ISSN 1819-7140, Russian Journal of Pacific Geology, 2024, Vol. 18, No. 4, pp. 452–466. © Pleiades Publishing, Ltd., 2024.

Study on Aquifer Contamination by Heavy Metals Using Finite Element Modeling with Freundlich Parameters in Traditional Metal Recycling Craft Village in Bac Ninh Province, Vietnam

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Received June 20, 2023; revised March 12, 2024; accepted March 29, 2024

Abstract—The traditional craft villages in Vietnam in general and in Bac Ninh province in particular have been exposing many negative impacts on the environment. The heavy metal-rich wastes from the metal recycling casting craft villages in the field of metal recycling and metal casting are causing severe heavy metal pollution not only to the air, soils, and sediments but also to the groundwater resources. In Da Hoi iron recycling craft village in Chau Khe ward, Tu Son town, Bac Ninh province, Vietnam, the Holocene aquifer is exposed to the Ngu Huyen Khe River's sediments contaminated with heavy metals Lead, Cadmium, Nickel, and Zinc. Freundlich isotherm parameters of the Holocene aquifer have been selected for finite element modeling of heavy metal transport with high temporal and spatial varying retardation factors to get reliable quantitative heavy metals' distribution in depth and time. Initial and boundary conditions have been augmented to be established. The retardation factors of the advection and dispersion transport in the Holocene aquifer for heavy metals Pb, Zn, Cd, and Ni are very highly none-linear and very much varying in time and space: 8.7–66.4 for Pb, 2.0–12 for Zn, 1.7–4.8 for Cd and 1.1–5.9 for Ni. The results of the numerical modeling show that heavy metal transport in the Holocene aquifer is very fast and the entire aquifer thickness has equilibrium aquifer formation and aquifer water heavy concentrations after around 2–2.5 years for Cd and Ni, around 4 years for Zn and around 27 years for Pb. The heavy metals' fluxes from the Holocene aquifer to the Pleistocene aquifer are maximal and more or less constant from the equilibrium time and would cause severe contamination of the Pleistocene aquifer.

Keywords: Freundlich Isotherm, Dispersion, Retardation Factor, Finite element (FE), Peclet number, Courant number

DOI: 10.1134/S1819714024700155

INTRODUCTION

Vietnam's economic development is very much associated with the formation and development of various occupational groups in craft villages, such as lacquer, ceramics, embroidery, rattan, rush, weaving, paper, folklore paintings, etc. About 3000 craft villages with over 400 traditional ones, are in operation in Vietnam, contributing significantly to the promotion of local socio-economic development. However, old production methods and out-of-date technology used in Vietnam's traditional craft villages have been exposing many negative impacts on the environment [1].

The soil and groundwater pollution and contamination by heavy metals is of a widely worldwide concern, some relevant studies of which are described as follows. Fatta et al. [2] carried out a study on the groundwater quality around the Ano Liosia landfill in Attica region, Greece. Based on the study results, the authors came to the conclusion that due to the pollution caused by the landfill, the groundwater near the landfill is not potable and not suitable for irrigation water, since most of the examined physical and chemical parameters, including heavy metals Fe, Ni and Pb exceeded the permissible limits. The authors also presented an application of the hydrologic evaluation of landfill performance (HELP) model for the determination of the yearly leakage from the base of the landfill after the final capping for supporting the future assessment of groundwater contamination in future long-term.

Regarding the issue of technogenic metallization of soils, [3] had pointed out that the soil metallization has covered almost the entire biosphere, the highest metal concentrations are found in areas of ore mining, the largest area and most dangerous concentrations of metals in soils for humans are typical for populated areas and are associated with the smelting of metals, the manufacture, wear and disposal of waste materials, and had recommended that it is necessary to take into account the increasing metallization of agricultural soils.

The relative abundance of the heavy metals above the median background in the administrative regions of Altai krai and the total soil pollution with heavy metals in the regions have been addressed by Morkovkin and Maksimova (2015) [4], who pointed out that the environment (air, water, soil) in the industrial cities and regional centers experiences the load of large amount of toxic substances, including heavy metals.

Kulakov et al. [5] through the study the changes in mineralogical composition occurring in the course of preparation of drinking water based on the data from the monitoring wells of the Tunguska groundwater abstraction field had shown that the solid products of the destruction of oxides and hydroxides of iron and manganese are formed in the process of interlayer oxidation of water, participate in the colmatation of cracks and the slit space of the well filters. This would cause a higher iron and manganese concentration of the pumped water, that needs to be considered.

