Critical review on uranium and arsenic content and their chemical mobilization in the groundwater: A case study of the Malwa region Punjab, India

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Abstract

Groundwater played a pivotal role in the social and economic development of the Malwa Region. With the advent of the green revolution, water for irrigation and domestic use led to the development of groundwater resources. Slowly, the green revolution changed into a greed revolution, and the exploitation of groundwater resources converted into their overexploitation. Groundwater's overexploitation not only led to groundwater depletion but also led to a change in the chemistry of the Malwa region's aquifers. Researchers from academia and institutions worked and published their findings of the uranium and arsenic contaminations in the Malwa region of Punjab. In this article, we are the first to bring all the dispersed data to one commonplace. By studying the physicochemical parameters of groundwater of all districts of the Malwa region and their correlation, this paper is going to highlight the various chemical reactions occurring in the Malwa region's aquifer and how they impact groundwater chemistry. For understanding, we devised a hypothetical model to understand the complex interplay of this region's natural dynamics of groundwater aquifers. Finally, we tried to describe how the
various chemical changes in the groundwater aquifer can be the reason for the mobilization of arsenic and uranium by making schematic chemical flow-charts of their mobilization. This article aims to highlight the importance of using a multidisciplinary and interdepartmental approach to comprehending the complex problem of groundwater management.

Keywords: groundwater, uranium, arsenic, hydrogeochemistry, chemical mobilization.
Introduction

Water covers three-quarters of the earth's surface, but only 0.3% of water, especially from lakes, rivers, and groundwater, is available for human utilization (Davis and De Weist 1966; Shiklomanov 1993). The demand for drinking/agricultural water keeps increasing, so the burden on freshwater resources from great rivers to underground aquifers also increases (Lall et al. 2020). Although these aquifers are renewable, the rate of pumping out water is faster than the rate of recovery; hence, water depletion occurs faster than enrichment (Fendorf and Benner 2016; MacDonald et al. 2016). Not only quantity but the quality of water also becomes a major concerning factor. According to the world water report by United Nations, the increasing withdrawal of groundwater decreases its quality worldwide. Among them, Asian countries draw a significant share of about 65%, and among Asian countries, groundwater sources of India are overexploited. In the Punjab state of India, where the green revolution occurred, the groundwater resources are highly overexploited. Hence, this overexploitation led to changes in hydrogeochemistry and deteriorated the water quality.

One region of Punjab, the Malwa region, was once known as the breadbasket of India, now called the cancer belt of Punjab. In collaboration with ICMR (Indian Council of Medical Research), a study by the State government confirmed this fact (Nanda et al. 2016). People also suffer from diseases like different types of Cancer, Arthritis, Sinusitis, Anemia, Fluorosis, Arsenicosis, Lead poisoning, Methaemoglobinemia, kidney-related problems etc., because of contaminated water. The leaching from natural chemical deposits and continual use of agrochemicals (fertilizers, pesticides, insecticides and herbicides) in agriculture contributes to the deterioration of water quality. As a result, surface and groundwater sources are polluted with toxic heavy metals like arsenic, uranium etc (Kaur et al. 2019b). People of this area mainly depend on the canal and groundwater for domestic use and continuously use this water and suffer from health-related problems. Several reports highlighted the quality of water in Punjab
and the presence of toxic metals, for instance, uranium and arsenic, in it. But the research’s finding describing the flow of these hazardous chemicals inside the earth's surface is very sparse. Here, we collected more than 200 scientific research papers describing the excess uranium and arsenic content in the groundwater of the Malwa region of Punjab. Whatever the reports or reviews are present in the literature, all those were missing the connecting links. So, it is difficult for policymakers to devise the proper control measure. So, to establish the connecting links, we proposed hypothetical models for earth geochemistry and chemical schematic flowcharts for the flow of uranium and arsenic inside the groundwater. These schematic flowcharts will explain all possible ways of the mobilizations of arsenic and uranium in the groundwater. Indeed, these developed models will be helpful for academician, scientists and policy makers to understand the problems and taking the necessary steps to mitigate the problems.

Here, to understand the changing groundwater chemistry, the physicochemical parameters of water from all districts of the Malwa region and their correlation studies were discussed. By getting their understanding, a hypothetical model about various chemical processes occurring under the earth's surface was proposed to understand the complex interplay of natural dynamics of the hydrological cycle. Later on, we tried to explain how the chemistry operating under the surface affects the mobilization of arsenic and uranium in the groundwater. This article attempts to underscore the complex interaction of groundwater contaminants and their transport process by understanding the various chemical processes. This paper will highlight the urgent need for interdisciplinary and interdepartmental initiatives to ensure sustainable groundwater quality. The model employed here could be utilized in other areas of the world where groundwater has been seriously polluted.

The Malwa region of Punjab
Punjab is the land of five rivers, but the Sutlej and Beas are the two major rivers that pass through the state, while the Ravi River touches the northern part of the state. This river pattern divides the state into three regions: Malwa, Majha and Doaba. Among the three areas, the Malwa region is the most significant part of the present Punjab state of India. Sutlej river's left bank separated the Malwa region from the other regions. Its southern border is shared with Haryana and Rajasthan, while the western edge is shared with Pakistan. The Malwa region geographically extends from 29°30' North to 31°10' North and longitudes 73°50' to 76°50' east. It occupies 65.1% (32808 km²) of the total Punjab area and bears 58% of the Punjab population. Cotton, rice and wheat are the major crops grown in this area, and the region is known as the cotton belt of India(Kaur and Kaur 2016).

![Figure 1. Map of Malwa region of Punjab.](image)

**The effect of the green revolution**

After the green revolution, the Malwa region of Punjab led from the front to feed the nation and made a discernible change in the economy of the state and the whole country(Khush 2001). This boom in agriculture made farmers of Punjab self-reliant. But, on the other hand, considerable investments in the agriculture sector, an increase in farm mechanization and the
excessive use of pesticides for 2 to 3-fold increase in production changed the green revolution to the greed revolution (Planning Commission of Punjab 2005; Nanda et al. 2016).

In 1995, Singh et al. reported uranium in the water of Bathinda and Amritsar (Singh et al. 1995). In the late 90s, Philipose et al. published an article in an Indian express newspaper that described the scenario of Punjab and warned about the future consequences (Philipose 1998). In 1999, Pandhar's article in the newspaper brought two villages, Gyana and Jajjal of district Bathinda, in the limelight by reporting cancer deaths and call them cancer-stricken villages (Panher 1999). In parliamentary question 2003, the government of Punjab ((Proceeding of Punjab Vidhan Sabha 2003) was initially in denial mode. Still, later on, the Punjab Pollution Control Board (PPCB) and Post-graduate Institute of Medical Education and Research (PGIMER) Chandigarh conducted a study in Talwandi Sabo and Chamkaur Sahib blocks of Bathinda and Rupnagar districts, respectively. This study found that females were more affected by different types of cancers than males. Moreover, they reported heavy metals (U, As, and other heavy metals) contamination in drinking water/groundwater at a higher concentration than the World Health Organization (WHO) permissible limit. Vegetables, Milk and blood samples of different patients also showed the presence of residue of pesticides (Thakur 2005; Thakur et al. 2008). Halder et al., in a survey, reported premature greying of hair, premature ageing and excessive cancer death in Jajjal village of Bathinda (Haldar 2007). After these eye-opening reports, many other research groups and organizations worked in this region and published their findings of uranium and arsenic contents in the groundwater, summarized in Table 1.

