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TEMPORAL VARIATIONS IN ARSENIC CONCENTRATIONS AND GROUNDWATER QUALITY ASSESSMENT IN VAN PHUC, NAM PHU, HANOI

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INTRODUCTION

1. Rationale of the study

Arsenic (As) contamination in groundwater is considered one of the most serious environmental and public health issues worldwide, particularly in young deltaic regions with strongly reducing geochemical conditions. Long-term exposure to arsenic through drinking water may cause adverse health effects, including skin lesions, cardiovascular and neurological disorders, and increased cancer risk.

In Vietnam, the Red River Delta is recognized as a high-risk area for arsenic contamination due to its young organic-rich sediments and favorable hydrogeochemical conditions for As release into groundwater. Previous studies have reported groundwater As concentrations in suburban Hanoi far exceeding the World Health Organization (WHO) guideline. However, most earlier studies were based on single-time-point surveys, despite the fact that groundwater As concentrations can vary significantly with seasonal conditions, hydrological regimes, and groundwater abstraction.

Van Phuc, Nam Phu, Hanoi is one of the typical arsenic contamination hotspots in the Red River Delta, with As concentrations reaching more than 500 µg/L. The area also exhibits a clear contrast between contaminated and uncontaminated zones within a narrow spatial scale, providing favorable conditions for investigating the geochemical mechanisms and temporal dynamics of As in aquifers. In addition, intensive groundwater extraction in Hanoi may alter groundwater flow and enhance contamination transport between aquifers.

In this context, investigating temporal variations in arsenic concentrations, elucidating the geochemical mechanisms controlling As mobilization, and assessing groundwater quality and associated health risks are scientifically and practically important for sustainable groundwater management. For these reasons, the dissertation entitled "***Temporal variations in arsenic concentrations and groundwater quality assessment in Van Phuc, Nam Phu, Hano****i*" was conducted to address existing research gaps and provide a scientific basis for risk assessment and sustainable groundwater management.

2. Research objectives

- To determine seasonal and long-term variations in arsenic concentrations and related hydrochemical parameters.
- To elucidate the geochemical mechanisms controlling the formation and distribution of As in the aquifers of Van Phuc.
- To apply machine learning approaches for objective groundwater quality assessment using the groundwater quality index (GWQI).
- To assess non-carcinogenic and carcinogenic human 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 physicochemical parameters in Van Phuc.
- Assessment of seasonal and temporal variations of arsenic concentrations
- Analysis of relationships between As and physicochemical parameters to elucidate the geochemical mechanisms controlling As mobilisation and distribution in groundwater.
- Application of machine learning approaches for objective calculation of the groundwater quality index (GWQI) to classify groundwater quality in Van Phuc
- Assessment of non-carcinogenic and carcinogenic health risks under the worse scenario of direct use of groundwater for domestic purposes.

4. Structure of the dissertation

The dissertation comprises 120 pages, including 30 figures and 14 tables, organized as: Introduction (3 pages); Chapter 1. Literature review (35 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 133 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 the dissertation were groundwater samples collected from the Holocene and Pleistocene aquifers in Van Phuc. Specifically:

- Groundwater samples from 17 monitoring wells at depths of 24-54m (below ground surface) were used for studies on seasonal and long-term variations of As in groundwater and for health risk assessment.

- Groundwater samples from 29 monitoring wells at depths of 20-54 m were used for studies on geochemical mechanisms and machine learning applications in groundwater quality assessment.
- The analyzed parameters included 22 physicochemical indicators of groundwater, 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, Mn^{2+}, PO_4^{3-}, NH_4^+, dissolved organic carbon (DOC) and CH_4.

The study area of the dissertation was Van Phuc, Nam Phu, Hanoi (Figure 2.1), one of the typical arsenic-contaminated areas in the Red River Delta, characterized by the following distinctive features:

