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## Article

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# Hydrogeochemical Appraisal and Human Health Risk Assessment of the Geogenic Fluoride Crisis in Al-Musaymir's Drinking Water: From Neurodevelopmental Hazards to Sustainable Remediation

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**ABSTRACT:** Drinking water quality in Yemen's Al-Musaymir District presents a severe geogenic crisis, masked by a dangerous 'Deceptive Visual Clarity' paradox. This pioneer study provides a multidimensional appraisal of 17 surface wells, integrating a 15-parameter suite with advanced multivariate modeling (PCA/HCA) and human health risk assessments. PCA (81.57% variance) and Pearson correlation ( $r=0.71$ ) confirmed that fluoride enrichment is driven by alkaline leaching within the Jurassic Nayfa formations. While 100% of samples met aesthetic standards, WQI modeling unmasked a catastrophic 82.35% failure rate were classified as 'Very Poor' to 'Unsuitable' (Class IV–V) due to geogenic fluoride enrichment (Mean 2.57 mg/L). Piper Trilinear analysis identified Na-Cl and Mixed Ca-Mg-Cl-SO<sub>4</sub> types, while irrigation appraisal revealed a 'Double Burden' of low sodicity (SAR 6.8) but extreme salinity (EC 1996.9  $\mu\text{S/cm}$ ). Toxicologically, the pediatric Hazard Quotient (HQ) reached 6.33, strictly aligning with NTP (2024) neurotoxicity standards. To resolve this, the study validated a sovereign remediation strategy using locally sourced, 99.73% pure Wadi Nakhleen limestone. The reactor reduced fluoride from critical peaks (5.7 mg/L) to <0.40 mg/L within three hours, providing an economically viable and culturally aligned blueprint to safeguard the cognitive and physical trajectory of groundwater-dependent communities in arid basins.

**Keywords:** Multivariate Statistical Modeling; Pediatric Neurotoxicity; Wadi Nakhleen Reactor; Hazard Quotient (HQ); IQ decline; Adsorptive filtration; Yemen; Drinking Water Quality.

## 1.Introduction

The scientific prioritization of Yemeni geological assets for environmental remediation represents a sovereign research trajectory initiated by our group at the University of Aden prior to 2019. This systematic journey began with the foundational geochemical mapping by **Ahmed et al.<sup>1</sup>**, which first identified the Jurassic Nayfa Formation in Wadi Nakhleen as a high-purity source of calcium carbonate. This baseline was subsequently solidified by **Saleh et al.<sup>2,3</sup>** whose chemical protocols revealed a unique purity fingerprint of 99.73 percent in these strata, pioneering their use for geogenic fluoride removal.

Expanding this conceptual framework, **Al Hariri et al.<sup>4</sup>** in an investigation conducted under the principal author's doctoral supervision utilized advanced spectroscopic techniques (FTIR, XRF, and TGA-DTA) to validate the selective efficiency of this mineral for toxic heavy metal sequestration. Building upon this cumulative expertise, the present 2026 investigation represents the operational culmination of our work, linking to the recent technical validations by **Nasser<sup>5</sup>** and the multi-regional hydrochemical expertise established in studies across Zabid <sup>6,7,8</sup>, the Tuban Delta<sup>9</sup> Sharaa and Kirsh, Lahj Governorate <sup>10</sup> and Al-Dhalea <sup>11</sup>.

Water intended for human consumption must be free from chemical concentrations that pose a hazard to health, a principle established by **WHO<sup>12</sup>** and reinforced in modern guidelines<sup>13,14</sup>. Crucially, fluoride ingestion triggers complex metabolic pathways, involving high-affinity binding to calcified tissues and potential systemic toxicity across multiple organ systems<sup>15</sup>. However, Al-Musaymir District faces a critical geogenic fluoride crisis, where visually pristine water masks toxic mineral burdens—a phenomenon we term the '**Deceptive Visual Clarity' paradox**. By integrating advanced multivariate modeling (**PCA/HCA**) and the **Water Quality Index (WQI)** with **high-resolution health risk assessments** aligned with **National Toxicology Program (NTP, 2024)<sup>16</sup> neurotoxicity standards**, this study provides the definitive scientific blueprint for resolving fluoride-induced developmental risks in rural Yemen.

**OVERARCHING GOAL:** To provide an integrated hydrogeochemical and toxicological appraisal of the geogenic fluoride crisis in Al-Musaymir's aquifers, quantifying pediatric neuro-developmental risks through the Hazard Quotient (HQ) model and validating a sustainable remediation strategy using high-purity locally sourced limestone.

**The primary objectives of this pioneer study are:**

1. To evaluate the physicochemical profile of Al-Musaymir's surface wells and determine compliance with **WHO and Yemeni National Standards**

2. To quantify the overall potability of the aquifer using the Water Quality Index (WQI) to unmask the '**Deceptive Visual Clarity**' paradox.
3. To decipher the hydrochemical evolution and geochemical facies of the basin through **Piper Trilinear Diagram analysis**.
4. To assess agricultural sustainability risks by evaluating **Salinity Hazards and the Sodium Adsorption Ratio (SAR)** in the context of arid-zone irrigation.
5. To isolate the hydrochemical drivers of fluoride enrichment through **multivariate modeling (PCA/HCA)**, distinguishing geogenic water-rock interactions from localized anthropogenic nitrate contamination.
6. To quantify the non-carcinogenic health hazards for children and adults using the **Hazard Quotient (HQ) model**, specifically modeling **pediatric developmental neurotoxicity risks** by aligning local exposure data with the **NTP (2024)** global benchmarks and the established **IQ-decline threshold (>1.5 mg/L)**.
7. To validate the technical efficacy of **99.73% pure locally sourced Wadi Nakhleen limestone** as a sustainable and cost-effective national remediation prototype.
8. To establish a strategic public health blueprint that bridges the analytical 'Deceptive Visual Clarity' paradox with field-validated engineering solutions to safeguard communities reliant on shallow surface-well water resources.

## 2. MATERIALS AND METHODS

### 2.1. Study Area and Sampling Design

This investigation was conducted in the Al-Musaymir District (Lahij, Yemen), where the community relies on 17 shallow surface wells for potable needs. Strategic sampling was executed between August and December 2021 to capture the dry-season hydrogeochemical profile. All sites were georeferenced via GPS, with well depths (6.8–28 m) recorded to characterize the shallow aquifer (**Fig. 1**). Detailed coordinate metadata and site-specific depths are curated in **Table 1** and **Table S1 (Supplementary Materials)**.

### 2.2. Instrumentation and Analytical Procedures

Surface water quality was assessed through an integrated suite of 15 physicochemical parameters following the standard protocols of the American Public Health Association (APHA)<sup>17</sup>. In situ measurements for pH, Temperature, Electrical Conductivity (EC), and Total Dissolved Solids (TDS) were conducted using a pre-calibrated HACH HQ40D multi-parameter meter. Laboratory determination of turbidity utilized a HACH DR 900 spectrophotometer, while Fluoride (F<sup>-</sup>) and Nitrate (NO<sub>3</sub><sup>-</sup>) were quantified via a HACH DR 5000 UV-VIS

spectrophotometer employing the SPADNS and cadmium reduction methods, respectively. Analytical validation was performed—covering linearity, sensitivity limits (LOD/LOQ), precision, and accuracy—to ensure the electrochemical integrity and reproducibility of the geogenic mineral data presented in this study.

### 2.3. Data Integrity and Quality Control (ICBE)

To guarantee the reliability of the **hydrogeochemical** dataset, the **Ionic Charge Balance Error (ICBE)** was calculated for the **15 measured parameters** across all **17 samples (Table S1; Supplementary Materials)**. In strict accordance with **Appelo and Postma**<sup>18</sup> and **Rashid et al.**<sup>19</sup> an acceptance limit of **±5%** was enforced to validate the electrochemical neutrality and analytical completeness of the data.

### 2.4. Integrated Water Quality and Irrigation Suitability Indices

To integrate the multi-parameter chemical suite into a single regulatory snapshot of drinking water suitability, the Water Quality Index (**WQI**) was calculated using the weighted arithmetic method. The computation followed a three-stage probabilistic approach: (i) assigning relative weights ( $w_i$ ) to the **15** parameters based on their toxicological significance; (ii) calculating the unit weight ( $Wi$ ); and (iii) determining the quality rating ( $qi$ ) for each ion using Equation (1):

$$Wi = \frac{wi}{\sum_{n=1}^n wi} \quad (1)$$

**Where:**

$Wi$ : The relative weight;  $w_i$ : The weight of each parameter; n: The number of parameters.

The calculated relative weight ( $Wi$ ) values and the **WHO standards** for each parameter were of each parameter<sup>7,13,20,21</sup> are presented in **Table S2 (Supplementary Materials)**.

The third step, quality rating scale ( $qi$ ) was calculated for each parameter calculated by using equations. (2):

$$qi = \frac{ci}{si} \quad (2)$$

**Where:**

$Ci$ : Concentration of Concentration of each chemical parameter in each water sample in mg/L;

$Si$ : The WHO standard for each chemical parameter in **mg/L**.

Finally, the ( $SLi$ ) calculated for each parameter calculated by using  $Wi$  and  $qi$ . Then the water quality index (**WQI**) was calculated as the following equations<sup>22</sup>:

$$SLi = Wi \times qi \quad (3)$$

$$WQI = \sum_{n=1}^n Sli \quad (4)$$

The classification framework used to categorize the 17 wells (ranging from 'Excellent' to 'Unsuitable')<sup>23-25</sup> is detailed in **Table S3 (Supplementary Materials)**.

Simultaneously, the Sodium Adsorption Ratio (SAR) was calculated to quantify the potential for soil permeability degradation and agricultural risk, using the deterministic model established by **Richards**<sup>26</sup>:

$$SAR = \frac{Na^+}{\sqrt{\frac{Ca^{+2} + Mg^{+2}}{2}}}$$

For Equation (SAR), all ionic concentrations were converted into milliequivalents per liter (meq/L) to ensure geochemical balance. The calculated SAR values were subsequently cross-referenced with the **Wilcox**<sup>27</sup> and USSL salinity diagrams to determine long-term irrigation viability, as summarized in **Table S4 (Supplementary Materials)**<sup>26,27</sup>.

## 2.5. Advanced Multivariate Statistical Modeling and Geochemical Facies Identification

To decipher the geogenic drivers and identify contamination hotspots, advanced statistical processing was conducted using **IBM SPSS Statistics (Version 25.0) (IBM Corp)** and **Origin**<sup>28,29</sup>. Descriptive statistics were compared against **WHO**<sup>13</sup> and **Yemeni standards**<sup>30</sup> to evaluate compliance. Spatial significance was confirmed via **one-way ANOVA (p < 0.05)**, while **Principal Component Analysis (PCA)** and **Hierarchical Cluster Analysis (HCA)** using **Ward's method**<sup>31</sup> were applied for source apportionment and spatial zonation. Furthermore, hydrogeochemical facies were mapped using the **Piper Trilinear Diagram**<sup>32</sup> with visual modeling performed via specialized **Geochemistry Software (e.g., Origin)**<sup>29</sup> to elucidate the dominant rock-water interaction mechanisms

## 2.6. Human Health Risk Modeling Framework (USEPA CDI/HQ Protocols)

To quantify the toxicological threat posed by geogenic fluoride, this study utilized the non-carcinogenic risk model established by the **U.S. Environmental Protection Agency (USEPA)**<sup>33</sup> and **Asgari et al.**<sup>34</sup>, adopting the validation protocols for fluoride-endemic arid regions as established by **Duggal & Sharma**<sup>35</sup> and **Rehman et al.**<sup>36</sup>. Notably, the assessment methodology for non-carcinogenic risks utilized in this study builds upon the successful implementation of the **USEPA health risk framework in Yemeni context (e.g., Al-Alaiy et al.)**<sup>8</sup>, which provided the foundational evidence for household water safety in Zabid City. The assessment focused on two vulnerable groups: **adults** and **children**. The mathematical

framework for calculating the **Chronic Daily Intake (CDI)** and the **Hazard Quotient (HQ)** were calculated in the following:

$$CDI = \frac{CM \times IR \times EF \times ED}{BW \times AT} \quad (1)$$

**Where:**

**CM (mg/L):** Concentration of fluoride in water; **IR:** Drinking water ingestion rate (L/day); **EF:** The exposure frequency (Days/year); **ED:** The exposure duration (year) **Ahada & Suthar**<sup>37</sup>; **BW:** Body weight (kg); **AT:** The average resident time (days/year).

$$HQ = \frac{CDI}{RfD} \quad (2)$$

**Where:**

**Rfd** is reference dose (in **mg/kg day**) for the fluoride (**USEPA; IRIS**)<sup>33,38</sup>.

The specific input parameters, exposure factors, and toxicological constants (such as body weight, ingestion rates, and the oral reference dose) utilized for the Al-Musaymir population are detailed in **Table 2**.

## **2.7. Forward-Looking Modeling Framework: Bridging External Exposure and Internal Dose**

Given the critical pediatric neuro-risk identified (**HQ = 6.33**), this study advocates a transition toward Physiologically Based Pharmacokinetic (PBPK) modeling, aligning with **NTP**<sup>16</sup> neurotoxicity benchmarks and **Tan et al.**<sup>39</sup>. This integrated framework aims to bridge the gap between external fluoride concentrations in Al-Musaymir's wells and internal biological doses (e.g., plasma and brain) to assess cognitive vulnerability in children under 12. Establishing this baseline is a prerequisite for future longitudinal tracking and high-resolution biosampling in this high-temperature geogenic hotspot.

## **2.8. Characterization of Geogenic Remediation Media and Technology**

The remediation media utilized in this study consist of three distinct geogenic natural raw limestones sourced from the Jurassic Nayfa Formation in Southern Yemen (Wadi Nakhleen, Wadi Saim, and the Bates region). Building upon the research trajectory of the University of Aden<sup>1-5</sup>, these materials were compared against industrial cement-grade samples to evaluate their geochemical superiority. Mineralogical purity and structural properties were verified using an integrated suite of X-ray Fluorescence (XRF - Axios Pw4400), ICP-OES (PerkinElmer), FTIR (Perkin-Elmer 1750X), and Simultaneous TG-DTA (STA449C, Netzsch).

## **2.9. Sovereign Mineral Sourcing: Selection of the Defluoridation Media**

The selection of the defluoridation media was strategically based on foundational geological surveys and mineral prospecting conducted between **2001** and **2005** by the Geological Survey and Mineral Resources Board (GSMRB-Aden) and the National Cement Company (NCC) <sup>1</sup>. These early investigations established the high-purity baseline of the Jurassic Nayfa Formation in Wadi Nakhleen, identifying it as a premium industrial asset for cement production. Building upon this established geological framework, the authors of the present study pioneered the application of these pristine geogenic resources for environmental remediation. While the deposits were historically identified for industrial use, this research represents the inaugural utilization of Wadi Nakhleen limestone as a high-efficiency adsorbent for fluoride removal from drinking water and the elimination of toxic heavy metals from industrial effluents <sup>4,20,40</sup>. To ensure a rigorous mineralogical appraisal, raw limestone samples (4-5 kg) were strategically collected from natural geogenic outcrops in three distinct regions: **(1) Wadi Nakhleen** (Jurassic Nayfa Formation), **(2) Wadi Saim**, and **(3) Bates Region**<sup>1</sup>. The preparation of the defluoridation media followed a dual-pathway protocol. For chemical fingerprinting, sub-samples were pulverized to a 0.07 mm grain size for comprehensive silicate analysis <sup>41</sup>. For adsorptive filtration, the limestone was crushed and sieved to a uniform chip size of 0.5–1.0 cm. Laboratory defluoridation trials were systematically conducted to evaluate the removal performance of these materials. These experiments utilized both natural water samples from the study area and synthetic solutions with high fluoride concentrations (10 mg/L)<sup>2,5,42</sup>. The analytical protocols for monitoring defluoridation efficiency and kinetics in the laboratory were performed in accordance with the established frameworks of **Saleh et al. and Nasser** <sup>2,5</sup>.