**Table 1. Collection of reports about uranium and other heavy metals content in groundwater of Malwa region**

<table>
<thead>
<tr>
<th>Area of Study</th>
<th>Metals content found</th>
<th>Concentration range (ppb or µg/l)</th>
<th>Sample Taken</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bathinda</td>
<td>Uranium</td>
<td>11.7 - 113 ppb</td>
<td>Groundwater</td>
<td>(Singh et al. 1995)</td>
</tr>
<tr>
<td>Bathinda, Rupnagar</td>
<td>Arsenic</td>
<td>&gt; 10 ppb</td>
<td>Groundwater</td>
<td>(Thakur et al. 2008)</td>
</tr>
<tr>
<td>Location</td>
<td>Parameter</td>
<td>Value</td>
<td>Sample Type</td>
<td>Reference</td>
</tr>
<tr>
<td>--------------------------------</td>
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<td>-----------------------------------------------</td>
</tr>
<tr>
<td>Bathinda</td>
<td>Uranium</td>
<td>2 - 87.5 µg/l</td>
<td>Groundwater</td>
<td>(Kumar et al. 2006)</td>
</tr>
<tr>
<td>Bathinda, Mansa</td>
<td>Uranium</td>
<td>7 - 316 ppb</td>
<td>Groundwater</td>
<td>(Kochhar et al. 2007)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Kochhar et al. 2012)</td>
</tr>
<tr>
<td>Malwa Region</td>
<td>Uranium</td>
<td>5.41 – 43.39 µg/l</td>
<td>Groundwater</td>
<td>(Mehra et al. 2007)</td>
</tr>
<tr>
<td>Bathinda, Mansa</td>
<td>Uranium</td>
<td>0.9-63.1 ppb</td>
<td>Groundwater</td>
<td>(Singh et al. 2009)</td>
</tr>
<tr>
<td>Bathinda, Mansa</td>
<td>Uranium</td>
<td>28.57 – 213.36 mBq/l</td>
<td>Milk</td>
<td>(Kumar et al. 2009)</td>
</tr>
<tr>
<td>Bathinda, Mansa, Faridkot,</td>
<td>Uranium</td>
<td>0.2 – 644 µg/l</td>
<td>Groundwater</td>
<td>(Kumar et al. 2011)</td>
</tr>
<tr>
<td>Firozpur</td>
<td></td>
<td></td>
<td></td>
<td>(Kumar et al. 2014)</td>
</tr>
<tr>
<td>Bathinda</td>
<td>Uranium</td>
<td>0.48 – 571.7 µg/l</td>
<td>Groundwater</td>
<td>(Singh et al. 2013b)</td>
</tr>
<tr>
<td>Muktsar</td>
<td>Uranium</td>
<td>4.5 – 330 µg/l</td>
<td>Groundwater</td>
<td>(Shenoy et al. 2012)</td>
</tr>
<tr>
<td>Malwa Region</td>
<td>Uranium</td>
<td>&gt;100 ppb</td>
<td>Groundwater</td>
<td>(Muhand et al. 2009)</td>
</tr>
<tr>
<td>Malwa Region</td>
<td>Uranium</td>
<td>13.9 – 172.8 µg/l</td>
<td>Groundwater</td>
<td>(Tripathi et al. 2013)</td>
</tr>
<tr>
<td>Faridkot, Bathinda, Mansa</td>
<td>Uranium</td>
<td>0.13 – 676 µg/l</td>
<td>Groundwater</td>
<td>(Saini et al. 2016)</td>
</tr>
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<td></td>
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<td></td>
<td></td>
<td>(Saini et al. 2017)</td>
</tr>
<tr>
<td>Bathinda, Mansa, Faridkot,</td>
<td>Uranium</td>
<td>0.5 – 571.7 µg/l</td>
<td>Groundwater</td>
<td>(Bajwa et al. 2017)</td>
</tr>
<tr>
<td>and Firozpur</td>
<td>Arsine</td>
<td>1 – 59.6 µg/l</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bathinda, Mansa, Faridkot,</td>
<td>Uranium</td>
<td>2.47 – 366 µg/l</td>
<td>Groundwater</td>
<td></td>
</tr>
<tr>
<td>Mansa</td>
<td>Uranium</td>
<td>0.13 – 1340 µg/l</td>
<td>Groundwater</td>
<td>(Sharma and Singh 2016)</td>
</tr>
<tr>
<td>Mansa, Bathinda</td>
<td>Uranium</td>
<td>2.3 – 357 µg/l</td>
<td>Groundwater</td>
<td>(Sharma et al. 2017a)(Sharma et al. 2020)</td>
</tr>
<tr>
<td>Firozpur, Sangrur, Moga Patiala</td>
<td></td>
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<tr>
<td>Bathinda, Moga, Faridkot</td>
<td>Arsine</td>
<td>16 – 76 µg/l</td>
<td>Groundwater</td>
<td>(Sidhu et al. 2014)</td>
</tr>
<tr>
<td>Bathinda, Mansa, Faridkot,</td>
<td>Arsine</td>
<td>2.2 – 120 µg/l</td>
<td>Groundwater</td>
<td>(Shah et al. 2015)</td>
</tr>
<tr>
<td>Firozpur, Sangrur, Moga Patiala</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bathinda</td>
<td>Arsine</td>
<td>&gt;10 µg/l in 1/3 samples</td>
<td>Groundwater</td>
<td>(Singh et al. 2013a)</td>
</tr>
<tr>
<td>Bathinda</td>
<td>Arsine</td>
<td>2.28 – 27.47 µg/l</td>
<td>Soil</td>
<td>(Kumar et al. 2016)</td>
</tr>
<tr>
<td>Bathinda, Faridkot, Firozpur,</td>
<td>Arsine</td>
<td>5 – 50 µg/l, 10 – 100 µg/l, 10 – 50 µg/l, 5 – 50 µg/l, 5 -50 µg/l</td>
<td>Groundwater</td>
<td>(Sharma et al. 2013)</td>
</tr>
<tr>
<td>Sangrur, Muktsar</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Faridkot Firozpur, Sangrur,</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moga, Barnala</td>
<td>Uranium</td>
<td>2.1 – 83.87 µg/l</td>
<td>Groundwater</td>
<td>(Kaur et al. 2021a)</td>
</tr>
<tr>
<td>Barnala, Ludhiana</td>
<td>Arsine</td>
<td>0.5 – 28.7 µg/l</td>
<td>Groundwater</td>
<td>(Kaur et al. 2017)</td>
</tr>
<tr>
<td></td>
<td>Uranium</td>
<td>0.5 – 432 µg/l</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bathinda, Mansa, Muktsar,</td>
<td>Arsine</td>
<td>4.35 – 23.94 µg/l</td>
<td>Groundwater</td>
<td></td>
</tr>
<tr>
<td>Faridkot</td>
<td></td>
<td></td>
<td></td>
<td>(Kaur et al. 2017)</td>
</tr>
<tr>
<td>Faridkot, Muktsar</td>
<td>Uranium,</td>
<td>3 – 190 µg/l</td>
<td>Groundwater</td>
<td>(Pant et al. 2017)(Pant et al. 2020a)</td>
</tr>
<tr>
<td>Location</td>
<td>Contaminant</td>
<td>Concentration</td>
<td>Type</td>
<td>Source</td>
</tr>
<tr>
<td>---------------------------</td>
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</tr>
<tr>
<td>Ludhiana</td>
<td>Arsenic</td>
<td>0 – 21 µg/l</td>
<td>Groundwater</td>
<td>(Singh et al. 2019)</td>
</tr>
<tr>
<td>Ferozpur, Patiala, Rupnagar</td>
<td>Arsenic</td>
<td>16 – 91 µg/l</td>
<td>Groundwater</td>
<td>(Virk 2019e)</td>
</tr>
<tr>
<td>Bathinda, Mansa, Firozpur, Faridkot</td>
<td>Uranium</td>
<td>3.2 – 60.5 ppb</td>
<td>Groundwater</td>
<td>(Prabhu et al. 2012)</td>
</tr>
<tr>
<td>Bathinda, Mansa, Firozpur, Faridkot</td>
<td>Uranium</td>
<td>1.78 – 261 µg/l</td>
<td>Groundwater</td>
<td>(Singh et al. 2018b)</td>
</tr>
</tbody>
</table>

