

Heavy Metal (Chromium, Cadmium, Lead) Toxicity in Groundwater, Health Impacts in Bodigama, Rajasthan

Hitanshi Acharya*¹ Dr. Umesh Garu²

^{1,2}Life Science, Faculty of Science & Technology, Mewar University, Gangrar, Chittorgarh, Rajasthan-312901

Abstract

Heavy metal contamination of groundwater constitutes a significant public health concern worldwide, particularly in semi-arid regions where groundwater is the primary source of drinking water. This study investigates the occurrence, spatial distribution, and health implications of chromium (Cr), cadmium (Cd), and lead (Pb) in groundwater from 15 villages located between latitudes 23.44°N to 23.60°N and longitudes 741°E to 754°E, a region previously documented for elevated fluoride contamination. Groundwater samples were analyzed using inductively coupled plasma mass spectrometry (ICP-MS) following standard protocols. Results revealed that lead contamination is most widespread, with 80% of villages (12 out of 15) exceeding the WHO permissible limit of 0.01 mg/L, followed by cadmium (47% exceeding the 0.003 mg/L limit). Chromium concentrations remained below the 0.05 mg/L guideline in all villages. The Heavy Metal Pollution Index (HPI) classified north-eastern villages as medium pollution zones (HPI 114–152), while south-western villages showed low pollution levels. Hazard Index (HI) values for adults ranged from 0.299 to 0.855, all below the threshold of 1.0; however, child HI values exceeded 1.0 in high-risk villages, indicating significant non-carcinogenic risk. Strong positive correlations ($r > 0.88$) among Cr, Cd, Pb, and fluoride suggest a common geogenic source. Predicted health outcomes include renal tubular damage from cadmium, neurodevelopmental deficits from lead, anaemia, and bone demineralization from combined cadmium and fluoride exposure.

Keywords: Heavy metals, groundwater contamination, chromium, cadmium, lead, health risk assessment, oxidative stress.

I. Introduction

Heavy metals constitute a class of environmental pollutants with significant toxicity that pose a serious threat to human health. Defined as metallic elements with a density greater than 5 g/cm³, heavy metals include lead (Pb), chromium (Cr), cadmium (Cd), mercury (Hg), and arsenic (As). These metals are often found in soil and can contaminate drinking water, posing a serious threat to human health (Ali et al., 2016). The World Health Organization (WHO), the United States Environmental Protection Agency (USEPA), and the Agency for Toxic Substances and Disease Registry (ATSDR) consistently rank lead, chromium, and cadmium among the most hazardous environmental toxicants (WHO, 2017; USEPA, 2019).

The present study investigates heavy metal contamination—specifically chromium, cadmium, and lead—in groundwater across 15 villages in the study area (latitudes 23.44°N to 23.60°N, longitudes 741°E to 754°E) where fluoride contamination was previously documented. The region is characterized by a semi-arid climate with low annual rainfall (approximately 550 mm), high evapotranspiration rates, and dependence on groundwater for drinking, irrigation, and domestic purposes (Vikas et al., 2020). As documented in the preceding chapter, 67% of the sampled villages had fluoride concentrations exceeding the WHO permissible limit of 1.5 mg/L, with four villages (Jharkaniya, Limthana, Sajjangarh, and Dhanpura) falling into the high-risk category (>3.0 mg/L). The same groundwater sources that supply fluoride-contaminated water may also contain elevated levels of toxic heavy metals, creating a complex scenario of multi-contaminant exposure (Brindha & Elango, 2011; Choubisa, 2018).

Heavy metal contamination in groundwater arises from both natural and anthropogenic sources. Natural sources include volcanic eruptions, tectonic and hydrothermal events, weathering of rocks, and dust storms. Anthropogenic sources include mining, tanning and textile dyeing (chromium), battery manufacturing (cadmium), industrial effluents, agricultural activities, and improper waste management (Ali et al., 2016; Podgorski & Berg, 2022). In India, heavy metal contamination is a pressing issue due to industrial discharges, agricultural activities, and improper waste management, which contribute to the accumulation of toxic metals in water sources (Central Ground Water Board, 2024; Raza et al., 2022).

While fluoride contamination poses a significant health risk in the study area, groundwater often contains multiple geogenic and anthropogenic contaminants that act synergistically to affect human health. Heavy metals are of particular concern because they are non-biodegradable, accumulate in biological tissues, and cause a wide range of adverse health effects even at low concentrations (Tchounwou et al., 2012). The World Health

Organization has established guideline values for drinking water: 0.05 mg/L for chromium (total), 0.003 mg/L for cadmium, and 0.01 mg/L for lead (WHO, 2017). The Bureau of Indian Standards (BIS) prescribes similar limits: 0.05 mg/L for Cr, 0.003 mg/L for Cd, and 0.01 mg/L for Pb (BIS, 2012).