### **3. RESULTS AND DISCUSSION**

The evaluation of **17 surface wells** in the Al-Musaymir District reveals a critical hydrogeochemical disparity: while the water appears physically pristine, it harbors a severe chemical crisis. This study transitions from baseline characterization to advanced health risk modeling, unmasking a **Deceptive Visual Clarity paradox** where **82.35% of samples** are chemically unfit for consumption due to **geogenic fluoride enrichment (Mean 2.57 mg/L; Max 5.7 mg/L)**.

#### **3.1. Technical Validation and Statistical Reliability**

Prior to hydrogeochemical interpretation, analytical rigor was confirmed via a comprehensive validation framework. The fluoride determination method exhibited exceptional linearity (**R<sup>2</sup>=0.9998**) with high sensitivity (LOD: **0.02 mg/L**; LOQ: **0.07 mg/L**), as detailed in **Figure 2 and Table S5 (Supplementary Materials)**. Precision and accuracy were verified through

intraday and interday assessments, yielding Relative Standard Deviation (RSD%) values below 1.185% and recovery rates ranging from 99.84% to 101% (**Table S6; SI**).

Most importantly, the Ionic Charge Balance Error (**ICBE**) for the 15-ion suite was maintained within  $\pm 5\%$  (**Mean ICBE = 2.15%**), providing the "**analytical backbone**" for the reported geochemical trends (**Fig. 3**). Spatial variations were further confirmed as statistically significant via **one-way ANOVA ( $p < 0.05$ )**, ensuring the observed fluoride "hotspots" are geogenic realities rather than random fluctuations.

This high degree of electrochemical balance confirms that all major cations and anions were accurately quantified, providing a robust 'analytical backbone' for the subsequent WQI modeling and health risk assessments.

### **3.2. Hydrogeochemical Characterization and Integrated Quality Appraisal**

The hydrogeochemical profile of Al-Musaymir's wells reveals a profound '**Deceptive Visual Clarity**' Paradox (**Table 3; Figure 3**)<sup>13,21,30</sup>. While **100%** of sources align with international aesthetic standards for **pH ( $7.48 \pm 0.19$ )** and **turbidity ( $1.37 \pm 0.85$  NTU)**, this physical transparency masks a catastrophic chemical burden. In contrast to the aesthetic compliance, the chemical integrity is severely compromised, showing massive failure rates for **fluoride (82.35%)**, **EC (100%)**, and **TDS (88.24%)**. This disparity creates a "**false sense of security**" among the community, who perceive the water as pristine despite its inherent geogenic toxicity. To ensure a comprehensive suitability appraisal, parameters lacking **WHO**<sup>13</sup> or **Yemeni benchmarks**<sup>30</sup> (e.g., **Mg<sup>+2</sup>**, **K<sup>+</sup>**, **PO<sub>4</sub><sup>-4</sup>**, **HCO<sub>3</sub><sup>-</sup>**), were evaluated against **USPHS standards**<sup>20</sup>. Notably, while the regional failure rate for **EC** appears low under **Yemeni limits (2500  $\mu\text{S/cm}$ )**, it escalates to a staggering **88.24%** when aligned with **WHO** palatability guidelines (**1500  $\mu\text{S/cm}$** ), confirming an intense, invisible mineral burden. Crucially, **Sample-16 (1.5 mg/L)** was intentionally categorized as '**Unsafe**' via a rigorous application of the precautionary principle. Given Al-Musaymir's high-temperature environment and the resulting pediatric **HQ of 1.67**, this 'borderline' well poses a significant neuro-skeletal risk for children, justifying immediate defluoridation priority.

#### **3.2.1. Systematic Failure of Mineral and Fluoride Integrity**

A cornerstone of this study is the application of the precautionary principle to borderline data. While 100% of samples meet physical limits, the chemical integrity is severely compromised:

- **Mineral Overload (EC & TDS):** Using the stringent **WHO** palatability guideline (**1000  $\mu\text{S/cm}$** ), we recorded a **100%** failure rate for Electrical Conductivity (**EC**). Even against flexible regional thresholds (**1500  $\mu\text{S/cm}$** ), the failure rate remains critical at **88.24%**. The **mean TDS (1257 mg/L)** is significantly higher than levels in other arid centers like **Riyadh**

(706.5 mg/L)<sup>43</sup>, serving as a "geochemical signature" of intense rock-water interaction within the Jurassic Nayfa formations<sup>1</sup>.

- **The Fluoride Crisis:** fluoride (F<sup>-</sup>) represents the most critical threat, ranging from 1.1 to 5.7 mg/L (Mean 2.57 ± 1.19 mg/L). Remarkably, 82.35% of samples fail safety limits. We deliberately classified **Sample-16 (1.5 mg/L)** as '**Unsafe**' because Al-Musaymir's high-temperature environment triggers elevated ingestion rates, resulting in a pediatric Hazard Quotient (HQ = 1.67) that significantly exceeds safety thresholds.
- **Anthropogenic Overlays:** A 23.53% failure rate for Nitrate (NO<sub>3</sub><sup>-</sup>) identifies localized anthropogenic 'hotspots' (e.g., **Samples 4 and 6**), likely linked to **agricultural runoff**, complicating the geogenic risk profile.

**Internationally**, the fluoride burden in Al-Musaymir parallels endemic zones in **Punjab, India** (Avg 2.54 mg/L)<sup>37</sup> and **Isa Khel, Pakistan** (Avg 1.8 mg/L)<sup>36</sup>, where similar hydrogeological interactions dictate toxicity. Collectively, these results confirm that visual clarity in Al-Musaymir is a mask for a verified public health emergency, necessitating the immediate deployment of the **Wadi Nakhleen Reactor**.

The comprehensive hydrogeochemical data for each individual well (n=17) is presented in the **Supplementary Material (Table S1)**.

### **3.2.2. Holistic Potability Assessment: The Water Quality Index (WQI) Analysis**

To provide a comprehensive evaluation of the 17 surface wells, the **Water Quality Index (WQI)** was computed following the weighted arithmetic framework of **Saleh et al.**<sup>7</sup>. As summarized in **Table 4**, the **WQI** values in Al-Musaymir exhibited a wide range from **89.80 to 221.40**, reflecting a systematic deterioration of chemical integrity despite deceptive physical clarity.

**Interpretation and Spatial Significance:** The **WQI** results reveal that **76.47%** of the sampled sources (13 out of 17 wells) fall into the '**Poor**' to '**Very Poor**' categories (**WQI > 100**), rendering them inherently unsuitable for direct human consumption. The identification of **Sample-5 (WQI = 221.40)** as a "**Very Poor**" quality hotspot is synergistically driven by extreme geogenic mineralization, specifically the peak levels of **TDS (2280 mg/L)** and **EC (3800 µS/cm)** recorded in the district. Crucially, the **WQI** analysis supports the study's application of the **precautionary principle** for borderline cases; **Sample-16 (Abdulkareem well)**, which technically sits at the WHO 1.5 mg/L fluoride limit, yielded an unsuitable **WQI of 101.64**, confirming that its chemical safety is compromised by the cumulative mineral burden. This holistic failure underscores the '**Deceptive Visual Clarity**' paradox, where visual transparency masks a chronic and invisible chemical toxicity.

**Comparative Appraisal: Multi-Regional Synthesis:** Comparing the WQI profile of Al-Musaymir with other arid and semi-arid regions highlights the severity of the geogenic crisis:

- **Local Context (Yemen):** The WQI failure rate in Al-Musaymir is significantly **higher than** that reported for the **Bir Nasser and Bir Ahmed fields (Tuban Delta)**<sup>9</sup>, where water quality was generally more stable despite localized threats. However, it aligns with findings in **Al-Dhalea basin**<sup>45</sup>, where **over-mineralization** and **fluoride** leaching have **similarly** compromised the potability index.
- **Regional Context (KSA):** A stark contrast is observed when compared to **Riyadh, Saudi Arabia**<sup>44</sup>, where over **88%** of samples are classified as 'Excellent' (Class I) with WQI values ranging from 17.5 to 42.0 due to advanced water treatment and management. Conversely, our results mirror the **geogenic patterns in Hafar Albatin (KSA)**<sup>47</sup>, where **47%** of untreated wells were found 'Unsuitable' for drinking (**WQI > 300 in some cases**), confirming that **geogenic basins in the Arabian Peninsula share a common mineral hazard**.
- **International Context:** Al-Musaymir's WQI profile is strikingly **similar** to the **Isa Khel region in Pakistan**<sup>36</sup>, where surface water suitability was severely degraded by fluoride concentrations (up to 5.35 mg/L), leading to a high percentage of non-potable classifications. Furthermore, the findings coincide with rural **Ethiopian highlands**<sup>48</sup>, where unimproved sources frequently failed WQI benchmarks, **necessitating urgent sustainable solutions like the Wadi Nakhleen reactor**.

### **3.2.3. Hydrogeochemical Risk to Agricultural Sustainability: SAR & Salinity Appraisal**

To evaluate the impact of geogenic mineralization on the district's agricultural productivity, the suitability of the 17 surface wells for irrigation was assessed using the Sodium Adsorption Ratio (SAR) and Electrical Conductivity (EC) frameworks of **Richards**<sup>26</sup> and **Wilcox**<sup>27</sup> (**Figure 5**):

#### **A. Salinity Hazard (EC Classification):**

The analysis reveals a severe salinity burden across the Al-Musaymir basin. The measured EC values ranged from 1409 to 3800  $\mu\text{S}/\text{cm}$  (Mean: 1996.9  $\mu\text{S}/\text{cm}$ ). According to the **Wilcox** classification<sup>27</sup>:

- **0% of samples fall into the Low (C1) or Medium (C2) salinity categories.**
- **70.59% of samples (12 wells) are classified as High Salinity (C3) water**, suitable only for plants with good salt tolerance and requiring special drainage management.

- **29.41% of samples** (5 wells, including S-5 and S-7) fall into the **Very High Salinity (C4) category**, rendering them generally unsuitable for irrigation under normal conditions as they may cause severe soil salinization.

#### **B. Sodium Hazard (SAR Classification):**

Despite the high fluoride and salinity, **the Sodium Adsorption Ratio (SAR) values (Mean: 6.8) remained relatively controlled:**

- **100%** of the wells fall into the **Low Sodium (S1)** category (**SAR < 10**), indicating that the immediate risk of soil permeability degradation (sodicity) is low.
- However, the coupling of **High Salinity (C3/C4)** with **Low Sodicity (S1)** creates a complex management scenario (**C3-S1 / C4-S1**), where constant leaching is required to prevent the accumulation of geogenic salts in the root zone.

**The agricultural profile of Al-Musaymir mirrors its drinking water crisis; the water is 'chemically aggressive' toward both human health and soil integrity. The dominance of C3-S1 and C4-S1 classes is a direct result of the intense rock-water interaction and evaporation characteristic of the Jurassic Nayfa formations.**

- **Locally (Yemen):** These findings align with the **Al-Dhalea basin** <sup>45</sup>, where **high mineralization** has compromised agricultural outputs.
- **Regionally (KSA):** The results are strikingly similar to the untreated wells in **Hafar Albatin** <sup>47</sup>, where **53.6% of samples** were grouped in the **C4-S2 category**, highlighting a shared geogenic salinity hazard across the Arabian Peninsula's arid basins.
- **Global Context:** This agricultural risk underscores the 'Double Burden' of fluoride zones; as documented in **Pakistan** <sup>36</sup> and **India** <sup>37</sup>, communities suffering from fluorosis often face simultaneous crop yield declines due to high-EC irrigation water.

#### **3.3. Spatial Dynamics and Geogenic Drivers of Fluoride Contamination**

Fluoride (F<sup>-</sup>) concentrations across the Al-Musaymir district exhibited alarming elevations, ranging from 1.1 to 5.7 mg/L (Mean: 2.57 ± 1.19 mg/L; **Table 3**). While only 17.65% of sources meet WHO safety standards, an overwhelming 82.35% exceed the 1.5 mg/L threshold. A critical feature of this study is the intentional categorization of Sample-16 (1.5 mg/L) as "unsafe" via the precautionary principle. In Al-Musaymir's high-temperature environment, elevated water ingestion rates ensure that even at this threshold, the calculated Hazard Quotient (HQ) remains significantly above the safe limit of 1.0, factoring in chronic exposure and cumulative physiological impacts<sup>36,49,50</sup>.

This pervasive contamination is primarily geogenic, where intense water-rock interactions facilitate the natural leaching of fluoride-bearing minerals (fluorite, apatite, micas) from the region's geological strata <sup>45,51,52</sup>. Spatial analysis confirms significant variability, identifying high-risk "hotspots" that require prioritized intervention <sup>49</sup>. The most critical extreme was recorded at Sample-12 (Ali Nusorah well), reaching 5.7 mg/L—nearly four times the international limit—posing an immediate threat of skeletal fluorosis. Collectively, these findings confirm the 'Deceptive Visual Clarity' paradox: physically pristine water masks a chronic chemical toxicity that is devastating to public health.

### 3.4. Geochemical Facies and Hydrochemical Evolution (Piper Diagram Analysis)

The application of the **Piper Trilinear Diagram (Figure 6)** provides a definitive 'geochemical fingerprint' of the 17 surface wells in Al-Musaymir. The **Cation Triangle** reveals a significant clustering toward the **Sodium (Na<sup>+</sup>)** pole (**Mean: 329.2 mg/L**), indicating advanced silicate weathering and cation exchange activities between the water and the clay-rich sedimentary strata. Simultaneously, the **Anion Triangle** shows a distinct lean toward the **Chloride (Cl<sup>-</sup>)** and **Sulfate (SO<sub>4</sub><sup>-2</sup>)** facies, which is a classic geochemical signature of high evaporation rates in arid environments.

The **Central Diamond** plot categorizes the majority of the sources as **Na-Cl type** and Mixed **Ca-Mg-Cl-SO<sub>4</sub> type**. This finding is critical as it identifies the 'chemical theater' where fluoride enrichment occurs; the dominance of sodium-rich, alkaline environments in Al-Musaymir (**Avg pH 7.48**) facilitates the desorption and solubility of fluoride from minerals like fluorite and apatite embedded in the local rocks. These results are robustly supported by regional and international studies.

**Locally**, Al-Amry et al. <sup>45</sup> observed similar geogenic drivers in the **Al-Dhalea basin**, where rock-water interaction was the primary mechanism for ion enrichment. **Regionally**, in **Hafar Albatin, Saudi Arabia** <sup>47</sup>, identified **Na-Cl and Ca-SO<sub>4</sub>-Cl** facies as indicators of evaporation-crystallization and gypsum-bearing sedimentary aquifers, mirroring the hydrochemical conditions of the Al-Musaymir basin. **Globally**, these findings align with **Rehman et al.** <sup>36</sup> in the **Isa Khel region, Pakistan**, where **Na-Cl** type dominance was directly linked to **geogenic fluoride enrichment and skeletal health hazards**, further validating the 'Pioneer' status of the present study in the Yemeni context.

### 3.5. Multivariate Statistical Modeling of Contamination Drivers (PCA & HCA)

To provide a deeper mechanistic understanding of the fluoride crisis and translate complex hydrochemical datasets into actionable management strategies, **Principal Component Analysis (PCA)** and **Hierarchical Cluster Analysis (HCA)** were performed (Table 5;

**Figure 7)** <sup>28,49,53,54</sup> . This multivariate approach successfully disentangles geogenic fluoride enrichment from complex hydrochemical matrices, providing a robust statistical precedent for interpreting high mineral loadings.