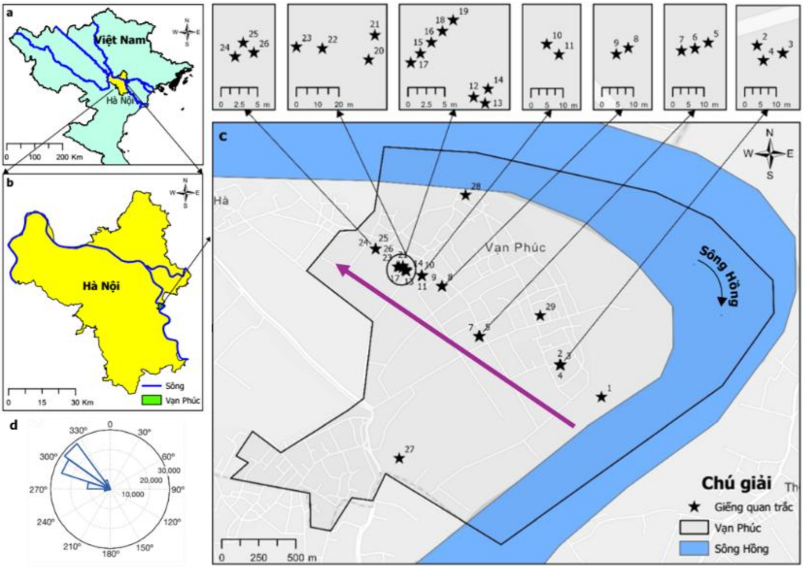

Figure 2.1. a) Location of Hanoi and major rivers in northern Vietnam. b) Location of Van Phuc. c) Locations of monitoring wells along the study transect. d) Groundwater flow direction in Van Phuc.

- Distinct spatial contrast in As contamination: As concentrations vary markedly, with very high levels in the southeastern area (>500 µg/L) and ow levels in the northwestern area (<10 µg/L).
- Strong anthropogenic influence on hydrology: 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 downward transport of arsenic and organic matter from the Holocene aquifer to the deeper Pleistocene aquifer, making the site suitable for investigating temporal variations and inter-aquifer transport processes.
- Integrated monitoring well system: Monitoring wells were installed along a hydrogeological transect following the groundwater flow direction and screened at multiple depths, enabling synchronized data collection for evaluating spatial and temporal variations in arsenic concentrations.

2.2. Chemicals, instruments and materials

2.3. Sampling and sample preservation

Before sampling, 3–5 well volumes were purged to completely remove stagnant water from the wells. Field parameters, including pH, oxidation-reduction potential (Eh), dissolved oxygen (DO), electrical conductivity (EC), and temperature, were measured in situ. Once these parameters stabilized, groundwater samples were collected and processed according to specific analytical requirements to optimize chemical stability. Samples for cation analysis were filtered into polyethylene (PE) bottles and immediately acidified with 65% HNO_3 to pH <2. Samples for anion analysis were filtered into PE bottles without acidification. Samples for NH_4^+ and PO_4^{3-} analyses were filtered into PE bottles and preserved with H_2SO_4 (1:1, v:v) to pH <2. Samples for dissolved organic carbon (DOC) analysis were stored in pre-combusted glass bottles then acidified with 37% HCl to pH <2. Samples for CH_4 analysis were collected directly into evacuated Labco

819W glass vials filled to approximately two-thirds of the vial volume, then immediately preserved on dry ice in the field and stored frozen in the laboratory until analysis.

Field blanks, duplicate samples, and reference samples were analyzed together with groundwater samples to ensure analytical reliability.

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 through ingestion and dermal contact pathways, were assessed to evaluate potential health impacts under the worst-case scenario of direct use of contaminated groundwater by 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.

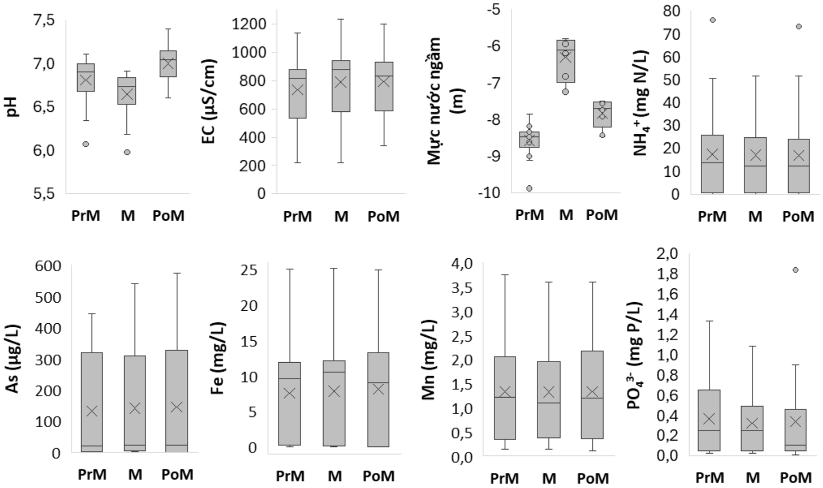

Figure 3.1. Box plots showing the concentrations of groundwater physicochemical parameters in Van Phuc during the pre-monsoon (PrM), monsoon (M), and post-monsoon (PoM) periods

3.1.2. Seasonal variation of arsenic concentrations in groundwater

Groundwater As concentrations in Van Phuc varied over a wide range, from <5–444 µg/L (mean: 132 µg/L) during the pre-monsoon period, <5–541 µg/L (mean: 141 µg/L) during the monsoon period, and <5–574 µg/L (mean: 145 µg/L) during the post-monsoon period. Groundwater quality assessment showed that 47% of the sampled wells exceeded the arsenic limit for groundwater in all three seasons according to QCVN 09:2023 issued 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 minerals under reducing conditions. These conditions are are enhanced in shallow aquifers by the high organic matter content and strongly reducing environment associated with the presence of organic-rich peat layers and gray sandy sediments.

