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Seasonal variation in arsenic concentration and hydrogeochemical dynamics in groundwater at Van Phuc, Thanh Tri, Ha Noi

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Abstract. Arsenic contamination in groundwater represents a significant public health threat to millions of people globally, particularly within the Red River Delta region of Vietnam. This investigation of seasonal variation of arsenic levels and the hydrogeochemical dynamics of groundwater in Van Phuc, Thanh Tri, Hanoi was conducted based on a study of samples collected from 17 wells at depths 25 to 54 meters across pre-monsoon, monsoon, and post-monsoon seasons. Findings reveal that local biogeochemical processes and year-round river recharge predominantly determine groundwater quality, while anthropogenic impacts are negligible. Arsenic concentrations increased slightly from 132 µg/L pre-monsoon to 145 µg/L post-monsoon, with greater variation noted in shallow wells (<30 meters). Seasonal changes are driven by arsenic mobility linked to fluctuating redox conditions and geohydrochemical processes, with high phosphate levels further influencing arsenic variation. Health risk assessments highlighted a high hazard index (HI > 1) and significant carcinogenic risks (ILCR > 10^{-4}) in most wells. This study provided insights into the seasonal hydrogeochemical processes governing arsenic contamination, with implications for groundwater management in affected regions. Further research is needed to refine mitigation approaches and ensure contribution reducing arsenic exposure risks.

Keywords: arsenic contamination, groundwater, seasonal variation, health risk assessment, Van Phuc village

Classification numbers: 3.2.1, 3.4.2, 3.6.2

1. INTRODUCTION

Groundwater serves as a critical source of drinking water for millions of people worldwide, particularly in developing countries and densely populated urban areas where surface water sources are often contaminated by wastewater. However, naturally occurring arsenic (As) in groundwater represents a significant public health concern. Prolonged exposure to elevated arsenic concentrations through the consumption of contaminated groundwater has been linked to a variety of chronic health conditions, including hyperpigmentation, keratosis, edema, necrosis, leukopenia, circulatory disorders, and an increased risk of several cancers, notably skin, bladder, and lung cancers [1-3]. It is estimated that between 94 and 220 million people, primarily in Asia, are at risk of exposure to arsenic-contaminated groundwater [4]. Elevated arsenic concentrations in groundwater are geographically widespread, with particularly affected regions including South and Southeast Asia (e.g., China, India, Bangladesh, Nepal, Vietnam, Myanmar, and Cambodia), Latin America (e.g., Mexico, Argentina, Bolivia, and Chile), and parts of Europe (e.g., Hungary, Romania, and Greece) [5]. Among the most notable hotspots for arsenic contamination is Red River Delta in Vietnam, specifically in Hanoi, where arsenic concentrations in groundwater frequently exceed the World Health Organization (WHO) guideline of 10 µg/L for drinking water [6-12].

Hanoi, the capital of Vietnam and the country's second most populous city had a population of over 8.5 million people in 2023 [13]. As a result of rapid urbanization and population growth, the city has increasingly relied on groundwater as its primary source of domestic water for over a century [14]. By 2017, groundwater extraction in Hanoi had reached nearly 1,000,000 m^3/day, accounting for approximately 70% of the city's domestic water supply [14, 15]. This heavy dependence on groundwater exacerbates the risks associated with arsenic contamination and further threatens water quality in the region's vulnerable aquifers.

Since the pioneering study published by Berg et al. (2001) [6] that first highlighted arsenic contamination in Hanoi's groundwater, extensive efforts have been made to characterize the distribution and dynamics of arsenic in the region. Numerous studies have been conducted in Hanoi and the broader Red River Delta, contributing to a comprehensive understanding of the spatial patterns of arsenic contamination in groundwater [7-9, 11, 16]. However, critical questions remain unanswered regarding the seasonal variability of arsenic concentrations and the underlying mechanisms driving these changes. Seasonal fluctuations in groundwater recharge, water table levels, and hydrochemical conditions, all influenced by the monsoonal climate of northern Vietnam, are likely to impact arsenic mobilization and concentration. Understanding these seasonal variations is essential for predicting periods of heightened exposure risk and implementing effective mitigation strategies.

Global studies reveal contrasting seasonal patterns in groundwater arsenic concentrations [17]. Higher concentration occurs during dry in Mexico's Zimapan Valley, coastal aquifers on Greece's Lesvos Island, and aquifers in Bolivia's Poopó Basin, while wet season increases are observed in Alaska (USA), confined Zimapan aquifers, and China's Jianghan Plain. Anthropogenic factors, particularly irrigation, influence arsenic levels in shallow aquifers across Asia (West Bengal, Jianghan Plain, Nepal's Terai) while groundwater extraction and well

construction affect arsenic concentrations in Spain's Duero Basin and Vietnam's Red River Delta.

Although many studies have investigated seasonal variations in groundwater quality in Vietnam, these efforts have primarily focused on overall water quality, with limited attention given to specific contaminants such as arsenic [18-21]. Understanding seasonal variations in arsenic concentrations and the controlling hydrogeochemical parameters (pH, redox conditions, and competing ions like phosphate), is essential for developing effective groundwater management strategies in densely urbanized regions like Hanoi.

Exposure to arsenic-contaminated groundwater typically occurs through ingestion and dermal absorption during daily activities such as drinking, cooking, and bathing. Health risk assessments provide essential frameworks for evaluating the potential impacts of arsenic exposure on human health. Two primary indices used in such assessments are: 1) the Hazard Index (HI), which assesses non-carcinogenic risks by comparing estimated arsenic intake to a reference dose; an HI value greater than 1 indicates potential adverse health effects, and 2) the Incremental Lifetime Cancer Risk (ILCR), which estimates the likelihood of developing cancer over a lifetime due to arsenic exposure, with values above 1×10^{-4} signifying unacceptable risk and the need for immediate mitigation measures. Understanding seasonal variations in arsenic concentrations is critical for assessing temporal fluctuations in health risks. Seasonal changes in groundwater chemistry can alter arsenic mobility, leading to periods of elevated exposure risk. Without a comprehensive understanding of these seasonal trends, risk assessments may underestimate or overestimate arsenic-related health threats' true extent [22, 23].