This issue of high uranium contamination in the groundwater came to the limelight after Prof. Carin Smit, a South Africa-based clinical toxicologist, visited Baba Farid Centre for Special Children, where children are being treated for autism cerebral palsy and neurological impairments. He took samples and analyzed them. He reported high Uranium, Barium, Cadmium, Manganese, and Lead contents in the patients' samples (Blaurock-busch et al. 2010; Blaurock-Busch et al. 2010). This finding became a front-page headline in various national and international newspapers, for instance, The Times of India, Down to Earth, The Telegraph (London) etc. As a result, this issue started thundering in the assembly of Indian parliament (State 2012), New Delhi. Hence, Center Ground Water Board (CGWB), Punjab Pollution Control Board (PPCB), Punjab Water Supply Sanitation Department (PWSSD), Punjab State Planning Board and other government and non-government agencies were employed to know more about the situation. In the study by Punjab State Planning Board, Punjab, India, Bhaba Atomic Research Center, India (BARC) and Guru Nanak Dev University, Punjab, India (GNDU), the researchers found the excessive use of phosphate fertilizers as a possible source of the high amount of uranium in the region by percolation through the soil (Kumar et al. 2011; Bajwa et al. 2017). Still, Srivastava et al. and Singh et al. reports ruled out that hypothesis (Srivastava et al. 2017; Singh et al. 2018a). After that, other theories were put forward, such as fly ash dump of the thermal power station, industrial effluents, etc., also prevailed. However, Alrakabi et al. 2012 suggested that the most plausible origin of high uranium content in the malwa region might be geogenic (Alrakabi et al. 2012). Overall, high uranium can cause severe
kidney problems, lung infection, autoimmune disorder, high blood pressure, reproductive system problems, and cancer (Leggett 1994; Domingo 1994; Leggett and Pellmar 2003).

According to the Ministry of Agriculture, India report-2013, 6500 metric tonnes (MT) of pesticides were consumed only in Punjab, and 75% was only consumed in the malwa region of Punjab alone (Misra 2007). Researchers published many reports about pesticide content in drinking water, food and vegetables, and all the studies are very well compiled in Mittal’s review article (Mittal et al. 2014). Pesticides also contains arsenic as a primary constituent and is commonly found in the form of Lead arsenate, Sodium arsenate, Calcium arsenate, Dimethyl arsenate, Chromated copper arsenate, Fluorochrome arsenate Phenoyl, etc. (Bencko and Yan Li Foong 2017). However, the source of arsenic in groundwater may be geogenic; Hundal et al. found that hand pump and canal water in the Malwa region of Punjab are also contaminated with arsenic more than the WHO permissible limit (Hundal et al. 2007, 2009). They reported that the arsenic contents in Patiala, Bathinda, Muktsar, Ludhiana, Mansa, Faridkot, Firozpur and Sangrur districts were more than the permissible limit. A study by PGIMER and PPCB reported that the Buddha nullah river became highly toxic due to effluents from industries and contained various harmful heavy metal ion content such as As. (Machhan 2019). Arsenic is a deadly poison considered a carcinogenic element that causes cancer through respiratory and gastrointestinal exposure. One study by Hong and co-workers confirmed the association of lung, skin and bladder cancer due to arsenic poisoning (Hong et al. 2014). Recent studies linked arsenic with other types of cancer, such as liver, prostate, leukaemia, etc. The relationship between arsenic and different diseases, for instance, diabetes, neurological effects, cardiac disorders, congenital disabilities and reproductive organs were also found (Lee et al. 2002; Tseng et al. 2002; Tsai et al. 2003; Claudia et al. 2003).

**Physicochemical parameters of groundwater of Malwa region**
The information about the quality of water and its suitability for drinking use are easily obtained by studying the physicochemical parameters, such as pH, electrical conductivity (EC), total dissolved solutes (TDS) and turbidity and by calculating the inorganic and organic components in the water and influence of biotic and abiotic factor (Kumar et al. 2007). The inorganic elements are essential for various body functions, but their higher concentrations create groundwater pollution and human health-related issues. Various natural and anthropogenic processes such as leaching of soils, rocks weathering, mining, chemical fertilizers and the metal industry can be the reason for deviation of these parameters (Thakur et al. 2016). Moreover, these parameters mentioned above vary with changes in weather, such as premonsoon and postmonsoon of the areas (CGWB 2018, 2019, 2020). These variations might be due to the change in geological location of the study area and the method used for sample collection. So here, the physicochemical parameters data of groundwater from recent publications/reports about all districts of the malwa region are compiled as shown in Table 2. The data of pH from Bathinda (6.9 -9.5), Mansa (7.5–9.1), Faridkot (7.0–9.8), Muktsar (6.8-9.0) and Fazilka (7.8 -9.6) district Southwest part showed slightly inclination toward the upper limit of WHO permissible parameters (Table 2). The pH value is affected by the presence of carbon dioxide and various inorganic ions. Electrical conductivity speaks for the measure of the total dissolved ions/salts and salinity. The High electrical conductivity and high TDS data of southwest part of the Malwa region {Bathinda [Ec(223 -3870), TDS(164-2500)], Mansa [Ec(268 – 5140), TDS(160-3400)], Faridkot [Ec(814 – 7542), TDS(446-4600)], Muktsar [Ec(513 - 11500), TDS(303-5785)] and Fazilka [Ec(745 - 8320), TDS(600-6800)]} is only due to dissolution or leaching of aquifer mineral or mixing of saline source or both respectively (Hounslow 2018). Due to the very high EC and TDS, the land of Muktsar and Fazilika districts became infertile. No crop has been sown in the Rattakheda and Sikhwala villages of Muktsar district and Shajrana village of Fazilka district since the last two decades (Shah 2013). Total
hardness depends upon calcium, magnesium, carbonate, sulphate, and chloride ion concentrations.