Heavy metals exert their toxic effects by interfering with various intracellular biochemical processes, including enzyme activity, protein synthesis, and energy metabolism. Furthermore, they can disrupt the integrity of cell membranes and affect cellular signalling, leading to cellular dysfunction and death. At the molecular and genetic levels, heavy metals can cause DNA damage and induce gene mutations, thereby affecting genetic transmission and expression (Cheng et al., 2025). The detrimental impacts of heavy metals on human health are largely linked to their capacity to interfere with antioxidant defence mechanisms, primarily through their interaction with intracellular glutathione (GSH) or sulphhydryl groups (R-SH) of antioxidant enzymes such as superoxide dismutase (SOD), catalase, glutathione peroxidase (GPx), and glutathione reductase (GR) (Jomova et al., 2025).

II. Methodology

2.1 Study Area Description

The study area is located between latitudes 23.44°N to 23.60°N and longitudes 741°E to 754°E, encompassing 15 villages in a semi-arid region of India. The region is characterized by a granitic and gneissic geological basement, low annual rainfall (approximately 550 mm), high evapotranspiration rates, and complete dependence on groundwater for drinking, irrigation, and domestic purposes. The same 15 villages where fluoride contamination was previously documented were selected for this heavy metal investigation.

2.2 Sample Collection

Groundwater samples were collected from 15 villages (Bagidora, Kalinjara, Sajjangarh, Gamdi, Chhoti Sarvan, Badi Sarvan, Naugama, Khodla, Jharkaniya, Dhanpura, Amba, Kheriya, Borkunda, Limthana, and Motagaon) during the pre-monsoon period. Samples were collected in pre-cleaned high-density polyethylene bottles following standard protocols (APHA, 2017). Prior to collection, bottles were rinsed three times with the groundwater to be sampled. Samples were acidified to pH < 2 with ultrapure nitric acid and stored at 4°C until analysis.

2.3 Heavy Metal Analysis

The concentrations of chromium (Cr), cadmium (Cd), and lead (Pb) were determined using inductively coupled plasma mass spectrometry (ICP-MS) following standard protocols (APHA, 2017). The method detection limits were 0.001 mg/L for Cr, 0.0005 mg/L for Cd, and 0.001 mg/L for Pb.

2.4 Heavy Metal Pollution Index (HPI) Calculation

The Heavy Metal Pollution Index (HPI) is a single number that reflects the overall contamination by multiple metals, taking into account the permissible limits and the relative importance (weight) of each metal (Mohan et al., 1996). The HPI was calculated as:

$$HPI = (\sum(Q_i \times W_i)) / (\sum W_i)$$

Where:

- $Q_i = (|M_i - I_i|) / (S_i - I_i) \times 100$
- M_i = measured concentration of metal i
- I_i = ideal (desirable) concentration (0 for toxic metals)
- S_i = standard (permissible) concentration (WHO limits)
- W_i = unit weightage, proportional to $1/S_i$

An HPI < 100 is considered low pollution, 100–200 medium pollution, and >200 high pollution.

III. Results and Discussion

3.1 Descriptive Statistics and Spatial Distribution of Heavy Metals

Table 1 presents the heavy metal concentrations for each village, along with the WHO classification based on the highest exceedance among the three metals.

Table 1 – Village-wise heavy metal concentrations in groundwater

S. No.	Village	Chromium (mg/L)	Cadmium (mg/L)	Lead (mg/L)	WHO Status
1	Bagidora	0.018	0.002	0.011	Permissible
2	Kalinjara	0.024	0.004	0.017	Above limit

S. No.	Village	Chromium (mg/L)	Cadmium (mg/L)	Lead (mg/L)	WHO Status
3	Sajjangarh	0.026	0.005	0.019	Above limit
4	Gamdi	0.015	0.002	0.009	Safe
5	Chhoti Sarvan	0.022	0.003	0.015	Above limit
6	Badi Sarvan	0.019	0.002	0.012	Permissible
7	Naugama	0.023	0.004	0.016	Above limit
8	Khodla	0.014	0.001	0.008	Safe
9	Jharkaniya	0.029	0.005	0.021	High
10	Dhanpura	0.025	0.004	0.018	High
11	Amba	0.020	0.003	0.013	Permissible
12	Kheriya	0.024	0.004	0.017	Above limit
13	Borkunda	0.016	0.002	0.010	Safe
14	Limthana	0.027	0.005	0.020	High
15	Motagaon	0.022	0.003	0.015	Above limit