This study aims to: 1) investigate the seasonal variation of arsenic concentrations in groundwater from the Van Phuc area, Thanh Tri, Hanoi, across three seasons – pre-monsoon, monsoon, and post-monsoon; and 2) assess the associated human health risks using HI and ILCR models. Van Phuc, which is directly impacted by over-extraction in Hanoi's urban center, serves as a representative site for understanding arsenic dynamics in the Red River Delta. By elucidating the seasonal mechanisms driving arsenic mobilization, this study contributes to developing more accurate arsenic risk assessments and supports the sustainable management of groundwater resources in arsenic-affected regions.

2. MATERIALS AND METHODS

2.1. Study area

The study area is in Van Phuc village, about 13 km southeast of Hanoi, outside the dyke system (Fig. 1). This region is historically known for groundwater arsenic contamination, with concentrations frequently surpassing established safety limits. A notable characteristic of the area is the juxtaposition of contaminated and uncontaminated wells, often located within just a few hundred meters of one another [7, 24]. Like Hanoi, the study area has a tropical monsoonal climate with a rainy season from May to October and a dry season from November to April. Traditionally, the region was subject to flooding during the rainy season, with groundwater primarily used for domestic purposes. However, in recent years, groundwater extraction has shifted toward irrigation for seasonal crops, such as bananas, corn, and various vegetables.

The geology of the study area is characterized by complex Quaternary sedimentary formations with a thickness ranging from 50 to 90 meters. The aquifer system comprises two interconnected, yet not entirely distinct, layers: the upper Holocene aquifer, under reducing

conditions, consists of alternating layers of sand and clay rich in organic peat material. The Pleistocene aquifer, formed under oxidizing conditions, is characterized by yellow-brown sands and compact gravel deposits [10, 24-26].

Intensive groundwater extraction in central Hanoi has created drawdown cones that disrupt natural groundwater flow patterns in surrounding areas. At Van Phuc, groundwater flows predominantly from southeast-to-northwest towards Hanoi [10, 11, 24, 27], with the Red River serving as the primary recharge source for both Holocene and Pleistocene aquifers within a 5 km corridor along the river [24, 26]. Similar to other nearby areas, although the flow regime has been altered, the site's relative distance from major groundwater exploitation plants for domestic use helps limit the influence of surface water intrusion and anthropogenic disturbances. Additionally, in Van Phuc, there is a natural boundary separating the arsenic-contaminated and uncontaminated zones [24, 27], offering a unique opportunity to investigate arsenic migration between Holocene and Pleistocene aquifers. Moreover, as the study area lies in the downstream part of the Red River Delta, it is characterized by frequent alluvial deposition, which promotes the development of reducing conditions favorable to arsenic mobilization. Taken together, these hydrogeological and geochemical characteristics make the site particularly well-suited for assessing the temporal variation in arsenic contamination under both natural and anthropogenic influences.

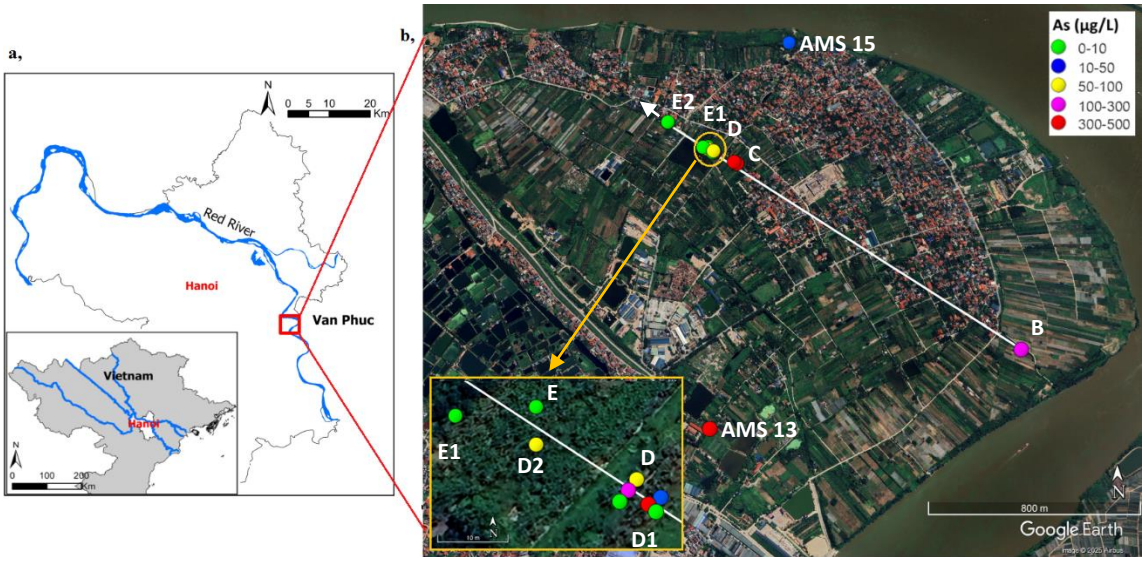

Figure 1. Sampling sites along a transect at Van Phuc. a, Geographical location of Van Phuc village. b, Satellite image (Google Earth 2025) illustrating this study's transect and monitoring wells. The white arrow represents the study transect, aligned with the groundwater flow direction.

2.2. Groundwater sampling and preservation

A total of 51 groundwater samples were collected from 17 monitoring wells along a transect in Van Phuc, spanning three seasons: pre-monsoon (PrM, April 2018), monsoon (M, July 2018), and post-monsoon (PoM, November 2018). The depths of the wells ranged from 25 to 54 meters below ground level (m.b.g.l). To ensure accurate sample collection, stagnant water was purged from the wells by removing at least three well volumes. Purging continued until

field measurements of pH, redox potential (Eh), electrical conductivity (EC), dissolved oxygen (DO), and temperature stabilized, using an HQ 40d multi-parameter meter (Hach, USA). Following stabilization, groundwater samples were filtered through 0.22 µm cellulose acetate (CA) Minisart syringe filters into polyethylene (PE) bottles for subsequent laboratory analysis. To preserve the integrity of the samples, the following preservation techniques were applied: 1) Cations and heavy metals: Samples were acidified to a pH < 2 using 65% HNO_3 . 2) Ammonium (NH_4^+) and phosphate (PO_4^{3-}): Samples were acidified to a pH < 2 with 1:1 (v/v) H_2SO_4. 3) Anion samples were filtered directly into PE bottles without acidification. All samples were stored in a cooling box in the field and refrigerated at 4 °C in the laboratory for later analysis. Alkalinity was measured in the field using a colorimetric titration method with a Merck MColortest kit (11109) to determine the total bicarbonate (HCO_3^-) concentration.

