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TEMPORAL VARIATION OF ARSENIC CONCENTRATION AND GROUNDWATER QUALITY INDEX ASSESSMENT IN VAN PHUC, NAM PHU, HANOI

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INTRODUCTION

1. Rationale of the study

Groundwater plays a crucial role in supplying drinking water to hundreds of millions of people worldwide, particularly in regions where surface-water resources are degraded or unreliable. In this context, arsenic contamination in groundwater has emerged as one of the most serious global environmental and public health challenges. Arsenic is a toxic metalloid of predominantly geogenic origin, and long-term exposure through drinking water has been linked to cancer and various chronic diseases.

In Vietnam, especially in the Red River Delta, many studies have reported elevated arsenic concentrations in groundwater that exceed national standards and World Health Organization guideline values. Suburban areas of Hanoi, where population density is high and groundwater has historically been a major domestic water source have been identified as regions with considerable arsenic-exposure risk. However, most previous studies relied on single-time sampling campaigns, whereas arsenic concentrations can vary over time due to hydrological fluctuations, groundwater abstraction, and evolving biogeochemical conditions.

The lack of long-term monitoring limits understanding of temporal arsenic dynamics and may lead to incomplete exposure and risk assessments. Therefore, investigating temporal variations in arsenic concentrations in representative contaminated areas such as Van Phuc, Thanh Tri, Hanoi, where arsenic contamination is well documented and aquifer conditions are strongly influenced by long-term pumping is both scientifically necessary and practically urgent.

Accordingly, the dissertation entitled ***“Temporal variation of arsenic concentration and groundwater quality index assessment in Van Phuc, Nam Phu, Hanoi”*** was conducted to address this research gap and provide a scientific basis for risk assessment and sustainable groundwater management.

2. Research objectives

- Characterize seasonal and long-term variations in arsenic concentration and groundwater hydrochemistry at Van Phuc.
- Elucidate the hydrogeochemical processes controlling arsenic mobilization and distribution in Holocene and Pleistocene aquifers.
- Apply machine-learning-based approaches to assess groundwater quality using the Groundwater Quality Index (GWQI).
- Evaluate non-carcinogenic and carcinogenic health risks associated with exposure to As, Fe, and Mn.

3. Main research contents

- Compilation and analysis of long-term monitoring data on arsenic and groundwater hydrochemistry composition at Van Phuc.
- Assessment of seasonal and temporal variations of arsenic concentrations
- Analysis of relationships between arsenic and hydrochemical parameters to clarify mechanisms controlling arsenic mobilization and distribution in groundwater at Van Phuc.
- Application of machine-learning techniques for GWQI-based groundwater quality classification.
- Calculation of non-carcinogenic and carcinogenic health risks under worst-case exposure scenarios assuming direct use of untreated groundwater for domestic purposes.

4. Structure of the dissertation

The dissertation comprises 126 pages, including 29 figures and 15 tables, organized as: Introduction (3 pages); Chapter 1. Literature review (43 pages); Chapter 2. Scope and Methodology (18 pages); Chapter 3. Results and Discussion (50 pages); Conclusions and Recommendations (2 pages); Novel contributions (1 page); List of publication (1 page) and 130 references.

CHAPTER 1. LITERATURE REVIEW

This chapter provides an overview of arsenic as an element and its occurrence in the environment and in human life. It reviews previous studies on arsenic contamination in groundwater and summarizes global and national research trends on arsenic in groundwater, with particular attention to the study area of Van Phuc, Nam Phu, Hanoi. The chapter also identifies four principal mechanisms responsible for elevated arsenic concentrations in groundwater. In addition, this chapter discusses recent trends in integrating machine-learning techniques with groundwater quality indices to evaluate and classify groundwater quality using more objective approaches compared with conventional methods. Furthermore, it presents background information on health risk assessment, including the procedures and key steps involved in evaluating potential health risks associated with the use of groundwater as a domestic water supply.

CHAPTER 2. STUDY AREA AND METHODOLOGY

2.1. Subject and study area

The subjects of this dissertation are groundwater samples collected from the Holocene and Pleistocene aquifers in Van Phuc, Nam Phu, Hanoi. Specifically:

- Groundwater samples from 17 monitoring wells at depths of 24-54 m (below ground surface) were used to investigate seasonal and long-term variations of As in groundwater and to assess associated health risks.
- Groundwater samples from 29 monitoring wells at depths of 20-54 m investigate the mechanisms controlling As occurrence and to apply machine-learning approaches for groundwater quality

assessment in Van Phuc.

- Analyzed parameters: A total of 22 physicochemical parameters representative of groundwater quality were measured, including pH, Eh, DO, EC, Na, K, Ca, Mg, Cl^-, HCO_3^-, SO_4^{2-}, F^-, Br^-, NO_2^-, NO_3^-, total As, total Fe, manganese (Mn^{2+}), phosphate (PO_4^{3-}), ammonium (NH_4^+), dissolved organic carbon (DOC) and methane (CH_4).

The study area of this dissertation is Van Phuc, Nam Phu, Hanoi (Figure 2.1), which represents a typical setting of the Red River Delta with the following distinctive characteristics:

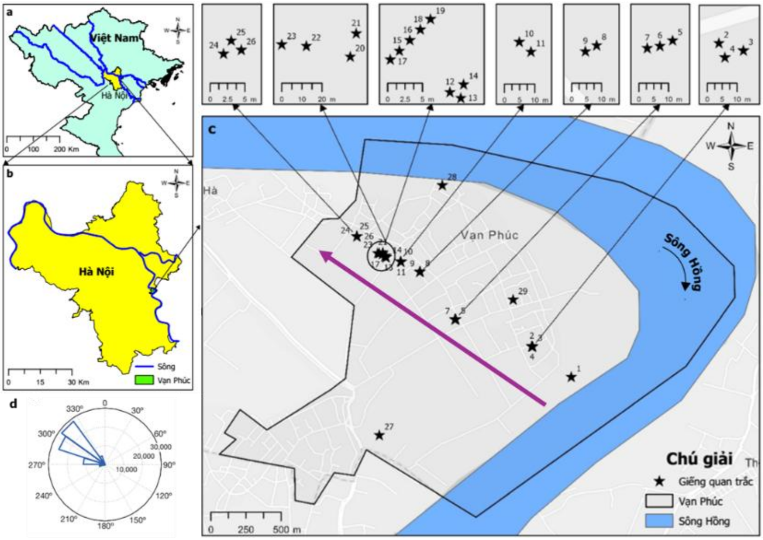

Figure 2.1. a) Location of Hanoi and major rivers in northern Vietnam. b) Location of Van Phuc relative to Hanoi and the Red River. c) Locations of monitoring wells along the study transect following the groundwater flow direction (purple arrow). d) Groundwater flow direction in Van Phuc.