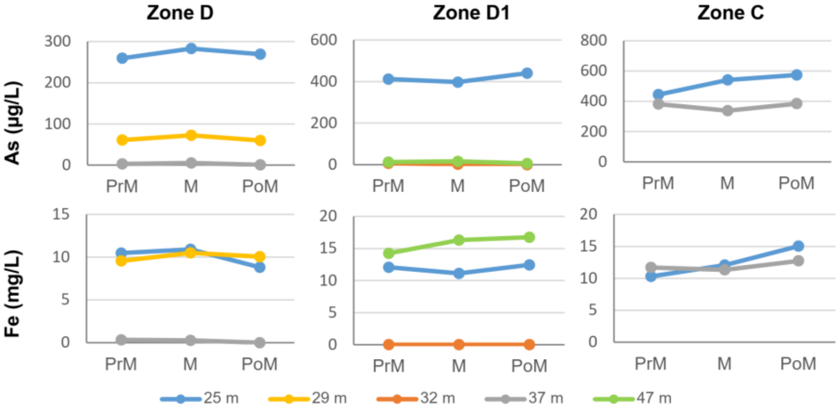

Figure 3.4. Seasonal variation of As and Fe in groundwater from wells at different depths in zones C, D1, and D during pre-monsoon (PrM), monsoon (M) and post-monsoon (PoM) periods

The mean arsenic concentrations of all wells indicated a relatively stable seasonal trend. However, slight seasonal variations in As concentrations were still observed, particularly in shallow wells.

Groundwater As concentrations in well C showed an increasing trend from the pre-monsoon to the monsoon and post-monsoon periods. In wells D1 and D2, As concentrations slightly decreased during the monsoon season, whereas well D exhibited increased groundwater As concentrations during this period. In contrast, As concentrations in wells B and E remained nearly stable throughout all three seasons (Figure 3.5).

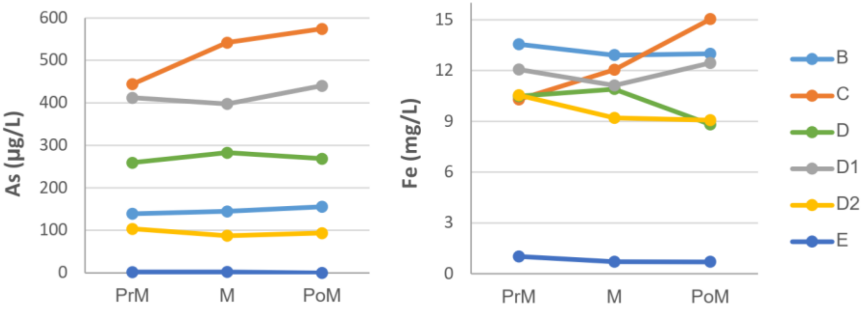

Figure 3.5. Seasonal variation of As and Fe in shallow groundwater from 25 m deep wells along the study transect during pre-monsoon (PrM), monsoon (M) and post-monsoon (PoM) periods

Overall, the results indicate that seasonal variations in arsenic at Van Phuc are not extreme but rather reflect slight adjustments of the groundwater system in response to cyclic hydrological changes. General physicochemical parameters remained relatively stable, whereas arsenic appeared more sensitive to subtle variations in redox conditions, depth, and sediment characteristics. In general, As concentrations and groundwater physicochemical compositions in Van Phuc showed only minor seasonal changes. This relative stability may partly be attributed to the slow groundwater flow velocity at Van Phuc, averaging approximately 40 m/year, which reduces short-term fluctuations. In addition, the presence of a thick aquitard overlying the aquifer likely limits the influence of dilution from rainfall and surface water.

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

Long-term monitoring data from 2010 to 2024 showed that the major ions in groundwater, including Na, K, Ca, Mg, Cl, HCO_3^- and SO_4^{2-} remained relatively stable in most wells throughout the study period. This indicates that the background hydrochemical composition of the aquifer was not strongly affected by short-term dilution or recharge processes, such as direct infiltration of rainfall and surface water on an annual basis. In contrast, the temporal variations of As and several physicochemical parameters related to As mobilization differed among the geochemical zones along the study transect.