2.3. Chemicals analysis and quality assurance

Chemical analysis was undertaken at the VNU Key Laboratory of Analytical Technology for Environmental Quality and Food Safety Control (KLATEFOS), VNU University of Science. Whereas, major cations and total arsenic (As), iron (Fe), and manganese (Mn) were quantified by atomic absorption spectroscopy (AA-6800, Shimadzu, Japan). Arsenic (As) was measured on the same instrument equipped with a hydride generation system (HVG-AAS). Internal quality control was ensured by analyzing ARS groundwater matrix solutions (certified by Eawag) alongside the sample. NH_4^+ and PO_4^{3-} concentrations were measured using the salicylate and molybdate methods, respectively, on a UV/Vis spectrophotometer (UV-1800, Shimadzu, Japan). Anions were quantified using ion-exchange chromatography (HIC-20A super, Shimadzu, Japan), with the Shimadzu PIA reference material employed to maintain analytical quality. All measurements were conducted under calibration conditions with R^2 values exceeding 0.999. The relative standard deviation (RSD) for triplicate analyses was less than 5%, and the recovery rates for reference materials consistently ranged between 90% and 110%, ensuring the precision and accuracy of the measurement.

2.4. Health risk assessment

Long-term exposure to arsenic has been demonstrated to cause several adverse health effects, including diseases of the lungs, kidneys, and cardiovascular system [28]. More dangerously, chronic arsenic exposure can lead to cancers such as skin cancer and other internal cancers, including those of the liver, bladder, kidneys, and lungs [29]. Based on published data, the International Agency for Research on Cancer (IARC) and the United States Environmental Protection Agency (USEPA) have classified arsenic as a human carcinogen (Group 1 and Group A , respectively). In this study, potential non-carcinogenic and carcinogenic health risks from arsenic exposure via two pathways, including ingestion and dermal absorption, for two population groups, adults and children, were calculated to assess the potential harm from arsenic exposure in groundwater in the study area.

To estimate non-carcinogenic health risks, the hazard quotient (HQ) was calculated using Eq. 1 and Eq. 2, based on the ratio between the chronic daily intake (CDI), which represents the average daily amount of arsenic absorbed into the body over a lifetime, and the reference dose (RfD) of arsenic, which indicates the daily intake level that is not expected to cause any adverse health effects over a lifetime. RfD values (0.30 and 0.12 µg/kg/day for ingestion and dermal exposure, respectively) were referenced from [22], while CDI values were calculated according to Eq. 3 and Eq. 4. Finally, the hazard index (HI) was determined by summing the HQ values for

all exposure pathways (Eq. 5). If the HI value is < 1, the health risk from arsenic exposure is considered low, while an HI > 1 indicates a higher risk of adverse health effects.

$$HQ_{Ingestion} = \frac{CDI_{Ingestion}}{RfD_{Ingestion}} \quad \text{(Eq. 1)}$$

$$HQ_{Dermal} = \frac{CDI_{Dermal}}{RfD_{Dermal}} \quad \text{(Eq. 2)}$$

$$CDI_{Ingestion} = \frac{C_{As} \times IR \times EF \times ED}{BW \times AT} \quad \text{(Eq. 3)}$$

$$CDI_{Dermal} = \frac{C_i \times SA \times K_p \times ET \times EF \times ED \times CF}{BW \times AT} \quad \text{(Eq. 4)}$$

$$HI = HQ_{Ingestion} + HQ_{Dermal} \quad \text{(Eq. 5)}$$

where C_{As} is the arsenic concentration in groundwater (μg/L), IR is the ingestion rate (2.50 L/day for adults and 0.64 L/day for children), EF is the exposure frequency (365 days/year), ED is the exposure duration (75 years for adults and 6 years for children), BW is the body weight (55 kg for adults and 20 kg for children), AT is the average time (ED × 365 days/year), SA is the skin area (16,000 cm^2 for adults and 8,000 cm^2 for children), ET is the exposure time (0.58 h/day for adults and 1 h/day for children), K_p is the dermal permeability coefficient for arsenic in groundwater (10^{-3} cm/h), and CF is the conversion factor (10^{-3}).

The increased lifetime cancer risks (ILCRs) were calculated using the oral slope factor for arsenic (CSF, 1.50×10^{-3} and 3.66×10^{-3} $(\mu g/kg/day)^{-1}$ for ingestion and dermal exposure, respectively)[30]and the mentioned CDI values as presented in Eq. 6 and Eq. 7. An estimated risk value of 1×10^{-6} means that one person per million is at risk of developing cancer, which is considered negligible. Risk levels from 1×10^{-6} to 1×10^{-4} are deemed acceptable by the USEPA, while values greater than 1×10^{-4} indicate unacceptable risk.

$$ILCR_{Ingestion} = CDI_{Ingestion} \times CSF_{Ingestion} \quad \text{(Eq. 6)}$$

$$ILCR_{Dermal} = CDI_{Dermal} \times CSF_{Dermal} \quad \text{(Eq. 7)}$$

2.5. Statistical analysis

Descriptive statistics were performed using Excel 365 (Microsoft, USA). The normality of the data was examined using the Shapiro-Wilk test. Since most of the dataset did not follow a normal distribution, the temporal variations of physicochemical parameters and health risks across the three seasons were compared using the Friedman test. All exploratory statistical analyses were performed using SPSS 27 software (IBM, USA), with a significance level set at 0.05.