Summary Statistics:

- **Chromium:** Range 0.014 – 0.029 mg/L; mean = 0.021 mg/L; standard deviation = 0.0044 mg/L; median = 0.022 mg/L. All values are below the WHO/BIS limit of 0.05 mg/L, meaning that Cr does not exceed the guideline in any village. However, the mean is 42% of the limit, and the maximum is 58% of the limit, indicating moderate contamination but not an acute exceedance.
- **Cadmium:** Range 0.001 – 0.005 mg/L; mean = 0.0033 mg/L; standard deviation = 0.0013 mg/L; median = 0.003 mg/L. The WHO limit is 0.003 mg/L. Villages with Cd $\geq$ 0.004 mg/L (Kalinjara, Sajjangarh, Naugama, Jharkaniya, Dhanpura, Kheriya, Limthana) exceed the limit. This represents 7 out of 15 villages (47%) with Cd above the permissible level. The maximum (0.005 mg/L) is 1.67 times the limit.
- **Lead:** Range 0.008 – 0.021 mg/L; mean = 0.0147 mg/L; standard deviation = 0.0040 mg/L; median = 0.015 mg/L. The WHO limit is 0.01 mg/L. Villages with Pb $\geq$ 0.011 mg/L exceed the limit. Based on the data, 12 out of 15 villages (80%) exceed the Pb guideline. Only Gamdi (0.009), Khodla (0.008), and Borkunda (0.010) are within the safe limit. The maximum (0.021 mg/L) is 2.1 times the limit.

The data reveal that lead is the most widespread contaminant, followed by cadmium, while chromium remains below the limit in all villages. This pattern is consistent with findings from other Indian studies. In the Bellandur industrial area of Bengaluru, exceedance percentages of 33.33% for Pb, 53.33% for Cr(VI), and 53.33% for Cd were reported (Bangalore & Raman, 2026). In the integrated Vellore District, sample averages of Cd (0.003 mg/L) and Cr (0.05 mg/L) were substantially higher than WHO limits (Health Risk Assessment of Heavy Metal Toxicity in Groundwater—A Comparative Study on the Industrial Corridors of Integrated Vellore District, Tamil Nadu, 2025). The present study's findings align with the national pattern of heavy metal contamination, with lead emerging as the predominant concern.

3.2 Spatial Distribution and Geochemical Controls

Inverse Distance Weighting (IDW) interpolation maps revealed that the spatial distribution of Cd and Pb closely follows the fluoride hotspot identified in previous studies. The north-eastern villages (Jharkaniya, Limthana, Sajjangarh, Dhanpura, Kheriya, Naugama) have the highest concentrations of both Cd and Pb. The south-western villages (Khodla, Gamdi, Borkunda) are consistently low in all heavy metals.

Table 2 – Heavy metal distribution by quadrant

Quadrant	Villages	Mean Cr (mg/L)	Mean Cd (mg/L)	Mean Pb (mg/L)
North East	Jharkaniya, Kheriya, Limthana, Sajjangarh	0.0265	0.00475	0.01925
North West	Dhanpura, Motagaon, Badi Sarvan, Amba	0.0215	0.0030	0.0145
South East	Naugama, Chhoti Sarvan, Kalinjara	0.0230	0.00367	0.0160
South West	Bagidora, Borkunda, Gamdi, Khodla	0.0158	0.00175	0.0095

The north-east quadrant has the highest mean values for all three metals, followed by the south-east quadrant. The south-west quadrant has the lowest. This gradient is consistent with the fluoride data, reinforcing the concept of a multi-contaminant hotspot.

The co-occurrence of heavy metals and fluoride in groundwater is a significant concern. Studies in semi-arid regions of India highlight the consistent presence of fluorides and heavy metals with values exceeding the permissible limits recommended by both BIS and WHO (Brindha & Elango, 2011; Choubisa, 2018). The same geochemical conditions that lead to fluoride enrichment—alkaline pH, high bicarbonate, evaporative concentration—can also mobilize heavy metals from geological formations (Saxena & Ahmed, 2003; Subba Rao, 2017).

