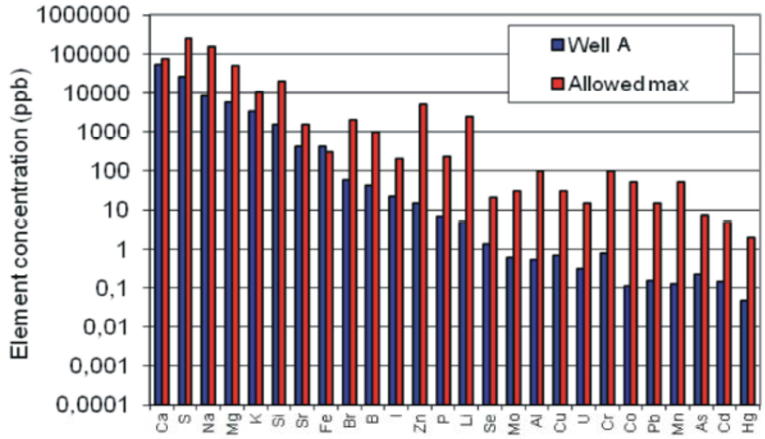


Fig. 3: Average elemental concentrations of trace elements(Ca, S, Na, Mg, K, Si, Sr, Fe, Br, B, I, Zn, P, Li, Se, Mo, Al, Cu, U, Cr, Co, Pb, Mn, As, Cd and Hg) from the sampling site A compared to the maximum allowed values for each element according to ( EPA) and (WHO) in the logarithmic scale

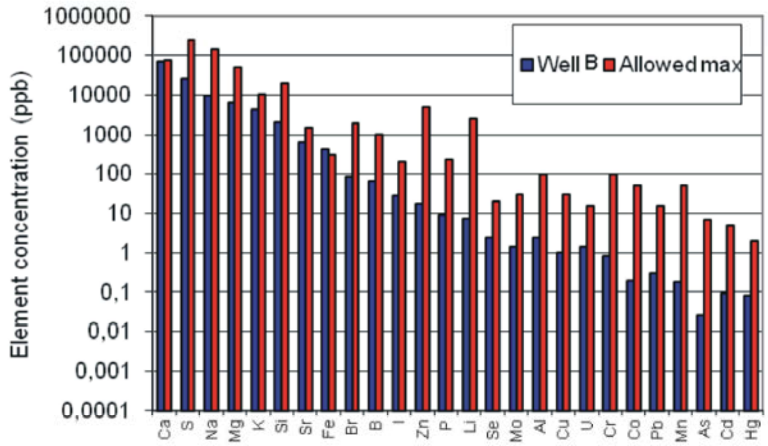


Fig. 4: Average elemental concentrations of trace elements (Ca, S, Na, Mg, K, Si, Sr, Fe, Br, B, I, Zn, P, Li, Se, Mo, Al, Cu, U, Cr, Co, Pb, Mn, As, Cd and Hg) from the sampling site B compared to the maximum allowed values for each element according to ( EPA) and (WHO) in the logarithmic scale

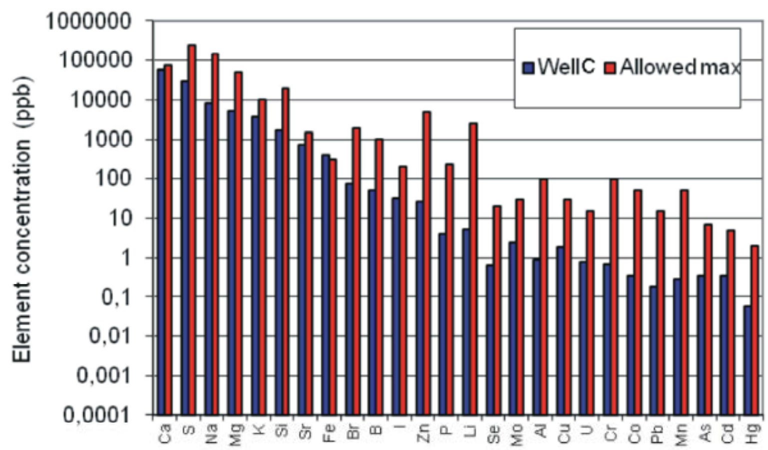


Fig. 5: Average elemental concentrations of trace elements(Ca, S, Na, Mg, K, Si, Sr, Fe, Br, B, I, Zn, P, Li, Se, Mo, Al, Cu, U, Cr, Co, Pb, Mn, As, Cd and Hg) from the sampling site C compared to the maximum allowed values for each element according to ( EPA) and (WHO) in the logarithmic scale

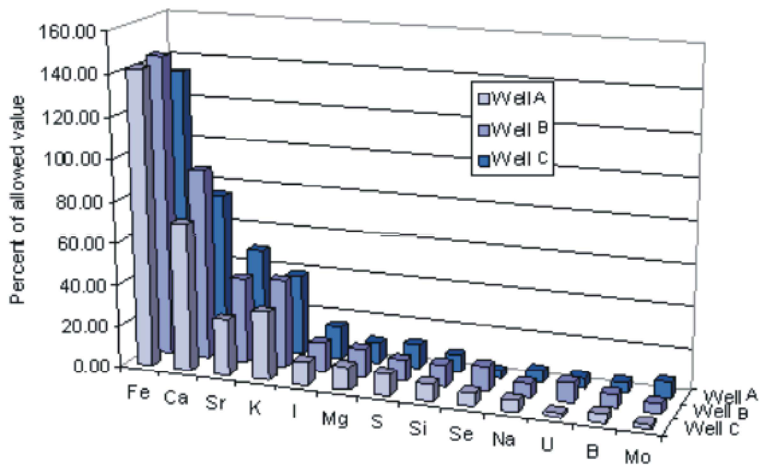


Fig. 6: Percentages of allowed value concentrations of the trace elements: Fe, Ca, Sr, K, I, Mg, S, Si, Se, Na, U, B, Mo from the all sampling sites A, B and C compared to the maximum allowed values as set by ( EPA) and (WHO).

bromide and usually in these forms it is readily dissolved in groundwater [30,31]. It is gradually released from rocks with concentrations usually increasing in time. Potassium is a dietary requirement for adults and children, with some of its vital functions including its role in nerve stimulus, muscle contractions, blood pressure regulations and protein dissolution [32]. Adverse effects from exposure to increased levels of potassium are unlikely in healthy people, nevertheless in cases of individuals with kidney or heart disease, hypertension or diabetes who depends on medication that would interfere with the way the body handles potassium there could be potential risk [32].

All other elements in our analysis such I, Mg, S, Si, Se, Na, U, B, Mo are well below the maximum allowed concentrations and represent a healthy and rich mineral profile in the Haier Basin groundwater.

## CONCLUSIONS

Our trace element analysis of groundwater using ICP-MS showed that the concentration of Li, B, Na, Mg, Si, P, K, S, Cr, Mn, Co, Cu, Zn, As, Se, Br, Sr, Mo, Cd, I, Hg, Pb, U and Al were all within the permissible limits for irrigation purposes and drinking consumption. In particular Fe showed elevated values of almost 140% of the permitted maximum levels according to the EPA and the WHO for the collected samples from the three wells.Furthermore, the amount of calcium was also increased showing hardness in the water quality. These findings represent important considerations in water quality evaluation as the samples are representative of the main three wells located within the largest established farming area within Haier. Monitoring such sources is very important for health purposes as well as for selecting appropriate purification methods in order the groundwater to be appropriate for irrigation and drinking purposes.

## ACKNOWLEDGEMENTS

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