- Distinct spatial contrast in As contamination: Groundwater As concentrations vary markedly, with very high levels in the southeast (>500 µg/L) and low levels in the northwest (<10 µg/L), providing favorable conditions for investigating As distribution and formation mechanisms.

- Impacted by anthropogenic activities: The natural groundwater flow direction in Van Phuc has been reversed from northwest-southeast to southeast-northwest (Figure 2.1d) due to intensive groundwater abstraction.
- Ideal area for studying As migration: The reversed hydraulic gradient enhances the potential downward migration of arsenic and organic matter from the Holocene aquifer to the Pleistocene aquifer, making the site suitable for investigating temporal variations and inter-aquifer transport processes.
- Integrated monitoring well system: Monitoring wells are arranged along a hydrogeological transect aligned with the groundwater flow direction and screened at multiple depths, enabling synchronized data collection to evaluate spatial and temporal variations of arsenic.

2.2. Chemicals, instruments and materials

2.3. Sampling and sample preservation

Groundwater samples were collected from monitoring well equipped with 1 m screen intervals to obtain samples from specific depths. Prior to sampling, each well was purged with at least 3-5 well volumes to remove stagnant water. Field parameters, including pH, oxidation-reduction potential (Eh), dissolved oxygen (DO), electrical conductivity (EC), and temperature, were measured in situ. Once field parameters stabilized, groundwater samples were collected and processed following specific protocols for each group of analytes to preserve chemical integrity: cations sample: filtered into Polyethylene (PE) and acidified with 65% HNO_3 to pH < 2. Anions sample filtered into PE bottles without acidification. Ammonium and phosphate samples: Filtered into PE bottles and preserved with H_2SO_4

1:1 (v/v) to pH < 2. DOC samples were collected in pre-combusted glass bottles (500 °C for 6 h) to remove trace carbon and acidified with 37% HCl to pH < 2. Samples for methane analysis were collected directly into evacuated glass vials (Labco, 819W) with approximately two-thirds of the vial volume filled with water. Vials were inverted and immediately preserved in dry ice in the field and stored frozen in the laboratory until analysis.

2.4. Analytical methods

Cations samples were analyzed using atomic absorption spectrometry (AAS), anions were determined by ion chromatography, ammonium and phosphate were measured using UV-Vis spectrophotometry, methane concentrations were analyzed using gas chromatography.

2.5. Machine learning-based method for groundwater quality assessment

Machine-learning models were applied to calculate the groundwater quality index (GWQI) to ensure objective evaluation and classification of groundwater quality. From the 22 analyzed physicochemical parameters, 11 key parameters were selected as input variables based on QCVN 09:2023. The dataset was preprocessed, normalized, and divided into training and testing sets. Decision Tree, Random Forest, and XGBoost algorithms were compared to identifying the most suitable model. The GWQI was calculated by deriving parameter weights using machine learning, computing sub-indices, and aggregating them into an overall GWQI score for groundwater quality classification in the study area.

2.6. Health risk assessment

In this study, non-carcinogenic health risks associated with exposure to As, Fe, and Mn, as well as carcinogenic risks associated with As exposure, were evaluated through both ingestion and dermal contact pathways. Health risks were calculated under a worst-case scenario assuming direct use of contaminated groundwater for both adults and children in the study area.

2.7. Data processing and statistical analysis

CHAPTER 3. RESULTS AND DISCUSSION

3.1. Seasonal variation of arsenic and physicochemical parameters in groundwater in the study area

3.1.1. Seasonal variation of physicochemical parameters

Analytical results indicate that the major physicochemical parameters of groundwater in Van Phuc exhibit only minor seasonal fluctuations, reflecting a hydrochemical system that is relatively stable over time.

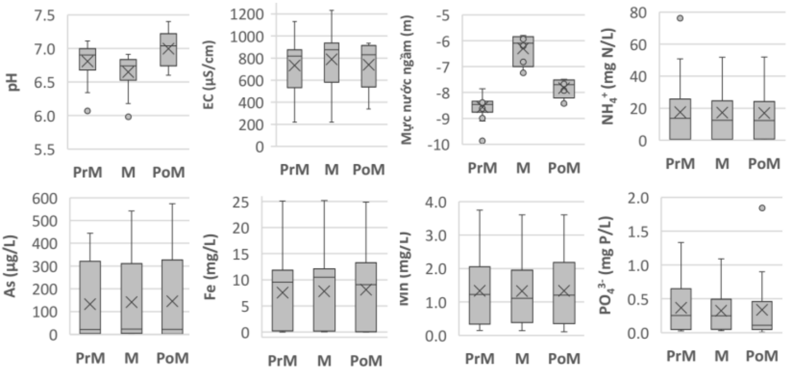

Figure 3.1. Box plots showing the concentrations of selected parameters in groundwater at Van Phuc across three seasons.