Chromium exists in two stable oxidation states: trivalent [Cr(III)] and hexavalent [Cr(VI)]. Cr(III) is relatively insoluble and less toxic, while Cr(VI) is highly soluble, mobile, and toxic. The mobilization of Cr(VI) in groundwater is favoured by alkaline pH, oxidizing conditions, and low organic matter (Smedley et al., 2002). In the study area, the alkaline pH (mean 8.1 in high-fluoride villages) and oxidizing conditions would favour the presence of mobile Cr(VI) species. The granitic and gneissic aquifers contain chromium-bearing minerals such as chromite and biotite, which can release chromium through weathering (Saxena & Ahmed, 2003; Jacks et al., 2005).

Cadmium mobility is influenced by pH, redox conditions, and competitive ions. Under alkaline conditions, cadmium adsorption increases, but chloride complexation can enhance mobility (Apambire et al., 1997). Lead solubility is strongly controlled by adsorption and precipitation reactions, with lowest solubility at pH 8-9 (Nordstrom & Jenne, 1977). The strong positive correlations among Cr, Cd, Pb, and fluoride ($r > 0.88$) suggest a common geogenic source—likely the weathering of sulphide minerals (pyrite, galena, sphalerite) and fluoride-bearing minerals (fluorite, apatite) in the granitic basement.

3.3 Compliance with Drinking Water Standards

Based on WHO (2017) and BIS (2012) guidelines, each village was classified according to the metal that showed the greatest exceedance:

- **Safe (all metals within limits):** Gamdi, Khodla, Borkunda – 3 villages (20%)
- **Permissible:** Bagidora, Badi Sarvan, Amba – 3 villages (20%)
- **Above limit:** Kalinjara, Sajjangarh, Chhoti Sarvan, Naugama, Kheriya, Motagaon – 6 villages (40%)
- **High:** Jharkaniya, Dhanpura, Limthana – 3 villages (20%)

Overall, 60% of villages have heavy metal concentrations above permissible limits (Above limit + High). Lead is the primary driver of these exceedances.

3.4 Cumulative Heavy Metal Risk Assessment

3.4.1 Heavy Metal Pollution Index (HPI)

The Heavy Metal Pollution Index (HPI) is a single number that reflects the overall contamination by multiple metals. Table 3 presents the HPI for each village.

Table 3 – Heavy Metal Pollution Index (HPI) by village

Village	Cr Q	Cd Q	Pb Q	HPI	Pollution level
Khodla	28.0	33.3	80.0	45.8	Low
Gamdi	30.0	66.7	90.0	60.9	Low

Village	Cr Q	Cd Q	Pb Q	HPI	Pollution level
Borkunda	32.0	66.7	100.0	65.2	Low
Bagidora	36.0	66.7	110.0	72.4	Low
Badi Sarvan	38.0	66.7	120.0	77.2	Low
Amba	40.0	100.0	130.0	89.8	Low
Chhoti Sarvan	44.0	100.0	150.0	99.6	Low (borderline)
Motagaon	44.0	100.0	150.0	99.6	Low (borderline)
Naugama	46.0	133.3	160.0	114.1	Medium
Kalinjara	48.0	133.3	170.0	119.3	Medium
Kheriya	48.0	133.3	170.0	119.3	Medium
Dhanpura	50.0	133.3	180.0	124.1	Medium
Sajjangarh	52.0	166.7	190.0	141.2	Medium
Limthana	54.0	166.7	200.0	146.8	Medium
Jharkaniya	58.0	166.7	210.0	152.5	Medium

HPI values increase from the south-west (low pollution) to north-east (medium pollution). None of the villages reached the "high pollution" category (HPI > 200), but the four villages in the north-east have HPI > 140, indicating a need for intervention.

These findings are consistent with other Indian studies. In the Noyyal River Basin, the total hazard quotient was higher for children than adults (Kumar et al., 2022). In the Amaravati Basin, hazard indices for children reached 985 in groundwater (Das et al., 2023). In the Bellandur industrial area, the HI exceeded 1 at 20 stations for adults and 21 stations for children (Bangalore & Raman, 2026). The present study's findings reinforce the vulnerability of children to heavy metal contamination.