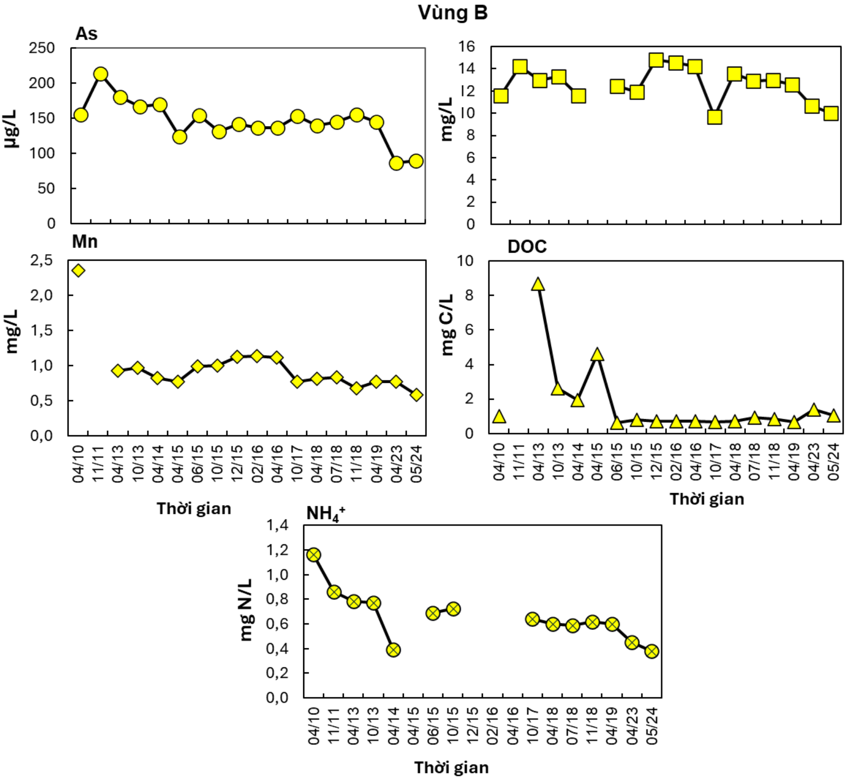

Figure 3.8. Temporal variation of As, Fe, Mn DOC and NH_4^+ concentrations in groundwater from 25 m deep wells in zones B

In zone B, the well located closest to the river showed a gradual decrease in As concentrations during the 2010-2019 period, while Fe, Mn, and DOC concentrations remained relatively stable over the same period (Figure 3.8). In this zone, the aquifer is continuously recharged by Red River water, and the decrease in $\delta^{18}O$ values from −7.6‰ to −8.6‰ indicates increased river water infiltration due to continuous groundwater abstraction in Hanoi. Therefore, the decline in As concentrations may be attributed to the flushing of dissolved As along the groundwater flow path. However, the relatively slow decrease suggests a continuous supply of dissolved As from riverbank sediments.

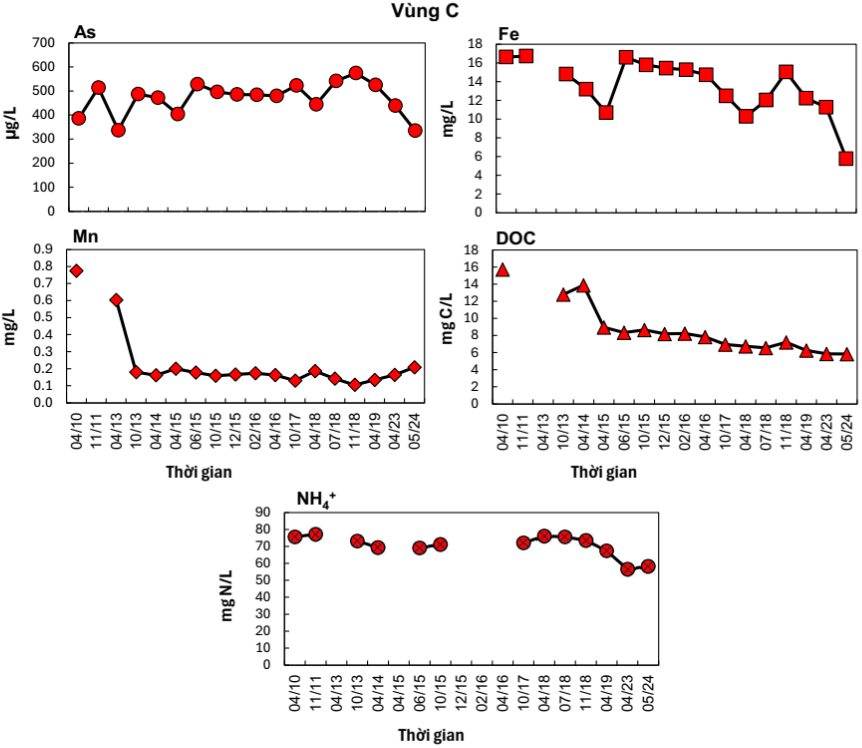

Figure 3.9. Temporal variation of As, Fe, Mn DOC and NH_4^+ concentrations in groundwater from 25 m deep wells in zones C

In zone C, located in the central part of the Holocene aquifer, As, Fe, Mn, and NH_4^+ concentrations remained relatively stable during the 2010-2019 period (Figure 3.9). This stability reflects relatively constant hydrogeochemical conditions in this zone throughout the monitoring period.

