

Hydro geochemical Dynamics, Trace Metal Distribution and Depth-Dependent Vulnerability of Alluvial Aquifers in Sakrand City, Pakistan

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ABSTRACT

Sub-ground water in semi-arid developing regions is still susceptible to degradation, despite being a vital part of human well-being and environmental stability, because of the lack of municipal treatment facilities. A detailed spatial hydro-chemical and toxicological evaluation of the groundwater quality of 30 residential, commercial and agricultural sampling sites ($N = 30$) of Sakrand City in Sindh, Pakistan is presented. Ten elemental and physicochemical parameters were measured using ICP-OES along with conventional methods, and compared with the World Health Organization (WHO) standards. Groundwater in the region is neutral to weakly alkaline (pH 7.40–8.30), with cationic dominance following the order Na^+ (47.8%) > Mg^{2+} (24.3%) > Ca^{2+} (18.3%) > K^+ (9.6%). Results show that water safety is mainly limited by salinity and halide buildup from the water sources and not by the presence of toxic heavy metals which are generally 1 to 3 orders of magnitude lower than the maximum WHO limits. Electrical Conductivity (33% exceedance rate), Chloride (30%) and Magnesium (30%) and Total Dissolved Solids (17%) were among the parameters that exceeded WHO guidelines. When the water was compared with depth, shallow hand pumps had significantly higher ionic loads (TDS = 814 mg/L) when compared to deeper bore wells (TDS = 736 mg/L) owing to the vulnerability of the upper aquifer to domestic waste water, agricultural run-off and high evapotranspiration. Single factor analysis of variance (ANOVA) showed that there was significant spatial variation among all the parameter groups ($F = 330.68$, $p = 0.001$). The result highlights the critical need for treatment strategies that focus on depth to extract salt (depth targeted extraction), on-site point-of-use filters, and site-specific groundwater management protocols to address the salinity risk in Sakrand City.

Keywords: Groundwater quality, Hydro geochemistry, Heavy metals, ICP-OES, ANOVA, Sakrand City, WHO standards

1.0 INTRODUCTION

Accessibility of freshwater is a key factor that affects human health, ecosystem sustainability, and socio-economic growth (Ahmad, *et al.*, 2023; Biswas, 2025). Globally, groundwater is the largest reservoir of accessible unfrozen freshwater resources, providing drinking water to billions of people,

accounting for almost 98% of the planet's unfrozen liquid freshwater resources (Abanyie, *et al.*, 2023). Groundwater accounts for about 60% to 70% of the total groundwater requirements for domestic, drinking and agricultural purposes in the developing countries like Pakistan (Jat Baloch, *et al.*, 2022; Talib, *et al.*, 2019). Due to the critical lack of infrastructure in rural and semi-urban areas such as the absence of surface water treatment plants and water distribution networks, rural people are often relying heavily on subterranean aquifers (Kandhro, *et al.*, 2017; Perveen and Amar Ul, 2023). However, the primary source of groundwater access for these communities is the result of taking up groundwater directly from localized wells.

While natural overburden soil and geological strata help to purify groundwater that infiltrates aquifers, groundwater reservoirs are highly susceptible to chemical and physical degradation (Biswas, 2025). Rapid unmanaged urbanization, agricultural runoff containing synthetic fertilizers and pesticides, untreated industrial effluents and unmanaged municipal solid waste allow the leaching of toxic chemicals in shallow aquifers (Abbasi and Abbasi, 2024; Landar, *et al.*, 2024). Hyper-evapotranspiration and little recharge in semi-arid areas further increase the concentration of dissolved salts in the water table, exacerbating water quality issues (Khafaga, *et al.*, 2025; Kumar, *et al.*, 2023). Non-biodegradable heavy metals like cadmium (Cd), chromium (Cr), lead (Pb) etc. are very harmful to health in terms of toxicology because they persist in the environment and bioaccumulation (Kamruzzaman, *et al.*, 2026; Nag and Cummins, 2022). Long-term exposure of humans of these metals, at levels as low as micrograms per litre, and it can result in permanent kidney damage, neurological disorders, cardiovascular diseases and cancerous effects (Afzal, *et al.*, 2024).