The groundwater from the Pleistocene aquifer had been being exploited for Hanoi city domestic supply since the beginning of the 20th century, when the Frenchmen in Hanoi evaluated the utilization of groundwater of aquifer for the city's water supply. However, the groundwater contamination are believed to be due to the inadequate sewage and solid waste handling and its disposal. Most of the landfills in Hanoi city were selected in the past from the locations where the surface clay layers have been excavated for brick and tile making. Therefore it makes it more possible for contaminants to enter the Pleistocene groundwater system. Nguyen Van Hoang et al. [6] carried out a finite element modeling using higher order shape functions to evaluate the spreading of contaminants in the Pleistocene confined aquifer provided that they have reached it from the Me Tri landfill. The result showed that upon the time for which the contaminants spread over the whole aquifer, the contaminants' concentrations would be higher than drinking standards.

Nguyen Van Hoang et al. [7] carried out finite element modelling of heavy metals transport by groundwater movement from Kieu Ky waste landfill leach pond through the underneath soil layer into the Pleistocene aquifer in the Northern East Hanoi along with Freundlich isotherm adsorption parameters with the Freundlich's adsorption isotherm parameters. The model results show that the soil and soil water would be contaminated by the heavy metals at levels higher than the allowable limits if the heavy metal concentrations are sufficiently high and exceeding the soil adsorption capacity at equilibrium concentration with pore water contamination.

Ahmad et al. [8] carried out chemical analysis to determined the concentration of toxic (Cr, Mn, Cu, As) and heavy metals (Cd, Ba, Hg, Pb) in soil and water samples near the landfill site of industrial waste in Sialkot, province of Punjab-Pakistan. The results show that the mean concentration of all metals in both soil and water samples was found under the standard limit set by regulatory agencies like EU, US EPA, and WHO, except Cr and Mn. The soil Cr and Mn concentration found to be high and the soil is categorized as moderately contaminated classified based on index of geoaccumulation. Based on the results of human health risk assessments, metals present in soil and water pose negligible non-carcinogenic and carcinogenic risks to the adults and children living in the area under study. But need for the attention and actions of the minimization and prevention of toxic and heavy metal contamination in soil and water by retardation of leachate movement, since these toxic and heavy metals can bio-accumulate.

Bac Ninh province has 18 and 10% of the total and traditional craft villages of Vietnam, respectively, which contributed more than 30% of the province's industrial production value [9]. Most craft villages of Bac Ninh province are located in Tu Son town, Yen Phong, and Gia Binh districts: 42 craft villages which are 68% of the province's total number of craft villages [10].

In Tu Son town and Yen Phong district there are some craft villages in the field of metal recycling and metal casting, where dust containing lignite dust and wastes containing high contents of acid and sulfur are directly disposed into the environment causing a severe environmental problem, for the reason of which some craft villages are classified as "cancer villages" [1]. In craft clusters of Chau Khe ward (Tu Son town), 123 production facilities of metal recycling craft village that had been inspected have not been installed with exhaust gas and wastewater treatment systems, and the generated solid wastes are arbitrarily dumped around the craft cluster area or even discharged into the common sewage channels of the craft villages which then flow to Ngu Huyen Khe River causing serious pollution of surface water [11]. Man Xa craft village which is specialized in alumina, lead, and zinc recycling in Van Mon commune, Yen Phong district, produces 30–40 tons of slag to be dumped in 7 waste fields of a total area of 76000 m^2 [11].

The determination of heavy metals Cu, Zn, and Pb of 65 soil samples in agricultural land during 2013–2017 years by Nguyen Thi Tham et al. [13] had shown