In addition, $\delta^{18}O$ values remained around −7‰, indicating that groundwater in this area originated from a mixture of infiltrated river water and evaporated water from the overlying aquitard, which helped sustain Fe reduction and subsequent As release.

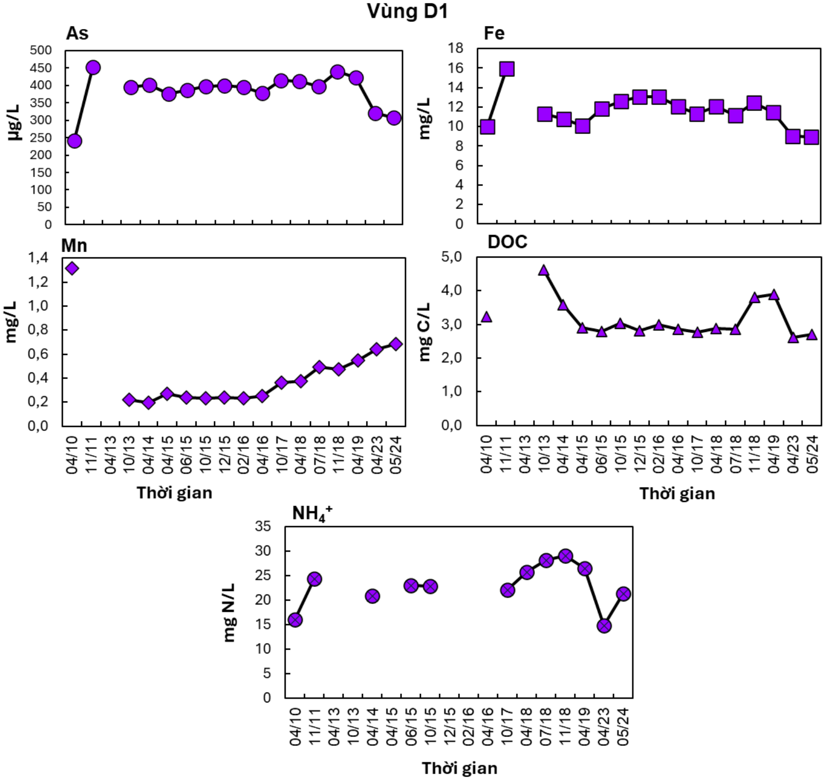

Figure 3.10. Temporal variation of As, Fe, Mn DOC and NH_4^+ concentrations in groundwater from 25 m deep wells in zones D1

In the RTZ zone, well D1, located between the RTZ and central Holocene aquifer, showed relatively stable As, Fe, and NH_4^+ concentrations from 2013 to 2019 (Figure 3.10). This indicates that hydrogeochemical conditions remained relatively unchanged and suggests a dynamic equilibrium within the RTZ, where As-rich groundwater flowing from the

Holocene aquifer was effectively buffered by Fe-related adsorption and co-precipitation processes. Notably, Mn concentrations in groundwater from this well showed a gradual increasing trend during 2013–2024. Although the increase was relatively small, approximately 0.46 mg/L (from 0.22 mg/L in 2013 to 0.69 mg/L in 2024), it remained consistent over time.