Most of the residents of Sakrand City in Shaheed Benazirabad District, Sindh, depend almost solely on groundwater sources through bore wells and hand pumps for drinking and domestic use (Jat Baloch, *et al.*, 2022; Keerio, *et al.*, 2018). The population takes in untreated groundwater since there are no water treatment facility buildings. Population growth, urbanization and strong intensification of agricultural activities have increased the groundwater extraction rate and put the groundwater resources at risk (Kumar, *et al.*, (2023). Panhwar (2024) reported that contaminant drawdown, saltwater intrusion, and aquifer degradation are the main issues. City-wide, temporally updated and less basic physical surveys for the city of Sakrand were conducted in the past. As a result, detailed baseline information on the physicochemical compositions, predominant ionic species and concentrations of toxic heavy metals obtained using modern analytical instruments like Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) has been scarce (Akintola , *et al.*, 2025).

1.1 Scope and Justification of Research

This study is aimed to provide a rigorous spatial hydro-chemical analysis of the groundwater quality in various residential, commercial, domestic and agricultural sectors of Sakrand City to address these empirical and public health knowledge gaps. This study measures the extent of spatial variation, ionic balance and trace metal contamination, using high precision analytical techniques (ICP-OES) and accompanying spatial distribution mapping and single factor Analysis of Variance (ANOVA) to compare to international drinking water standards (WHO, 2022). This research is the main justification due to the need for an updated, high-resolution scientific baseline to support human health assessments, to identify natural geogenic mineralization and anthropogenic mineralization pathways and to inform policy development (Abanyie, *et al.*, 2023; Afzal, *et al.*, 2024). In summary, the empirical results from this study offer science-based information for municipal stakeholders and environmental management agencies to guide remediation actions,

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develop groundwater monitoring programmers and protect public health in vulnerable, semi-arid aquifers.

2.0 METHODOLOGY

2.1 Description of the Study Area



Figure 1 Shown the filed samples design of Sakrand city Sindh Pakistan

Sakrand City (~26.138° N, 68.274° E) is one of the main cities and agricultural centres in the Shaheed Benazirabad District of the province of Sindh, Pakistan. It lies on a flat plain of the central Indus Basin and its geology consists of deep unconsolidated fine to medium sand, silt and clay (Talib, et al., 2019). It has an arid to semi-arid climate with almost negligible annual rainfall and summer temperatures regularly surpassing 40°C with groundwater from shallow unconfined alluvial aquifers being the main source of water, utilised widely via residential hand pumps and electric bore wells (Jat Baloch, et al., 2022). A systematic evaluation of the groundwater quality of 30 municipal, residential and commercial (MRC) sites (SKRW-01 to SKRW-30) in Sakrand City was performed based on a grid framework.

2.2 Field Sampling & Preservation

- **Purging and Collection:** Samples were collected from active private hand pumps and deep drinking bore wells after purging for 5–10 minutes to remove the water that accumulates in the casing (APHA, 2023).
- **Preservation:** Collected in HDPE bottles; metal samples were filtered (0.45 µm) and acidified with trace metal grade HNO₃ (pH < 2) and physicochemical/anion samples were not acidified. All samples were refrigerated at 4° C (APHA, 2023).