3. RESULTS AND DISCUSSION

3.1. Seasonal variation of groundwater quality and general chemicals analysis

The seasonal variation of analyzed physicochemical parameters across the pre-monsoon (PrM), monsoon (M) and post-monsoon (PoM) seasons is shown in Fig. 2 and Table 1. In general, the pH of the groundwater changed from slightly acidic to neutral: this value ranges from 6.07 to 7.11 (mean 6.81) in PrM; from 5.98 to 6.91 (mean 6.65) in M, and from 6.60 to 7.40 (mean 6.95) in PoM, which is within the permissible limits of 5.5 – 8.5 for groundwater quality set by Vietnam Ministry of Natural Resources and Environment (MONRE) [31]. However, the pH values of groundwater from 3 wells in PrM and 4 wells in M seasons fall below the 6.5 – 8.5 range specified by the Vietnam Ministry of Health (MOH) for domestic water quality [32]. The measurement results show that the pH value tended to be lower in the monsoon season and higher in the post-monsoon season, possibly due to dilution by rainfall. This result was in contrast to the findings by Nguyen et al, (2015), which reported a slightly higher pH range for Hanoi groundwater during dry and wet seasons (6.7-8.8 (mean 7.1) and 7.1-8.0 (mean 7.5), respectively) [20].

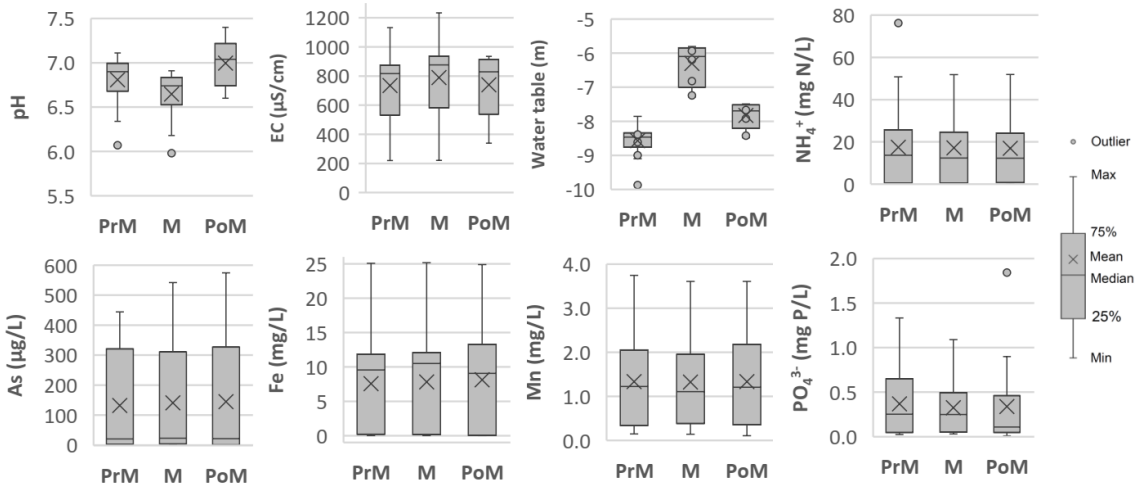

Figure 2. Box plot of analyzed physicochemical parameters in groundwater at Van Phuc in pre-monsoon (PrM), monsoon (M), and post-monsoon (PoM) seasons.

Table 1. Statistical summary of the analyzed physicochemical parameters in groundwater at Van Phuc across three seasons

Season	PrM				M				PoM			
Parameters	Min	Max	Mean	Median	Min	Max	Mean	Median	Min	Max	Mean	Median
Water level (m.b.g.l)	7.86	9.87	8.57	8.46	5.80	7.28	6.30	6.10	7.49	8.48	7.83	7.70
pH	6.07	7.11	6.81	6.90	5.98	6.91	6.65	6.74	6.60	7.40	7.00	7.04
EC (µS/cm)	220	1132	734	817	221	1233	789	876	339	935	740	829
As (µg/L)	1.03	444.12	132.21	20.48	0.99	541.76	140.91	23.04	0.00	574.23	145.09	21.64
Fe (mg/L)	0.00	25.08	7.55	9.55	0.00	25.16	7.82	10.50	0.00	24.89	8.10	9.07
Mn (mg/L)	0.15	3.75	1.33	1.22	0.14	3.61	1.32	1.11	0.11	3.61	1.34	1.21
NH_4^+ (mg N/L)	0.02	76.20	17.47	13.67	0.00	75.60	17.18	12.37	0.06	73.50	16.92	12.28
PO_4^{3-} (mg P/L)	0.02	1.33	0.37	0.25	0.03	1.09	0.32	0.25	0.01	1.84	0.34	0.11
Na (mg/L)	5.29	41.35	16.53	11.77	5.37	45.17	16.91	11.62	4.97	38.18	15.32	13.68
K (mg/L)	1.81	8.13	4.90	5.22	1.95	8.40	4.86	4.91	2.79	8.43	4.85	4.86
Ca (mg/L)	2.68	125.71	76.42	90.60	4.02	132.71	77.13	93.83	18.28	131.71	79.29	96.56
Mg (mg/L)	5.24	66.73	28.89	30.01	5.24	64.75	28.94	30.49	17.94	63.94	30.22	29.12

Cl^- (mg/L)	3.84	21.55	12.82	12.99	3.68	21.86	12.42	13.31	4.06	28.93	13.95	12.25
SO_4^{2-} (mg/L)	0.17	45.03	3.75	0.21	0.00	46.79	3.89	0.18	0.12	30.37	2.83	0.20
HCO_3^- (mg/L)	134	781	520	574	0.00	812	500	574	262	830	532	561
NO_2^- (mg/L)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NO_3^- (mg/L)	0.00	0.07	0.00	0.00	0.00	0.10	0.01	0.00	0.00	0.42	0.03	0.00

The fluctuation of EC value in groundwater in the study area ranged between 220 – 1132 µS/cm (mean 734 µS/cm), 221 – 1233 µS/cm (mean 789 µS/cm), 339 – 935 µS/cm (mean 740 µS/cm) in the PrM, M and PoM seasons, respectively. The EC was notably higher in the monsoon season, reflecting increased mineralization due to recharge from rainwater and river water, which enhances water-sediment interactions. Previous studies have reported similar recharge dynamics in the Hanoi aquifer system [10, 26, 33].

The Piper diagram (Fig. 3) reveals that most groundwater samples belong to the Ca^{2+} /Mg^{2+} -HCO_3^- type, while a few samples fall into the Na^+ /K^+ -HCO_3^- type. This groundwater type is typical for As affected water bodies in young alluvial deltaic aquifers in Asia [7]. There were no significant seasonal trends or major changes in the groundwater's hydrochemical composition.