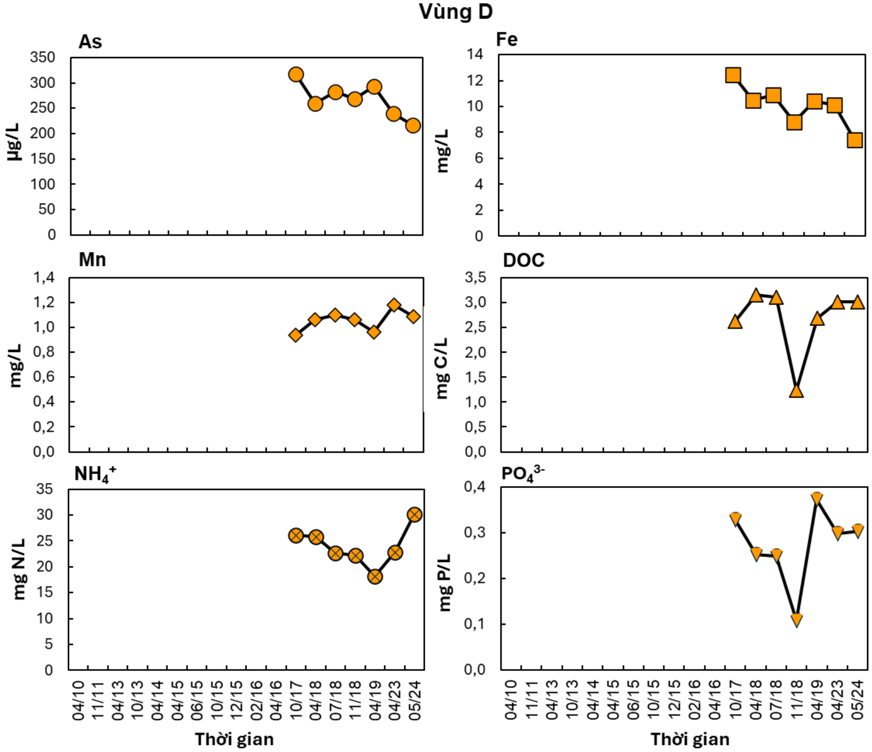

Figure 3.11. Temporal variation of As, Fe, Mn DOC, NH_4^+ and PO_4^{3-} concentrations in groundwater from 25 m deep wells in zones D

In the central RTZ zone, well D, despite having limited data from only 2017 to 2024, still showed a decreasing trend in As and Fe concentrations together with a slight increase in phosphate concentrations (Figure 3.11), while other parameters remained relatively stable. This suggests that the variations in As and Fe were more likely associated with in situ redox adjustments within the RTZ rather than changes in water sources or dilution processes. Specifically, the simultaneous decrease in Fe may be related to Fe^{2+} oxidation and the formation of secondary Fe(III) phases capable of adsorbing As, whereas the slight increase in PO_4^{3-} may reflect As redistribution through competitive adsorption between phosphate and As on newly formed mineral surfaces.

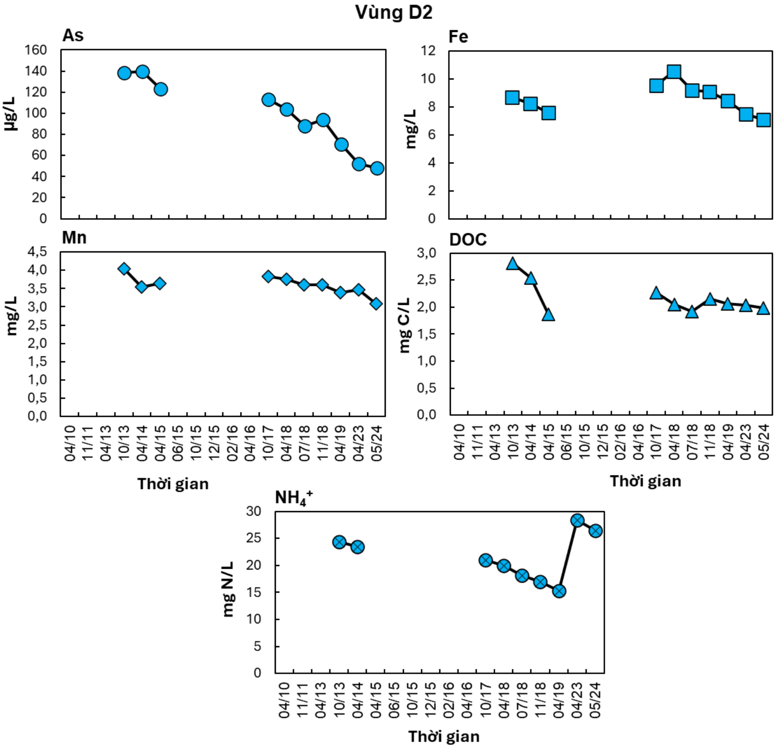

Figure 3.12. Temporal variation of As, Fe, Mn DOC and NH_4^+ concentrations in groundwater from 25 m deep wells in zones D2

Located near the Pleistocene aquifer, well D2 showed a rapid decline in As concentrations from 138 µg/L in 2013 to 48 µg/L in 2024, whereas Fe, Mn, DOC, and NH_4^+ only slight decreases (Figure 3.12). This trend reflects the dominant role of As sequestration within the RTZ as As-rich groundwater from the Holocene aquifer approached the Pleistocene aquifer enriched in Fe(III) and Mn(III/IV) phases. At D2, Fe^{2+} transported from the Holocene aquifer was more strongly oxidized, promoting the formation of secondary Fe(III) phases capable of efficiently adsorbing As, resulting in a faster decline in As concentrations than in other hydrochemical parameters. The minor decreases in Fe, Mn, DOC, and NH_4^+ suggest that the hydrogeochemical conditions at D2 remained stable and strongly reducing.