Table 2 showed high value for TH (0-1490), which may be due to the calcareous texture of the soil. According to the Davis-DeWeist classification for TDS (Davis and De Weist 1966) and Durfor-Becker classification of TH (Durfor and Becker 1964) (Table 3), the groundwater of the malwa region comes in the category of very hardwater and unfit for drinking.
Table 2. Physiochemical parameters of groundwater of all the district of the Malwa region of Punjab.*

<table>
<thead>
<tr>
<th>Districts</th>
<th>pH</th>
<th>Ec</th>
<th>TH</th>
<th>CO₃⁺</th>
<th>TDS</th>
<th>HCO₃⁻</th>
<th>NO₃⁻</th>
<th>SO₄⁻</th>
<th>F⁻</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Na⁺</th>
<th>In addition to CGWB, 2021 Other Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bathinda</td>
<td>6.9 - 9.5</td>
<td>223 - 3870</td>
<td>60 - 1125</td>
<td>0 - 156</td>
<td>164 - 2500</td>
<td>85 - 818</td>
<td>5.28 - 245</td>
<td>0.5 - 201</td>
<td>0.29 - 4.79</td>
<td>20 - 285</td>
<td>50 - 900</td>
<td>8.5 - 1120</td>
<td>(Sharma et al. 2021a)</td>
</tr>
<tr>
<td>Mansa</td>
<td>7.5 - 9.1</td>
<td>268 - 5140</td>
<td>50 - 1440</td>
<td>0 - 204</td>
<td>160 - 3400</td>
<td>100 - 1062</td>
<td>3.6 - 71</td>
<td>5 - 548</td>
<td>0.4 - 2.0</td>
<td>12 - 60</td>
<td>2 - 77</td>
<td>43 - 1100</td>
<td>(Sharma et al. 2021b)</td>
</tr>
<tr>
<td>Faridkot</td>
<td>7.0 - 9.8</td>
<td>814 - 7542</td>
<td>50 - 767</td>
<td>0 - 190</td>
<td>446 - 2700</td>
<td>104 - 756</td>
<td>1 - 711</td>
<td>28 - 1379</td>
<td>0.23 - 4.2</td>
<td>1 - 182</td>
<td>2 - 132</td>
<td>41 - 1397</td>
<td>(Ahada and Suthar 2018)</td>
</tr>
<tr>
<td>Firozpur</td>
<td>8.0 - 8.9</td>
<td>478 - 1641</td>
<td>105 - 273</td>
<td>0 - 102</td>
<td>246 - 1740</td>
<td>118 - 370</td>
<td>2.4 - 172</td>
<td>31 - 305</td>
<td>0.14 - 1.21</td>
<td>13 - 46</td>
<td>13 - 51</td>
<td>37 - 310</td>
<td>(Ahada and Suthar 2018)</td>
</tr>
<tr>
<td>Muktsar</td>
<td>6.8 - 9.0</td>
<td>513 - 11500</td>
<td>179 - 761</td>
<td>0 - 263</td>
<td>303 - 5785</td>
<td>74 - 816</td>
<td>9 - 2000</td>
<td>31 - 2500</td>
<td>0.39 - 6.4</td>
<td>16 - 408</td>
<td>17.3 - 348</td>
<td>34 - 1123</td>
<td>(Pant et al. 2020b)</td>
</tr>
<tr>
<td>Sangrur</td>
<td>7.7 - 9.1</td>
<td>329 - 1715</td>
<td>90 - 560</td>
<td>0 - 156</td>
<td>150 - 683</td>
<td>5.7 - 105</td>
<td>12 - 175</td>
<td>0.15 - 1.2</td>
<td>4 - 48</td>
<td>17 - 106</td>
<td>19 - 385</td>
<td>(Ahada and Suthar 2018)</td>
<td></td>
</tr>
<tr>
<td>Patiala</td>
<td>7.6 - 8.9</td>
<td>355 - 4060</td>
<td>20 - 821</td>
<td>0 - 84</td>
<td>171 - 573</td>
<td>0.35 - 358</td>
<td>5 - 1022</td>
<td>0.19 - 4.12</td>
<td>4 - 72</td>
<td>2 - 156</td>
<td>20 - 650</td>
<td>(Ahada and Suthar 2018)</td>
<td></td>
</tr>
<tr>
<td>Rupnagar</td>
<td>7.1 - 8.5</td>
<td>330 - 1701</td>
<td>57 - 833</td>
<td>0 - 27</td>
<td>199 - 983</td>
<td>70 - 409</td>
<td>0.14 - 53</td>
<td>37.7 - 522</td>
<td>0.11 - 1.03</td>
<td>13 - 220</td>
<td>3 - 138</td>
<td>15 - 387</td>
<td>(Ahada and Suthar 2018)</td>
</tr>
<tr>
<td>Ludhiana</td>
<td>6.7 - 8.3</td>
<td>80 - 1940</td>
<td>60 - 695</td>
<td>0 - 96</td>
<td>57 - 1370</td>
<td>110 - 696</td>
<td>0.5 - 209</td>
<td>1 - 258</td>
<td>0.08 - 2.75</td>
<td>15 - 250</td>
<td>15 - 620</td>
<td>6.7 - 235</td>
<td>(Kumar et al. 2021)</td>
</tr>
<tr>
<td>Moga</td>
<td>7.5 - 8.8</td>
<td>73 - 2332</td>
<td>60 - 495</td>
<td>36 - 132</td>
<td>352 - 1472</td>
<td>134 - 549</td>
<td>107 - 163</td>
<td>20 - 59</td>
<td>0.09 - 10.5</td>
<td>8 - 98</td>
<td>9 - 102</td>
<td>36 - 260</td>
<td>(Shashi and Bhardwaj 2011)</td>
</tr>
<tr>
<td>Fatehgarh Sahib</td>
<td>6.7 - 8.5</td>
<td>206 - 1452</td>
<td>110 - 650</td>
<td>0 - 27</td>
<td>146 - 1109</td>
<td>168 - 629</td>
<td>0.5 - 65</td>
<td>12 - 120</td>
<td>0.05 - 0.65</td>
<td>15 - 88</td>
<td>30 - 60</td>
<td>30 - 122</td>
<td>(Kumar et al. 2020)</td>
</tr>
<tr>
<td>Mohali</td>
<td>7.7 - 9.0</td>
<td>450 - 6480</td>
<td>95 - 1490</td>
<td>0 - 14</td>
<td>182 - 699</td>
<td>0.4 - 407</td>
<td>0.1 - 880</td>
<td>0.31 - 1.52</td>
<td>8 - 360</td>
<td>14 - 163</td>
<td>30 - 820</td>
<td>(Ahada and Suthar 2018)</td>
<td></td>
</tr>
<tr>
<td>Fazilka</td>
<td>7.8 - 9.6</td>
<td>745 - 8320</td>
<td>74 - 911</td>
<td>0 - 240</td>
<td>600-6800</td>
<td>74 - 574</td>
<td>1.5 - 253</td>
<td>43 - 2005</td>
<td>0.32 - 3.1</td>
<td>8 - 206</td>
<td>5 - 418</td>
<td>110 - 1600</td>
<td>(Ahada and Suthar 2018)</td>
</tr>
<tr>
<td>Barnala</td>
<td>6.8 - 8.6</td>
<td>41 - 2340</td>
<td>20 - 825</td>
<td>12 - 72</td>
<td>29 - 1657</td>
<td>159 - 317</td>
<td>0.5 - 242</td>
<td>1 - 392</td>
<td>0.37 - 2.3</td>
<td>10 - 225</td>
<td>10 - 650</td>
<td>30 - 182</td>
<td>(Ahada and Suthar 2018)</td>
</tr>
<tr>
<td>WHO recommended Values</td>
<td>6.5 - 8.5</td>
<td>750 - 2000</td>
<td>0 - 500</td>
<td>0 - 500</td>
<td>0 - 1000</td>
<td>-</td>
<td>0 - 50</td>
<td>0 - 400</td>
<td>0.6 - 1.5</td>
<td>0 - 100</td>
<td>0 - 50</td>
<td>200</td>
<td>(Ahada and Suthar 2018)</td>
</tr>
</tbody>
</table>