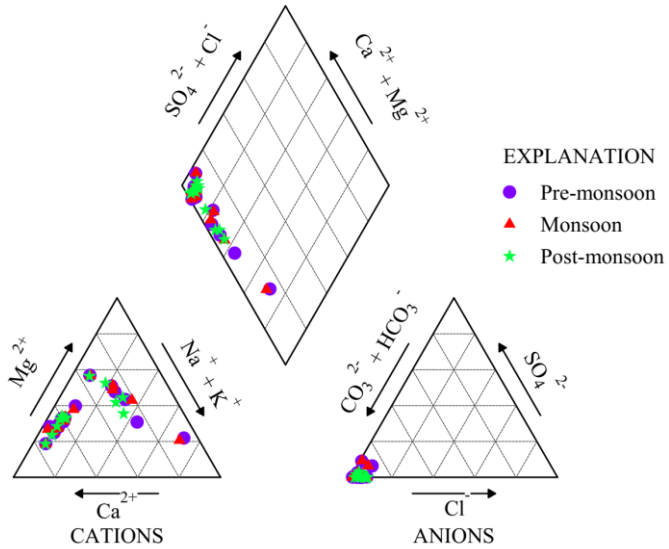

Figure 3. Piper diagram illustrating the major ions composition of groundwater samples.

Nitrate (NO_3^-) and nitrite (NO_2^-) ions were undetectable in the groundwater samples from Van Phuc. Instead, inorganic nitrogen species were predominantly present in the form of ammonium (NH_4^+) ions. Ammonium concentrations varied from less than 0.2 mg N/L to 76.20 mg N/L (mean 17.47 mg N/L), 75.60 mg N/L (mean 17.18 mg N/L), and 73.50 mg N/L (mean 16.92 mg N/L) in PrM, M and PoM season, respectively. The analysis revealed only minor seasonal variations in ammonium concentrations, and the observed patterns of change were inconsistent and unclear. These ammonium levels consistently exceeded the regulatory thresholds for both domestic and groundwater quality, as set by the MOH and MONRE of 1 mg N/L [31, 32]. Specifically, over 65% of the wells (11 out of 17) exhibited ammonium concentrations above the permissible limit outlined by these regulations. Elevated ammonium concentrations in the groundwater of Hanoi have been reported in previous studies [9, 20, 26]. The absence of detectable NO_3^- and NO_2^-, in conjunction with consistently low concentrations

and negligible seasonal variation in sulfate (SO_4^{2-}) and phosphate (PO_4^{3-}) ions (Fig. 2), suggests that the groundwater in the study area is unlikely to be significantly influenced by agricultural activities, such as irrigation, fertilizer application, or wastewater discharge. These findings suggest that seasonal fluctuations in groundwater hydrochemistry are primarily driven by local biogeochemical processes and the recharge of groundwater from river water rather than direct anthropogenic inputs.

Iron (Fe) and manganese (Mn) showed high concentrations in groundwater samples (Fe: 0.3 – 25 mg/L; Mn: 0.2 – 3.6 mg/L) with no significant seasonal variation. Most wells exceeded regulatory standards set by MOH and MONRE, with Fe violations in 59 – 76% of wells and Mn violations in 76 – 100% of wells. Consumption of drinking water with elevated concentrations of iron and manganese has been linked to severe health effects, including neurological disorders (Parkinson's and Alzheimer's diseases), cardiovascular complications, pigmentation changes, hyperkeratosis, and various disorders affecting liver, kidney, and respiratory systems [34].

3.2. Seasonal variation of arsenic concentration in groundwater

Arsenic (As) concentration in groundwater varied from less than 5 µg/L to 444 µg/L (mean 132 µg/L), 541 µg/L (mean 141 µg/L) and 574 µg/L (mean 145 µg/L) in PrM, M and PoM seasons, respectively. An assessment of groundwater quality revealed that more than 59% and 53% of the sampled wells exhibited As concentrations exceeding the 10 µg/L threshold guided by WHO and MOH for drinking water in all three seasons Additionally, up to 47% of the sampled wells surpassed the permissible limit for arsenic as per the MONRE [31] of 50 µg/L for groundwater quality across all three seasons. The mean As concentrations exhibited a slight but consistent seasonal increase, from 132.2 µg/L in PrM to 140.9 µg/L in M and reaching 145.1 µg/L in PoM. However, these changes were statistically insignificant, and no clear trend was observed across all wells. The data further revealed substantial spatial and depth-related variability in As concentrations, highlighting the complex influence of local hydrogeochemical conditions and groundwater dynamics.

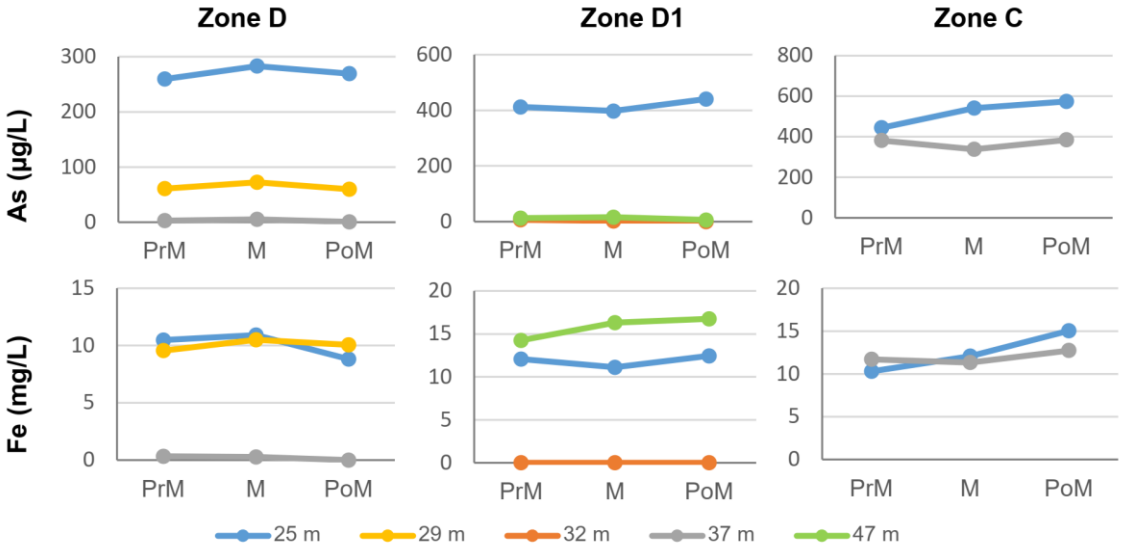

Figure 4. Seasonal and depth variations of As and Fe in groundwater at zones C, D1 and D.