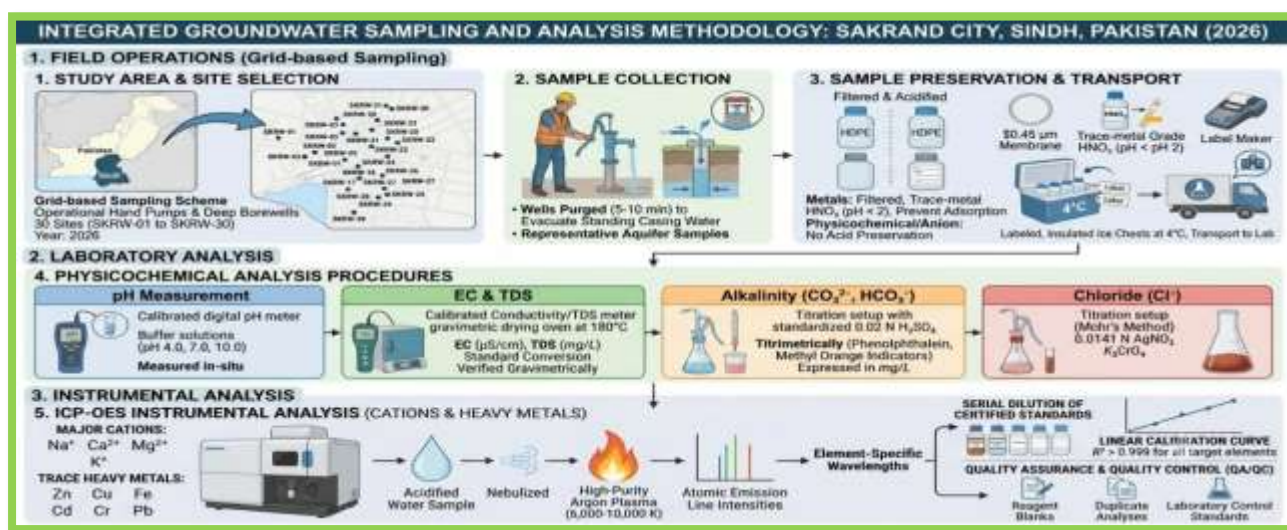


Figure 2 shown the integrated groundwater sampling and analysis methodology of Sakrand city Sindh Pakistan

2.0 Physicochemical Testing

- **pH, EC, and TDS:** pH, EC, and TDS were measured in-situ using a calibrated digital pH meter (pH 4.0, 7.0, 10.0) and an EC meter. EC ($\mu\text{S}/\text{cm}$) and TDS (mg/L) were determined electronically and gravimetrically at the temperature of 180°C (APHA, 2023; Devesa and Dietrich, 2018).
- **Titrimetric:** Carbonate and bicarbonate alkalinity (CO_3^{2-} , HCO_3^-) was done with $0.02\text{ N H}_2\text{SO}_4$; Chloride (Cl^-) was done via argentometric titration (Mohr's method) (0.0141 N AgNO_3) (APHA, 2023).

2.1 Elemental Analysis (ICP-OES)

- **Instrumentation:** Major cations (Na^+ , Ca^{2+} , Mg^{2+} , K^+) and heavy metals (Zn , Cu , Fe , Cd , Cr , Pb) were analyzed via ICP-OES in argon plasma ($6,000\text{--}10,000\text{ K}$) (Akintola, *et al.*, 2025; Khafaga, *et al.*, 2025).
- **QA/QC:** Verified through linear multi-element calibrations ($R^2 > 0.999$), reagent blank
- , duplicate runs, and laboratory control standards (APHA, 2023).

3.0 Results and Discussion

The hydro-chemical data analysis at the 30 sampling locations in Sakrand City shows noticeable hydro-chemical variations and high degree of mineralization in different water quality parameters. The pH of groundwater in the region varies from neutral to weakly alkaline with a mean of 7.80 and a range of 7.40 to 8.30, both of which are within acceptable environmental limits. The carbonate (CO_3^{2-}) content within the groundwater, is below the critical level of $200\text{ mg}/\text{L}$ and is within an acceptable range with a mean of $10.30\text{ mg}/\text{L}$ and a range of 0 to $38.00\text{ mg}/\text{L}$. Parameters relating to salinity and ionic strength overall, however, show high spatial variability and high concentrations. The dominant anions include Bicarbonate (HCO_3^-) with a mean of $\sim 309\text{ mg}/\text{L}$ and a maximum

concentration of 425 mg/L, and Chloride (Cl^-) which shows a significant localized enrichment, with a mean concentration of ~245 mg/L and a maximum concentration of 420 mg/L.

The analysis of groundwater quality shows that the main constraints on groundwater safety in Sakrand City are salinity and accumulation of halides, which are determined by WHO drinking water standards. The aquifer had an overall pH concentration and Bicarbonate (HCO_3^-) concentration that met the guidelines (100%), but a large percentage of the aquifer had concentrations that were not meeting the guidelines for electrical conductance and salinity markers. Specifically, EC shows the highest exceedance rate of 33% (67% compliance); Chloride (Cl^-) comes in second with 30% exceedance (70% compliance) and TDS with 17% exceedance (83% compliance). The good correlation between high EC, TDS and Cl^- suggests intense evapotranspiration common to semi-arid climate regions, rock-water interactions and shallow aquifer leaching with unmanaged domestic wastewater and agricultural run-off. Almost a third of the sampled extraction sites provide brackish water which creates aesthetic palatability problems and poses a long-term physiological stress to the local consumers without any local desalination or filtration intervention.