3.1.2. Seasonal variation of arsenic concentrations in groundwater

Arsenic concentrations in groundwater at Van Phuc vary over a wide range: from <5 to 444 µg/L (mean 132 µg/L) in the pre-monsoon season, <5 to 541 µg/L (mean 141 µg/L) during the monsoon season, and <5 to 574 µg/L (mean 145 µg/L) in the post-monsoon season. Groundwater-quality assessment indicates that approximately 47% of sampled wells exceeded the permissible arsenic limit set by the Ministry of Agriculture and Environment under QCVN 09:2023 in all three seasons.

Shallow wells (<30 m) generally exhibit higher As concentrations than deeper wells (Figure 3.4), primarily due to arsenic release from Fe-bearing minerals under reducing conditions. These conditions are more pronounced in shallow aquifers because of higher organic-matter content and strongly reducing environments associated with organic-rich layers and gray sandy

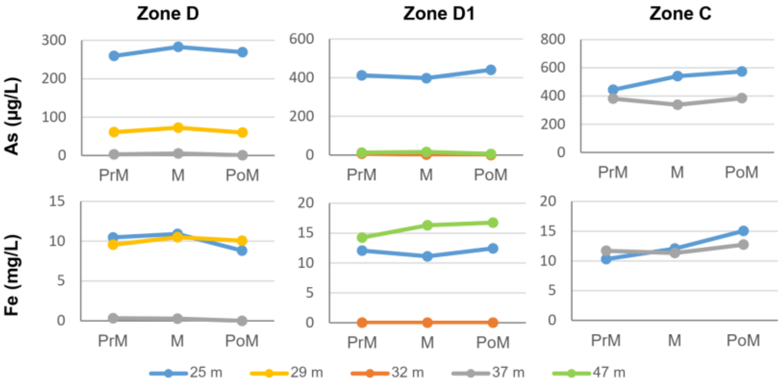

Figure 3.4. Seasonal variation of As and Fe in groundwater from wells at different depths in zones C, D1, and D.

Although average As concentrations suggest an overall stable annual trend, minor seasonal differences are evident, particularly in shallow wells.

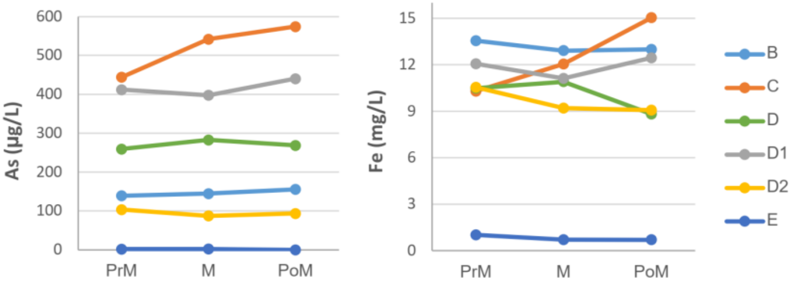

Figure 3.5. Seasonal variation of As and Fe in shallow groundwater from 25 m deep wells along the study transect.

Arsenic concentrations at well C show a gradual increase from the pre-monsoon to monsoon and post-monsoon seasons. In contrast, wells D1 and D2 show a slight decrease in As during the monsoon season, while well D exhibits an increase during the same period. Arsenic concentrations in wells B and E remain relatively stable across all three seasons (Figure 3.5).

Overall, seasonal variability of arsenic in the Van Phuc area is moderate rather than extreme, reflecting subtle adjustments of the groundwater system to hydrological changes associated with seasonal climatic cycles. General physicochemical parameters remain relatively stable, whereas arsenic appears more sensitive to minor variations in redox conditions, depth, and sediment characteristics. In general, arsenic concentrations and groundwater physicochemical parameters at Van Phuc do not change substantially between seasons. This limited variability may partly result from the relatively slow groundwater flow velocity at Van Phuc (approximately 40 m per year), which dampens short-term fluctuations. Additionally, the presence of a thick low-permeability aquitard overlying the aquifer reduces the influence of dilution by rainfall and surface-water recharge.

3.2. Temporal variation of arsenic and physicochemical parameters in groundwater in the study area

Long-term monitoring data from 2010 to 2024 indicate that the major dissolved ions in groundwater including Na, K, Ca, Mg, Cl, HCO_3^- and SO_4^{2-} remained relatively stable over time in most wells. This stability suggests that the hydrochemical composition of the aquifer has not been strongly influenced by short-term dilution or recharge processes, such as direct infiltration of rainfall or surface water on an annual basis.

In zone B, closest to the river, a gradual decrease in As concentrations was observed during 2010-2019, while Fe, Mn, and DOC remained relatively stable (Figure 3.7). In this zone, the aquifer is frequently recharged by Red River water. A decrease in $\delta^{18}O$ values from -7.6‰ to -8.6‰ indicates increased river-water infiltration, likely driven by continuous groundwater abstraction in Hanoi. The observed decrease in As may therefore reflect flushing of dissolved arsenic along the groundwater flow path. However, the decline is relatively slow, possibly due to continued input of dissolved As from riverbank sediments.