In a previous study, the groundwater transect was classified into five hydrogeochemical

zones along the groundwater flow path, each representing distinct conditions and processes related to arsenic mobilization. Zone A (Riverbank), where arsenic is strongly mobilized from newly deposited sediments. Zone B (Net transport zone), approximately 200 meters from the riverbank, where arsenic is transported without significant mobilization or removal. Zone C (Strongly reducing zone) is located approximately 1.6 km from the riverbank, where arsenic is additionally mobilized from Holocene aquifer sediments. Zone D (Redox transition zone – RTZ), is subdivided into three subzones: D1: closer to Zone C, where strong reducing conditions prevail; D: the central of the RTZ; and D2: situated closer to the Pleistocene aquifers (Fig. 1), approximately 1.6 to 1.7 km from the riverbank, representing the natural barrier between the Holocene and Pleistocene aquifers; and Zone E (Pleistocene aquifer), located about 1.8 to 1.9 km from the riverbank, characterized by low arsenic concentrations [10].

This study investigates groundwater quality across Zones B to E, with sampling from wells at a depth of 25 m and additional multi-depth sampling conducted in Zones C, D, and E. Arsenic (As) concentrations in wells from Zone E were found to be below the detection limit, and thus, seasonal variations in As concentrations in these wells are not discussed.

Shallow wells (<30 m) generally exhibited higher As concentrations than deeper wells (Fig. 4), primarily due to arsenic desorption from iron (Fe) minerals under reducing conditions. These conditions are enhanced in shallow aquifers by high organic matter content and strongly reductive environments [5, 9, 10]. In contrast, yellow-to-brown oxidized sediments observed at depths greater than 30 m within the redox transition zone (RTZ) in Zones D [7, 35] contain Fe(III) oxyhydroxides that adsorb As, thereby reducing groundwater As concentrations. This phenomenon may be attributed to the stabilization of As by persistent Fe minerals such as hematite and goethite in the RTZ, which immobilize As in solid phases and limit its re-release into groundwater under varying seasonal conditions. Seasonal fluctuations in As concentrations were most pronounced in shallow groundwater due to direct influence from recharge processes (rainfall and river water infiltration) and varying redox conditions. The magnitude of these seasonal variations decreased in the order: Zone C > Zone D > Zone B > Zone E, though without consistent seasonal pattern across all wells (Fig. 5).

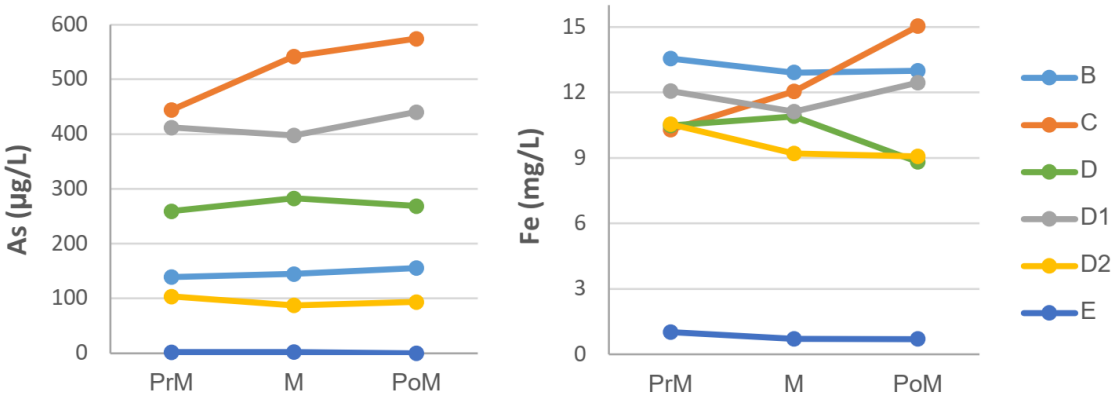

Figure 5. Seasonal variation of As and Fe in shallow groundwater (25 m) across the transect.

Zone C, located within the central region of the Holocene aquifer, is particularly influenced by the infiltration of evaporative water through the overlying aquitard layers. The resulting high organic matter influx, combined with strongly reducing conditions, facilitates the dissolution of As-bearing Fe minerals, thus releasing arsenic into the groundwater [10]. As a result, As

concentrations in this zone are the highest, showing progressive seasonal increases from pre-monsoon (PrM) through monsoon (M) to post-monsoon (PoM) seasons, paralleling Fe concentration patterns across all three seasons (Fig. 5).

In Zone D, arsenic (As) concentrations decrease along the groundwater flow path (D1→D→D2) due to re-adsorption onto Fe oxyhydroxide minerals within the sediments. Well D1, situated near Zone C, retains higher As levels due to ongoing Fe reduction processes and serves as a transitional point for arsenic migration between Zones C and D.

As a transitional area between the Holocene aquifer and the RTZ, seasonal As variations in well D1 show a distinctive pattern: slight decrease from PrM to M, followed by more substantial increase in PoM, reflecting the simultaneous influence of strong reduction conditions in the Holocene aquifer and the re-adsorption of As onto Fe minerals in the sediments. Within the RTZ (well D), As is effectively immobilized on Fe(III) minerals, preventing its advection into the deeper Pleistocene aquifer. Seasonal increases in Fe and As concentrations during the monsoon season are likely related to pH variations, as groundwater recharges from river and rainwater during this period leads to lower pH levels, enhancing the solubility of metals. Although the increase in Fe concentration during the monsoon is not statistically significant, it may still contribute to the dissolution of As from weakly bound sediment phases into groundwater.

As the study progresses toward Zone E (Pleistocene aquifer), well D2 exhibits a marked decrease in As concentration, coupled with a significant increase in manganese (Mn) concentration (ranging from less than 0.2 mg/L in Zone C to 0.5 mg/L in well D1, 1.0 mg/L in well D, and reaching 3.6 mg/L in well D2). This pattern reflects ongoing redox transitions that progressively alter the groundwater characteristics towards those typical of the Pleistocene aquifer, which explains the minimal seasonal variation in As concentrations observed at well D2. And the slight decrease in arsenic concentration observed at this well during the monsoon season may be attributed to dilution effects associated with the recharge of river water/rainwater.