### 3.5.1. Source Apportionment via Principal Component Analysis (PCA)

The selection of two principal components, governed by the Kaiser criterion <sup>55</sup>, explains 81.57% of the total hydrochemical variance in Al-Musaymir.

- **Component 1 (58.45% of variance):** Exhibits **strong positive** loadings ( $>0.70$ ) for **Fluoride, EC, TDS, and pH**. This statistically validates that **F<sup>-</sup> enrichment** in Al-Musaymir is a **geogenic process** driven by intense **water-rock interaction**. The alkaline environment (**Mean pH 7.48**) and high ionic strength (**Mean EC 1996.9  $\mu\text{S/cm}$** ) facilitate the leaching of fluoride-bearing minerals (fluorite and apatite) from the local strata, a mechanism consistent with the findings of **Sridhar et al.** <sup>52</sup> in similar semi-arid basins.
- **Component 2 (23.12% of variance):** Dominated by **Nitrate and Turbidity**, identifying a separate, localized anthropogenic driver likely linked to domestic waste or agricultural runoff.

The statistical decoupling of Nitrate from Fluoride confirms that the crisis is a regional geochemical phenomenon<sup>50,56</sup>. Crucially, the significant **significant communality value ( $h^2 = 0.761$ ) for fluoride** reinforces its dominant geogenic origin, indicating that over **76%** of its variance is governed by the same drivers as mineralization (**Table 5**). The proximity to high-purity (**99.7%**) carbonate formations of Wadi Nakhleen further confirms a mature geochemical environment conducive to F<sup>-</sup> release.

### 3.5.2. Hierarchical Cluster Analysis (HCA) and Risk Zonation

The HCA dendrogram (**Ward's Method**) <sup>31</sup> delineates the study area into three distinct management zones based on **the 15-ion hydrogeochemical fingerprint (Figure 7)**:

- **Cluster I (Safe/Moderate):** Includes wells with limited rock-water interaction.
- **Cluster II (Chronic Endemic):** Represents the widespread geogenic crisis affecting the majority of villages.
- **Cluster III (Emergency Hotspot Zone):** Isolates high-mineralization peaks (e.g., **Sample-12**) where fluoride reaches **5.7 mg/L** and pediatric **HQ reaches 6.33**, necessitating immediate intervention via the **Wadi Nakhleen Reactor**.

### 3.6. Inter-ionic Relationships and Geochemical Leaching Mechanisms

To decipher the geochemical processes governing ionic enrichment in the Al-Musaymir aquifer, a **Pearson Correlation Matrix** was executed (**Table S7; SI**). Following the

interpretative frameworks of **Salifu et al.** <sup>53</sup> and **Naik et al.** <sup>57</sup>, these results provide robust statistical evidence for a predominantly geogenic origin of the fluoride crisis, driven by two primary mechanisms: alkaline leaching and evaporative concentration.

### 3.6.1. Alkaline Leaching and Ion-Exchange Dynamics

A critical finding is the strong positive correlation between **Fluoride** and **pH** ( $r=0.71^{**}$ ;  $p < 0.01$ ). In the alkaline environment of Al-Musaymir (Mean pH 7.48), this relationship indicates an ion-exchange mechanism where **hydroxyl groups** ( $\text{OH}^-$ ) in the surface water displace fluoride ions from the crystal lattices of minerals such as **fluorite** ( $\text{CaF}_2$ ) and **micas** <sup>45,51,52</sup>. This "**Alkaline Leaching**" is a classic hallmark of fluoride-endemic arid basins, where high alkalinity facilitates the mobilization of fluoride into shallow aquifers, as corroborated by **Sridhar et al. and Brindhya and Elango**<sup>52,58</sup>. Furthermore, the significant correlation between  **$\text{Na}^+$  and  $\text{F}^-$**  ( $r = 0.65^{**}$ ;  $p < 0.01$ ) validates the geogenic model, where fluoride enrichment reflects mature rock-water interactions within the Jurassic Nayfa formations<sup>1</sup>.

### 3.6.2. Evaporative Concentration and Mineral Synergy

The exceptionally strong correlation between  **$\text{Cl}^-$  and  $\text{SO}_4^{2-}$**  ( $r = 0.86^{**}$ ;  $p < 0.01$ ) coupled with the high  **$\text{F}^-$  vs. TDS** ( $r = 0.82^{**}$ ;  $p < 0.01$ ) and  **$\text{Na}^+$**  ( $r = 0.65^{**}$ ;  $p < 0.01$ ) relationships provides irrefutable evidence of a unified geogenic mechanism driven by evaporation-dominated interactions. Fluoride exhibits a highly significant synergy with **Electrical Conductivity** (EC;  $r = 0.86^{**}$ ;  $p < 0.01$ ), suggesting that enrichment is intrinsically linked to the overall mineralization of the aquifer. This is consistent with findings in other semi-arid regions where high evaporation rates increase the ionic strength, promoting the leaching of fluoride-bearing minerals <sup>52</sup>. The nearly perfect correlation between **EC and TDS** ( $r=0.99$ ;  $p < 0.01$ ) serves as an internal validation of the analytical precision and consistency of our laboratory measurements.

### 3.6.3. Source Differentiation: Geogenic vs. Anthropogenic

Most importantly, the matrix provides a clear differentiation between natural and human-induced components. The negligible correlation between **Fluoride and Nitrate** ( $r=0.25$ ) confirms that the fluoride burden is not derived from anthropogenic sources such as agricultural fertilizers or domestic sewage, which are instead represented by localized nitrate hotspots. These results, aligning with the source apportionment patterns observed by **Abdipour et al.** <sup>50</sup>, justify the deployment of the **Wadi Nakhleen Reactor**. Using **99.73% pure local limestone** targets this specific geogenic mineral fingerprint, safeguarding the pediatric population from chronic neurotoxic exposure.

## 3.7. Toxicological Risk Appraisal and Clinical Correlation

The evaluation of health risks in Al-Musaymir transitions from qualitative impact classification to quantitative toxicological modeling, revealing a deep-seated public health crisis hidden behind deceptive water clarity.

### 3.7.1. Qualitative Health Risk Categorization and Tiered Pathologies

Following the international frameworks established by **Dissanayake**<sup>59</sup> and **Rehman et al.**<sup>36</sup>, the water sources were categorized into distinct classes based on their potential to induce dental and skeletal pathologies is presented in the **Supplementary Material (Tablets S3 & S8)**. The analysis shows that **58.82%** of the samples fall into **Class 3 (1.5– 3.0 mg/L)**, a range known to promote dental fluorosis in children. More alarmingly, a significant portion of the aquifer represents a severe orthopedic hazard; **17.65%** of the samples fall into **Class 4 (3.0–5.0 mg/L)**, which is associated with both dental and mild skeletal fluorosis, while **5.88%** reach the extreme **Class 5 (5.0–10.0 mg/L)**. Collectively, **23.53%** of the assessed wells **exceed the critical 3.0 mg/L threshold**, posing a direct and irreversible risk of debilitating skeletal fluorosis, a condition characterized by abnormal bone mass accumulation, joint calcification, and spontaneous fractures<sup>60,61</sup>. Crucially, 82.35% of the sources exceed the 1.5 mg/L threshold, which aligns with the **NTP**<sup>16</sup> and **Taylor et al.**<sup>62</sup> consensus linking these concentrations to developmental neurotoxicity and potential declines in children's IQ. While the current study primarily focuses on non-carcinogenic risks, it is essential to note that international classifications include **Class 6 (>10 mg/L)**, where fluoride exposure is under rigorous scientific scrutiny for potential oncogenic associations alongside the threat of crippling skeletal deformities.<sup>14,63</sup> These findings provide the toxicological context for the 'alarming stage' of fluorosis observed among the inhabitants, highlighting that **children under 12** are the most vulnerable cohort to this geogenic chemical burden<sup>16,37</sup>.

### 3.7.2. Quantitative Exposure Modeling and Pediatric Vulnerability

The quantitative **HHRA** modeling, validated against **USEPA** frameworks<sup>33</sup> and **EFSA**<sup>64</sup> benchmarks, provides mathematical proof of a district-wide public health crisis. While 82.35% of samples exceed the chemical fluoride limit, the toxicological model reveals a **100% failure rate for pediatric safety (HQ > 1.0)** (Table 6). Even **Sample-3**, with the **lowest fluoride (1.1 mg/L)**, yields a pediatric **HQ of 1.22**, proving that children in Al-Musaymir are physiologically defenseless against current exposure levels.

### 3.7.3. Strategic Priority Zonation and the Precautionary Principle

To bridge the gap between analytical data and emergency intervention, a priority-based hierarchy was established (Table 6; Table S9; SI). This classification isolates **Sample-12**, **Sample-2**, and **Sample-6 as Level 1 (Critical Emergency) hotspots**, where fluoride peaks at

**5.7 mg/L** and pediatric **HQ reaches 6.33**, necessitating immediate well closure or filtration. A pivotal feature of this assessment is the classification of **Sample-16 (1.5 mg/L)** under 'Precautionary Failure' (Level 3). Although it technically meets the WHO limit, its pediatric **HQ of 1.67** in Yemen's high-temperature environment necessitates a proactive safety approach to prevent cumulative neuro-skeletal damage.

**Scientific Precedence and Priority:** The remediation strategies and priority rankings established in this study are grounded in the academic and chemical blueprints first published by **Ahmed et al.**<sup>1</sup> and **Saleh et al.**<sup>2,3</sup>. These studies originally identified and validated Wadi Nakhleen limestone (**99.73% CaCO<sub>3</sub>**) as the sovereign national benchmark for defluoridation, providing the scientific foundation upon which subsequent international field applications (e.g., **Das et al.**)<sup>42</sup> were later operationalized.

#### **3.7.4. Alignment with Global Neurotoxicity Consensus**

Beyond physical complications, the elevated fluoride levels in Al-Musaymir align with the emerging global consensus regarding developmental neurotoxicity. According to the **National Toxicology Program (NTP)**<sup>16</sup> and systematic reviews by **Taylor et al.**<sup>62</sup>, there is moderate confidence that fluoride concentrations exceeding 1.5 mg/L are consistently associated with declines in children's IQ scores.

These authoritative sources, supported by the **European Food Safety Authority (EFSA)**<sup>64</sup>, highlight that the children of Al-Musaymir face significant cognitive impairments alongside dental disfigurement. This underscores the urgent need for a transition toward Physiologically Based Pharmacokinetic (PBPK) modeling, as advocated by **Tan et al.**<sup>39</sup> and the **U.S. EPA**<sup>65</sup>, to accurately correlate external well exposure with internal biological doses, particularly for sensitive life-stages such as children under 12.

#### **3.7.5. Spatial Risk Zonation and Pediatric Neuro-Toxicological Implications**

The demarcation of **Zone III (Emergency Hotspot)**, centered on **Sample-12 (Ali Nusorah Well)**, unmasks a profound public health emergency. With a peak fluoride concentration of **5.7 mg/L**—nearly four times the international limit—this zone subjects children to a **Hazard Quotient (HQ) of 6.33**. This exposure dose, over six times the safe reference limit (**RfD = 0.06 mg/kg/day**), provides the definitive mathematical evidence for the high prevalence of dental fluorosis, rickets, and skeletal curvatures clinically observed in the district. These multifaceted findings, synthesized in the **Pediatric Neuro-Toxicological Risk Dashboard (Figure 8)**, underscore that routine monitoring is no longer sufficient; the data mandates an immediate shift toward sustainable engineering interventions.

To bridge the gap between multivariate modeling and localized intervention, a spatio-chemical zonation framework was derived from the Hierarchical Cluster Analysis (HCA) (**Table S10; SI**). While **Zone I (Safe/Moderate)** represents only **17.65%** of the sources, **Zone II (Chronic Endemic)** encompasses the majority of the district, where fluoride-induced neuro-vulnerability remains a persistent threat. Most critically, the zonation confirms that **Zone III represents a 'Chemical Emergency'**, dictating the **urgent priority** for deploying **validated 99.7% pure Wadi Nakhleen limestone filters** to safeguard the physical and cognitive trajectory of Al-Musaymir's children.

### **3.8. Comparative Appraisal: Regional and International Synthesis**

The findings in Al-Musaymir reflect a broader national endemic<sup>10,11</sup>. As illustrated in **Table 7**, fluoride concentrations in Al-Musaymir (avg **2.57 mg/L**) rank among the highly contaminated regions in **Yemen**, being notably higher than **Dhamar** city (0.30–1.84 mg/L) reported by **Al-Aizari et al.**<sup>44</sup> and the **Bir Nasser** fields (avg 1.019 mg/L) analyzed by **Saleh and Al-Sallami**<sup>9</sup>. However, these levels are surpassed by extreme peaks in the **Al-Dhalea** basin (up to **18.30 mg/L**) and the hot springs of Shara'a and Kirsh<sup>10</sup>, which exhibit **100%** exceedance rates<sup>45</sup>. This regional variability underscores the urgent need for a comprehensive national study to correlate specific geological formations with population-wide health outcomes.

Beyond the national context, the mineralization levels in Al-Musaymir (Mean TDS **1257 mg/L**) are significantly higher than those reported in urban assessments in **Riyadh, Saudi Arabia** (Mean TDS 706.5 mg/L)<sup>43</sup>. This comparison places Al-Musaymir's water in a high-salinity and high-toxicity category relative to other arid regional capitals. Furthermore, a comparative synthesis of geogenic fluoride and pediatric health risks across **different regions** highlights the critical nature of the Al-Musaymir basin (**Figure 9**). While urban centers like **Riyadh, Saudi Arabia** ( $F^-$ : 0.70 mg/L<sup>43</sup>; HQ: 0.40) and **Romania** ( $F^-$ : 0.14 mg/L; HQ: 0.13)<sup>68</sup>, remain in the safe zone, Al-Musaymir presents a significantly higher chronic risk profile (Mean HQ: 2.85) than reported cases in **Isa Khel, Pakistan** ( $F^-$ : 1.80 mg/L; HQ: 1.62)<sup>36</sup> and **Zahedan, Iran** ( $F^-$ : 2.13 mg/L; HQ: 2.45)<sup>50</sup>. Crucially, Al-Musaymir's peak pediatric HQ reaches 6.33, identifying it as a critical chemical emergency hotspot that surpasses most regional benchmarks documented in recent literature.

### **3.9. Clinical-Environmental Correlation and Verified Health Emergency**

The mathematical evidence provided by the pediatric Hazard Quotient (HQ) values—reaching a critical peak of **6.33**—is directly corroborated by the qualitative humanitarian findings from the **South24 Center report**<sup>69</sup> and the regional hydrogeochemical assessments of **Al-Mahrabi et al.**<sup>66</sup> Field surveys in the neighboring Al-Hussein district, which shares the same Jurassic

Nayfa hydrogeological strata, identified **1,020** infected individuals out of 1,330 sampled (**76.7%**), documenting **high prevalences of spontaneous bone fractures among students** and **chronic skeletal** rickets. These clinical outcomes are chemically justified by the regional benchmarks of **Al-Mahrabi et al.** <sup>66</sup>, who documented extreme geogenic fluoride peaks reaching **13.30 mg/L** (mean **3.67 mg/L**) (see of **Table 7**) <sup>9,10,11,44,46,66,67</sup>.

**Notably, a strategic comparison reveals that while the Al-Hussein district recorded higher individual peaks, the Al-Musaymir basin (present study) exhibits a significantly higher systematic failure rate (82.35% vs 66.7%) (Table 7).** This indicates that the fluoride crisis in Al-Musaymir is more pervasive and spatially consistent, affecting a larger proportion of the population relative to the sampled sources. The synergy between these clinical reports and chemical failure rates confirms that the geogenic fluoride crisis has transitioned from a hidden chemical burden into a verified public health emergency. This necessitates the immediate nationwide deployment of the **Wadi Nakhleen Reactor** to safeguard the physical and cognitive integrity of communities in Al-Musaymir and beyond.