*Most recent published data is used to make this table (CGWB 2020)

Except Ph and Ec(uS/cm), all other parameters are in mg/l
A report by the Planning Commission of India showed the considerable area of four districts of southwestern Punjab, such as Fazilka, Muktsar, Bathinda, and some parts of Mansa, is facing the condition of waterlogging and salinization, as shown in Figure 2 (Shah 2013). Except Rupnagar (0.14 – 53 mg/l) and Fatehgarh sahib (0.5 -65 mg/l) district, the high average nitrate content than the WHO permissible limit in all districts of the malwa region was reported (Aulakh and Malhi 2005) and this is due to excessive use of fertilizers and pesticides, organic and other human wastes (Aulakh et al. 2009).

![Figure 2. Hypothetical sample model showing waterlogging problem in the southwestern part of the Malwa region (Shah 2013).](image)

Table 3. Durfor-Becker and Davis-DeWeist and classification of groundwater from physicochemical parameter TH and TDS respectively.

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Parameters</th>
<th>Range</th>
<th>Water class</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TH (Durfor and Becker 1964)</td>
<td>0 - 60</td>
<td>Soft</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60 - 120</td>
<td>Moderately Hard</td>
</tr>
<tr>
<td></td>
<td></td>
<td>120 - 180</td>
<td>Hard</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt;180</td>
<td>Very Hard</td>
</tr>
<tr>
<td>2</td>
<td>TDS</td>
<td>&lt; 500</td>
<td>Desirable for drinking</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500 - 1000</td>
<td>Permissible for drinking</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1000 - 3000</td>
<td>Useful for irrigation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt;3000</td>
<td>Unfit for both</td>
</tr>
</tbody>
</table>

In 9 districts, Bathinda (0.29 -4.79 mg/l), Mansa, Faridkot, Muktsar, Patiala, Ludhiana, Moga, Fazilka and Barnala, the average value of fluoride ions is above WHO permissible limits that may be due to fluoride bearing minerals, fluorite, in aquifers (Wenzel and Blum 1992). The high bicarbonates and sodium ions concentrations increase the fluoride pollution in
groundwater (Kumar and Singh 2015). The highest content of fluoride ions (10.5 mg/l) was reported in the Moga district. Lower and higher concentrations of fluoride ions have serious implications on health. Its lower concentration below 0.5 mg/l leads to tooth decay, but a higher concentration above 1.5 mg/l causes dental fluorosis (Rathore et al. 2017). The sodium ion, commonly called salinity’s indicator, were found in higher concentration than the recommended limits of WHO (200 mg/l) in all district of the malwa region except Fatehgarh Sahib and Barnala (Ahada and Suthar 2018). The weathering of feldspar minerals and the utilization of fertilizers are the most common source of sodium. The high sulphate ions concentration than WHO permissible limits (400 mg/l) in the Faridkot (28 –1379 mg/l), Muktsar (31 – 2500 mg/l), Mansa (5 – 548 mg/l), Patiala (5 – 1022 mg), Fazilka (43 – 2005 mg/l) and Mohali (0.1 – 880 mg/l) districts was reported (Kaur et al. 2017). The breakdown of organic substances from the weathered soils, human activities, fertilizers and pesticide utilization may be the reason for its excess.

The physicochemical parameters study about groundwater quality generated large and perplexing data. Therefore, software-based statistical techniques such as Pearson's correlation analysis, Principal component analysis, hierarchical correlation analysis, etc., are frequently used to predict the common origin and sources of contaminants in the groundwater (Ofungwu 2014). These statistical techniques, called multivariate statistical analysis, tell about correlation and variance among the variables and find common factors responsible for pollutants in the water from the complex datasets. In table 4, the data about the linear correlation among different physicochemical parameters are compiled for understanding. For example, electrical conductivity is attributed to various total dissolved ions (cation and anions), total hardness, calcium, sodium and chloride concentration. Thakur et al. delineated the correlation of high EC with increased dissolved salts content (Thakur et al. 2016) and Tubonimi et al. 2010 described the correlation of total dissolved (TDS) with other ions such as sodium. The positive
The correlation of sodium ions with Ec and TDS gave information about the salinity content of the soil. The correlation analysis showed that TH is mainly due to calcium and magnesium, along with carbonates, sulphate and chloride. Through these studies, it can be realistic to expect that weathering of limestone, dolomite and other calcium-rich minerals dissolution frequently occurring in the aquifer of this region and the reason for the high content of carbonate and bicarbonate in the groundwater (Tubonimi et al. 2010).

Interestingly, these physicochemical parameters also influenced the uranium and arsenic concentration in the groundwater. Sharma et al. showed a positive correlation between uranium and high TDS in the Mansa district (Sharma et al. 2021b). Through an in-depth study, Sharma et al. found a strong correlation between uranium and total alkalinity. They claimed that high alkalinity might be one of the reasons for the mobilization of uranium in groundwater (Sharma et al. 2019). Hundal and co-workers showed that various geochemical conditions influenced the arsenic concentrations in groundwater (Hundal et al. 2007). The strong correlation between arsenic contamination with a high concentration of iron, phosphate, ammonium ions and anthropogenic activities were demonstrated by Kumar and colleagues (Kumar et al. 2010).

Geographically, the Kasoor district of west Punjab of Pakistan lies adjacent to the malwa region. After a thorough study, they claimed that the distribution of the heavy metals in groundwater is highly irregular, which might be due to anthropogenic sources of pollution such as fly-ash from the thermal power plant, vehicle pollution, pesticides and fertilizers, corrosion of pipes, chemical industries etc. in addition to geochemical reactions (Afzal et al. 2014). Inclusively, it is evident that the concentration of uranium and arsenic ions is somehow dependent upon one or other geochemical conditions such as oxidation-reduction, associated or competing ion, pH, dissolved salts, alkali content, arid environment and anthropogenic factors etc. Contemporary researchers also use multivariate analysis techniques to find the correlation between different metal ions and their sources of origin. The strong positive
correlation among these ions indicates their common origin and source of groundwater contamination in the study area. So, to understand the geochemical changes, there is a need to understand the mechanism of hydrogeochemistry.