In Zone B, situated near the river within the Holocene aquifer, groundwater is influenced by arsenic transported from newly deposited riverbank sediments [10]. This zone is characterized by concurrent Fe(III) and sulfate reduction progress, coupled with arsenic adsorption and re-precipitation of arsenic. The relatively minor seasonal variations in Fe concentrations (Fig. 5) suggest that groundwater in this zone remains stable throughout the year.

Additionally, seasonal As fluctuations tend to decrease with increasing distance from the river, except in Zone B, suggesting that local biogeochemical and hydrological processes, including recharge from river and evaporative sources, are the primary drivers of seasonal As variability. The natural occurrence of redox transition zones plays a crucial role in both controlling As contamination and mitigating seasonal fluctuations in As concentrations. Furthermore, elevated phosphate (PO_4^{3-}) concentrations in groundwater may also contribute to the mobilization of As from sediments (Fig. 2). Given the strong affinity between arsenate and phosphate for Fe minerals, high PO_4^{3-} concentrations can enhance competition for adsorption sites on metal oxides, displacing As into the aqueous phase [5, 10, 36]. This finding underscores the importance of considering competitive ion interactions when studying As contamination in groundwater within the study area and across the broader Red River Delta.

Although seasonal variations in As concentrations were observed in several wells, the patterns were inconsistent, indicating that groundwater in this region is influenced by a complex interplay of hydrological, geochemical, microbiological processes, and recharge dynamics from both river and rainfall sources. These findings emphasize the need for sustainable groundwater

management and continuous monitoring of As contamination to protect public health.

3.3. Health risk assessment

The assessment of health risk associated with seasonal arsenic exposure from groundwater for local residents was conducted using non-carcinogenic health hazard index (HI) and the incremental lifetime cancer risk (ILCR). The HI was evaluated for two primary exposure pathways: direct oral ingestion and dermal contact, while the ILCR was assessed exclusively for ingestion. The detailed results of this risk assessment are presented in Tables 2 and 3.

Table 2. Evaluation of the seasonal non-carcinogenic hazard index (HI) by arsenic exposure for adults and children.

Zone	Well name	Depth	PrM		M		PoM	
		(m.b.g.l)	Adult	Child	Adult	Child	Adult	Child
B	AMS 12	25	21.14	15.34	21.95	15.92	23.63	17.14
C	AMS 5	25	67.35	48.85	82.16	59.59	87.09	63.17
	VPNS 5	37	57.95	42.04	51.30	37.21	58.29	42.28
D1	AMS 11 - 25	25	62.46	45.30	60.33	43.76	66.80	48.45
	AMS 11 - 32	32	0.98	0.71	0.34	0.25	0.09	0.07
	AMS 11 - 47	47	1.97	1.43	2.43	1.76	0.96	0.70
D	AMS 31	25	39.34	28.53	42.90	31.11	40.79	29.59
	PC 43	29	9.22	6.69	10.97	7.96	9.06	6.57
	PC 44	37	0.44	0.32	0.78	0.57	0.10	0.07
D2	AMS 32	25	15.74	11.42	13.32	9.66	14.21	10.30
E	AMS 36	25	0.36	0.26	0.39	0.28	0.04	0.03
E1	AMS 4	25	0.16	0.11	0.88	0.64	0.06	0.05
E2	VPML A - 24	24	0.41	0.30	0.21	0.15	0.11	0.08
	VPML A - 38	38	0.19	0.13	0.15	0.11	0.04	0.03
	VPML A - 54	54	1.19	0.87	1.19	0.86	1.01	0.73
	AMS 13	25	58.85	42.68	70.47	51.12	68.54	49.71
	AMS 15	25	3.11	2.25	3.49	2.53	3.28	2.38
Mean			20.05	14.54	21.37	15.50	22.01	15.96
Min			0.16	0.11	0.15	0.11	0.04	0.03
Max			67.35	48.85	82.16	59.59	87.09	63.17

The analysis of health risks associated with arsenic exposure revealed that the potential risks from direct ingestion were significantly higher than those from dermal contact for both adults and children (Table 2). Adult HI values were consistently higher than those for children ($p < 0.05$), likely due to prolonged exposure durations in adults. Seasonal trends in HI values were observed, with increasing values in the following order: pre-monsoon < monsoon < post-monsoon. However, these variations did not reach statistical significance ($p > 0.05$). Specifically, during the pre-monsoon season, HI values for adults ranged from 0.16 to 67.35 (mean 20.05), while for children, they ranged from 0.11 to 48.85 (mean 14.54). In the monsoon season, HI values were slightly higher, ranging from 0.15 to 82.16 (mean 21.37) for adults and from 0.11 to 59.59 (mean 15.50) for children. During the post-monsoon season, HI values ranged from 0.04 to 87.09 (mean 22.01) for adults and from 0.03 to 63.17 (mean 15.96) for children. Among the 17 wells surveyed, only six wells (AMS 11-32, PC 44, AMS 36, AMS 4, VPML A-24, and VPML A-38) during the pre-monsoon and monsoon seasons showed minimal health risks associated with arsenic exposure. This number increased to seven wells during the post-monsoon season, including AMS 11-47. Notably, the deepest well in Zone E2 (VPML A-54), located at 54 m, posed a potential health risk for adults (with HI values ranging from 1.01 to

1.19), though it did not present a significant risk to children (HI < 1). The HI values observed in this study were notably higher compared to those reported in studies conducted in India [22, 23].

In terms of carcinogenic risk, arsenic exposure via ingestion resulted in unacceptable risks for both adults and children in the majority of wells across all three seasons, except for two wells in Zone E1 and E2 (AMS 4 and VPML A-38) in the pre-monsoon season, two well in Zone E2 (VPML A-24 and VPML A-38) in the monsoon season, and one well in zone D1 (AMS 11-32), one well in zone D (PC 44), and four wells in Zone E, E1 and E2 (AMS 36, AMS 4, VPML A-24, and VPML A-38) in the post-monsoon season. For these wells, the $ILCR_{ingestion}$ values were within the acceptable range (1.14×10^{-5} to 9.50×10^{-5}). In contrast, for dermal exposure, the carcinogenic risk for adults remained negligible or acceptable across all three seasons ($ILCR_{dermal}$ values ranging from 1.46×10^{-8} to 3.55×10^{-5}). However, for children, there were no samples exhibiting non-risk levels during the pre-monsoon and monsoon seasons, and 7 wells (AMS 12, AMS 5, AMS 11-25, AMS 11-32, AMS 31, AMS 32, and AMS 13) demonstrated unacceptable carcinogenic risk across all three seasons (Table 3). These findings indicate that groundwater in the study area should be treated to remove arsenic before being used for drinking or bathing purposes.