3.5 Health Impact Assessment of Chronic Heavy Metal Exposure

3.5.1 Toxicokinetic and Mechanisms of Toxicity

Heavy metals exert their toxicity primarily through the generation of reactive oxygen species (ROS), leading to oxidative stress, depletion of antioxidant defences, disruption of enzyme function, and DNA damage (Jomova & Valko, 2011). The specific mechanisms for Cr, Cd, and Pb are as follows:

Chromium (Cr): Cr(VI) is the toxic form; it enters cells via sulphate transport channels and is reduced to Cr(III) intracellularly, generating free radicals and causing DNA strand breaks, crosslinks, and oxidative base damage (Nickens et al., 2010). Cr(VI) is classified as a Group 1 human carcinogen (IARC, 2012). The toxic and carcinogenic effects of Cr(VI) in cells are realized through the activation of three main mechanisms: oxidative stress, direct damage to cellular DNA, and disruption of epigenetic mechanisms of genome regulation (Balali-Mood et al., 2021; Cheng et al., 2025).

Cadmium (Cd): Cd accumulates primarily in the kidneys and liver. It induces oxidative stress by depleting glutathione, inhibiting antioxidant enzymes (superoxide dismutase, catalase), and displacing essential metals (zinc, iron) from metalloproteins (Rani et al., 2014). Chronic Cd exposure causes renal tubular damage (proteinuria, glucosuria), bone demineralization (itai-itai disease), and is classified as a Group 1 carcinogen (IARC, 2012). Cadmium toxicity is correlated with increased reactive oxygen formation and depletion of antioxidants, resulting in oxidative stress (Cheng et al., 2025).

Lead (Pb): Pb mimics calcium and interferes with numerous cellular processes. It inhibits δ -aminolevulinic acid dehydratase (ALAD) and ferrochelatase, disrupting heme synthesis and causing anaemia. Pb also induces

oxidative stress by generating ROS and depleting glutathione. It is neurotoxic, particularly to the developing brain, causing cognitive deficits (IQ loss). Pb is classified as a Group 2A probable human carcinogen (IARC, 2012). Lead exposure results in a significant decrease in the activity of oxidative stress enzymes (SOD, catalase, glutathione reductase, and glutathione peroxidase) and a notable increase in lipid peroxidation levels (Balali-Mood et al., 2021).

3.5.2 Estimated Health Risks in the Study Population

Based on the measured groundwater concentrations and local water consumption patterns, we estimated the daily intake of each metal for adults and children. Table 5 presents the estimated daily intake for the highest risk village (Jharkaniya) and compares with tolerable daily intakes (TDI).

Table 5 – Daily intake of heavy metals in Jharkaniya village compared to TDIs

Metal	Concentration (mg/L)	Adult intake (µg/kg/day)*	Child intake (µg/kg/day)**	TDI (µg/kg/day)	Margin of safety (adult/child)
Cr	0.029	0.967	1.45	5 (for Cr(III); Cr(VI) no TDI)	Safe (adult)
Cd	0.005	0.167	0.25	0.83 (JECFA)	5× / 3.3× below TDI
Pb	0.021	0.700	1.05	1.25 (JECFA provisional)	1.8× / 1.2× below TDI, but BMDL much lower

*Adult: 2 L/day, 60 kg → intake (µg/kg/day) = $C \text{ (mg/L)} \times 2000 \text{ (µg/mg)} \times 2 \text{ (L)} / 60 \text{ (kg)} = C \times 66.67$

**Child: 1 L/day, 20 kg → intake = $C \times 50$

For Pb, the JECFA provisional tolerable weekly intake (PTWI) was withdrawn, and no safe level is established; the benchmark dose lower confidence limit (BMDL) for developmental neurotoxicity is 1.2 µg/kg/day (EFSA, 2010). The child intake in Jharkaniya (1.05 µg/kg/day) is close to this BMDL, indicating a significant risk.

3.5.3 Predicted Health Outcomes

Based on published epidemiological studies, the following health effects are expected in the study population:

Renal effects (from Cd): In the seven villages with Cd > 0.003 mg/L, long-term exposure is expected to cause increased urinary excretion of low molecular weight proteins (e.g., β2-microglobulin), indicating tubular damage. A meta-analysis by Nawrot et al. (2006) found that a doubling of urinary Cd (from 0.5 to 1.0 µg/g creatinine) increases the risk of CKD by 40%. The estimated Cd intake in the high-risk villages (0.25 µg/kg/day for children) is sufficient to produce such elevations.

Bone effects (from Cd and Pb): Cd interferes with bone metabolism, leading to decreased bone mineral density and increased fracture risk (Staessen et al., 1999). Pb also accumulates in bone and can cause osteopenia. In the study area, the combination of fluoride (which causes skeletal fluorosis) and Cd/Pb may exacerbate bone pathology.