### **3.10. Performance of Sovereign Remediation Media: Validation of the Wadi Nakhleen Reactor**

#### **3.10.1. Geochemical Superiority and Molecular Fingerprinting**

The chemical characterization (**Table 8**) confirms that Wadi Nakhleen limestone possesses an exceptional geogenic purity of **99.73% CaCO<sub>3</sub>**. This unique 'purity fingerprint'—originally established and validated by **Saleh et al.** <sup>2</sup>—identifies it as the national benchmark for defluoridation in Yemen. This exceptional mineralogical quality, characterized by minimal levels of **silica (1.107%)** and **alumina (0.197%)**, allows **Wadi Nakhleen media** to significantly outperform other natural raw samples by providing a superior density of active adsorption sites (**Figure 8**). These geochemical attributes, rooted in the Jurassic Nayfa formations, establish the molecular foundation for the reactor's high kinetic efficiency.

This geogenic excellence is robustly consistent with the authors' strategic vision; as synthesized in **Table S11(a) (Supplementary Materials)**, this study achieved a significant chemical enrichment compared to industrial mining debris used in earlier phases. Specifically, targeting pristine outcrops within the Jurassic Nayfa Formation yielded a superior profile (**55.025% CaO**) with minimal silica (**1.107%**) and alumina (**0.197%**) impurities. Beyond elemental mapping, the structural and thermal stability of the remediation media was validated via **FT-IR and TG-DTA** (curated in **Figures S1a-c and S2a-c, Supplementary Materials**). Spectroscopic fingerprints (e.g., **1393–1404 cm<sup>-1</sup>** and **1798 cm<sup>-1</sup>**) confirmed a dominant calcite crystalline phase, while thermal profiles demonstrated a stable residual weight of **56.06%**,

matching the theoretical signature of **pure  $\text{CaCO}_3$** . This high calcium-to-impurity ratio distinguishes it from samples obtained near industrial plants; the minimal levels of silica (1.107%) and alumina (0.197%) provide a high-purity matrix rich in oxygen-containing surface sites (silanols and aluminols). This establishes the geochemical backbone for high-selectivity ion exchange and coordination bonding required for efficient defluoridation. Such efficiency underscores the strategic potential of regulating crystalline phases in natural adsorbents to elevate performance, a direction strongly advocated by the latest global syntheses of **Jaiswal et al.** <sup>70</sup>.

### **3.10.2. Textural Blueprint and Adsorptive Kinetics**

Building upon this chemical purity, the textural performance of the Nakhleen media is physically justified by the appraisal presented in **Table S11(b) (Supplementary Materials)**. Detailed BET analysis, adapted from **Das et al.** <sup>42</sup>, confirmed a well-developed mesoporous structure (Type IV isotherm) with an average pore diameter of 9.55 nm and a total pore volume of  **$3.24 \times 10^{-3} \text{ cm}^3/\text{g}$** . These properties, coupled with a high mineral density of  **$2.99 \text{ g/cm}^3$**  indicate a stable calcite matrix that maximizes the available surface area ( **$1.267 \text{ m}^2/\text{g}$** ) for fluoride adsorption compared to the Saim and Bates samples physical robustness ensures that the material maintains its structural integrity within the acid-enhanced crushed limestone reactors, facilitating efficient ion diffusion and precipitation **without clogging the filter bed**, even under high-load fluoride conditions.

### **3.10.3. Laboratory Benchmarking and Field Validation**

Across twelve experimental trials (**Table 9**), integrating benchmarks from **Saleh et al.** <sup>2</sup> and **Nasser** <sup>5</sup>, **Wadi Nakhleen limestone emerged as the superior national adsorbent**. This superiority is attributed to its exceptional mineralogical purity ( **$99.73\% \text{ CaCO}_3$** ), which consistently outperformed the National and Unity cement media by providing more active adsorption sites. A critical milestone was achieved in **Trial 6 ( $0.0007\text{M PA}$ )**, where a  **$10 \text{ mg/L}$**  stress-concentration was reduced to a **safe residual of  $0.20 \text{ mg/L}$**  within **three hours**—far **below the WHO limit**. This performance was operationalized using the district’s peak geogenic contamination—**Sample-12 (Ali Nusorah well)** at  **$5.7 \text{ mg/L}$** —where the reactor achieved  **$89.6\%$  efficiency, reducing fluoride to  $<0.40 \text{ mg/L}$**  while ensuring a stable neutral pH (**Table 10**). Crucially, the Nakhleen media demonstrated exceptional buffering capacity, stabilizing post-treatment **pH at  $7.52 \pm 0.1$**  from an acidified influent of  **$3.55$** , ensuring chemical neutrality and palatability.

**Operational Field Validation:** The scalability of the Wadi Nakhleen reactor was definitively confirmed through large-scale implementation by **ZOA International (2022, 2024)**<sup>71,72</sup>, as

documented by **Das et al.**<sup>42</sup> The successful restoration of water safety for **over 700 households** and the installation of a **18,000L** community-scale filtration unit (**Table S9**) provide the real-world 'proof-of-concept' for the hydrogeochemical models and pediatric safety thresholds (**HQ=6.33**) presented in this study. These internal successes are further corroborated by recent global findings; specifically, **Budania et al.**<sup>73</sup> validated limestone powder as an effective medium, yet our field application reached even more stringent safety levels (**<0.40 mg/L**), emphasizing the superior kinetics of the localized Wadi Nakhleen media.

#### **3.10.4. Global Context and Longitudinal Trajectory**

By utilizing these unique mineralogical properties within decentralized adsorptive filtration units, conceptually aligned with the field experiences of **Mohan et al.**<sup>74</sup>, this study addresses the critical '**Socio-Technical Gap**' emphasized by **Dhiman**.<sup>75</sup> This approach fulfills the urgent global need for remediation strategies that are not only chemically effective but also culturally accepted and sustainable in groundwater-dependent developing countries, as highlighted in the recent synthesis by **Ahmad et al.**<sup>76</sup>. Ultimately, this trajectory transitions the Wadi Nakhleen limestone from a raw geological material to a **Sovereign National Blueprint** for safeguarding the cognitive and physical well-being of communities in Yemen.

The longitudinal evolution of this research, detailed in **Table S11(c) (Supplementary Materials)**, delineates a significant scientific trajectory from 2020 to 2026. This journey transitioned from basic geological mapping<sup>76</sup> and laboratory protocols<sup>2,3</sup>, to Demonstrate the material's versatility in sequestering Lead and Cadmium.<sup>4</sup> Following the field scaling for **700+ households** by **Das et al.**<sup>42</sup>, the present study provides the critical '**Crown of Evidence**'. By integrating multivariate modeling (81.57% variance) with high-resolution pediatric risk assessments (**HQ = 6.33**), this trajectory has successfully evolved from a geogenic discovery into a definitive **public health shield**, safeguarding the cognitive well-being of Yemen's children.

Consequently, this **pioneer study provides** a comprehensive hydrogeochemical appraisal of Al-Musaymir's surface water, integrating human health risk assessment with sustainable remediation strategies.

## **4. Conclusion and Recommendations**

### **4.1. Conclusion**

This study unmasks a severe geogenic fluoride crisis in Al-Musaymir, Yemen, defined by the '**Deceptive Visual Clarity**' paradox. While 100% of samples meet aesthetic standards for turbidity (Avg 1.37 NTU) and pH (Avg 7.48), an alarming **82.35% exceed the 1.5 mg/L**

**chemical safety limit**, with peaks reaching **5.7 mg/L**. Multivariate modeling (PCA/HCA) confirms a predominantly geogenic origin, where intense water-rock interactions within the **Jurassic Nayfa formations** govern toxicity.

Toxicological modeling via the **USEPA** framework reveals a **100% failure rate for pediatric safety**, with the Hazard Quotient (**HQ**) reaching a critical **6.33—over six times the safe reference limit**. These findings align with the **NTP (2024)<sup>16</sup>** consensus linking concentrations **>1.5 mg/L** to **developmental neurotoxicity and IQ decline**. However, the validation of **99.73% pure Wadi Nakhleen limestone** provides a sustainable solution, reducing fluoride to **<0.40 mg/L within 3 hours** while maintaining chemical neutrality.

## **4.2. Strategic Recommendations: The 6-Point National Blueprint**

- 1. Immediate Engineering Intervention:** Deploy decentralized defluoridation units using locally sourced **99.7% pure Wadi Nakhleen media**, a field-proven technology for low-resource arid zones.
- 2. Pediatric & Maternal Policy:** Establish a "**Safe Water Priority Protocol**" for schools and maternal clinics to protect critical neurodevelopmental windows in children under 12.
- 3. Precautionary Monitoring:** Implement rigorous tracking for borderline sources (**Sample-16; 1.5 mg/L**), as cumulative intake in Yemen's high-temperature environment poses high chronic risk.
- 4. Awareness on Deceptive Clarity:** Launch community campaigns to dismantle the "**false sense of security**" provided by visual water transparency.
- 5. Geospatial Risk Management:** Integrate the identified **Level 1 Hotspots (HQ=6.33)** into a GIS-based national database to prioritize NGO and international aid resources.
- 6. Transition to PBPK Modeling:** Future research must prioritize **Physiologically Based Pharmacokinetic (PBPK) modeling** to accurately correlate external well exposure with internal biological doses.

## **Data Availability Statement**

**The raw data supporting the findings of this study are available from the corresponding author upon reasonable request.** While preliminary fluoride levels and remediation blueprints were discussed in our baseline work (Saleh et al., 2022), the present manuscript introduces a significant scientific overhaul for the 2024–2026 period. These transformative original updates include: **(i)** a rigorous data integrity framework validated by an **Ionic Charge Balance Error (ICBE)** within  $\pm 5\%$ ; **(ii)** the application of a multidimensional **Water Quality Index (WQI)** framework to unmask chemical toxicity hidden behind physical clarity; **(iii)** advanced multivariate statistical modeling (**PCA/HCA**) accounting for **81.57%** of hydrogeochemical variance to isolate geogenic drivers; **(iv)** the first comprehensive appraisal of **hydrochemical facies** and **rock-water evolution** via **Piper trilinear analysis**; and **(v)** a **dual-risk assessment framework** encompassing agricultural sustainability (**SAR** and **salinity indices**) and a **critical pediatric neurotoxicity risk assessment (HQ=6.33)** strictly aligned with the latest National Toxicology Program (NTP, 2024) consensus.

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## Sociated Content

### Appendix A. Supplementary data

Supplementary material related to this article can be found online at [Insert DOI]. This material provides the analytical and statistical foundation for the study, including:

**Table S1:** Comprehensive **15-parameter hydrogeochemical matrix** and **Ionic Charge Balance Error (ICBE) validation** for all 17 surface wells in Al-Musaymir.

**Tables S2–S4:** Detailed **Water Quality Index (WQI)** modeling, including parameter weighting, relative weights ( $W_i$ ), and WQI-based quality classifications (Class I–V).

**Table S5:** Linear regression parameters and sensitivity metrics (**LOD/LOQ**) for the fluoride determination method.

**Table S6 (a & b):** Analytical performance and cross-validation metrics (**ISE vs. Spectrophotometry**) for fluoride quantification.

**Table S7:** Full **Pearson Correlation Matrix (r)** identifying geogenic vs. anthropogenic ion associations (e.g.,  $F^-$  vs.  $pH$ ,  $r=0.71$ )

**Tables S8–10:** Advanced **Health-Risk Assessment** datasets: including tiered classification of pathologies, spatio-chemical zonation, and the risk-based priority ranking for water management.

**Tables S11 (a,b,c): Sovereign Remediation Benchmarks:** Multi-year chemical fingerprinting of raw limestone (**99.73% purity**), textural BET benchmarks, and the longitudinal trajectory of the **Wadi Nakhleen research (2020–2026)**.

**Figures S1(a,b,c): Fourier Transform Infrared (FT-IR)** spectroscopic fingerprints validating the dominant calcite crystalline phase of the geogenic media.

**Figures S2(a,b,c): Simultaneous Thermal Analysis (TG-DTA)** profiles confirming the 56.06% stable calcination residual and mineralogical purity of Wadi Nakhleen limestone.

## **Author Contributions - CRediT Style**

**Shaif M. K. Saleh:** Conceptualization, Resources, Supervision, Formal analysis, Writing original draft, Writing review and editing, Project administration, and Correspondence; **Radhwan M. Saleh:** Data curation, Investigation, Methodology (Field implementation), and Writing – original draft; **Rawan S. M. Kasem:** Writing – review & editing, and Formal analysis.

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## **Competing interests**

The authors declare no competing interests

## **Ethical approval**

This study is an environmental assessment of water quality and did not involve any experiments on human participants or animal subjects. All water samples were collected from public and private wells in Al-Musaymir District with the necessary local permissions.

**Table 1. Descriptive location details and spatial georeferencing (GPS/Depth) of the sampled surface wells in Al-Musaymir District**

| ID | Name sample | Name of well | Village            | Depth (m) | Latitude      | Longitude     |
|----|-------------|--------------|--------------------|-----------|---------------|---------------|
| 1  | Sample-1    | Fadhal Saeed | Al-Sarhan'a        | 11        | 13°20'47"N    | 44°40'35"E    |
| 2  | Sample-2    | Fara a       | Fara'a             | 16        | 13°27'47.25"N | 44°41'35.75"E |
| 3  | Sample-3    | Nakhela a    | Nakhela a          | 14        | 13°24'9.99"N  | 44°41'43"E    |
| 4  | Sample-4    | Mutein       | Nakhela a          | 16        | 13°24'15"N    | 44°42'42"E    |
| 5  | Sample-5    | Qayif        | Qaaf               | 10        | 13°24'37"N    | 44°38'49" E   |
| 6  | Sample-6    | Qaaf         | Qaaf               | 13        | 13°25'55"N    | 44°39'59" E   |
| 7  | Sample-7    | Bashria      | Bashria            | 12        | 13°29'11.6"N  | 44°35'40.7"E  |
| 8  | Sample-8    | Alhaqaf      | Al-Musaymir Center | 20        | 13°26'39"N    | 44°36'42"E    |
| 9  | Sample-9    | Majwer       | Goal Madram        | 14        | 13°20'24"N    | 44°41'14.3"E  |
| 10 | Sample-10   | Mareeb       | Mareeb             | 11        | 13°25'36"N    | 44°37'43"E    |
| 11 | Sample-11   | Dagran       | Dagran             | 10        | 13°27'48"N    | 44°35'51"E    |
| 12 | Sample-12   | Ali Nusorah  | Qaaf               | 12        | 13°25'12.9"N  | 44°39'34.9"E  |
| 13 | Sample-13   | Yaseen       | Mucadium           | 28        | 13°28'19.06"N | 44°35'23.67"E |
| 14 | Sample-14   | Ahmed        | Allugma a          | 17        | 13°30'41.32"N | 44°35'31.74"E |
| 15 | Sample-15   | Alsaeed      | Top asel           | 10        | 13°31'08.24"N | 44°34'49.57"E |
| 16 | Sample-16   | Abdulkareem  | Habeel Alaf        | 13        | 13°28'01"N    | 44°35'44"E    |
| 17 | Sample-17   | Shatha a     | Shatha a           | 6.8       | 13°34'23.27"N | 44°32'59.5"E  |