Table 3. The incremental lifetime cancer risk (ILCR) estimated values from ingestion and dermal contact exposure pathway for adults and children.

Zone	Well name	PrM				M				PoM			
		$ILCR_{ingestion}$ ($\times10^{-5}$)		$ILCR_{dermal}$ ($\times10^{-5}$)		$ILCR_{ingestion}$ ($\times10^{-5}$)		$ILCR_{dermal}$ ($\times10^{-5}$)		$ILCR_{ingestion}$ ($\times10^{-5}$)		$ILCR_{dermal}$ ($\times10^{-5}$)	
		Adult	Child	Adult	Child	Adult	Child	Adult	Child	Adult	Child	Adult	Child
B	AMS 12	951	669	0.86	20.41	987	695	0.89	21.19	1062	748	0.96	22.81
C	AMS 5	3028	2132	2.74	65.02	3694	2600	3.35	79.31	3915	2756	3.55	84.07
	VPNS 5	2606	1834	2.36	55.95	2307	1624	2.09	49.53	2621	1845	2.37	56.27
D1	AMS 11-25	2808	1977	2.54	60.29	2712	1910	2.46	58.24	3003	2114	2.72	64.49
	AMS 11-32	44.25	31.15	0.04	0.95	15.47	10.89	0.01	0.33	4.22	2.97	0.00	0.09
	AMS 11-47	88.35	62.20	0.08	1.90	109	76.91	0.10	2.35	43.19	30.40	0.04	0.93
D	AMS 31	1769	1245	1.60	37.97	1929	1358	1.75	41.41	1834	1291	1.66	39.38
	PC 43	414	292	0.38	8.90	493	347	0.45	10.59	407	287	0.37	8.74
	PC 44	19.83	13.96	0.02	0.43	35.09	24.71	0.03	0.75	4.49	3.16	0.00	0.10
D2	AMS 32	708	498	0.64	15.20	599	421	0.54	12.86	639	450	0.58	13.71
E	AMS 36	16.05	11.30	0.01	0.34	17.53	12.34	0.02	0.38	1.62	1.14	0.00	0.03
E1	AMS 4	7.00	4.92	0.01	0.15	39.76	27.99	0.04	0.85	2.92	2.05	0.00	0.06
E2	VPML A-24	18.65	13.13	0.02	0.40	9.50	6.69	0.01	0.20	4.98	3.50	0.00	0.11
	VPML A-38	8.33	5.87	0.01	0.18	6.76	4.76	0.01	0.15	1.70	1.20	0.00	0.04
	VPML A-54	53.62	37.75	0.05	1.15	53.41	37.60	0.05	1.15	45.46	32.01	0.04	0.98
	AMS 13	2646	1863	2.40	56.81	3168	2231	2.87	68.03	3081	2169	2.79	66.16
	AMS 15	140	98.32	0.13	3.00	157	111	0.14	3.37	148	104	0.13	3.17

4. CONCLUSIONS

This study provides a comprehensive analysis of seasonal variations in arsenic contamination and the associated hydrogeochemical dynamics of groundwater in Van Phuc village. The physicochemical analysis of groundwater reveals minimal seasonal fluctuations, with notable exceptions in pH, which exhibited a slight decrease during the monsoon season, and electrical conductivity (EC), which increased during the same period. These relatively subtle seasonal variations suggest that the groundwater system in the study area is predominantly influenced by local biogeochemical processes, with limited impact from anthropogenic activities such as irrigation, fertilization, and wastewater discharge.

Although arsenic concentrations showed slight but statistically significant seasonal fluctuations, the highest mean concentrations were observed during the post-monsoon season. However, these fluctuations were only evident in a limited number of wells and did not follow a consistent trend. In general, seasonal variations in arsenic concentrations were most pronounced in shallow groundwater samples (depths < 30 m). The relative stability of arsenic concentrations in deeper groundwater and the Pleistocene aquifer throughout the study period can be attributed to the presence of oxidized sediment layers and stable iron minerals, such as hematite and goethite, which effectively immobilize arsenic in solid phases. In the shallow aquifers, the magnitude of seasonal fluctuations in arsenic concentrations diminished progressively with increasing distance from the Red River. These variations are primarily controlled by local biogeochemical processes, which are influenced by dilution effects from groundwater recharge, as well as by evaporative processes. Furthermore, the high concentrations of phosphate in groundwater appear to exacerbate the seasonal variation in arsenic, likely due to competitive adsorption between arsenate and phosphate on iron oxides.

This study also highlights the critical role of redox transition zones as natural barriers that limit the migration of arsenic into deeper aquifers, thereby mitigating seasonal variations in arsenic concentrations. However, it is important to note that groundwater extraction and land-use changes could disrupt these natural processes, potentially exacerbating contamination risks.

Health risk assessments indicate that arsenic exposure through drinking water represents a significant public health concern, particularly with long-term ingestion. The hazard index (HI) values for most sampled wells exceed safety thresholds, and carcinogenic risk assessments reveal an unacceptably high incremental lifetime cancer risk (ILCR > 10^{-4}) for several of the wells. These findings underscore the urgent need for mitigation strategies, including groundwater treatment, well management, and the development of alternative water sources.

In conclusion, the results of this study emphasize that arsenic contamination in the study area is predominantly governed by local hydrogeochemical processes within the aquifer system. However, the results are based on data from 17 wells in a single region, necessitating further research with a larger sample size and expanded geographical coverage to enhance the generalizability of these findings. Given the significant health risks associated with arsenic exposure, future research should focus on long-term monitoring of groundwater quality, the development of advanced water treatment technologies, and the formulation of policy interventions aimed at protecting public health. By integrating hydrogeochemical insights with sustainable water management practices, the risks associated with arsenic contamination can be effectively mitigated in Hanoi and other regions facing similar challenges.

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Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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