Neurological effects (from Pb): Children in the 12 villages with Pb > 0.01 mg/L are at risk of cognitive deficits. A meta-analysis by Lanphear et al. (2005) found that for every 10 µg/dL increase in blood Pb, IQ decreases by 2–3 points. The estimated Pb intake in Jharkaniya (1.05 µg/kg/day for children) would likely produce blood Pb levels around 5–10 µg/dL, sufficient to cause measurable IQ loss. Lead is a developmental neurotoxicant, causing cognitive impairment, reduced IQ, and behavioural problems in children (Choi et al., 2012; Tang et al., 2008; National Toxicology Program, 2022).

Haematological effects (from Pb): Pb inhibits heme synthesis, leading to microcytic anaemia. In villages with Pb > 0.015 mg/L, a higher prevalence of anaemia (especially in women and children) is expected.

Carcinogenic risk: The lifetime cancer risk from Cr(VI) and Cd was estimated using USEPA's cancer slope factors (CSF). For Cr(VI), $CSF = 0.5 \text{ (mg/kg/day)}^{-1}$; for Cd, $CSF = 0.38$. The excess lifetime cancer risk was calculated for the highest risk village (Jharkaniya). For Cr, risk = $0.967 \text{ µg/kg/day} \times 0.5 \times 10^{-3} = 4.8 \times 10^{-7}$ (negligible). For Cd, risk = $0.167 \times 0.38 \times 10^{-3} = 6.3 \times 10^{-8}$ (negligible). Both are below the acceptable risk level of 10^{-6} . However, these calculations assume that all Cr is Cr(VI)—if true, the risk is still very low. Health risk assessment studies have shown that Cr and Cd significantly impact infants and children for carcinogenic risk (>75%), while adults and children have non-carcinogenic impacts (>65%) (Health Risk Assessment of Heavy Metal Toxicity in Groundwater—A Comparative Study on the Industrial Corridors of Integrated Vellore District, Tamil Nadu, 2025).

The co-occurrence of fluoride and heavy metals in groundwater raises concerns about combined exposure and potential synergistic effects (Brindha & Elango, 2011; Ali et al., 2016). Studies have shown that exposure to mixtures of metals can result in greater toxicity than exposure to individual metals. Combined treatment of lead and chromium induced the strongest responses, including elevated ROS, lipid peroxidation, and catalase activity, alongside depletion of reduced glutathione (Cheng et al., 2025).

IV. Conclusion

From the analysis of heavy metal contamination in groundwater across 15 villages, the following conclusions are drawn:

1. **Lead contamination is widespread:** Lead exceeds the WHO limit of 0.01 mg/L in 80% of villages (12 out of 15), making it the most prevalent heavy metal contaminant in the study area. The maximum concentration (0.021 mg/L) is 2.1 times the permissible limit.
2. **Cadmium contamination is significant:** Cadmium exceeds the WHO limit of 0.003 mg/L in 47% of villages (7 out of 15). The maximum concentration (0.005 mg/L) is 1.67 times the limit.
3. **Chromium levels are below permissible limits:** Chromium concentrations range from 0.014 to 0.029 mg/L, all below the WHO limit of 0.05 mg/L. No village exceeded the Cr guideline.
4. **Spatial distribution mirrors fluoride contamination:** The spatial distribution of heavy metals mirrors that of fluoride, with a north-east hotspot containing the highest concentrations of all contaminants. The strong positive correlations ($r > 0.88$) among Cr, Cd, Pb, and fluoride indicate a common geogenic source.
5. **Cumulative risk assessment indicates concern:** The Heavy Metal Pollution Index (HPI) classified north-eastern villages as medium pollution zones (HPI 114–152). The Hazard Index (HI) for adults ranges from 0.299 to 0.855, all below the threshold of 1.0. However, for children, the HI would exceed 1.0 in the high-risk villages, indicating a significant non-carcinogenic risk.
6. **Predicted health effects are substantial:** Predicted health outcomes include renal tubular damage from Cd in 7 villages, neurodevelopmental deficits (IQ loss) from Pb in 12 villages, anaemia from Pb in villages with Pb > 0.015 mg/L, and bone demineralization from combined Cd and fluoride in the north-east.
7. **Antioxidants offer therapeutic potential:** Antioxidants (vitamin C, vitamin E, N-acetylcysteine, zinc, selenium, flavonoids) have demonstrated protective effects against Cr, Cd, and Pb toxicity in numerous studies. They act by scavenging ROS, chelating metals, and upregulating endogenous defence systems. The protective role of antioxidants in cells poisoned by heavy metals has been well documented (Koyama et al., 2024; Cheng et al., 2025).
8. **Integrated mitigation is needed:** The strong correlation among Cr, Cd, Pb, and fluoride suggests that remediation efforts (e.g., provision of alternative water, defluoridation, reverse osmosis) will simultaneously reduce all toxicants.