**TABLE 5. Linear correlation analysis among different Physico-chemical parameters.**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Physicochemical parameter</th>
<th>Positive correlation with other parameters</th>
<th>Information derived out</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ec</td>
<td>TDS, Total alkalinity (TA), TH, Ca\textsuperscript{2+}, Cl\textsuperscript{-}, Na\textsuperscript{+}</td>
<td>High EC informs about the mechanism of groundwater circulation, surface infiltration and cation exchange</td>
<td>(Jothivenkatachalam et al. 2010)</td>
</tr>
<tr>
<td>2</td>
<td>TDS</td>
<td>EC, TA, TH, Ca\textsuperscript{2+}, Cl\textsuperscript{-}, Na\textsuperscript{+}, K\textsuperscript{+}</td>
<td>TDS delineates some features about precipitation, atmospheric temperature, evapotranspiration and saline intrusion underground sources</td>
<td>(Tubonimi et al. 2010)</td>
</tr>
<tr>
<td>3</td>
<td>TH</td>
<td>TDS, EC, TS, TA, Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, K\textsuperscript{+}</td>
<td>TH tells about the calcareous rock dissolution and ion exchange in the aquifer</td>
<td>(Thakur et al. 2016)</td>
</tr>
<tr>
<td>4</td>
<td>Ca\textsuperscript{2+}</td>
<td>EC, TDS, TA, TH</td>
<td>High Ca\textsuperscript{2+} may be due to calcium-rich minerals in the aquifer</td>
<td>(Zare Garizi et al. 2011)</td>
</tr>
<tr>
<td>5</td>
<td>Na\textsuperscript{+}</td>
<td>EC, TDS, Cl\textsuperscript{-}</td>
<td>High sodium ion concentration talks about the salinity</td>
<td>(Kaur et al. 2021b)</td>
</tr>
<tr>
<td>6</td>
<td>F\textsuperscript{-}</td>
<td>Na\textsuperscript{+}, pH, HCO\textsubscript{3}\textsuperscript{-}</td>
<td>High fluoride and high pH lead to high HCO\textsubscript{3}\textsuperscript{-} ion concentration and dissolutions of fluorite.</td>
<td>(Li et al. 2015)</td>
</tr>
</tbody>
</table>

**The mechanism controlling the groundwater chemistry: hydro-geochemical evolution**

Malwa region comes under the Indo-Gangetic plains, and its north-eastern part is at a higher elevation than the southwestern region (Jain 2014). The groundwater flows from higher to lower elevations, so there is a strong probability that the mobilization of minerals from the Himalayas influences the Malwa region's underground water quality (CGWB 2017). The
minerals-water’s interactions affected the groundwater chemistry. Multiple techniques, for instance, Gibbs plot, saturation index and ion exchange index, etc., are used to study the various hydrogeochemical processes, such as precipitation, rock-water interaction, and evaporation (Gibbs 1970; Feth and Gibbs 1971)

To establish the relationship between water composition and aquifer lithological characteristics, Gibbs draws a graph between TDS and cation ratio \([\text{Na}^+/(\text{Na}^+ + \text{Ca}^{2+})]\) and anions ratio \([\text{Cl}^-/(\text{Cl}^- + \text{HCO}_3^-)]\) and explains the mechanism that controls the groundwater chemistry. Through the Gibbs plot’s study, the various research groups (Thakur et al. 2016; Kaur et al. 2017; Kumar et al. 2021) suggested that the groundwater chemistry of shallow and deep aquifers is mainly controlled in the Malwa region by the rock water interaction. In the southwestern part, along with rock-water interactions, the evaporation processes also played an important role(Pant et al. 2020c). The saturation index talks about the mineral dissolution and precipitation processes by measuring the equilibrium between minerals and water. In the malwa region, groundwater is supersaturated with calcite and dolomite minerals by various processes, for instance, silicate mineral dissolutions, carbonate mineral's weathering, common ions effect, evaporation, temperature, infiltration of wastewater and irrigation return flows (CGWB 2013). In alkaline conditions, precipitation of calcite governs fluorite dissolution and high fluoride content in the groundwater as shown in scheme 1 (Saxena and Ahmed 2001; Kumar and Singh 2015)

\[
\text{CaF}_2 + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 + 2\text{F}^- + \text{H}_2\text{O} + \text{CO}_2
\]

Scheme 1. Calcite precipitation governs fluorite dissolutions

The chemical compositions of groundwater change during its movement to the subsurface, and these changes are found by the ion exchange index. The Ion exchange index describes the exchange of ions either directly or indirectly. In direct exchange, \(\text{Na}^+\) and \(\text{K}^+\) ions from the
water exchange with the \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \) ions from the rock, but in indirect exchange, \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \) ions from the water exchange with \( \text{Na}^+ \) and \( \text{K}^+ \) ions from the rock. The groundwater showed reverse ion exchange trends in most malwa regions: alkali metals such as \( \text{Na}^+ \) replaced alkaline earth metals (Sharma et al. 2017b; Pant et al. 2020d). These replacements most commonly happened in clay minerals and can be displayed as in Scheme 2.

\[
\text{Na}_2\text{Clay} + \text{Ca}^{2+}(\text{Mg}^{2+}) \rightarrow 2\text{Na}^+ + \text{Ca}^{2+}(\text{Mg}^{2+}) - \text{clay}
\]

Scheme 2. Ion exchange mechanism with clay

The number of direct and indirect interactions between aquifer and bedrock controls the mineral content of groundwater. By software-based bivariate methods, the researcher found that carbonate and silicate minerals’ dissolutions control the malwa region's groundwater chemistry (CGWB 2020; Singh et al. 2020)

\[
\begin{align*}
\text{(Na}^+, \text{Ca}^{2+}\text{Mg}^{2+}) \text{ Silicate} + \text{H}_2\text{CO}_3 & \rightarrow \text{H}_2\text{SiO}_4 + \text{HCO}_3^- + \text{Na}^+ + \text{Ca}^{2+} + \text{Mg}^{2+} + \text{clay} \\
2\text{NaAlSi}_3\text{O}_8 + 2\text{H}_2\text{CO}_3 + 9\text{H}_2\text{O} & \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{Na}^+ + 4\text{H}_4\text{SiO}_4 + \text{HCO}_3^- \\
\text{Kalonite} & \\
\text{CaMg(CO}_3\text{)}_2 + \text{H}_2\text{CO}_3 & \rightarrow \text{HCO}_3^- + \text{Ca}^{2+} + \text{Mg}^{2+} \\
\text{Dolomite} & \\
\text{CaCO}_3 + \text{H}_2\text{CO}_3 & \rightarrow \text{HCO}_3^- + \text{Ca}^{2+} \\
\text{Calcite} & \\
\text{CaSO}_4 + 2\text{H}_2\text{O} & \rightarrow \text{Ca}^{2+} + \text{SO}_4^- + 2\text{H}_2\text{O} \\
\text{Gypsum} & \\
\text{CaSO}_4 & \rightarrow \text{Ca}^{2+} + \text{SO}_4^- \\
\text{Anhydrite} & \\
\text{NaCl} & \rightarrow \text{Na}^+ + \text{Cl}^- \\
\text{Halite} & 
\end{align*}
\]

Scheme 3. Silicate, feldspar, dolomite, calcite, fluorite, gypsum and halite weathering.

The silicates weathering occurs upon coming in contact with carbonic acid. The albite ore silicate weathering and halite dissolutions increased the concentration of sodium ions in
groundwater. Dolomite and calcite weathering cause high content of calcium and magnesium (Keesari et al. 2014). The gypsum and anhydrite minerals' dissolutions release sulphate ions in water, as shown in Scheme 3. However, there might be other reasons for high sulphate content, such as the breakdown of the organic material and the use of fertilizers (Keesari et al. 2014). In this Indo-Gangetic region of Punjab, sediment deposition occurred due to the erosion of the Himalayan sedimentary rocks by the Indo-Gangetic river system. Each layer contains mixed mineralologic assemblage; from one region to another, wide variation in mineralologic assemblage can happen (Freeze and Cherry 1979). The alluvium soil of the malwa region is made up of sand, silt and clays, and their layering pattern in different areas can be different (CGWB 2020). But, a general hypothetical model was designed to prove the various hydrogeochemical reactions operating under the surface, as shown in Figure 3.