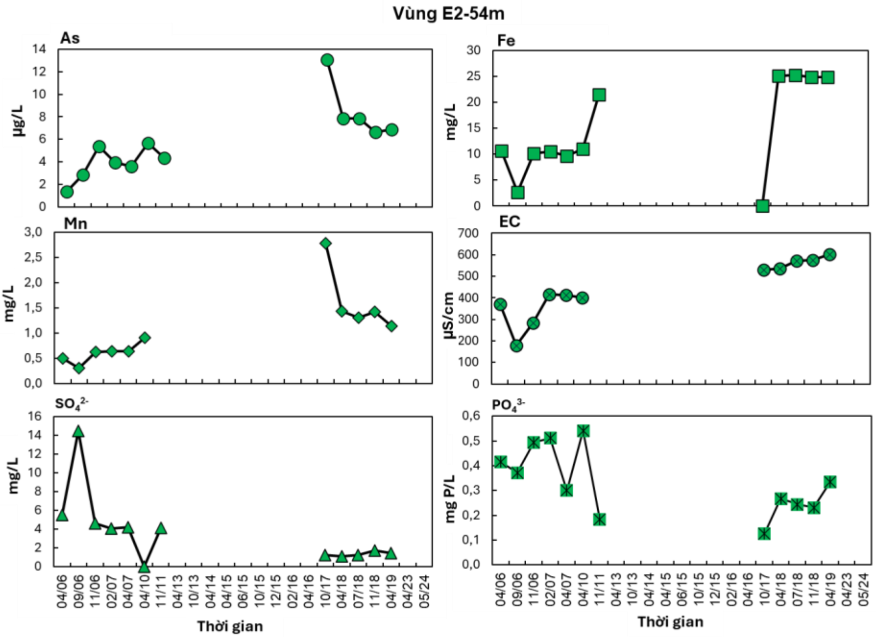

Figure 3.13. Temporal variation of As, Fe, Mn, EC, SO_4^{2-} and PO_4^{3-} in Pleistocene groundwater at a depth of 54 m

A notable exception within the Pleistocene aquifer is a well at a depth of 54 m. 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 3.13). 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.

The temporal variation results presented above indicate that the groundwater system in Van Phuc is relatively stable over short timescales but exhibits significant changes over longer periods, with distinct As variation patterns among different geochemical zones. These findings suggest that As dynamics in Van Phuc do not follow a simple common trend, but rather result from complex interactions among redox conditions, sediment characteristics, aquifer structure, and the cumulative effects of forced groundwater flow induced by long-term groundwater abstraction.

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, recent studies have demonstrated that phosphate and sulfate reduction processes also play important roles in As transport within aquifers. In addition, Fe mineral phases in sediments, microbial communities, and the formation of methane and sulfide play critical role in arsenic occurrence within aquifer systems. These findings indicate that As is not only released but also maintained and spatially distributed through complex and overlapping 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.

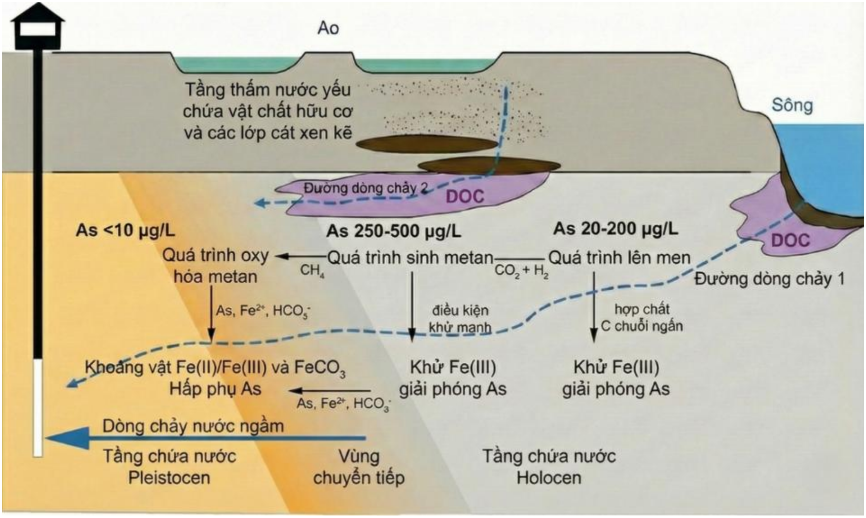

Figure 3.18. Conceptual model illustrating sources and cycling of organic matter associated with arsenic release mechanisms in aquifers at Van Phuc

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 3.18).

- 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.
- 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 in Van Phuc was assessed using 11 physicochemical parameters (out of the total 22 analyzed parameters) from 29 monitoring wells based on QCVN 09:2023. The most suitable groundwater quality assessment model for conditions in Van Phuc was selected by comparing the performance of three machine learning algorithms: Decision Tree (DT), Random Forest (RF), and XGBoost.

The results showed that the XGBoost model performed best for the hydrogeochemical conditions and input dataset in Van Phuc. The calculated parameter weights and importance scores indicated that eight parameters, including As, Mn, Fe, NH_4^+, F^-, and hardness, had non-zero importance, whereas pH, SO_4^{2-}, and TDS contributed negligibly (Table 3.7). Among the significant parameters, As was identified as the most influential factor controlling groundwater quality, while NH_4^+ showed relatively low importance.