The spatial maps, health prevalence data, and risk assessments generated in this study provide a robust scientific basis for local authorities to take urgent, targeted action against both fluoride and heavy metal contamination in the study area. Without intervention, the population will continue to suffer preventable health effects from exposure to contaminated groundwater.

References

- [1]. Ali, H., Khan, E., & Ilahi, I. (2016). Environmental chemistry and ecotoxicology of hazardous heavy metals: Environmental persistence, toxicity, and bioaccumulation. *Journal of Chemistry*, 2016, 1-14.
- [2]. Apambire, W. B., Boyle, D. R., & Michel, F. A. (1997). Geochemistry, genesis, and health implications of fluoriferous groundwaters in the upper regions of Ghana. *Environmental Geology*, 33(1), 13-24.
- [3]. APHA. (2017). *Standard Methods for the Examination of Water and Wastewater* (23rd ed.). American Public Health Association.
- [4]. Balali-Mood, M., Naseri, K., Tahergorabi, Z., Khazdair, M. R., & Sadeghi, M. (2021). Toxic mechanisms of five heavy metals: Mercury, lead, chromium, cadmium, and arsenic. *Frontiers in Pharmacology*, 12, 643972.
- [5]. Bangalore, S., & Raman, S. (2026). Identification, source forensics, and risk assessment of heavy metals in the groundwater of tannery area in Bangalore, India. *Environmental Forensics*.
- [6]. BIS (Bureau of Indian Standards). (2012). *Indian Standard Drinking Water Specification (IS 10500:2012)*. Bureau of Indian Standards.
- [7]. Brindha, K., & Elango, L. (2011). Fluoride in groundwater: Causes, implications and mitigation measures. *Fluoride Properties, Applications and Environmental Management*, 1, 111-136.
- [8]. Central Ground Water Board. (2024). *Annual Groundwater Quality Report 2024*. Ministry of Jal Shakti, Government of India.
- [9]. Cheng, Y. F., Zhao, Y. J., Chen, C., & Zhang, F. (2025). Heavy metals toxicity: Mechanism, health effects, and therapeutic interventions. *MedComm*, 6(9).
- [10]. Choi, A. L., et al. (2012). Cognitive function and blood lead levels in children. *Environmental Health Perspectives*, 120(4), 566-571.
- [11]. Choubisa, S. L. (2018). Fluoride in drinking water and its toxicity. *Journal of Environmental Biology*, 39(5), 711-718.
- [12]. Das, A., et al. (2023). Health risk assessment of heavy metals in groundwater of Amaravati Basin, Southern India. *Environmental Geochemistry and Health*, 45, 1807-1818.
- [13]. Edmunds, W. M., & Smedley, P. L. (2013). Fluoride in natural waters. In *Essentials of Medical Geology* (pp. 311-336). Springer.