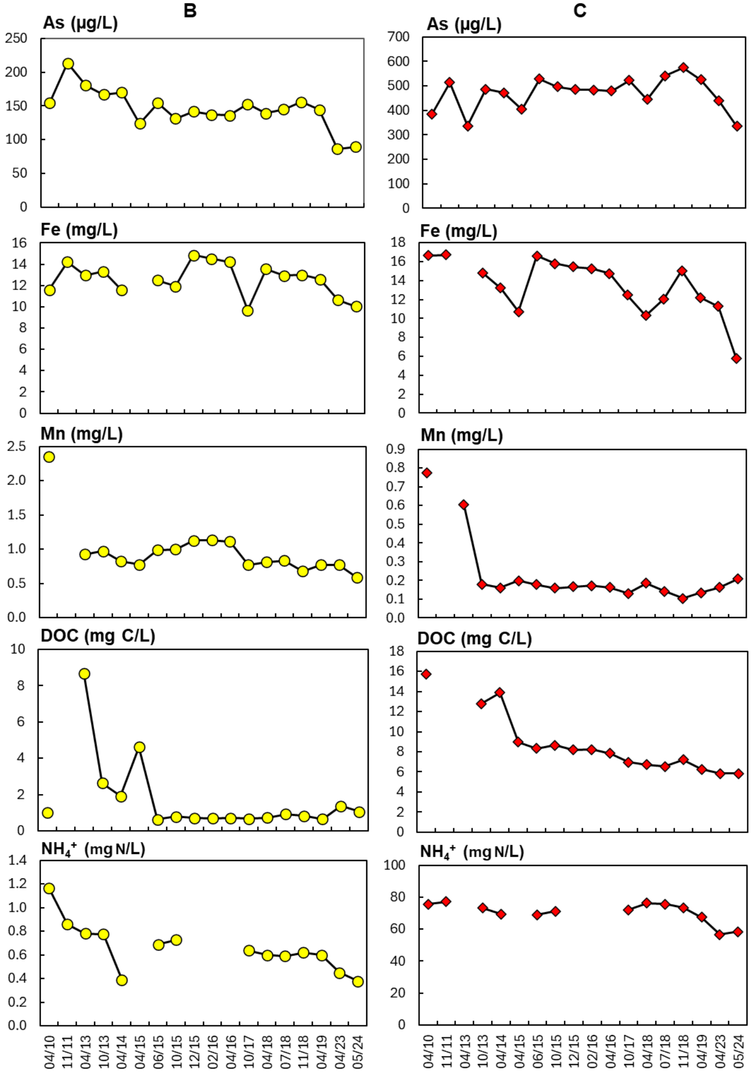

Figure 3.7. Temporal variation of As, Fe, Mn DOC and NH_4^+ concentrations in groundwater from 25 m deep wells in zones B and C.

In zone C, representing the center of the Holocene aquifer, concentrations of As, Fe, Mn, and NH_4^+ remained relatively stable during 2010-2019 (Figure 3.7), indicating stable hydrogeochemical conditions over the monitoring period. The $\delta^{18}O$ values remained around -7‰, suggesting that groundwater in this zone originates from a mixture of river recharge and evaporated water, conditions that help sustain Fe-reducing environments and ongoing As release.

In the redox transition zone (RTZ), well D1, located between the RTZ and Holocene aquifer, showed stabilization of As, Fe, and NH_4^+ concentrations from 2013 to 2019 (Figure 3.9). This pattern suggests relatively stable geochemical conditions and a dynamic equilibrium in the RTZ, where As-rich groundwater migrating from the Holocene aquifer is effectively buffered by adsorption and co-precipitation processes involving Fe phases. Notably, Mn concentrations in this well increased gradually from 2013 to 2024, although the magnitude of change was modest (about 0.46 mg/L, from 0.22 mg/L in 2013 to 0.69 mg/L in 2024). Dissolved Mn is a sensitive indicator of Mn(III/IV) reduction under redox conditions generally less reducing than those required for Fe(III) reduction.

At the center of the RTZ, well D shows a decreasing trend in As and Fe from 2017 to 2024, despite limited data availability (Figure 3.9), along with a slight increase in phosphate concentrations, while other parameters remain relatively stable. These patterns suggest that changes in As and Fe are unlikely to be driven by variations in recharge sources or dilution but rather by in situ redox adjustments within the RTZ. The concurrent decline in Fe may reflect oxidation of Fe^{2+} and formation of secondary Fe(III) phases capable of adsorbing As. The slight increase in PO_4^{3-} may indicate redistribution of As through competitive adsorption between phosphate and arsenic on newly formed mineral surfaces.

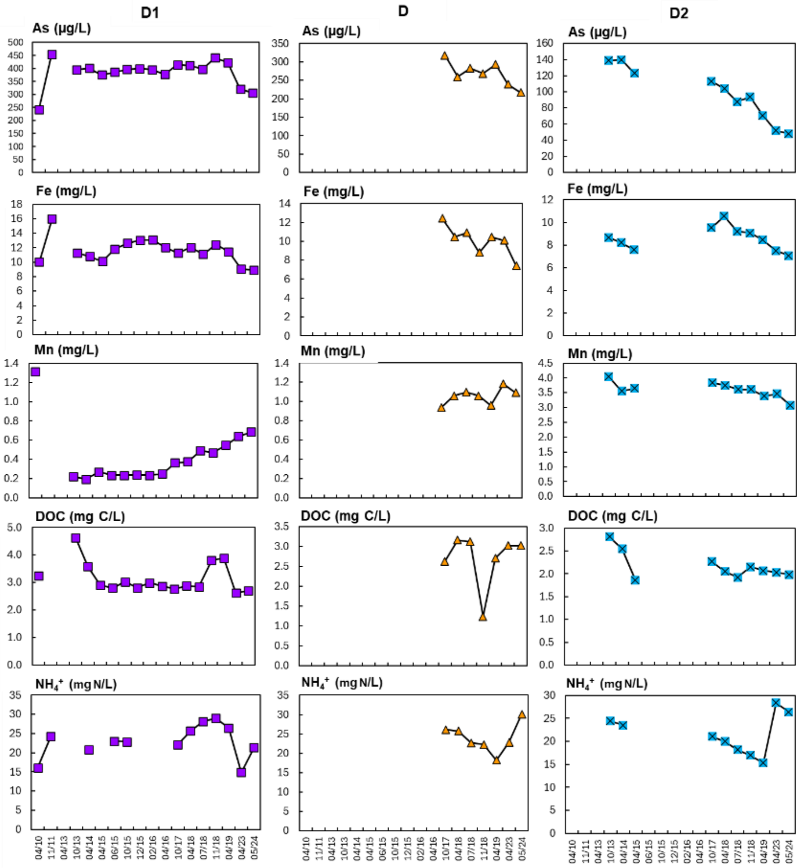

Figure 3.9. Temporal variation of As, Fe, Mn, DOC, and NH_4^+ concentrations in groundwater from 25 m deep wells in subzones D1, D, and D2.