**Table 2. Standardized input parameters, exposure factors, and toxicological constants utilized for Al-Musaymir population modeling**

| Parameter              | Symbol     | Unit      | Value (Adults)             | Value (Children)           | Source                    |
|------------------------|------------|-----------|----------------------------|----------------------------|---------------------------|
| Fluoride Concentration | <i>C</i>   | mg/L      | Variable (Sample-specific) | Variable (Sample-specific) | Present Study             |
| Daily Water Intake     | <i>IR</i>  | L/day     | 2.0                        | 1.0                        | USEPA(2001); WHO, (2017)  |
| Exposure Frequency     | <i>EF</i>  | days/year | 365                        | 365                        | Rehman et al., (2022)     |
| Exposure Duration      | <i>ED</i>  | years     | 30                         | 12                         | Ahada & Suthar (2019)     |
| Body Weight            | <i>BW</i>  | kg        | 70                         | 15                         | USEPA (2001); IRIS (2022) |
| Averaging Time         | <i>AT</i>  | days      | <i>ED x 365</i>            | <i>ED x 365</i>            | USEPA (2001)              |
| Oral Reference Dose    | <i>RfD</i> | mg/kg/day | 0.06                       | 0.06                       | USEPA (2001); IRIS 2022)  |

**Note:** An  $HQ > 1.0$  indicates that the exposed population is at **significant risk** of non-carcinogenic toxicity (Duggal & Sharma, 2022; Rehman et al., 2022; Asgari et al., 2025)

**Table 3. Statistical summary of physicochemical parameters and compliance status relative to WHO, (2017) and Yemeni standards (1999) (n=17)**

| Parameters                                   | Unit       | Range (Min-Max)    | Mean $\pm$ SD                     | WHO Limit         | Yemeni Standard | Compliance (%) | Status             |
|----------------------------------------------|------------|--------------------|-----------------------------------|-------------------|-----------------|----------------|--------------------|
| Temp                                         | (°C)       | 25-25              | 25 $\pm$ 0                        | 25                |                 | 100%           | Pass               |
| pH                                           | -          | 7.33 – 7.76        | 7.48 $\pm$ 0.19                   | 8.5               | 6.5–9.0         | 100%           | Pass               |
| Turbidity                                    | NTU        | 0.20 – 2.69        | 1.37 $\pm$ 0.85                   | 1-5               | 1–15            | 100%           | Pass               |
| EC                                           | $\mu$ S/cm | 1409– 3800         | 1996.9 $\pm$ 574                  | <b>1500</b>       | 2500            | <b>11.76%</b>  | <b>Fail* (WHO)</b> |
| TDS                                          | mg/L       | 950 – 2280         | 1257 $\pm$ 336                    | 1000              | 1500            | <b>11.76%</b>  | <b>Fail*</b>       |
| Nitrate                                      | mg/L       | 11.9 – 68.0        | 35.4 $\pm$ 16.5                   | 50                | 50              | 76.47%         | Pass               |
| Fluoride                                     | mg/L       | <b>1.10 – 5.70</b> | <b>2.57 <math>\pm</math> 1.19</b> | <b>1.5</b>        | <b>0.5–1.5</b>  | <b>17.65%</b>  | <b>Critical* *</b> |
| TH (Hardness)                                | mg/L       | 310–1400           | 497 $\pm$ 259                     | 500               | 500             | 70.6%          | Pass               |
| Sulfate (SO <sub>4</sub> <sup>2-</sup> )     | mg/L       | 210–1100           | 443 $\pm$ 220.2                   | 250               | 200–600         | <b>6%</b>      | Pass               |
| Chloride (Cl <sup>-</sup> )                  | mg/L       | 160–750            | 292.6 $\pm$ 142.2                 | 250               | 250             | 47%            | Pass               |
| Sodium (Na <sup>+</sup> )                    | mg/L       | 48.4–581           | 329.2 $\pm$ 151.7                 | 200               | 200–400         | <b>11.76%</b>  | Pass               |
| Calcium (Ca <sup>2+</sup> )                  | mg/L       | 58.4–228           | 90.5 $\pm$ 40.6                   | 75                | 75–200          | 94%            | Pass               |
| Magnesium (Mg <sup>2+</sup> )                | mg/L       | 23.2–199           | 64.4 $\pm$ 44.6                   | 30 <sup>a</sup>   | 30–150          | 23.5%          | Pass               |
| Potassium (K <sup>+</sup> )                  | mg/L       | 3.2–22             | 7.6 $\pm$ 4.0                     | 12 <sup>a</sup>   | 8–12            | 94%            | Pass               |
| Phosphate (PO <sub>4</sub> <sup>4-</sup> )   | mg/L       | 0.26–1.0           | 0.57 $\pm$ 0.21                   | 0.45 <sup>a</sup> | 0.5             | 70.6%          | Pass               |
| Bicarbonate (HCO <sub>3</sub> <sup>-</sup> ) | mg/L       | 244–390.4          | 334.7 $\pm$ 45.4                  | 500 <sup>a</sup>  | 500             | 100%           | Pass               |
| Mean ICBE                                    | (%)        | -1.8 to +2.5       | 2.15%                             | —                 | —               | 100% Valid     | Elite Quality      |

Notes: <sup>a</sup> USPHS Standards (1962)

**Table 4. Calculated WQI Values and Quality Status for Al-Musaymir Surface Wells (n=17)**

| Sample ID   | WQI Value      | Quality Status (Classification) | Primary Driver                          |
|-------------|----------------|---------------------------------|-----------------------------------------|
| Sample-3    | 93.07          | Good Water                      | Trace F <sup>-</sup>                    |
| Sample-12   | 89.80          | Good Water                      | Marginal Compliance                     |
| Sample-13   | 90.58          | Good Water                      | Low Mineralization                      |
| Sample-14   | 97.09          | Good Water                      | Acceptable TDS                          |
| Sample-16   | <b>101.64</b>  | <b>Unsuitable (Poor)</b>        | <b>Precautionary F<sup>-</sup></b>      |
| Sample-5    | <b>221.40</b>  | <b>Very Poor Water</b>          | <b>Peak TDS / EC</b>                    |
| Sample-6    | <b>168.68</b>  | <b>Poor Water</b>               | <b>Fluoride / Nitrate</b>               |
| Other Wells | <b>109–149</b> | <b>Poor / Unsuitable</b>        | <b>Geogenic F<sup>-</sup> &amp; TDS</b> |

| <b>Table 5. Principal Component Analysis (PCA) Loadings for Physicochemical Parameters in Al-Musaymir Surface Water (n=17)</b> |                               |                                    |                                    |                                            |
|--------------------------------------------------------------------------------------------------------------------------------|-------------------------------|------------------------------------|------------------------------------|--------------------------------------------|
| <b>Parameter</b>                                                                                                               | <b>Component 1 (Geogenic)</b> | <b>Component 2 (Anthropogenic)</b> | <b>Communality (h<sup>2</sup>)</b> | <b>Interpretation</b>                      |
| F <sup>-</sup>                                                                                                                 | <b>0.865</b>                  | 0.112                              | <b>0.761</b>                       | <b>Aquifer Mineralization</b>              |
| EC                                                                                                                             | <b>0.942</b>                  | 0.085                              | <b>0.895</b>                       | <b>Aquifer Mineralization</b>              |
| TDS                                                                                                                            | <b>0.938</b>                  | 0.091                              | <b>0.888</b>                       | <b>Aquifer Mineralization</b>              |
| Na <sup>+</sup>                                                                                                                | <b>0.812</b>                  | 0.115                              | 0.673                              | <b>Water-Rock Interaction</b>              |
| Cl <sup>-</sup>                                                                                                                | <b>0.785</b>                  | 0.201                              | 0.657                              | <b>Water-Rock Interaction</b>              |
| SO <sub>4</sub> <sup>-2</sup>                                                                                                  | <b>0.720</b>                  | 0.145                              | 0.539                              | <b>Water-Rock Interaction</b>              |
| pH                                                                                                                             | <b>0.712</b>                  | -0.245                             | 0.567                              | <b>Alkaline Leaching Environment</b>       |
| NO <sub>3</sub> <sup>-</sup>                                                                                                   | 0.204                         | <b>0.841</b>                       | <b>0.749</b>                       | <b>Surface/Human Contamination</b>         |
| Turbidity                                                                                                                      | -0.156                        | <b>0.789</b>                       | 0.647                              | <b>Localized Surface Runoff</b>            |
| Temperature                                                                                                                    | 0.045                         | 0.102                              | 0.012                              | Non-Significant                            |
| T.H                                                                                                                            | 0.685                         | 0.320                              | 0.572                              | Aquifer Mineralization                     |
| Ca <sup>+2</sup>                                                                                                               | 0.654                         | 0.211                              | 0.472                              | Water-Rock Interaction                     |
| Mg <sup>+2</sup>                                                                                                               | 0.612                         | 0.345                              | 0.494                              | Water-Rock Interaction                     |
| HCO <sub>3</sub> <sup>-</sup>                                                                                                  | 0.540                         | -0.150                             | 0.314                              | Non-Significant / Buffering                |
| PO <sub>4</sub> <sup>-3</sup>                                                                                                  | 0.210                         | 0.450                              | 0.247                              | Non-Significant                            |
| <b>% Variance Explained</b>                                                                                                    | <b>58.45%</b>                 | <b>23.12%</b>                      | <b>Total: 81.57%</b>               | <b>Total Cumulative Explained Variance</b> |
| <i>Ref.: Salifu et al., 2012 ; Yidana &amp; Yidana, 2012 ; Balasubramaniyan et al.,2026)</i>                                   |                               |                                    |                                    |                                            |

**Table 6. Summary of calculated Hazard Quotient (HQ) for adults and children across 17 surface water samples in Al-Musaymir District.**

*Source: Calculated based on the USEPA (2001) Human Health Risk Assessment (HHRA) model and toxicological constants from IRIS (2022) and Rehman et al., (2022)*

| Sample ID                                | Village/Location | Fluoride (mg/L) | HQ (Children) | HQ (Adults) | Risk Status (HQ)                       |
|------------------------------------------|------------------|-----------------|---------------|-------------|----------------------------------------|
| Sample-1                                 | Fadhal Saeed     | 2.10            | 2.33          | 1.00        | High Risk                              |
| Sample-2                                 | Fara a           | 4.40            | 4.89          | 2.10        | High Risk                              |
| Sample-3                                 | Nakhela a        | 1.10            | 1.22          | 0.52        | Significant Risk (C*)                  |
| Sample-4                                 | Mutein           | 2.24            | 2.49          | 1.07        | High Risk                              |
| Sample-5                                 | Qayif            | 2.17            | 2.41          | 1.03        | High Risk                              |
| Sample-6                                 | Qaaf             | 4.30            | 4.78          | 2.05        | High Risk                              |
| Sample-7                                 | Bashria          | 2.52            | 2.80          | 1.20        | High Risk                              |
| Sample-8                                 | Alhaqaf          | 1.40            | 1.56          | 0.67        | Significant Risk (C)                   |
| Sample-9                                 | Majwer           | 1.70            | 1.89          | 0.81        | Significant Risk (C)                   |
| Sample-10                                | Mareeb           | 2.40            | 2.67          | 1.14        | High Risk                              |
| Sample-11                                | Dagran           | 2.00            | 2.22          | 0.95        | Significant Risk (C)                   |
| Sample-12                                | Ali Nusorah      | 5.70            | 6.33          | 2.71        | Critical Emergency                     |
| Sample-13                                | Yaseen           | 1.47            | 1.63          | 0.70        | Significant Risk (C)                   |
| Sample-14                                | Ahmed Allugma a  | 3.10            | 3.44          | 1.48        | High Risk                              |
| Sample-15                                | Alsaed           | 2.80            | 3.11          | 1.33        | High Risk                              |
| Sample-16                                | Abdulkareem      | 1.50            | 1.67          | 0.71        | Precautionary Risk                     |
| Sample-17                                | Shatha a         | 2.80            | 3.11          | 1.33        | High Risk                              |
| Average                                  | District Mean    | 2.57            | 2.85          | 1.22        | Regionally Unsafe                      |
| Min-Max                                  |                  | 1.10-5.70       | 1.22-6.33     | 0.52-2.71   |                                        |
| % Samples more than criteria-Failure (%) |                  | 82.35%          | 100%          | 64.7%       | Significant Risk to Critical Emergency |

**Notes:** HQ>1.0 indicates significant non-carcinogenic risk. (Full 17-sample data provided in Table S9; SI)

| <b>Table 7. Comparative appraisal of geogenic fluoride levels in Al-Musaymir versus other endemic regions in Yemen</b>                                                                                                                                                                                                                                                                                                                                                                                                          |                                             |                                                |                                   |                          |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------|------------------------------------------------|-----------------------------------|--------------------------|
| <b>Area</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | <b>Water sample type (surface/ground) *</b> | <b>Fluoride Conc. (mg/L) ranges, (average)</b> | <b>Higher than the WHO limits</b> | <b>Ref.</b>              |
| Al-Dhalia                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | Ground water                                | BDL- <b>9.46</b>                               | 31.25% (n=16)                     | Taher et al., 2020       |
| Al-Hussein district, Al-Dhalia                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | Surface/ground                              | 0.60- <b>13.30 (3.67)</b>                      | 66.7% (n=15)                      | Al-Mahrabi et al., 2021  |
| Al-Dhalia basin                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | Ground water                                | 0.31- <b>18.30 (6.03)</b>                      | 71% (n=28)                        | Al-Amry et al., 2020     |
| Tuban delta basin (Lahij & Aden)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | Ground water                                | 0.015-2.4 (1.019)                              | 20% (n=20)                        | Saleh & Al-Sallami, 2022 |
| Shara a springs, Lahij                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | Surface water (Hot spring)                  | <b>4.33-5.1</b>                                | <b>100%</b> (n=8)                 | Taher et al. 2023        |
| Kirsh springs, Lahij                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                             | <b>6.17-7.63</b>                               | <b>100%</b> (n=7)                 | Taher et al., 2023       |
| Dhamar city                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | Drinking water                              | 0.30-1.84                                      | 25% (n=16)                        | Al-Aizari et al., 2020   |
| Rasyan Aquifer, Taiz                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | Ground water                                | 0.1 to 6                                       | 71% (n=93)                        | Naser et al., 2017       |
| <b>Al-Musaymir district</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | Surface water                               | 1.1- <b>5.7 (2.57)</b>                         | <b>82.35%</b> (n=17)              | <b>This Study</b>        |
| <p><b>* All types of water are used as drinking water; n=Total of samples</b><br/> <b>Note:</b> The comparative appraisal identifies Al-Musaymir District as a unique '<b>Chemical Hotspot</b>' in Yemen. While extreme values in the Al-Dhalea basin and hot springs reach higher peaks, Al-Musaymir exhibits a higher systematic failure rate (<b>82.35%</b>) compared to major aquifers like Rasyan (71%) and Tuban Delta (20%), necessitating the immediate localized defluoridation strategies proposed in this study.</p> |                                             |                                                |                                   |                          |

| <b>Table 8. Chemical characterization of the limestone used in the present study</b> |                                         |                                                   |                                                 |
|--------------------------------------------------------------------------------------|-----------------------------------------|---------------------------------------------------|-------------------------------------------------|
| <b>Components</b>                                                                    | <b>Wadi Nakhleen (Lahj Governorate)</b> | <b>National Cement Company (Lahj Governorate)</b> | <b>Unity Cement Company (Abyan Governorate)</b> |
| <b>Silica (SiO<sub>2</sub>) %</b>                                                    | 1.107                                   | 1.793                                             | 6.348                                           |
| <b>Alumina (Al<sub>2</sub>O<sub>3</sub>) %</b>                                       | 0.197                                   | 0.239                                             | 1.833                                           |
| <b>Fe<sub>2</sub>O<sub>3</sub>%</b>                                                  | 0.129                                   | 0.386                                             | 1.016                                           |
| <b>Lime (CaO) %</b>                                                                  | <b>55.025</b>                           | 51.983                                            | 44.718                                          |
| <b>MgO %</b>                                                                         | 0.096                                   | 2.349                                             | 3.399                                           |
| <b>SO<sub>3</sub>%</b>                                                               | 0.005                                   | 0.239                                             | 0.767                                           |
| <b>Na<sub>2</sub>O%</b>                                                              | 0.003                                   | 0.015                                             | 0.085                                           |
| <b>K<sub>2</sub>O%</b>                                                               | 0.139                                   | 0.186                                             | 1.004                                           |
| <b>Cl%</b>                                                                           | 0.081                                   | 0.084                                             | 0.063                                           |
| <b>Loss on Ignition (LOI) %</b>                                                      | 42.95                                   | 41.4497                                           | 37.387                                          |
| <b>Purity (CaCO<sub>3</sub>)</b>                                                     | <b>99.73</b>                            | 98.72                                             | 96.62                                           |