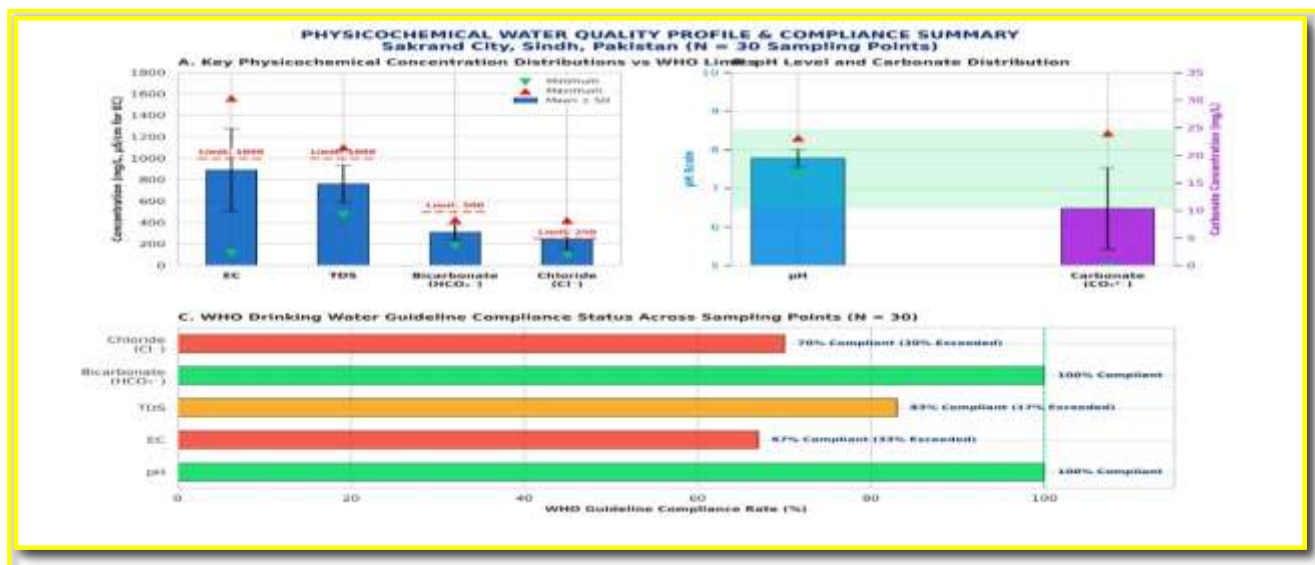
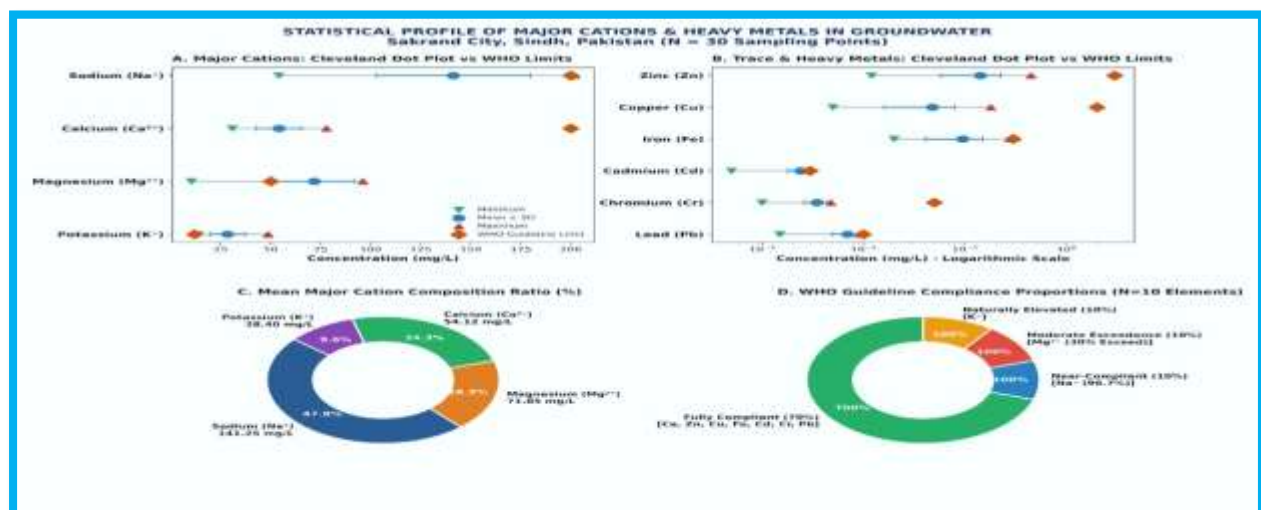