Located near the boundary with the Pleistocene aquifer, well D2 shows a rapid decrease in As concentrations from approximately 138 µg/L in 2013 to 48 µg/L in 2024, whereas Fe, Mn, DOC, and NH_4^+ isplay only slight declines. This trend highlights the dominant role of As sequestration processes within the RTZ as As-rich groundwater from the Holocene aquifer approaches the Pleistocene aquifer, which is enriched in Fe(III) and Mn(III/IV) phases. At this location, Fe^{2+} transported from the Holocene aquifer is more strongly oxidized, leading to formation of secondary Fe(III) phases that efficiently adsorb As and cause a faster decline in As relative to other parameters. The minor decreases in Fe, Mn, DOC, and NH_4^+ suggest that baseline geochemical conditions at D2 remain strongly reducing and relatively stable.

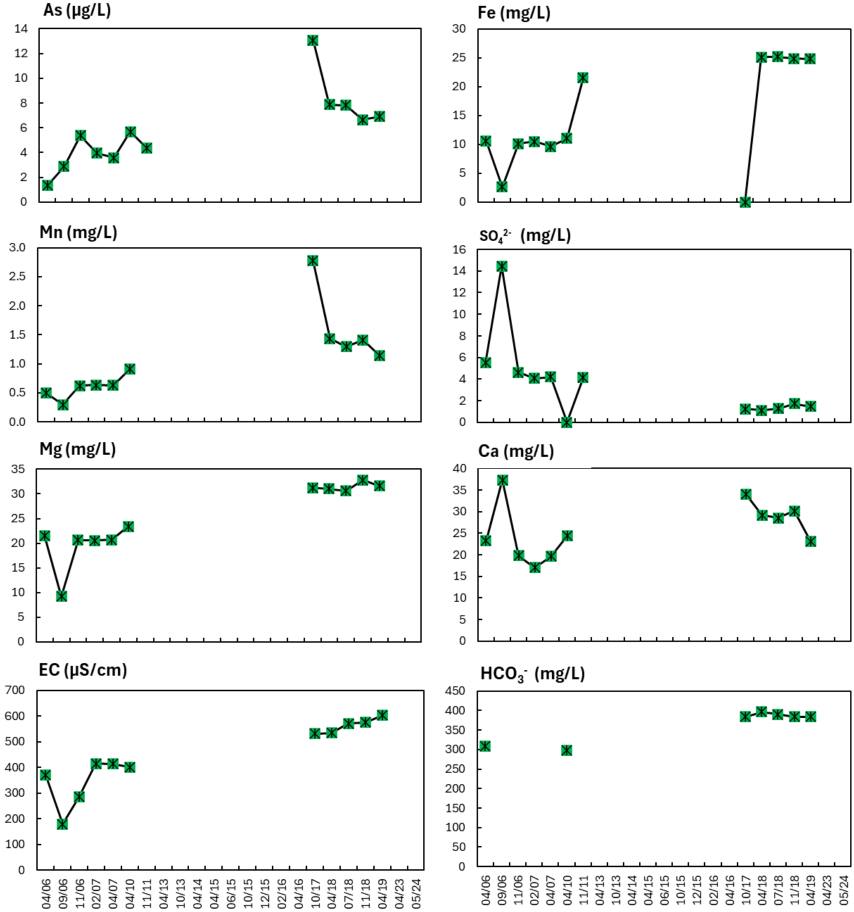

Figure 3.11. Temporal variation of As, Fe, Mn, and major ions in Pleistocene groundwater at a depth of 54 m.

A notable exception within the Pleistocene aquifer is a well at a depth of 54 m, which has been overlooked in previous studies. At this site, simultaneous increases in As concentrations were observed during 2006-2019, together with increases in Fe, Mn, Ca^{2+}, Mg^{2+}, HCO_3^- and EC, while SO_4^{2-} and PO_4^{3-} decreased (Figure 3.11). These trends indicate significant temporal changes in geochemical conditions. The pattern suggests increasingly reducing and mineralized groundwater, likely associated with enhanced Fe(III) and Mn(III/IV) reduction and accumulation of dissolved inorganic carbon (DIC) from organic-matter degradation, leading to carbonate dissolution and higher electrical conductivity.

Overall, temporal analysis indicates that the groundwater system in the Van Phuc area is relatively stable over short timescales but exhibits substantial long-term changes and pronounces spatial variability. Within a study transect of only about 2 km, monitoring wells reveal considerable heterogeneity in hydrogeochemical conditions, reflected in contrasting trends of As and associated parameters among river-proximal zones, the central Holocene aquifer, the RTZ, and the Pleistocene aquifer. These findings suggest that As dynamics at Van Phuc do not follow a single uniform trend but instead result from complex interactions among redox conditions, sediment characteristics, aquifer structure, and the cumulative effects of long-term pumping-induced groundwater flow.

3.3. Interpretation of arsenic formation mechanisms in groundwater in the study area

Unlike the classical model that considers Fe(III) reduction as the sole mechanism controlling arsenic mobilization, recent studies have demonstrated that phosphate and sulfate reduction processes also play important roles in arsenic transport within aquifers. In addition, Fe mineral phases in sediments, microbial communities, and the formation of methane and sulfide are key controls on arsenic occurrence in groundwater. These findings indicate that arsenic is not only released but also maintained and spatially distributed through overlapping and complex biogeochemical cycles. Therefore, examining the relationships between arsenic and other physicochemical components in groundwater is essential for understanding its mobility within aquifers.

Analytical results from groundwater samples collected from 29 monitoring wells show a strong positive correlation between As and Fe, reflecting the dominant role of reductive dissolution of As-bearing Fe(III) oxyhydroxide minerals in sediments. The close association NH_4^+ and PO_4^{3-} with As indicates intensive degradation of organic matter and mineralization of nitrogen- and phosphorus-bearing compounds under anoxic conditions, which helps maintain reducing environments within the aquifer. In addition to serving as an indicator of organic-matter mineralization, phosphate directly influences arsenic mobilization through competitive adsorption on Fe(III) mineral surfaces. When Fe(III) oxyhydroxide phases are reduced, the decrease in available adsorption sites lowers phosphate retention and simultaneously enhances arsenic mobility in the aqueous phase.