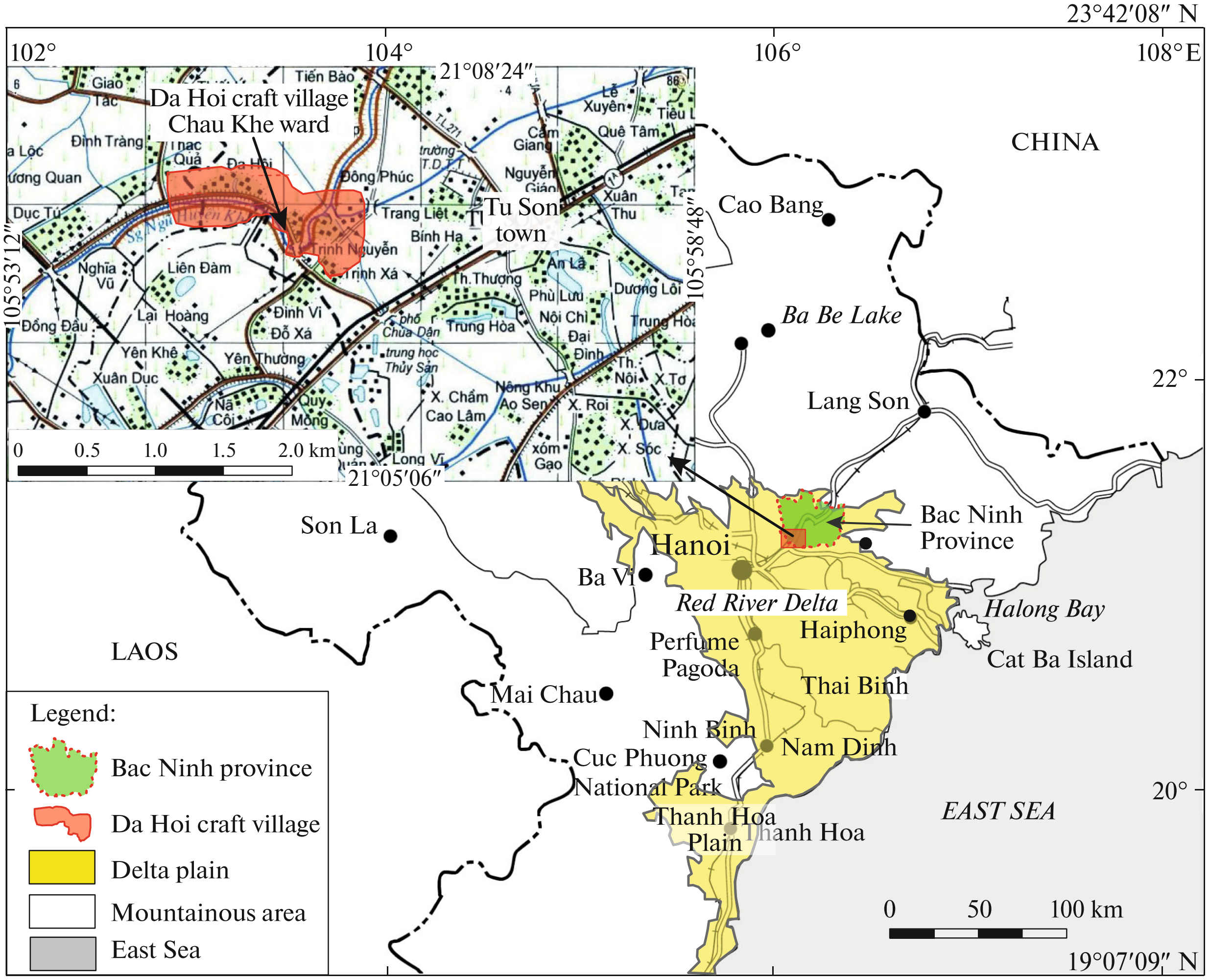


Fig. 1. Map of the study area.

soil pollution by Pb and Zn in the areas which are adjacent or near to Da Hoi iron recycling craft village in Chau Khe ward, Tu Son town, while the study of Le Van Thang et al. [1] had shown that the surface water in Da Hoi iron recycling craft village is polluted by ammonia, Fe and Pb. The analysis results of most soil and sediment samples were made within the research grant DTDLCN.86/21 [14] also showed that the soil and sediment in the Man Xa craft village (Yen Phong district) and Da Hoi craft village are polluted with Fe, Pb, Cu, Zn, and Ni. Meanwhile, groundwater in Bac Ninh province in general, and Tu Son town and Yen Phong district, in particular, is currently abstracted for domestic supply. The total groundwater abstraction rate in Bac Ninh province is 78686 m^3/day from which 18316 m^3/day in Tu Son town and 4180 m^3/day in Yen Phong district [15]. Da Hoi iron recycling craft village is just 3 km to the West of the groundwater abstraction well field of Tu Son town, where the overall groundwater level drawdown is great, would be at significant risk of groundwater contamination by heavy metals from the ground surface, especially from the bottom of lakes and streams where the sediments are heavily polluted by heavy metals. Figure 1 presents Bac Ninh province in Bac Bo delta plain and Da Hoi craft village on the southern-west edge of the province.