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

From a geochemical perspective, the parameter importance ranking obtained from the XGBoost model is consistent with the As mobilization mechanisms in the study area. As shown the highest importance, corresponding to its frequent exceedance of QCVN 09:2023 limits and its high toxicity. Hardness ranked second, representing Ca-Mg carbonate equilibrium and the mixing between recharged river water and groundwater, a process that may facilitate contaminant transport into the aquifer. The high importance of Mn^{2+} reflects the progression of redox reactions toward more strongly reducing conditions, which may promote As release in the Pleistocene aquifer under the influence of reversed groundwater flow in Van Phuc. NH_4^{+} showed moderate importance, indicating its role primarily as an indicator of reducing conditions and organic matter degradation rather than direct involvement in As release. The smaller contributions of Fe and F^{-} further support the role of water-sediment interactions and reductive dissolution of Fe oxyhydroxides in As mobilization, whereas pH, SO_4^{2-}, and TDS had negligible influence due to their relative stability and concentrations generally remaining within permissible limits.

Groundwater quality in Van Phuc was classified based on GWQI scores calculated from the sub-indices and parameter weights derived from the model. The results showed that among the 29 groundwater samples, only one sample was classified as Good (GWQI = 83), while 12 samples (41.4%) were classified as Moderate, and the remaining 55.2% were classified as Poor (20.7%) and Very Poor (34.5%).

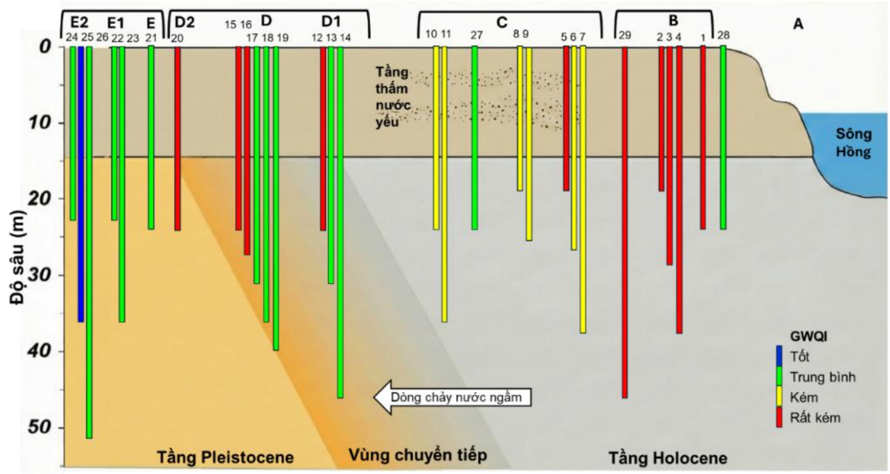

Figure 3.21. Groundwater quality classification in Van Phuc by depth based on GWQI scores calculated using the NSF aggregation function

Based on the geochemical zonation proposed by Stopelli et al. (2020), the wells were divided into four zones: zone B (wells 1–4 and well 29), representing the river-proximal Holocene aquifer; zone C (wells 5–10), representing the central Holocene aquifer; zone D (wells 12–21), corresponding to the redox transition zone (RTZ); and zone E (wells 22–26), representing the Pleistocene aquifer. Based on GWQI scores, poor to very poor groundwater quality was mainly concentrated in zones B and C and in shallow wells of zone D. In zone D, groundwater quality improved with depth, whereas moderate to good groundwater quality was mainly observed in the Pleistocene aquifer of zone E (Figure 3.21). Overall, the spatial distribution of GWQI in Van Phuc reflects the combined processes of As mobilization and attenuation within the Holocene-Pleistocene aquifer system.

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

In this study, carcinogenic and non-carcinogenic health risks were assessed under the worst-case scenario of direct groundwater use for drinking and domestic purposes through two main exposure pathways, namely ingestion and dermal contact, for both adults and children across different seasons based on As, Fe, and Mn concentration data collected in 2018.

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

The results showed that the mean HI values for As far exceeded the safety threshold of 1 in all seasons. For adults, the mean HI increased from 20.22 during the pre-monsoon period to 21.55 during the monsoon period and reached the highest value of 22.19 in the post-monsoon period. For children, the mean HI ranged from 14.54 to 15.96 and was also highest during the post-monsoon period.

The HI values of Mn ranged from 0.04 to 1.33 for adults, with only one well exceeding the safety threshold, whereas for children the values ranged from 0.06 to 2.19, with five wells exceeding the threshold in zones D, D2, E, and the shallow well in zone E2. The contribution of Fe was smaller, with average HI values of approximately 0.5 for adults and 0.4 for children. Only one deep well (54 m) in zone E2 exceeded the threshold for children, while 1–3 wells exceeded the threshold for adults depending on the season.

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 wells. 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
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