Isotope and Hydro-chemical Investigation on Uranium in Groundwater of South-west Punjab and Central Rajasthan

igh uranium concentrations are reported in groundwater of Punjab, Rajasthan, Madhya Pradesh, Andhra Pradesh, Chhattisgarh and Haryana by researchers. These high concentrations are not limited to one kind of geological formation but are spread across the diverse geological setups in India. Hence, it is very important to understand the role played by aquifer geology, geochemistry and dynamics towards the mobilization of uranium into groundwater. This study focuses on uranium contamination in groundwater, analyzing its occurrence, mobilization mechanisms, and hydro-chemical controls in Punjab and Rajasthan, two regions with different geological settings but similar climatic and agricultural conditions. Environmental isotopes (δ²H, δ¹⁸O, ³H), hydrochemistry (Cl⁻, NO₃⁻, SO₄⁻², F⁻, HCO₃⁻, Na^{+} , K^{+} , Mg^{2+} , Ca^{2+}), total uranium and its isotope activity ratio $(^{^{234}}\text{U}/^{^{238}}\text{U}),$ geochemical and statistical modeling approaches were applied to address the stated objectives.

The study reveals that a significant percentage of groundwater samples in both Punjab and Rajasthan exceed WHO's permissible limit of 30 µg/L, making the water unsafe for human consumption. In Punjab, the percentage of contaminated samples decreases in the postmonsoon season due to dilution, whereas in Rajasthan, contamination levels increase postmonsoon, worsening the health risks. In Punjab, uranium levels are higher in the premonsoon season due to increased oxidation of U(IV) to U(VI), driven by elevated nitrate concentrations. However, in the postmonsoon season, recharge from rainfall leads to dilution and reduced contamination levels. In contrast, Rajasthan experiences an increase in uranium concentration in the postmonsoon season, attributed to delayed recharge and the dissolution of salts from the vadose zone. Stable isotope analysis supports these findings. In Punjab, contamination is higher in shallow aquifers due to active oxidation processes, while deep aquifers show occasional pockets of high uranium concentrations due to mixing with shallow water. In Rajasthan, uranium contamination is more uniformly distributed across different depths, with both alluvial and hard rock aquifers exhibiting similar contamination patterns. In Punjab, where alluvial aquifers dominate, uranium mobilization is primarily driven by oxidative dissolution facilitated by high nitrate concentrations from agricultural runoff and irrigation return flow (Fig.1). The study reveals that uranium contamination is more pronounced in shallow aguifers, where oxidation processes are more active, and decreases in the postmonsoon season due to dilution effects. In Rajasthan, which has both alluvial and hard rock formations, uranium mobilization occurs through leaching and prolonged water-rock interactions. The study also examines uranium isotopic activity ratios $(^{234}U/^{238}U)$ as a tool for understanding groundwater dynamics. In Punjab, the activity ratio remains close to equilibrium, suggesting oxidative dissolution as the dominant mobilization process. In Rajasthan, higher activity ratios indicate disequilibrium caused by alpha recoil and selective leaching, which are influenced by the long residence time of groundwater (Fig.1). Optimal use of fertilizers and using surface sources or deep groundwater for drinking can help mitigate



A: NO3⁻ acting on ²³⁸U (IV)

- B: Oxidative Leaching of ²³⁸U (IV) to ²³⁸U (VI)
- C: NO3 acting on 234U (IV)
- D: Oxidative Leaching of ²³⁴U (IV) to ²³⁴U (VI)
- E: Complexation of 238U (VI) and 234U (VI) with HCO3



D: Alpha recoil imbedding ²³⁴U(IV)

E: Complexation of released ²³⁸U (VI) and ²³⁴U(VI) with HCO₃

Fig.1: Conceptual model of uranium release in I) alluvial formation of Punjab and II) hard rock formation of Rajasthan

uranium contamination in Punjab while removal of uranium through membranes or ultrafiltration techniques can be applied to in the case Rajasthan. The study provides a comprehensive understanding of uranium contamination in groundwater, highlighting its complex geochemical behavior, seasonal and spatial variations, and the influence of hydrochemical drivers.

Highlights of the work carried out by **Diksha Pant** under the supervision of **Dr. K. Tirumalesh** as a part of her doctoral thesis work. She was awarded PhD degree from Homi Bhabha National Institute in Chemical Sciences in 2021.