**Table 9. Comparative Appraisal of Defluoridation Efficiency using Sovereign Limestone Media: Integrating 2025 Thesis Benchmarks with 2026 Analytical**

| Synthesis (Saleh et al. protocols, 2022).                                                                                                                                                                                                                                                        |                                       |                                     |                           |                           |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------|-------------------------------------|---------------------------|---------------------------|
| n                                                                                                                                                                                                                                                                                                | Limestone                             | Remaining F <sup>-</sup> at 3 hours |                           |                           |
|                                                                                                                                                                                                                                                                                                  |                                       | Wadi Nakhleen (Al-Milah)            | Wadi Saim (Near National) | Bates Region (Near Unity) |
| 1                                                                                                                                                                                                                                                                                                | 0.01M of PA & 10 ppm F <sup>-</sup>   | 2.52                                | 2.17                      | 2.28                      |
| 2                                                                                                                                                                                                                                                                                                | 0.01M of PA & 10 ppm F <sup>-</sup>   | 0.79                                | 0.97                      | 1.12                      |
| 3                                                                                                                                                                                                                                                                                                | 0.0007M of PA & 10 ppm F <sup>-</sup> | 0.37                                | 0.62                      | 0.97                      |
| 4                                                                                                                                                                                                                                                                                                | 0.0007M of PA & 10 ppm F <sup>-</sup> | 0.31                                | 0.64                      | 0.79                      |
| 5                                                                                                                                                                                                                                                                                                | 0.0007M of PA & 10 ppm F <sup>-</sup> | 0.28                                | 0.78                      | 0.62                      |
| 6                                                                                                                                                                                                                                                                                                | 0.0007M of PA & 10 ppm F <sup>-</sup> | 0.2                                 | 0.71                      | 0.58                      |
| 7                                                                                                                                                                                                                                                                                                | 0.0007M of PA & 10 ppm F <sup>-</sup> | 0.46                                | 0.81                      | 0.67                      |
| 8                                                                                                                                                                                                                                                                                                | 0.0007M of PA & 10 ppm F <sup>-</sup> | 0.58                                | 1.04                      | 1.23                      |
| 9                                                                                                                                                                                                                                                                                                | 0.0007M of PA & 10 ppm F <sup>-</sup> | 0.94                                | 1.02                      | 1.18                      |
| 10                                                                                                                                                                                                                                                                                               | 0.0007M of PA & 10 ppm F <sup>-</sup> | 0.82                                | 0.75                      | 0.93                      |
| 11                                                                                                                                                                                                                                                                                               | 0.0007M of PA & 10 ppm F <sup>-</sup> | 0.78                                | 0.84                      | 1.14                      |
| 12                                                                                                                                                                                                                                                                                               | 0.0007M of PA & 10 ppm F <sup>-</sup> | 0.72                                | 1.07                      | 1.25                      |
| <b>Note:</b> While preliminary efficiency data originated from the doctoral work of <b>Nasser (2025)</b> , this table provides an <b>updated 2026</b> comparative synthesis, incorporating rigorous laboratory re-validation and optimization against <b>2024/2025 geogenic exposure peaks</b> . |                                       |                                     |                           |                           |

| Table10. Operational validation of localized defluoridation filters utilizing high-purity Wadi Nakhleen limestone (optimized by Saleh et al. protocols, 2022a,b).<br>(Influent [F <sup>-</sup> ] = 5.7 mg/L; Contact Time = 3 Hours) |                                   |          |          |          |          |          |          |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------|----------|----------|----------|----------|----------|----------|
| Samples (A-E)                                                                                                                                                                                                                        | n=1                               | n=2      | n=3      | n=4      | n=5      | n=6      | n=7      |
|                                                                                                                                                                                                                                      | Residual [F <sup>-</sup> ] (mg/L) |          |          |          |          |          |          |
| Sample-A                                                                                                                                                                                                                             | 2.39                              | 0.61     | 1.41     | 0.97     | 1.03     | 0.45     | 0.46     |
| Sample-B                                                                                                                                                                                                                             | 1.73                              | 0.48     | 0.93     | 0.81     | 0.99     | 0.48     | 0.80     |
| Sample-C                                                                                                                                                                                                                             | 2.45                              | 0.66     | 0.87     | 1.02     | 0.96     | 0.57     | 0.61     |
| Sample-D                                                                                                                                                                                                                             | 1.81                              | 1.15     | 0.76     | 0.41     | 1.31     | 0.86     | 0.40     |
| Sample-E                                                                                                                                                                                                                             | 2.32                              | 1.09     | 1.09     | 1.17     | 1.23     | 1.12     | 0.67     |
| Mean ± SD                                                                                                                                                                                                                            | 2.14±0.3                          | 0.80±0.3 | 1.01±0.3 | 0.88±0.3 | 1.10±0.2 | 0.70±0.3 | 0.59±0.2 |
| Removal Efficiency (%)                                                                                                                                                                                                               | 62.5%                             | 85.9%    | 82.3%    | 84.6%    | 80.7%    | 87.7%    | 89.6%    |
| (Acidified Influent pH = 3.55)                                                                                                                                                                                                       |                                   |          |          |          |          |          |          |
| Samples (A-E)                                                                                                                                                                                                                        | n=1                               | n=2      | n=3      | n=4      | n=5      | n=6      | n=7      |
|                                                                                                                                                                                                                                      | Post-treatment pH                 |          |          |          |          |          |          |
| Sample-A                                                                                                                                                                                                                             | 7.23                              | 7.40     | 7.53     | 7.40     | 7.51     | 7.30     | 7.53     |
| Sample-B                                                                                                                                                                                                                             | 6.55                              | 7.15     | 7.35     | 7.42     | 7.18     | 7.55     | 7.45     |
| Sample-C                                                                                                                                                                                                                             | 7.11                              | 7.22     | 7.30     | 7.42     | 7.46     | 7.62     | 7.43     |
| Sample-D                                                                                                                                                                                                                             | 6.87                              | 7.25     | 6.89     | 7.57     | 7.89     | 7.35     | 7.65     |
| Sample-E                                                                                                                                                                                                                             | 6.98                              | 7.19     | 7.38     | 7.49     | 7.48     | 7.50     | 7.52     |
| Mean ± SD                                                                                                                                                                                                                            | 6.95±0.3                          | 7.24±0.1 | 7.29±0.2 | 7.46±0.1 | 7.50±0.3 | 7.46±0.1 | 7.52±0.1 |



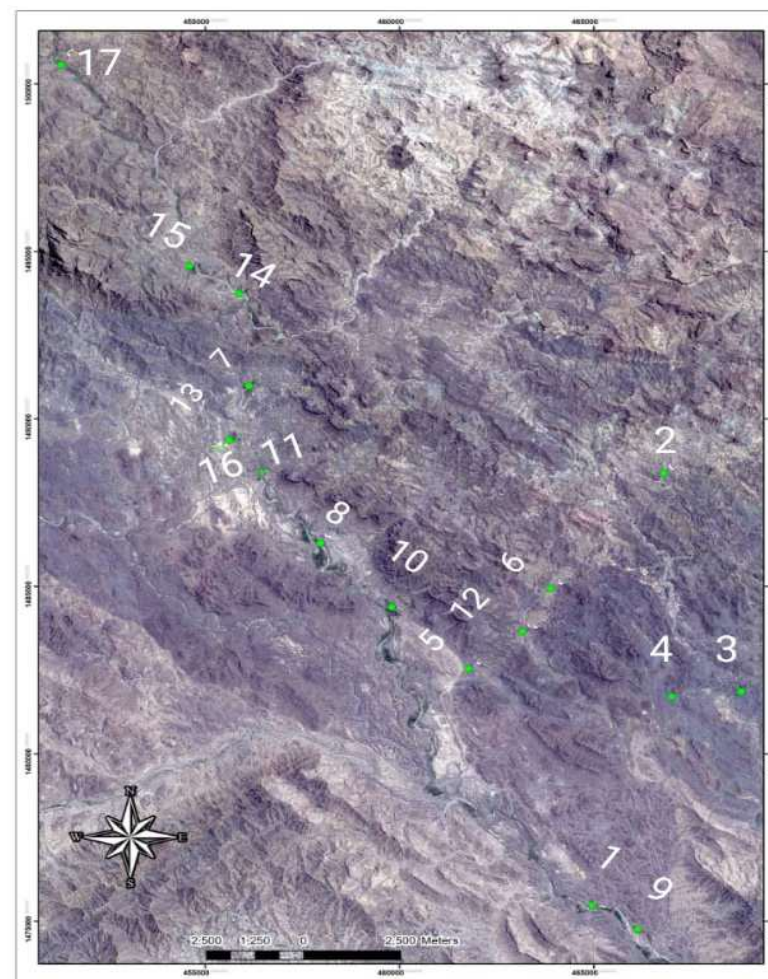
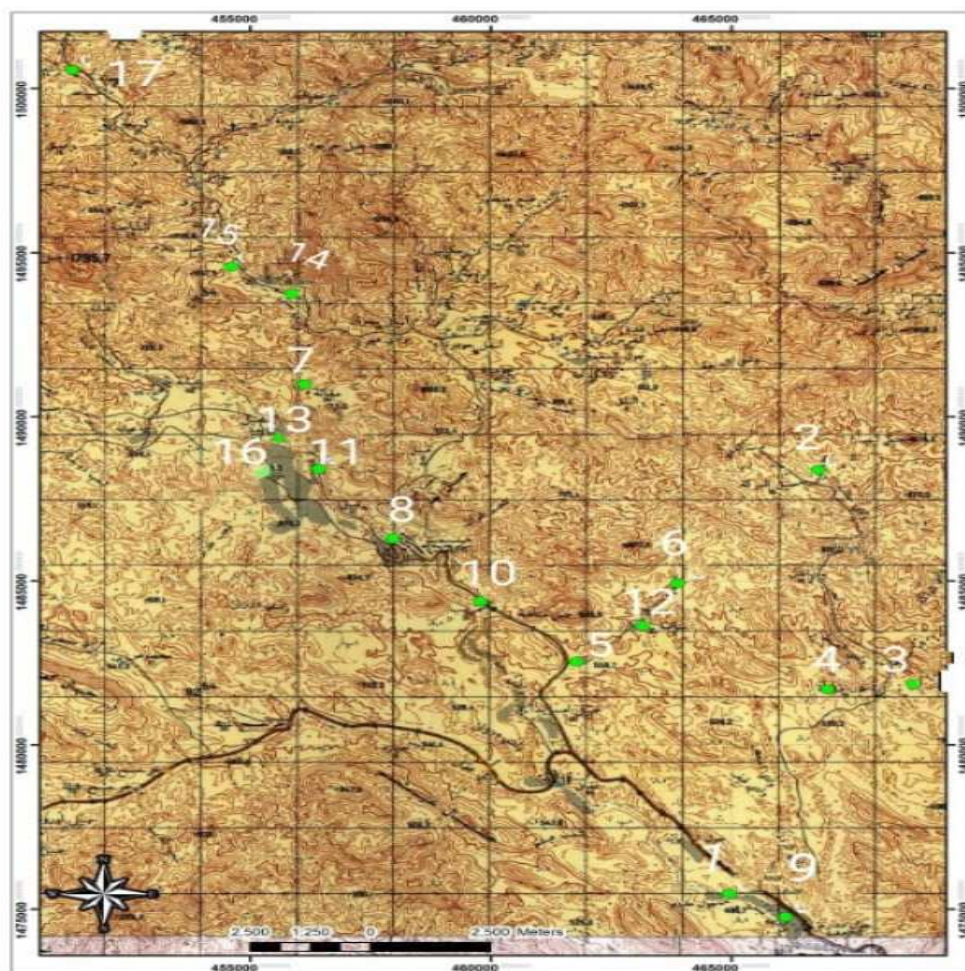


**Fig. 1. Geographic location of the study area and spatial distribution of the 17 surface water sampling sites in Al-Musaymir District, Yemen**

**Description:** This map illustrates the geographic distribution of the seventeen (17) strategically selected surface wells within the Al-Musaymir District, Lahij Governorate, Yemen. The sampling sites are plotted using precise GPS coordinates, covering various topographical features to capture the hydrogeochemical variability of the geogenic fluoride-affected aquifers in the region.

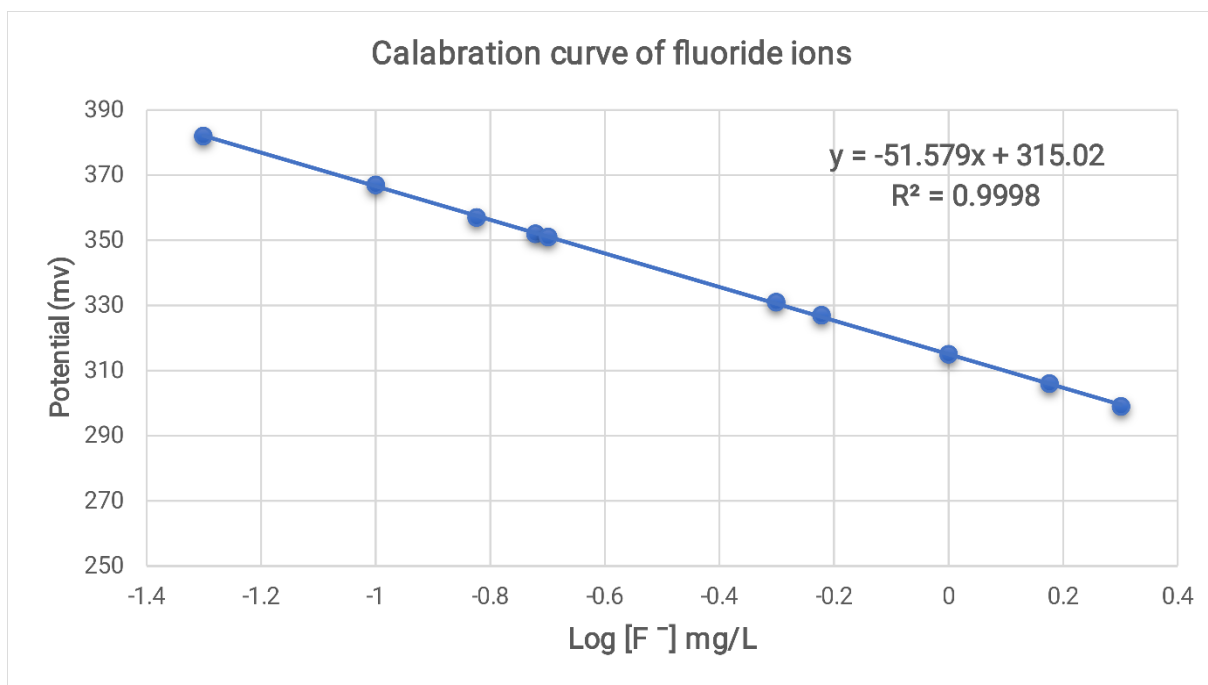


**Fig. 2. Potentiometric calibration curve for fluoride ion determination showing high analytical linearity ( $R^2 = 0.9998$ )**