As the water moves, it encounters several types of minerals. First, the high oxygen content decays the organic matter in the uppermost layer, and the excess water content releases the bicarbonate ions in the aquifer (Singh et al. 2020). The groundwater of the malwa region is hard, and calcium carbonate nodules are there (Masuda et al. 2010). The movement of groundwater through limestone, shown as the 2nd layer in Figure 3, calcite or dolomite dissolution occurs, and water becomes rich Ca-HCO$_3^-$ composition. Clay (3rd layer in figure 3) is rich in quartz, montmorillonite and feldspar-type minerals (Jassal et al. 2001). The interaction of these minerals leads to the supersaturation of calcite ore due to the common ion effect. As the water moves through the gypsum bed (4th layer in Figure 3), sulphate dissolution occurs, and calcite precipitation leads to the re-establishing of calcite equilibrium and sulphates becoming dominant ions (Kaur et al. 2017; Ahada and Suthar 2018) Bonsor et al. proposed that the aquifers in this region were saline and rich in halite minerals. Because of the high solubility of these minerals in the water, the groundwater becomes enriched with sodium and chloride ion concentrations (Bonsor et al. 2017).
Figure 3. Hypothetical model of various hydro-chemical evolution undergoing the groundwater. The first layer (Green layer) is the uppermost layer rich in organic matter. The second layer, shown as a light green layer, contains calcite type minerals. The third layer (Orange layer) is demonstrated as a clay layer rich in montmorillonite and feldspar-type minerals. The gypsum bed (brownish layer) is designated as the fourth layer. Finally, the last layer (dark grey) contains halite-type minerals that make the soil saline in nature.

The chemistry operating under the surface impacts the mobilization of other elements such as U, As and other heavy metals, etc. After a thorough study, Acosta and co-workers validated that salinity increased the movement of heavy metals in the groundwater (Acosta et al. 2011). It isn't easy to include everything in this review article. So, here, we are considering arsenic and uranium elements and trying to describe their mobilization in groundwater.
Chemical Mobilization of Arsenic the aquifer of Malwa regions

In malwa region aquifers, arsenic is found in neutral arsenite (H$_3$AsO$_3$) and arsenate (H$_2$AsO$_4^-$) forms (Saha 2014). In the Himalayan range, arsenic-rich pelitic and argillaceous rocks are commonly found. During the late Pleistocene and early Holocene, weathering processes led to the deposit of these materials as sediments in Pleistocene alluvium and Holocene alluvium (Herath et al. 2016). The movement of these species in the groundwater is mainly controlled by pH, organic matter reduction, redox reactions, and adsorbents such as oxides and hydroxides of iron, manganese, aluminium and clay minerals (Bauer and Blodau 2006). In reducing environment As(III), form is more prevalent and harmful. After the green revolution, frequent tube wells were dug for drinking water and irrigation water diffusing atmospheric oxygen into this region's aquifers. This diffusion will be resulted in changes in groundwater chemistry and thus causes the oxidation of As(III) into As(V) as shown in Figure 4. (Welch and Lico 1998; Hundal et al. 2007)

![Figure 4. illustration of redox transformation of arsenic in aquifer sediments.](image)

The various geochemical and biological processes play a crucial role in mobilizing and transforming arsenic in the groundwater. In the below proposed schematic representation, we tried to show the various reasons for releasing arsenic in the groundwater. Dissolved organic matter is one of the reasons for the release of arsenic from the soil and sediment of aquifers (Sharma et al. 2011). Frequent withdrawal of water from the aquifers by tube-well diffuses
oxygen in the aquifer and cause the oxidation of arsenopyrite (FeAsS) and pyrite (FeS₂) minerals, as shown in Figure 5 (reaction 1). (Shankar et al. 2014). The Fe(III) deposited in the aquifers can also oxidize these minerals and be the reason for the mobilization of arsenic to groundwater (reaction 2, Figure 5) (Welch and Lico 1998). The nitrate leaching can also oxidize these minerals at low pH (reaction 3, Figure 5) (Zhang et al. 2020). The ferrihydrite sulfidization also liberate arsenites in aquifers (reaction 4, Figure 5) (O’Day et al. 2004). After the reductive dissolution of iron oxides containing orpiment minerals discharges arsenite in the groundwater (Reaction 5, Figure 5) (Wang and Mulligan 2006).

Figure 5. Proposed chemical illustration of various mechanisms about the mobilization of arsenic in groundwater
The anthropogenically-induced chemical fertilizers containing phosphate leached through the soil. During the downward movement, phosphate ions react with arsenic-adsorbed minerals to replace arsenic from adsorbed surfaces and let go of the arsenate in the groundwater (reaction 6, Figure 5) (Cui and Weng 2013). The oxyanion of arsenite and arsenate adsorbed on the Fe(OH)₃, Al(OH)₃ and clay minerals (Manning and Goldberg 1996; Goldberg 2002). The alkaline conditions oxidize the oxyanion of arsenite to arsenate adsorbed on Fe(OH)₃ (reaction 7, Figure 5). At high pH, the desorption of arsenite and arsenate adsorbed on ferric hydroxide happened (reaction 8, Figure 5) (Masue et al. 2007). Generally, the arsenate oxyanions are found on clay minerals because trace metal impurities oxidize arsenite to arsenate (reaction 9, Figure 5). At high pH, Clay-bounded arsenite and arsenate are release into groundwater aquifers (reaction 10, Figure 5) (Frost and Griffin 1977). Here, we proposed a model for understanding the mobilization of arsenic in groundwater. We think this will be helpful for the researcher and policymakers in mitigating the arsenic problem.

**Chemical Mobilization of Uranium in the aquifer of the Malwa region**

The radiological and toxicological impact of uranium is shattering the socioeconomic model of society (Coyte et al. 2018; Sahoo et al. 2021). To deal with this dangerous metal, a roundtable discussion of experts from different areas, such as chemists, physicists, microbiologists, geologists, zoologists, botanists, and pedologists, is necessary. Indeed, the interaction of soil and water minerals with Uranium species is changing every day (Ginder-Vogel and Fendorf 2007). To understand this complicated natural chemical and physical interaction system, we proposed a chemical model of uranium mobilization in the aquifers of the malwa region, as shown in the schematic diagram (Figure 6). Uranium exists in two forms uranous or uranium⁴⁺ [U(IV)] and uranyl or uranium⁶⁺ [U(VI)]. U(VI) is more mobilized and generally found in water, whereas U(IV) is relatively insoluble and makes stable compounds (Ginder-Vogel and Fendorf 2007; Qafoku and Icenhower 2008). The dissolution and
mobilization of uranium in the groundwater depend upon various chemical and physical factors such as the climate of that region, rock-water interaction, hydrogeochemical conditions etc (Langmuir 1978). In the presence of oxygen and highly alkaline conditions, U(VI) is more prevalent and exists as $\text{UO}_2(\text{CO}_3)_3^{4+}$ and at pH above 8.5, the latter species exists in equilibrium with $(\text{UO}_2)_3(\text{OH})_5^{5+}$ (Reaction 2, Figure 6) (Langmuir 1978). In the presence of high calcium ion concentration, uranyl carbonyl ion form $\text{Ca(UO}_2)(\text{CO}_3)_3^{2-}$ (Reaction 4, Figure 6) and this also forms from $\text{Ca}_2(\text{UO}_2)(\text{CO}_3)_2$ in the presence of bicarbonate ion concentration and oxic conditions (Reaction 5, Figure 6) (Dong and Brooks 2006). The oxidation of liebigite ore also yielded the same result (Reaction 6, Figure 6) (Gorman-Lewis et al. 2008). At neutral conditions (pH = 7) and high phosphate ion concentrations, the equilibrium between Uranophane and autunite shifts towards autunite (Langmuir 1997; Cuney 2010) Autunite is one of the predominant species around pH 6-7.5 (Reaction 8, Figure 6) (Langmuir 1997). However, uranyl carbonyl complexes predominate at higher pH and high carbonate ion concentrations (Reaction 9, Figure 6) (Barnett et al. 2000; Phillippi et al. 2007). Through the process of biosorption, the uranium ion sorption occurs on the organic matter and forms $\text{UO}_2(\text{organic matter})$ complexes (Tsezos and Volesky 1982; Newsome et al. 2014). Still, in the presence of a sufficient amount of carbonates/bicarbonates ions, this $\text{UO}_2(\text{organic matter})$ dissolution happens, and uranyl carbonyl complexes form (Reaction 1, Figure 6) (Cumberland et al. 2016).