Previous studies have identified thick peat layers within Holocene sediments in Hanoi, and similar peat deposits have been observed at Van Phuc. These peat layers likely serve as important sources of organic matter (OM) for the aquifers in the study area. In the Holocene aquifers at Van Phuc, degradation and fermentation of OM play a fundamental role in establishing strongly reducing conditions, thereby controlling the formation, persistence, and redistribution of arsenic in groundwater.

Results from this study indicate that DOC in groundwater at Van Phuc is supplied and transported into the aquifer through two main flow pathways, each characterized by distinct geochemical features and functional roles in arsenic formation and distribution (Figure 3.17).

- Flowpath 1: DOC is transported horizontally with groundwater flow through recharge from Red River water infiltrating young, Fe- and OM-rich riverbank sediments into adjacent aquifers. This process occurs particularly along the forced groundwater-flow path from the Holocene aquifer toward the RTZ and the Pleistocene aquifer. In this zone, fermentation and Fe reduction dominate, leading to arsenic release into groundwater with concentrations typically ranging from 20 to 200 µg/L.

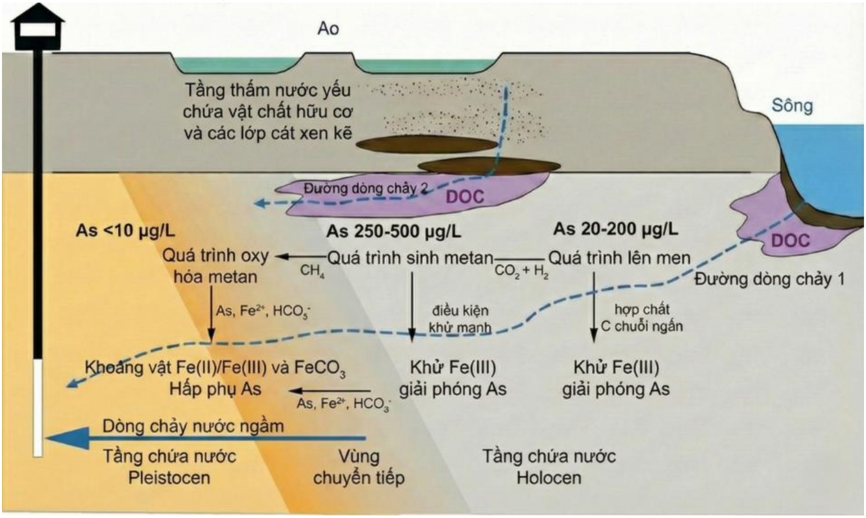

Figure 3.17. Conceptual model illustrating sources and cycling of organic matter associated with arsenic release mechanisms in aquifers at Van Phuc.

- Flowpath 2: DOC infiltrates vertically from OM-rich, low-permeability aquitard layers and from surface sources such as ponds. This pathway introduces relatively high DOC concentrations (approximately 5–7 mg C/L). Upon entering the Holocene aquifer, DOC is rapidly consumed by microorganisms through hydrolysis and fermentation, producing acetate, H_2, and CO_2. These processes stimulate microbial Fe(III) reduction by genera such as *Geobacter* and *Bacillus*, leading to arsenic release and methane production. Consequently, methane concentrations in this area reach 40–58 mg/L. This DOC supply pathway, combined with slow groundwater flow, likely contributes to the formation of geochemical "hotspots" where strongly reducing conditions develop, methane is generated in situ, and groundwater arsenic concentrations reach the highest levels observed in the study area, exceeding 500 µg/L.

Geochemical, isotopic, microbiological, and mineralogical analyses collectively indicate that arsenic contamination in groundwater at Van Phuc is not the result of a single process but rather the outcome of complex interactions among multiple biogeochemical cycles within the aquifer system. Organic matter serves as the primary driving force controlling redox evolution through degradation, fermentation, Fe(III) reduction, and methanogenesis, ultimately leading to arsenic release and accumulation in groundwater. The coexistence of two DOC supply and transport pathways contributes to spatial heterogeneity in methanogenic zones and arsenic "hotspots." Conversely, within the RTZ, methane oxidation and formation of secondary Fe phases act as natural attenuation mechanisms that reduce arsenic concentrations before groundwater enters the Pleistocene aquifer. This carbon–methane-cycle framework provides a coherent explanation for the formation, persistence, and redistribution of arsenic in groundwater at Van Phuc.

3.4. Application of machine learning in groundwater quality assessment at Van Phuc

Groundwater quality at Van Phuc was evaluated using 11 physicochemical parameters as input variables for the machine-learning (ML) model. These parameters were selected from a total of 22 measured variables obtained from 29 groundwater samples collected from monitoring wells. Previous studies integrating ML and groundwater quality indices (GWQI) have applied various algorithms, and no single method has been universally identified as the most effective. Each algorithm has its own strengths and limitations, and performance often depends on input data characteristics and local hydrogeological conditions. Therefore, three widely used ML algorithms: Decision Tree (DT), Random Forest (RF), and XGBoost were selected to determine the most suitable approach for groundwater-quality classification in the study area.

Table 3.7. Feature-importance ranking and ROC-derived weights of groundwater quality indicators based on the XGBoost model

Parameter	**Importance**	**Rank**	**ROC weight**
As	0,3994	1	0,3397
HN	0,1649	2	0,2147
Mn^{2+}	0,1153	3	0,1522
Na^+	0,1052	4	0,1106
Cl^-	0,0840	5	0,0793
NH_4^+	0,0571	6	0,0543
Fe	0,0452	7	0,0335
F^-	0,0290	8	0,0156
pH	0	-	0
SO_4^{2-}	0	-	0
TDS	0	-	0

The results indicate that the XGBoost model performs best for the dataset and hydrogeochemical conditions at Van Phuc. Analysis of parameter weights and importance shows that, among the 11 input variables, eight parameters including As, Mn, Fe, NH_4^+, F^- and hardness exhibit non-zero importance values, whereas the remaining three parameters (pH, SO_4^{2-} and TDS) contribute negligibly to the model (Table 3.7). Among the parameters with non-zero importance, As is predicted to have the greatest influence on groundwater quality classification, while NH_4^+ shows relatively low importance despite its positive correlation with As in the aquifers at Van Phuc.