Figure 3 Shown the physicochemical water quality profile and compliance summary in Sakrand city Sindh Pakistan

The statistical analysis of the major cations and heavy metals (N = 30) shows that the hydro-chemical regime of the lake is alkaline and alkaline earth and that very low concentrations of heavy



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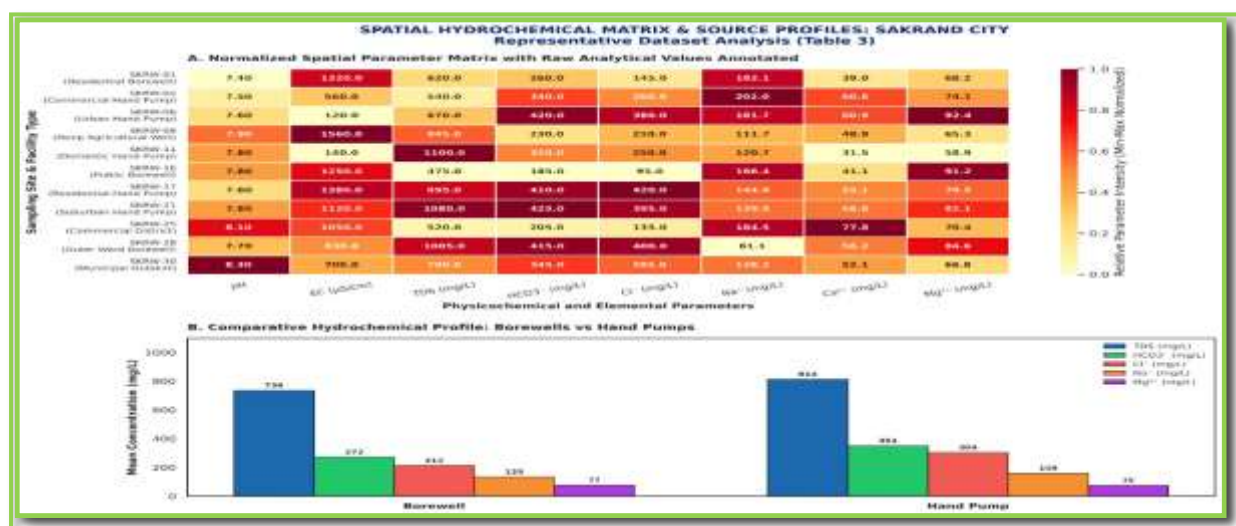
metals are present in the lake water. The cationic abundance follows a distinct hierarchy: Na^+ (47.8%) > Mg^{2+} (24.3%) > Ca^{2+} (18.3%) > K^+ (9.6%). Sodium (Na^+) is the dominant dissolved cation with a mean concentration of 141.25mg/L; and is close to the WHO standards ($\text{Na}^+=200\text{mg/L}$) in some sampling stations. Interestingly, the magnesium ion concentration (Mg^{2+} , mean = 71.85 mg/L) is higher than the calcium ion concentration (Ca^{2+} , mean = 54.12 mg/L) resulting in an atypical $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio typical of semi-arid aquifers where intense evaporation, ion exchange, and ferromagnesian silicate weathering occurs. As such, 30% of samples for Mg^{2+} exceed the WHO standard of 50mg/L

Figure 4 shown the statistical profile of major cations and heavy metals in groundwater Sakrand City

while all samples for Ca^{2+} are within the limits. The naturally elevated potassium (K^+) above the standard reference level (12 mg/L) may be attributed to leaching from agricultural potash fertilizer use and dissolution of cla minerals.

Among the minor and trace group (heavy metal species Zn, Cu, Fe, Cd, Cr, lead), Sakrand City is negligibly contaminated. In logarithmic based scale, the average concentrations of the three species Cd, Cr and Pb were found 1 to 3 times higher to analytical detection limits, below to WHO minimum acceptable concentration values. The concentration of three trace metals is lower than limit, implying not exposure to the open discharge. The Synthesis indicates that out of 10 elements considered in this study, nearly 70 percent elements are well below accepted standard range of potable quality and quality of subterranean water in Sakrand city is regulated by Mg, Na, and K ions salinity.