The insoluble uraninite in the presence of carbonate/bicarbonate ions and iron oxides (FeOOH, $\text{Fe}_2\text{O}_3$) and oxic environment leads to the formation of uranyl carbonyl complexes (Reaction 3, Figure 6) (Stewart et al. 2015). The oxidation of uraninite ore leads to the formation of uranyl ionic species (Reaction 10, Figure 6) (Bala et al. 2022). The latter ions in high carbonate concentrations form uranyl carbonate complexes mobilized in the groundwater (Reaction 26, Figure 6) (Chandrasekar et al. 2021). The introduction of oxygen and nitrate oxidized the
reduced Fe$^{2+}$ to amorphous FeOOH which are capable of oxidizing the uraninite (Senko et al. 2005).

Figure 6. Proposed chemical illustration of various mechanisms for the mobilization of uranium in groundwater

All over the globe, the deposits of uranium ores were identified within the granite plutons, roll-front deposits, sandstones, breccia and organic matters (Cumberland et al. 2016 and reference cited therein). In these deposits, the uranium exists as insoluble uraninite form UO$_2$ adsorbed on the surfaces of minerals like iron oxides (FeO), manganese oxides, alumina, gibbsite, granite, quartz and natural sediments etc (Qafoku and Icenhower 2008) and
The literature data showed that uranium adsorbed on the surfaces of FeO as bidentate or tridentate complexes at low pH, but bidentate complexes are more common (Reaction 11, Figure 6). (Ching-kuo Daniel Hsi and Langmuir 1985) The adsorbed uraninite on the surface of FeO oxidized by NO₃⁻, microbial oxidation, O₂ or other factors changes into uranyl [U(VI)] complexes (Reaction 12, Figure 6) (Liesch et al. 2015) (Bonotto et al. 2019). At high pH, desorption of uranyl ion occurred, and uranyl ion mobilized in the groundwater (Reaction 13, Figure 6) (Ching-kuo Daniel Hsi and Langmuir 1985). Sometimes, the surface-adsorbed uranium complexes also make complexes with carbonates ion (Reaction 14, Figure 6), but these complexes are not very stable (Bargar et al. 2000). Above pH 8, the adsorption affinity of these complexes towards the FeO surfaces decreases, and uranyl carbonate complexes dissolve into the water (Reaction 15, Figure 6) (Wazne et al. 2003). Similar kind of studies was also reported with other metal oxides, for instance, MnO (Wang et al. 2013), Al₂O₃ (Sylwester et al. 2000), Granite (Baik et al. 2004), SiO₂ (Reich et al. 1998), etc. Sometimes bidentate FeO adsorbs PO₄³⁻ ions and makes (FeO)₂PO₄³⁻ type complexes that show better affinity and holding capacity for uranium ions than simple FeO (Reaction 16, Figure 6) (Finch and Murakami 1999; Del Nero et al. 2011; Seder-Colomina et al. 2015). However, in oxic conditions, this bounded uraninite form converted into FeO-associated uranyl [U(VI)] phosphate complexes (Reaction 17, Figure 6). According to literature data, PO₄³⁻ has 3 to 4 orders of lower affinity than Carbonates (Sahoo et al. 2022). Hence in the presence of high carbonate ion concentration and high pH, these uranium species dissolve as uranyl carbonyl complexes (Langmuir 1978; Wazne et al. 2003).

Sediments and soil are both replete in clay minerals. These clay minerals showed strong chemical and physical interactions with the dissolved species because of small particle size, complex porous structure, high specific surface area etc (Schulze 2018). Uraninite is also adsorbed on the clay minerals at low pH (Reaction 19, Figure 6) (Davey and Scott 1956;
Hennig et al. 2020). However, U(IV) is readily converted into a uranyl-clay complex by microbial oxidation or other oxidation processes (Reaction 20, Figure 6). This uranyl clay complex mobilized in the water as $[(UO_2^{2+})_3(OH)_5]^+$ at high pH (Reaction 21, Figure 6) (Bachmaf and Merkel 2011). Clay minerals contain a high negative charge on their surface, so they adsorb positive metal ions or metal oxides on their surface (Geckeis et al. 2013). These metal or metal oxides ion provide better space for holding uranium species (Reactions 22 and 23, Figure 6) (Payne et al. 2004; Catalano and Brown 2005; Křepelová et al. 2007). But at high pH conditions, by ion exchange mechanisms, these mobilized in the groundwater as Uranyl carbonate complexes (Reactions 24 and 25, Figure 6) (Greathouse and Cygan 2005; Křepelová et al. 2006).

**Conclusion**

The study of physicochemical parameters of all districts of the Malwa region showed that the groundwater quality of all the Malwa regions is not suitable for drinking purposes. Moreover, uranium and arsenic are making the situation worse and posing significant threats. As a result, cancer and other life-threatening diseases are prevalent in this region and have devastating effects on the socioeconomic conditions of the people of this region. From the literature data, one thing is evident the southwestern districts of the Malwa region are badly affected by uranium and arsenic. Although the various government agencies, such as the Indian Council of Medical Research (ICMR), Punjab Pollution Control Board (PPCB), Central Groundwater Board (CGWB), Department of Drinking Water Supply and Sanitation (DWSS), Bhaba Atomic Research Centre (BARC), Department of Agriculture (DoA), Economic Protection Agency (EPA), Economic and Statistical Organization of Punjab (ESOP) and others were asked to conduct to do research and take appropriate actions. But the Malwa region needs special and serious attention, where groundwater is a lifeline to people and is utilized for agriculture and domestic use. Through this paper, we tried to explain the various chemical
changes below the earth's surface by a hypothetical model and how these changes affect the mobilization of arsenic and uranium in the groundwater of the Malwa region. Our designed models will be helpful in developing better control measures in the future to tackle the problem of arsenic and uranium contamination. Finally, the need of time is for better interdepartmental strategy and inter-disciplinary approach and research with sound science and adaptive policy and management practice.

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