From a hydrogeochemical perspective, the feature-importance ranking obtained from XGBoost is consistent with the current understanding of arsenic mobilization in the study area. The dominating role of As as the top-ranked feature is consistent with its high exceeding frequency and toxicity. Arsenic was released from sediment into groundwater through the reductive dissolution of Fe oxyhydroxides in the aquifer systems, supported by reducing bacteria, when the natural organic matter (NOM) is sufficiently available. The second-ranked indicator, hardness, acts as an integrated proxy for Ca-Mg carbonate equilibria and mixing between river-derived recharge and deeper Pleistocene groundwater, both of which control contaminant transport pathways. High importance of Mn^{2+} reflects the progression of redox reactions towards more reducing conditions that may lead to the further mobilization of As. Na^+ and Cl^- likely capture mixing between young river derived recharge and more mineralized, partly saline or anthropogenically impacted groundwater. Although NH_4^+ is a widespread pollutant in the study area, its moderate importance suggests that it indirectly reflects reducing conditions, which is coherent with the release of As in the Holocene aquifer as mentioned above. The minor contributions of Fe and F^- further support the role of redox-controlled mobilization of iron oxyhydroxides and water-sediment interactions in shaping groundwater quality in Van Phuc. The negligible contributions of pH, SO_4^{2-} and TDS in the model reflect their relatively limited variability within the dataset and their compliance with the guideline ranges.

Using sub-indices and parameter weights, GWQI scores were calculated for groundwater at Van Phuc. Based on the classification scale, among the 29 samples analyzed, only one was classified as Good (GWQI = 83), 12 samples (41.4%) as Fair, and the remainder as Marginal (20.7%) and Poor (34.5%).

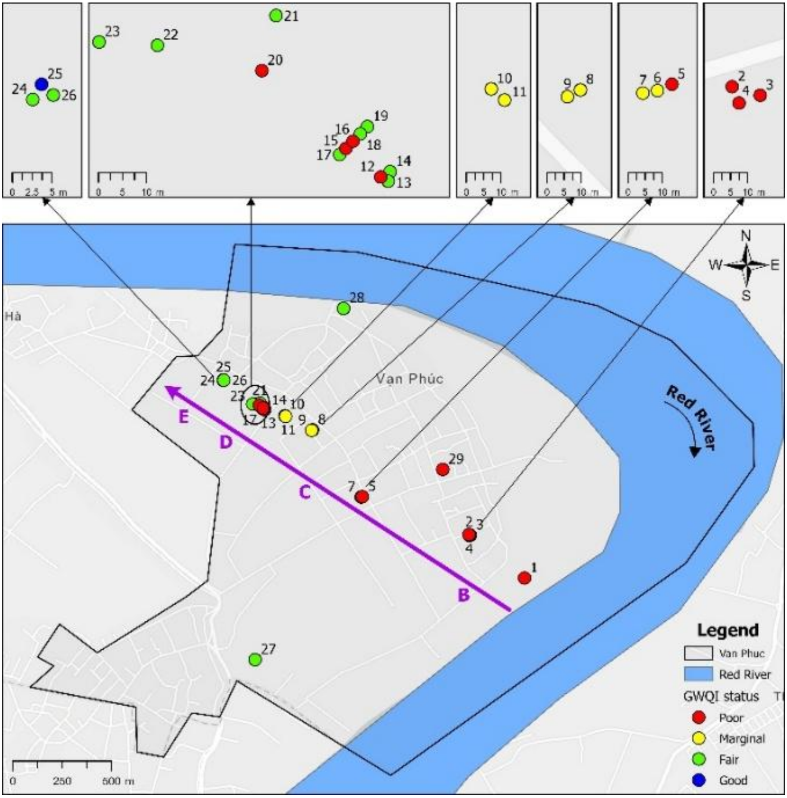

Figure 3.17. Spatial distribution of groundwater quality at Van Phuc based on GWQI scores calculated using the NSF method.

Most monitoring wells were installed along the dominant groundwater-flow direction. Based on the hydrogeochemical zonation proposed by Stopelli et al. (2020), these wells can be grouped into four zones: Zone B (wells 1–4 and 29), representing the river-proximal Holocene aquifer; Zone C (wells 5–10) within the Holocene aquifer; Zone D (wells

12–21) corresponding to the redox transition zone (RTZ); and Zone E (wells 22–26) representing the Pleistocene aquifer (Figure 3.17). GWQI scores reveal clear spatial variability consistent with these zonation, reflecting the complex hydrogeochemical dynamics of the Holocene–Pleistocene aquifer system.

Overall, the spatial distribution of GWQI at Van Phuc reflects combined effects of arsenic release and attenuation within the Holocene–Pleistocene system. Zones B and C act as primary arsenic sources, with groundwater quality classified as very poor to poor. Zone D functions as a transition zone where adsorption and co-precipitation reduce contaminant concentrations, improving water quality. Zone E represents a relatively stable aquifer with generally better groundwater quality.

3.5. Health risk assessment associated with the use of groundwater for domestic purposes

Seasonal and long-term results, together with previous studies, indicate that groundwater in Van Phuc has been persistently contaminated by As, Fe, and Mn, posing potential health risks if used directly for domestic purposes. Health risks were evaluated under a worst-case scenario considering exposure to As, Fe, and Mn through ingestion and dermal contact for both adults and children across seasons, in order to propose recommendations for water treatment prior to use.