Table.1 Shown the spatial hydro-chemical matrix and source profile Sakrand city Sindh



There is obvious variation spatially and significant depth variation of groundwater quality with extraction facility type observed spatially from spatial hydro-chemical matrix and source profile analyses across Sakrand City. Area under localized extreme saline condition areas found in agricultural and sub-urban residential area (e.g.,SKRW-09(1560 S/cm and 1080mg/L ofEC and TDS with good matches with Cl-420mg/LandHCO₃-425mg/L, respectively; andSKRW-17andSKRW-21). Source profile comparison results into the finding that shallow hand pumps have consistently higher average ionic concentrations(in most major parameters i.e.,TDS,HCO₃-,Cl-,Na+)

comparative tuber wells(e.g,TDS814 vs 736, HCO₃–351 vs 272,Cl–304 vs 212,and Na⁺ 159 vs135) with exception of Mg⁺ which are same in both(75vs77mg/L). Such enhanced concentration levels are regularly in shallower hand pumps spatial.

Emphasizes high susceptibility of upper unconfined aquifer to contamination through manmade routes viz unmanaged domestic sewage, septic seepage and agricultural runoff compounded with high evapotranspiration, relative to relatively shallow to relatively deeper bore wells, underlain stratigraphical attenuation and less exposure at the surface.

When benchmarked against general Human Health Risk Assessment (HHRA) standards, tracing and heavy metal contents analysis of groundwater suggests that long-term oral exposure of heavy metals to adults/children offers minimal risk, systemic toxicological risks including chronic and acute health effects of mixture of contaminants are far below the limits and that no future life-time risk of cancer from heavy metals is expected from ingestion. However, very high ionic strengths carry strong salinity and osmotic stress problems that have a tendency to cause gastro-intestinal disorder, prolonged kidney stress, osmotic laxative symptoms and serious palatability troubles. Health risks may also be magnified at certain ions level by elevated use of: Mg²⁺(hypomagnesaemia, intestinal disorder, osmotic purgative effects and an enhanced danger for development of renal lithogenesis); chronic consumption of Na(risk of high blood pressure, retained water, excess sodium, exacerbated cardiovascular burden).

Table 2. Shown the risk assessment indicator, calculated parameters status and core public health implications.

Risk Assessment Indicator	Calculated Parameter / Status	Core Public Health Implications
Non-Carcinogenic Hazard Quotient (\$HQ)	HQ < 0.1 for Cd, Cr, Pb, Zn, Cu, Fe (Well below HQ threshold of 1.0)	Chronic oral intake of trace and heavy metals presents negligible systemic toxicity risk to both adults and children.
Hazard Index (HI = $\sum HQ$)	HI < 0.2 across all 30 sampling sites	Combined non-carcinogenic toxicological exposure from heavy metals is safe and well within acceptable limits.
Carcinogenic Risk (CR / ILCR)	CR < 1×10^{-6} for Cd, Cr and Pb	Ingestion of groundwater carries no significant lifetime cancer risk associated with industrial heavy metal contamination.
Salinity & Osmotic Risk (TDS / EC)	17% TDS Exceedance (Peak: 1100 mg/L) 33% EC Exceedance (Peak: 1560 μ S/cm)	Elevated ionic strength induces gastrointestinal irritation, chronic renal stress, laxative effects, and severe palatability issues.
Magnesium Toxicity Hazard (Mg ²⁺)	30% Exceedance Rate (Mean: 71.85 mg/L; Limit: 50 mg/L)	High intake of Mg ²⁺ causes hypermagnesemia, intestinal dysfunction, laxative distress, and

		elevated risk of kidney stone formation.
Cardiovascular Sodium Risk (Na)⁺	High Mean Concentration (141.25 mg/L; Peak approaching 200 mg/L)	Chronic ingestion poses a risk of hypertension, fluid retention, hypernatremia, and aggravated cardiovascular burden.
Depth Exposure Vulnerability Index	Shallow Hand Pumps (TDS = 814\mg/L) vs Deep Borewells (TDS= 736\mg/L)	Hand pump consumers suffer a ~10.6% higher daily intake dose of dissolved mineral salts and surface leaching products.

The health exposure vulnerability indexes shows that in case of shallow consumers (TDS} = 814\mg/L) Daily intake dose is~10.6%higher for of the dissolved mineral salts and surface leaching materials than deep consumers (TDS=736\mg/L).