**Fig. 3. Analytical Data Integrity and Quality Assurance: ICBE Validation Framework**

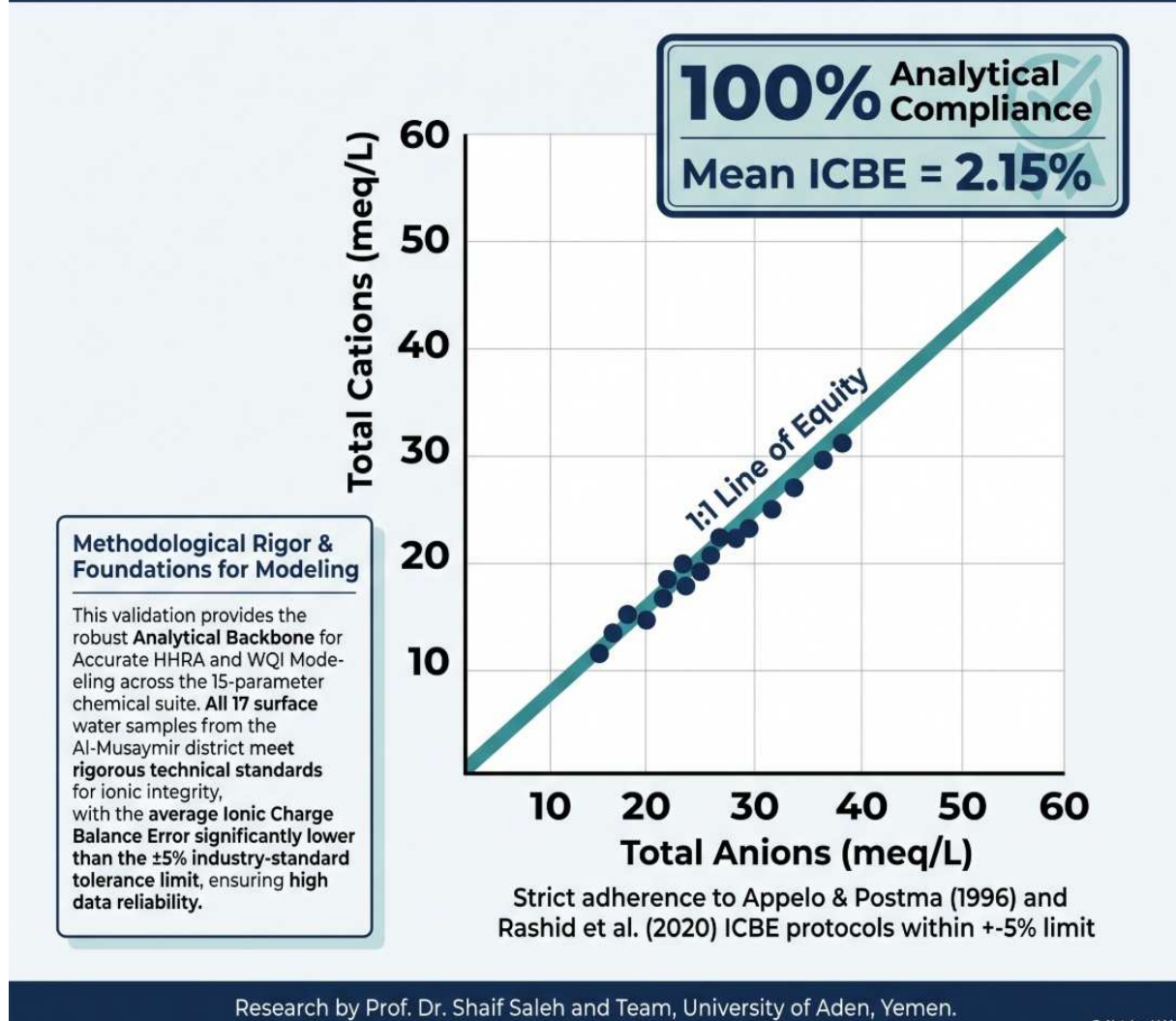


**Fig. 3. Analytical Data Integrity and Quality Assurance: ICBE Validation Framework**

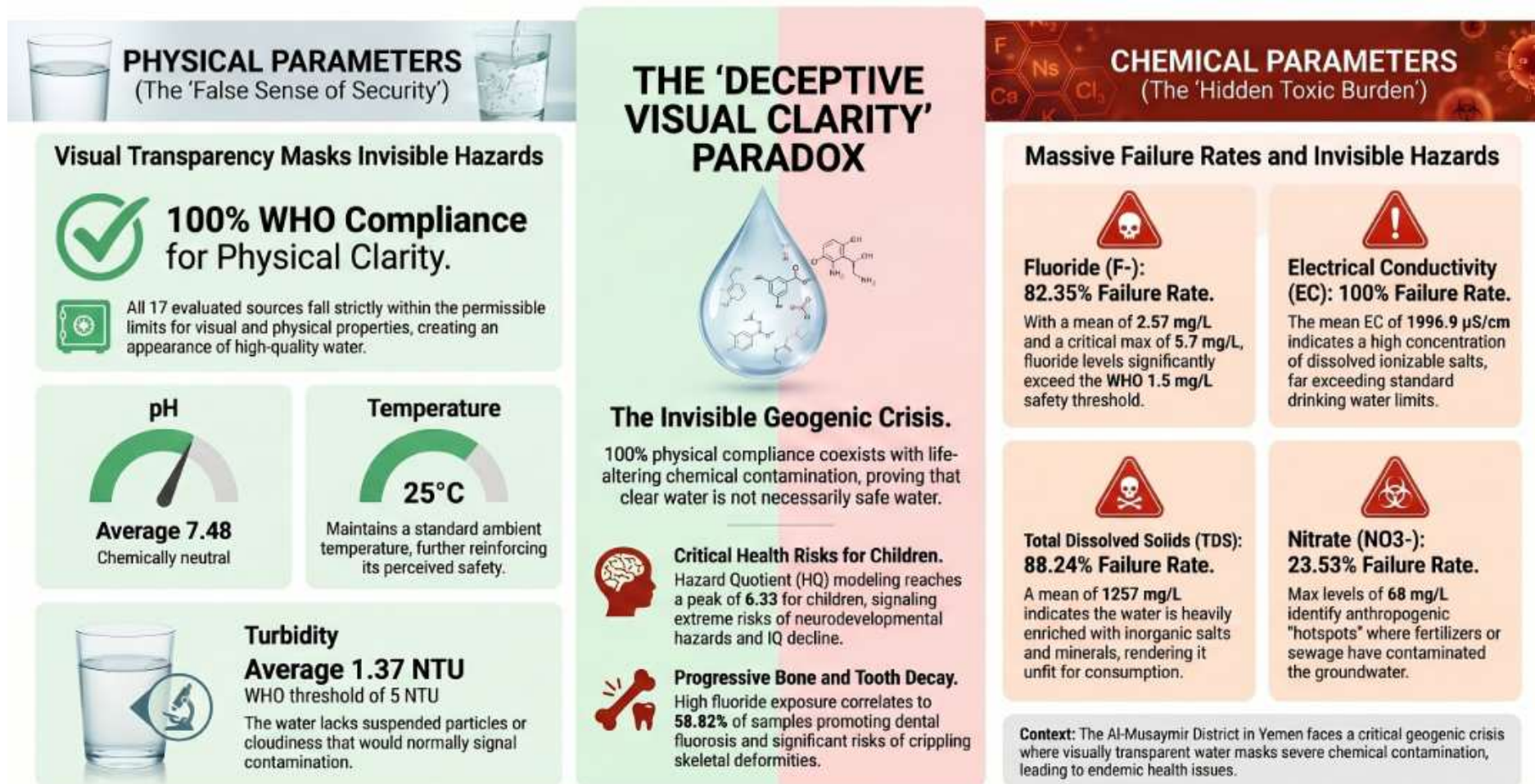


**Fig. 4. Physicochemical Appraisal of Drinking Water: The Disparity Between Physical Clarity and Chemical Toxicity**

**Description:** This technical dashboard visualizes the "Deceptive Visual Clarity" paradox observed in Al-Musaymir. It highlights that while 100% of samples meet international standards for physical parameters—pH (Avg 7.48) and Turbidity (Avg 1.37 NTU)—there is a catastrophic chemical failure. The dashboard underscores the **hidden toxic burden**, showing an **82.35% failure rate for fluoride**, **100% for Electrical Conductivity (EC)**, and **88.24% for Total Dissolved Solids (TDS)**, warning against the false sense of security provided by visually clear water.

An analysis of 17 surface wells in the Al-Musaymir District reveals a “Deceptive Clarity” paradox. While the water appears physically pristine, it harbors a severe chemical crisis characterized by extreme salinity and geogenic fluoride, creating a dual threat to both agricultural productivity and human biological safety.

### Irrigation Suitability Analysis

#### 100% High to Very High Salinity (C3-C4)

Mean Electrical Conductivity (EC) recorded at 1996.9  $\mu\text{S}/\text{cm}$  across the basin.

| Parameter                     | Mean Value                     | Classification/Risk            |
|-------------------------------|--------------------------------|--------------------------------|
| Electrical Conductivity (EC)  | 1996.9 $\mu\text{S}/\text{cm}$ | High-Very High Salinity Hazard |
| Sodium Adsorption Ratio (SAR) | 6.8                            | Low Sodium Hazard (S1)         |
| Salinity Exceedance           | 100%                           | Severe Agricultural Risk       |

#### Low Sodium Hazard (S1) but High Burden

Mean Sodium Adsorption Ratio (SAR) is 6.8, indicating low sodicity risk.

#### Severe Risk of Soil Salinization

High salinity dictates urgent management to prevent total crop yield decline.



### The ‘Double Burden’ Paradox

#### Geogenic Mineralization Synergy

Co-occurrence of high EC and geogenic Fluoride creates a unique environmental stressor.



**Threat to Health:**  
Toxic levels impact neurodevelopment in children

**Threat to Food Security:** Salinization degrades the agricultural landscape

#### Threat to Health and Food Security

Toxic levels impact neurodevelopment in children while salinization degrades the agricultural landscape.

Research by Prof. Dr. Shalf Saleh and Team – University of Aden, Yemen

Fig.5. Irrigation Suitability and Agricultural Risk Assessment: Al-Musaymir Surface Basin

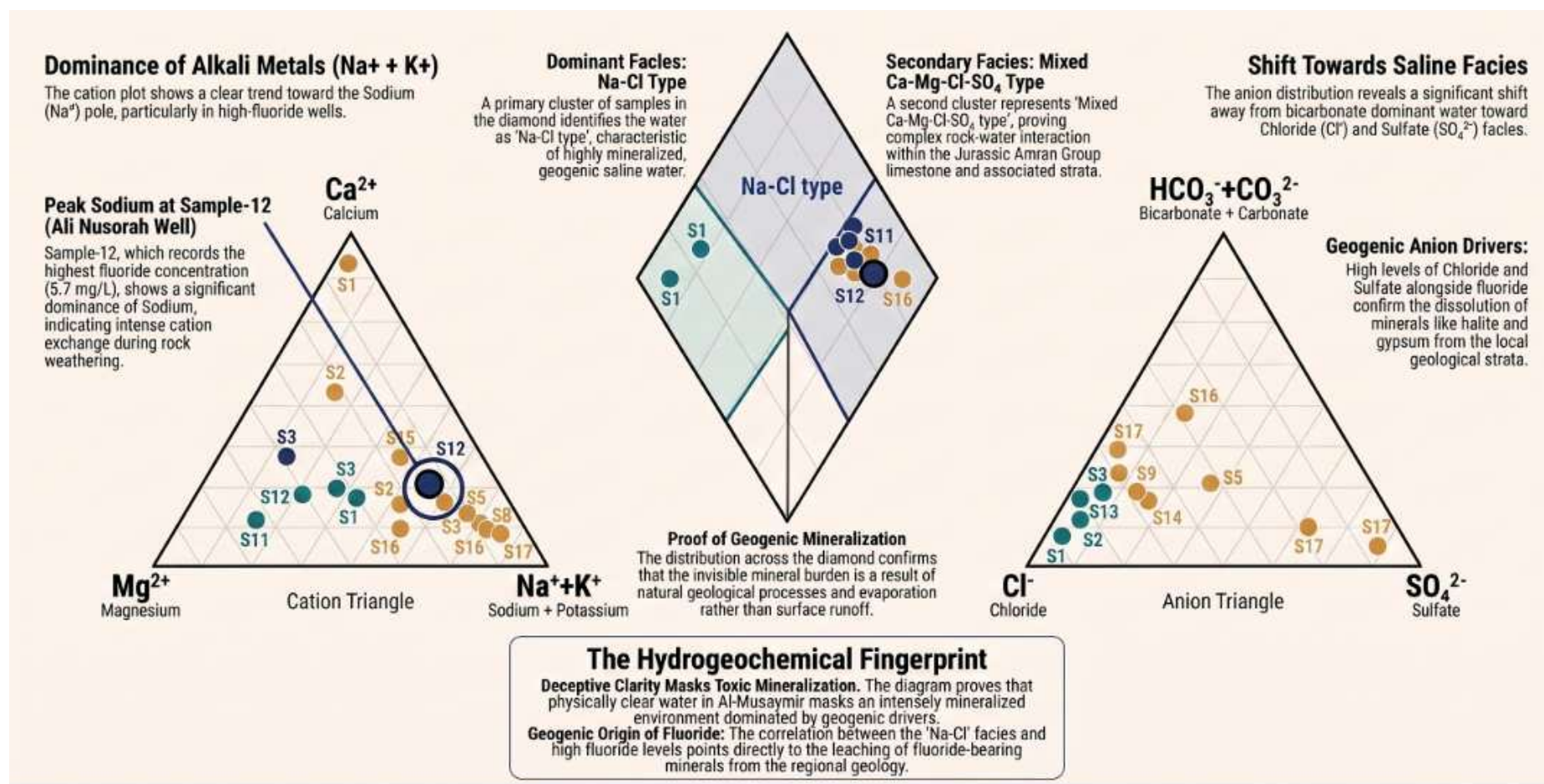


Fig. 6. Piper Trilinear Diagram: Mapping hydrogeochemical facies and rock-water interactions in Al-Musaymir surface aquifers (n=17). The diagram illustrates a clear evolutionary trajectory from Mixed Ca-Mg-Cl- $\text{SO}_4$  types to dominant Na-Cl facies, particularly in high-fluoride hotspots like Sample-12. This clustering confirms that groundwater chemistry is dictated by intense silicate weathering and evaporation-crystallization processes within the Jurassic Nayfa formations.

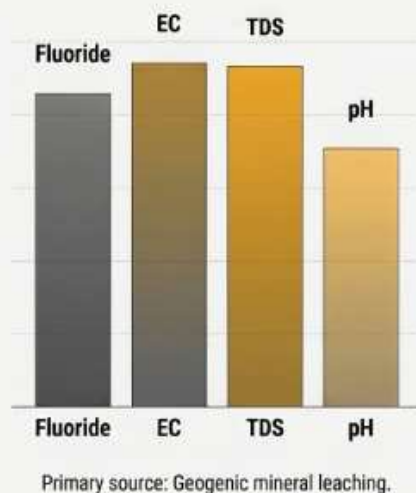
Rigorous statistical visualization of drivers behind water contamination and spatial risk categorization across 17 surface wells in the Al-Musaymir District, Yemen, highlighting a "Deceptive Visual Clarity" paradox where 82.35% of sources fail chemical safety limits despite passing aesthetic checks.