At the time of this study, households in Van Phuc had already been supplied with piped water from the Hanoi municipal system; therefore, groundwater from private wells is no longer used directly for drinking. However, groundwater from small household wells is still used for irrigation, livestock, or as a backup water source in case of supply interruptions.

3.5.1. Non-carcinogenic risks associated with As, Fe, and Mn

Non-carcinogenic risks were assessed using the hazard index (HI).

The average HI for As consistently exceeded the safety threshold (HI > 1) in all seasons. For adults, mean HI increased from 20.22 (pre-monsoon) to 21.55 (monsoon) and reached 22.19 (post-monsoon). For children, mean HI ranged from 14.54 to 15.96 and peaked in the post-monsoon season.

Mn and Fe are co-occurring contaminants contributing to overall risk. Mn HI ranged from 0.04-1.33 for adults (one well exceeding the threshold) and 0.06-2.19 for children (five wells exceeding), mainly in zones D, D2, and E. Fe contributed less, with mean HI values of ~0.5 for adults and ~0.4 for children; only a few wells exceeded the threshold.

Considering the combined effects of As, Fe, and Mn, most surveyed wells in Van Phuc show total HI values exceeding the safety threshold, confirming that direct use of untreated groundwater poses potential adverse health effects and requires treatment prior to use.

3.5.2. Carcinogenic risks associated with arsenic

Incremental lifetime cancer risk (ILCR) associated with arsenic was calculated for ingestion and dermal pathways. According to USEPA guidelines, acceptable risk ranges from 10^{-6} to 10^{-4}, while values greater than 10^{-4} are considered unacceptable. Results indicate that cancer risks via ingestion are generally unacceptable for most wells in all seasons, with ILCR values exceeding 10^{-4} at most sampling points. Children tend to face higher risks due to greater water intake per body weight. Dermal risks are substantially lower; for adults, dermal ILCR values for 12 of 17 wells fall within acceptable or negligible ranges (4.63×10^{-8}–1.26×10^{-5}). However, for children, 7 of 17 wells (~41%) exceed 10^{-4}, indicating continued concern.

Overall, under a worst-case scenario of direct groundwater use, residents in Van Phuc may face significant non-carcinogenic (HI > 1) and carcinogenic (ILCR $>10^{-4}$) risks, particularly in shallow wells and during the post-monsoon period. Although centralized water supply has reduced direct exposure, the results highlight persistent risks and the need for treatment to remove As, Fe, and Mn before groundwater is used for any purpose.

CONCLUSIONS

1. Regarding seasonal variability, As concentrations exhibited the most pronounced variability in shallow wells (~25 m), primarily due to recharge from rainfall and river water. The magnitude of these fluctuations varied across hydrogeochemical zones and generally decreased along the sequence from the Holocene center → transition zone → river-proximal zone → deeper Pleistocene aquifer.
2. Over the long-term period (2010–2024), As concentrations showed substantial temporal changes and marked spatial heterogeneity. The Holocene aquifer maintained persistently high and relatively stable As levels. In contrast, the transition zone displayed decreasing As concentrations, likely associated with the formation of secondary Fe mineral phases. The deeper Pleistocene aquifer exhibited increasing trends in both As and Fe, suggesting potential downward migration of contaminants driven by intensive groundwater abstraction.
3. The occurrence of As in groundwater at Van Phuc is primarily controlled by microbially mediated reductive dissolution of Fe oxyhydroxides under reducing conditions, closely linked to the carbon-methane cycle. Organic matter (OM) supplied from river inputs and rich OM aquitard layer provides dissolved organic carbon that promotes reducing conditions and enhances As mobilization in identified hotspots. Conversely, methane oxidation in the transition zone may contribute to partial attenuation of As before groundwater enters the deeper aquifer.
4. The preliminary application of machine-learning approaches to groundwater quality assessment indicates that As is the dominant

factor governing overall water quality. Among 29 sampled wells, only one was classified as good quality, while the remainder ranged from fair to poor, with the poorest quality concentrated in the Holocene aquifer. Groundwater quality generally improved with depth and was comparatively better in the Pleistocene aquifer.

5. Under the worst-case scenario, direct use of untreated groundwater in Van Phuc poses significant health risks, with hazard index (HI) values exceeding 1 and incremental lifetime cancer risk (ILCR) values greater than 10^{-4} in most surveyed wells. The highest risks occur after the rainy season; children represent the most vulnerable group, and exposure through ingestion presents a greater risk than dermal absorption.

LIST OF THE PUBLICATION RELATED TO THE DISSERTATION

1. Emiliano Stopelli, **Vu T. Duyen**, Henning Prommer, Martyna Glodowska, Andreas Kappler, Magnus Schneider, Elisabeth Eiche, Alexandra K. Lightfoot, Carsten J. Schubert, Pham K.T. Trang, Pham H. Viet, Rolf Kipfer, Lenny H.E. Winkel, Michael Berg, AdvectAs team members, Carbon and methane cycling in arsenic-contaminated aquifers, *Water Research*, 200, pp. 117300, 2021, DOI: https://doi.org/10.1016/j.watres.2021.117300
2. **Vu T. Duyen**, Thanh Dam Nguyen, Pham T.K. Trang, Viet Pham Hung, M. Berg, Seasonal variation in arsenic concentration and hydrogeochemical dynamics in groundwater at Van Phuc, Thanh Tri, Hanoi, *Vietnam Journal of Science and Technology*, 6x(x), 2026, pp 1-17, DOI: https://doi.org/10.15625/2525-2518/22409
3. **Thi Duyen Vu**, Thanh Dam Nguyen, Thi Kim Trang Pham, Michael Berg and Viet Hung Pham, Evaluating groundwater quality in an arsenic-contaminated aquifer in the Red River Delta using machine learning: a case study in Van Phuc, Hanoi, Vietnam, *Environmental Science: Advances*, 2026, DOI: http://doi.org/10.1039/D5VA00368G