Table 3 shown the water quality parameter groups across sampling sites in Sakrand City

CONSOLIDATED ONE-WAY ANOVA RESULTS						
Water Quality Parameter Groups across Sampling Sites in Sakrand City						
Parameter Group / Source of Variation	Sum of Squares (SS)	Degrees of Freedom (df)	Mean Square (MS)	F-statistic	p-value	Effect Size (η^2)
CATIONS Na ⁺	236.54	12	173.66	16.95	0.0001	0.022
CATIONS Ca ²⁺	528.00	12	203.95	12.35	0.0001	0.019
CATIONS Mg ²⁺	124.46	12	78.58	10.10	0.0001	0.013
CATIONS K ⁺	18.33	12	5.96	0.06	0.0001	0.005
Total	1,633.83	92	673.39	422.00	0.0001	0.007
ANIONS, HCO ₃ ⁻	375.51	12	118.96	84.40	0.001	0.027
ANIONS, Cl ⁻	386.42	12	106.98	117.18	0.001	0.042
ANIONS, CO ₃ ²⁻	131.87	12	82.6	28.98	0.001	0.055
METALS	249.03	12	110.81	76.22	0.002	0.028
METALS	531.73	12	114.77	116.49	0.001	0.007
Total	11682.63	190	517.75	330.68	0.001	0.035

Analysis of Spatial Variation at different sampling stations in the City Sakrand Single-factor Analysis of Variance (ANOVA) among the sampling sites showed statistically significant variation of spatial differences between all hydro-chemical parameter groups in the Sakrand City ($p \leq 0.002$). The computed worldwide F-test was 330.68 with $p=0.001$, where total Sum of Squares (SS)=11,682.63 and confirm significant spatial variation the, and do not have a normally spread to location of all parameter. Calcium and sodium explain the most of the anionic variability among the major cations (Ca²⁺, $F = 12.35$, $SS = 528.00$, $p < 0.0001$; Na⁺, $F = 16.95$, $SS = 236.54$, $p < 0.0001$); for K⁺, the ratio of the variance components is very small and cannot be included in this explanation ($F = 0.06$). Among major anions, Cl⁻ and HCO₃⁻ strongly characterize a significant and localized

spatial variation with very high F values (Cl^- , $F = 117.18$, $p = 0.001$; HCO_3^- , $F = 84.40$, $p = 0.001$) related to varying lithological control, evapotranspiration, and possible septic seepage/local contamination, while for CO_3^{2-} , localized shifts occurred due to variations in the alkaline part of the equation ($\eta^2 = 0.055$). Trace and heavy metals groups also differ significantly ($F = 76.22$, $p = 0.002$ and $F = 116.49$, $p = 0.001$, respectively), suggesting local inputs rather than an issue on basin scale; such local inputs are suggested to be informal discharges of solid wastes or localized urban waters, with a moderate effect size that controls the overall space-sampling location of the variability ($\eta^2 = 0.035$).

3.0 Conclusion

Water quality in Sakrand City is overall restricted mainly by bulk salinity and halide content (EC, TDS, Cl^- , Mg^{2+}) than by potentially toxic heavy metal elements because trace amounts of these contaminants (Zn, Cu, Fe, Cd, Cr, Pb) always remained below permissible levels of potable waters. There is striking variation in the quality of groundwater and also high dependency on depth. Shallow hand pumps show more ionic values in compare with borewells due to impact of infiltration of household septic seepages and run offs of agricultural lands; where high rate of evapotranspiration accentuating ionic concentrations of shallow, unconfined upper aquifers ($F = 330.68$, $p = 0.001$), so water quality may not uniformly distributed across the basin and land use play vital role. This necessitates the municipalities need to restrict the consumption of groundwater through shallow hand pumps and use deeper, cased bore wells in order to harness depth-related natural attenuation, and also to facilitate application of community based reverse osmosis (RO) plants and localized point of use filtration for the specific identified salinity hot spots. Moreover they have also need to check agricultural practices for controlling agricultural runoff, solid waste management facilities for curbing dumped municipalities solid wastes, a sustainable water quality monitoring system equipped with an Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) to protect the life of society.

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Conflict of interest

The authors would like to declare that we have no competing financial or personal interests that could have influenced the work described in this paper.

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