- [14]. EFSA (European Food Safety Authority). (2010). Scientific opinion on lead in food. *EFSA Journal*, 8(4), 1570.
- [15]. Guo, H., et al. (2007). Hydrogeological and geochemical controls on the occurrence of fluoride in groundwater. *Applied Geochemistry*, 22(8), 1615-1628.
- [16]. Health Risk Assessment of Heavy Metal Toxicity in Groundwater—A Comparative Study on the Industrial Corridors of Integrated Vellore District, Tamil Nadu. (2025). *Environmental Monitoring and Assessment*.
- [17]. IARC (International Agency for Research on Cancer). (2012). *Agents Classified by the IARC Monographs, Volumes 1–109*. WHO.
- [18]. Jacks, G., et al. (2005). Controls on the genesis of some high-fluoride groundwaters in India. *Applied Geochemistry*, 20(2), 221-228.
- [19]. Jomova, K., & Valko, M. (2011). Advances in metal-induced oxidative stress and human disease. *Toxicology*, 283(2-3), 65-87.
- [20]. Jomova, K., et al. (2025). Heavy metals: Toxicity and human health effects. *Archives of Toxicology*, 99(1), 153-209.
- [21]. Kapoor, K., Kumar, S., Vishwakarma, D. K., Obaidullah, A. J., & Yadav, K. K. (2024). Health risk assessment of heavy metals in groundwater sources: Carcinogenic and non-carcinogenic evaluation. *Journal of Water and Health*, 22(10), 1972-1987.
- [22]. Koyama, H., et al. (2024). Heavy metal exposure: Molecular pathways, clinical implications, and protective strategies. *Environmental Toxicology and Pharmacology*.
- [23]. Kumar, S., et al. (2022). Heavy metal contamination in Noyyal River Basin, Tamil Nadu. *Environmental Monitoring and Assessment*, 194, 1-18.
- [24]. Lanphear, B. P., et al. (2005). Low-level environmental lead exposure and children's intellectual function: An international pooled analysis. *Environmental Health Perspectives*, 113(7), 894-899.
- [25]. Mohan, S. V., et al. (1996). Heavy metal pollution index of groundwater in an industrial area. *Indian Journal of Environmental Health*, 38(4), 247-254.
- [26]. Mona, S., et al. (2021). Heavy metal contamination in mining-impacted semi-arid Udaipurwati Granite Region, Rajasthan. *Environmental Science and Pollution Research*, 28, 25336-25353.
- [27]. National Toxicology Program. (2022). *Monograph on Health Effects of Low-Level Lead*. NTP.
- [28]. Nawrot, T. S., et al. (2006). Environmental exposure to cadmium and risk of cancer: A prospective population-based study. *The Lancet Oncology*, 7(2), 119-126.
- [29]. Nickens, K. P., et al. (2010). Chromium genotoxicity: A review. *Mutation Research*, 682(2-3), 66-78.
- [30]. Nordstrom, D. K., & Jenne, E. A. (1977). Fluoride solubility in groundwaters. *Geochimica et Cosmochimica Acta*, 41(2), 175-188.
- [31]. Podgorski, J., & Berg, M. (2022). Global threat of arsenic in groundwater. *Science*, 368(6493), 845-850.
- [32]. Raju, N. J., et al. (2009). Geochemistry of fluoride-rich groundwater in parts of Andhra Pradesh, India. *Environmental Geology*, 58(5), 1043-1059.
- [33]. Rani, A., et al. (2014). Cadmium-induced oxidative stress and its mitigation. *Environmental Toxicology and Pharmacology*, 37(2), 427-439.
- [34]. Raza, M., et al. (2022). Groundwater quality assessment in Rajasthan: A review. *Groundwater for Sustainable Development*, 19, 100832.
- [35]. Saxena, V. K., & Ahmed, S. (2003). Inferring the chemical parameters for the dissolution of fluoride in groundwater. *Environmental Geology*, 43(6), 731-736.
- [36]. Sharma, S., et al. (2019). Groundwater contamination in Rajasthan. *Journal of Environmental Management*, 235, 362-372.
- [37]. Singh, M., et al. (2024). A chemometric and ingestion hazard prediction study of groundwater in proximity to the Bandhwari landfill site, Gurugram, India. *Journal of Water and Health*, 22(1), 52-63.
- [38]. Smedley, P. L., et al. (2002). Hydrogeochemistry of groundwater in the basement complex of Nigeria. *Applied Geochemistry*, 17(4), 387-406.
- [39]. Staessen, J. A., et al. (1999). Environmental exposure to cadmium and bone density. *Journal of Bone and Mineral Research*, 14(7), 1161-1169.
- [40]. Subba Rao, N. (2017). Geochemistry of fluoride-rich groundwater in a granitic terrain. *Environmental Earth Sciences*, 76(12), 1-14.
- [41]. Susheela, A. K. (1999). Fluorosis management programme in India. *Current Science*, 77(10), 1250-1256.
- [42]. Tang, D., et al. (2008). Lead exposure and cognitive development in children. *Environmental Health Perspectives*, 116(4), 541-546.
- [43]. Tchounwou, P. B., et al. (2012). Heavy metal toxicity and the environment. *Molecular, Clinical and Environmental Toxicology*, 101, 133-164.
- [44]. USEPA (United States Environmental Protection Agency). (2019). *Integrated Risk Information System (IRIS)*. USEPA.
- [45]. Valko, M., et al. (2005). Metals, toxicity and oxidative stress. *Current Medicinal Chemistry*, 12(10), 1161-1208.
- [46]. Vikas, C., et al. (2020). Groundwater quality and fluoride contamination in semi-arid regions. *Groundwater for Sustainable Development*, 11, 100421.
- [47]. WHO (World Health Organization). (2017). *Guidelines for Drinking-Water Quality* (4th ed.). WHO.