### Principal Component Analysis (PCA) – Geochemical Drivers

Two-Component Model Explains **81.57%** Total Cumulative Variance

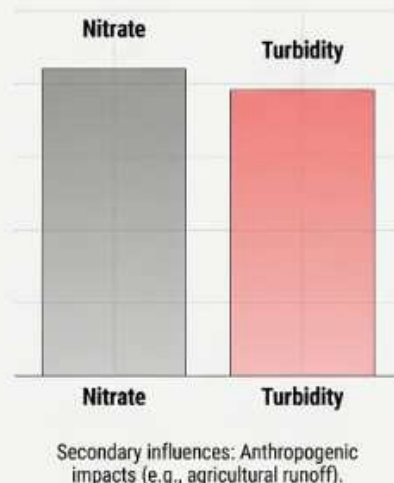
#### Component 1: Water-Rock Interaction Driver (58.45% Variance)

Primary source: Geogenic mineral leaching.



#### Component 2: Localized Surface Contamination Driver (23.12% Variance)

Secondary influences: Anthropogenic impacts (e.g., agricultural runoff).



### Hierarchical Cluster Analysis (HCA) – Spatial Risk Zones

Grouping of 17 sampled wells into distinct spatial management zones based on chemical risk.

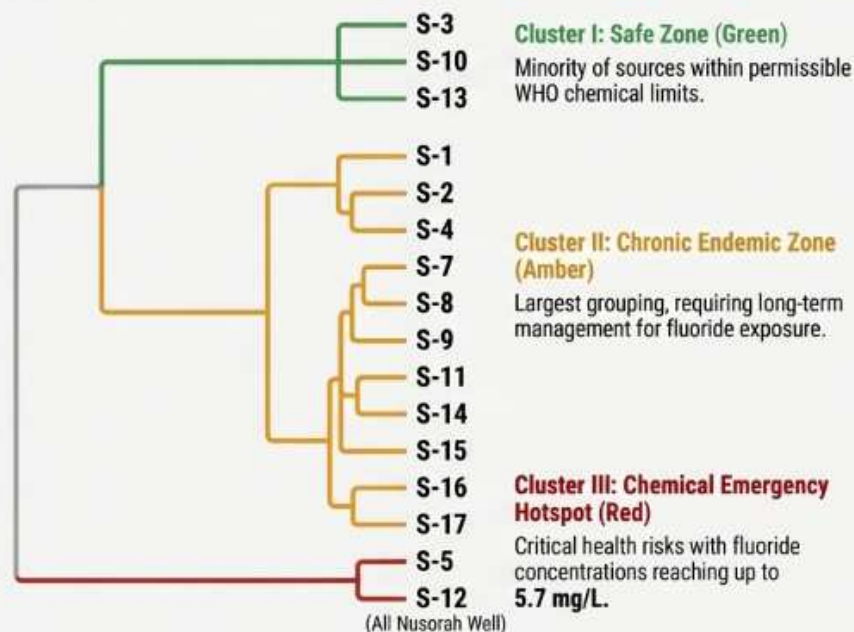


Fig. 7. Advanced Statistical Dashboard: Multivariate modeling of geogenic drivers and spatial management clusters via PCA and HCA

Note: Hierarchical Cluster Analysis (HCA) of 17 surface wells in Al-Musaymir: Integrating Spatio-Chemical Zonation with Pediatric Neuro-Toxicological Hazards. The dendrogram (Ward's Method) delineates the study area into three distinct management zones based on the total 15-ion hydrogeochemical fingerprint. **Cluster I (Safe/Moderate)** identifies wells with lower mineralization; **Cluster II (Chronic Endemic)** represents the widespread geogenic fluoride crisis affecting the majority of villages; and **Cluster III (Emergency Hotspot)** isolates high-mineralization peaks (e.g., S-12) where fluoride reaches 5.7 mg/L and pediatric HQ reaches 6.33, necessitating immediate engineering intervention.

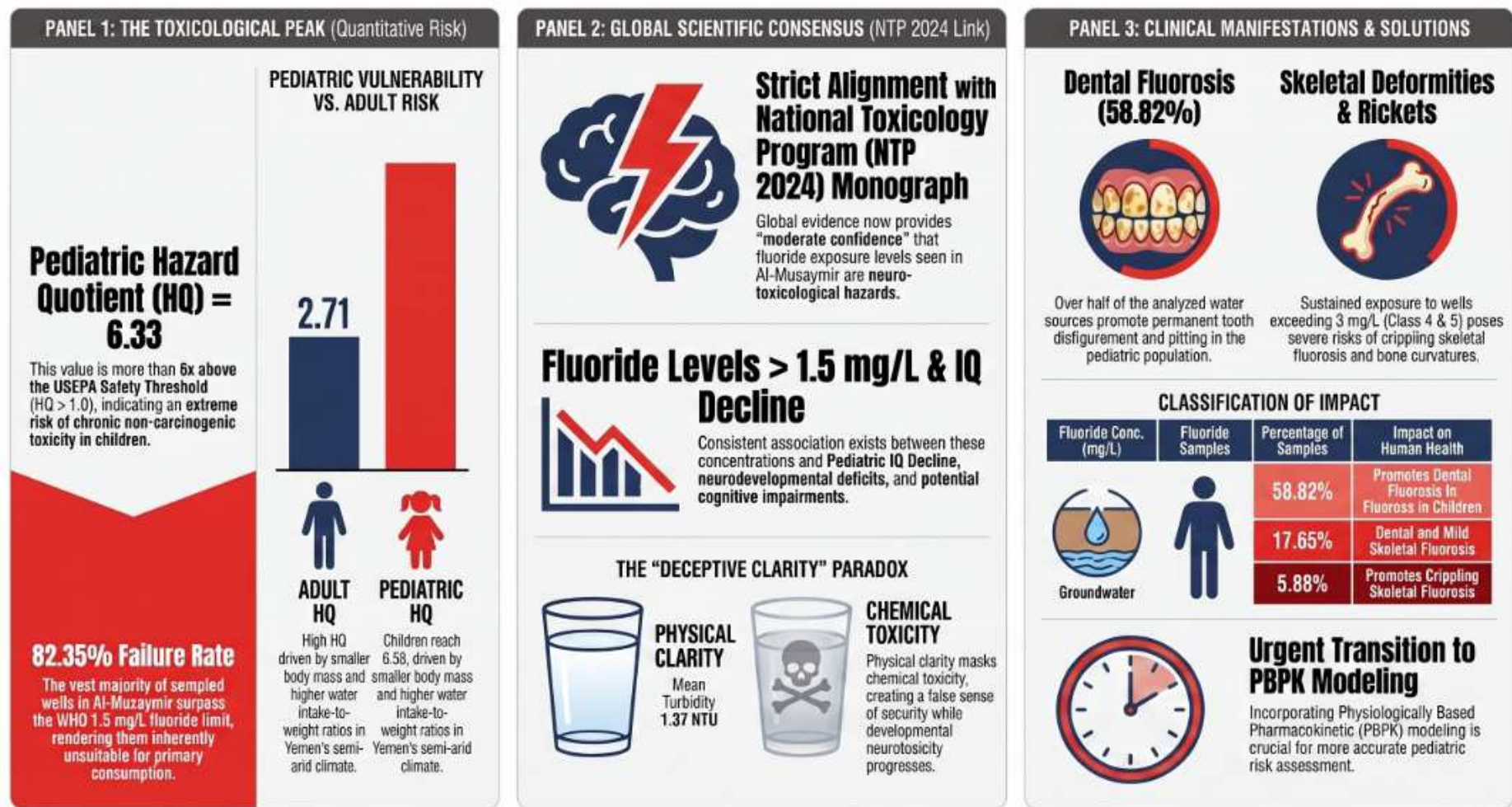
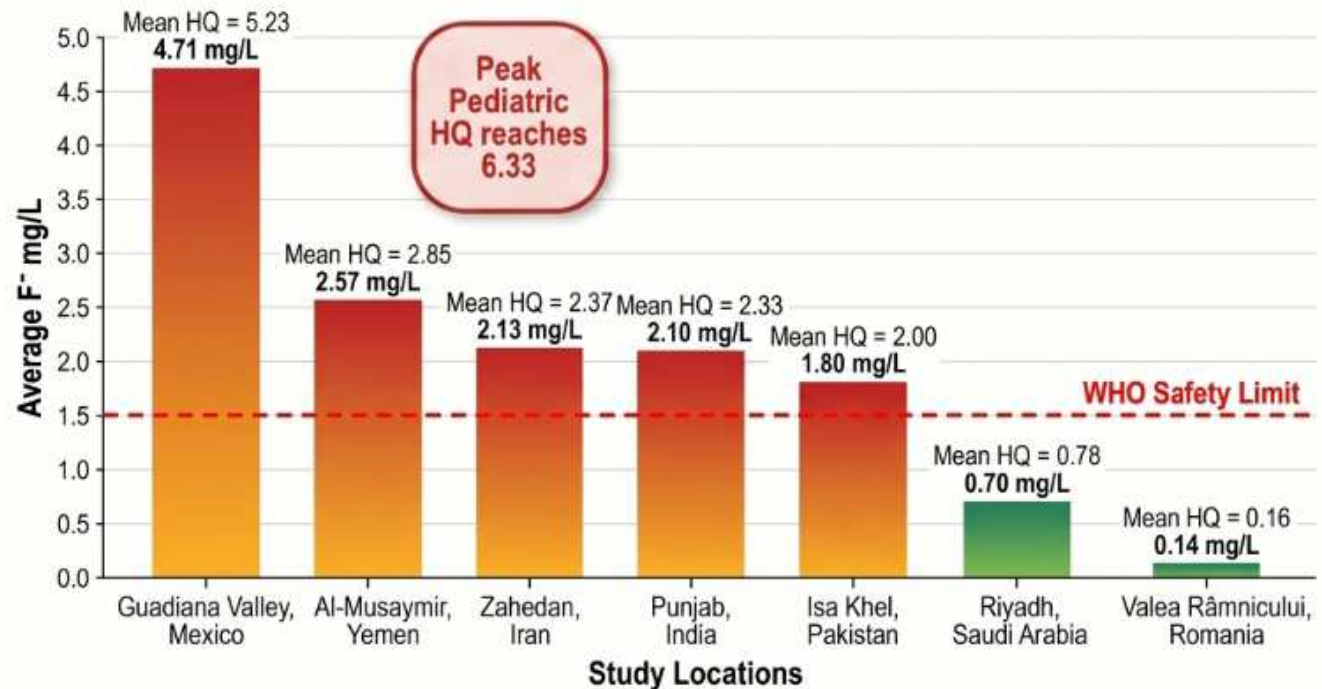


**Fig. 8.** Pediatric Neuro-Toxicological Risk Dashboard: Aligning local exposure data with NTP (2024) developmental neurotoxicity benchmarks.

## Context Summary

This infographic synthesizes geogenic fluoride ( $F^-$ ) data from international studies to illustrate the disparity between compliant water sources and those posing severe health risks. Geogenic fluoride originates from water-rock interactions. Concentrations exceeding the World Health Organization (WHO) safety threshold of 1.5 mg/L are linked to systemic health issues in children.



## Risk Classification Logic

**Hazard Quotient (HQ) Proportion:** Non-carcinogenic risk increases proportionally with chemical concentration; HQ values > 1.0 represent a failure of safety standards.

**Color-Coded Safety Compliance:** Water sources are categorized as "Safe/Compliant" (Green) if below 1.5 mg/L and "Unsafe/Risk" (Amber/Red) if exceeding the WHO limit.

Fig. 9. Comparative Synthesis of Average Geogenic Fluoride Concentrations and Pediatric Health Risks (Mean HQ) across Different Regions.

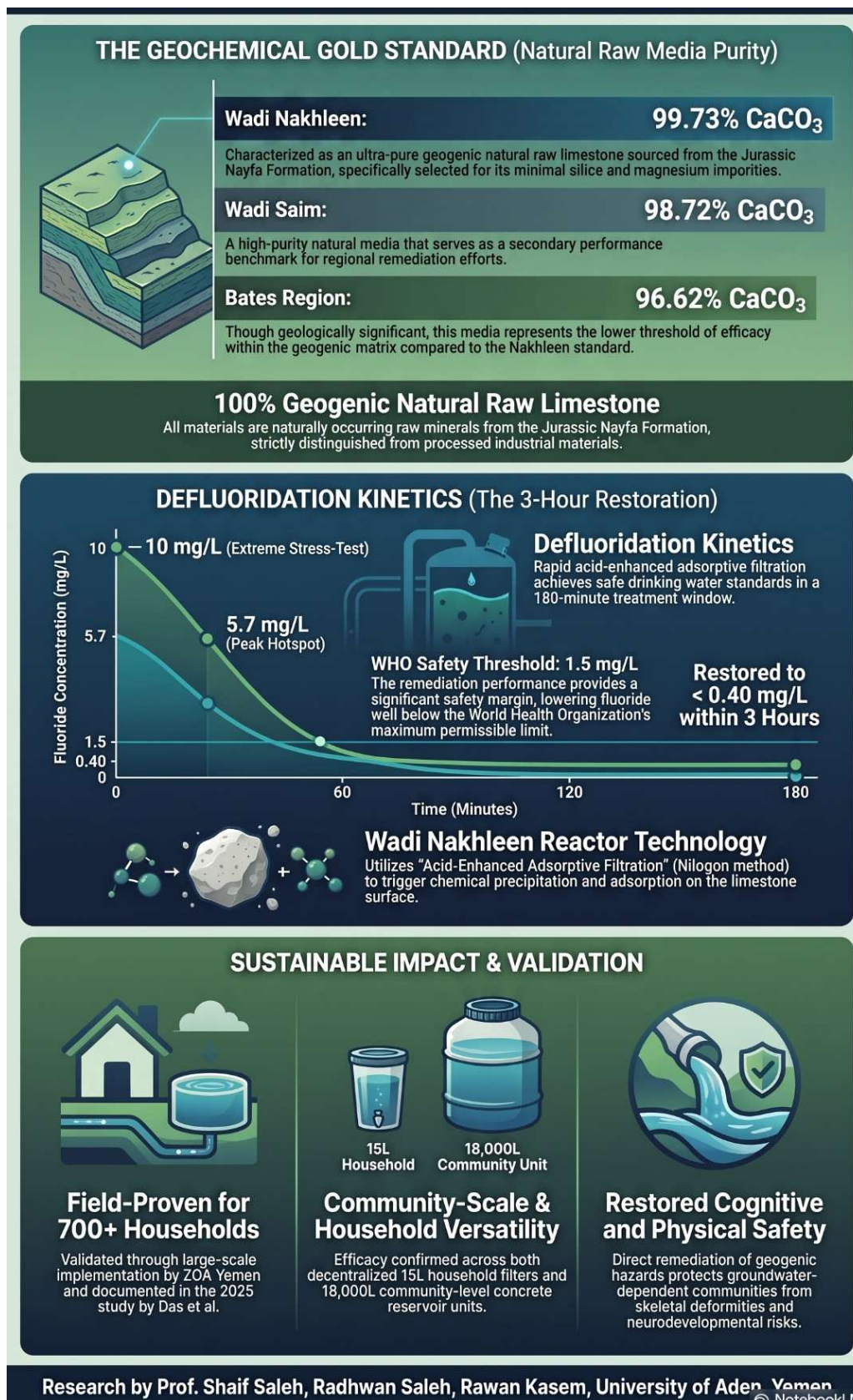


Fig. 10. Sovereign Remediation Performance Matrix: Comparative performance of the three natural raw limestone media in restoring water safety

## Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [SupplementaryMaterialsFiguresS1abcS2abc.pdf](#)
- [SupplementaryMaterialsTablesS1toS7.docx](#)
- [SupplementaryMaterialsTablesS8toS11c.docx](#)