The study aims to access the possible groundwater contamination and its magnitude by heavy metals from Chau Khe iron recycling craft village where high contents of heavy metals in soil and sediment are observed.

1. MATERIALS AND METHODS

The hydrogeological conditions, i.e., the groundwater aquifer system including the semi-permeable layers of the study area have been well established along with the hydraulic parameters such as hydraulic conductivities, total porosity and specific yield etc. in several fundamental hydrogeological investigation projects and groundwater exploitation feasibility studies. The most recent and comprehensive report is the report on groundwater protection in large cities, stage II: Bac Ninh City, Vietnam under the implementation of the National Center for Water Resources Planning and Investigation-MoNRE [15]. The very specific hydrogeological conditions of the study area of the Da Hoi craft village in Chau Khe Ward, Tu Son town, Bac Ninh province are based on the field hydrogeological survey within the Research grant DTDLCN.86/21 from the Ministry of Science and Technology of Vietnam [14].

The samples of the wastes, soils, sediments and water had been mostly sampled in 2022 and 2023 within the implementation of the approved field works of the Research grant DTDLCN.86/21 from the Ministry of Science and Technology of Vietnam [14]. The samples had been prepared and processed for heavy metal analysis strictly in accordance with relevant required procedures for analysis by ICP-MS are described in paragraph 3.1.

The heavy metals transport had been modelled by the Galerkin finite element method which may be well referred to the book *Finite Elements and Approximation* by Zienkiewicz and Morgan [26] which is described in paragraph 4.2 with the Freundlich's adsorption isotherm parameters of the soil in the solute advection-dispersion transport partial differential equation which is described in paragraph 4.1. The finite element modelling code used is from the work of Nguyen Van Hoang [27]. The Freundlich's adsorption isotherm parameters' values for the soil are described in paragraph 4.3 while the advection and dispersion parameters are described in paragraph 4.4.

2. HYDROGEOLOGICAL CONDITIONS AND GROUNDWATER ABSTRACTION OF BAC NINH PROVINCE

2.1. Hydrogeological Conditions

The hydrogeological conditions of the study are described in accordance with Trieu Duc Huy [15] as follows.

The semi-permeable layer 2 consists of silts with sands and clay of the upper parts of the Thai Binh formation (aQ_2^3tb) and Hai Hung ($aQ_2^{1-2}hh$) formation. This semi-permeable layer is existing in an area of 141.8 km^2 which is 39.9% of Bac Ninh province's area of 355.4 km^2. The layer's thickness of the layer varies from 0 m to 25.0 m with an average of 7.2 m. The layer's hydraulic conductivity is from 0.0181 to 0.0415 m/day with an average of 0.0334 m/day.

The Holocene unconfined aquifer (qh) is underlying the semi-permeable layer 1 and mainly consists of silty sands and fine sands of Thai Binh (aQ_2^2tb) and Hai Hung ($ambQ_2^{1-2}hh$) formations. This aquifer is existing in an area of 168.7 km^2 which is 47.5% of Bac Ninh province. Mostly, 84% area of this aquifer's distribution area is covered by a low permeable layer of upper Holocene clay, silty clay, and silt. In the remaining area, i.e., in the South of Tu Son town and along Duong, Cau, and Ngu Huyen Khe rivers, this aquifer is exposed to the ground surface. The aquifer has the average particle composition as follows: clay (<0.005 mm)–2.8%; fine silts (0.005–0.01 mm)–14.9%; coarse silts (0.01–0.05 mm)–5.6%; very fine sands (0.05–0.1 mm)–20.8%; fine sands (0.1–0.25 mm)–26.0%, medium sands (0.25–0.5 mm)–20.7% and coarse sands (0.5–2.0 mm)–9.2%. Therefore, the aquifer has a fairly uniform particle composition with 55.9% of fine and coarse sands 0.1–2.0 mm. The aquifer's average hydraulic conductivity is 9.1 m/day. The vertical hydraulic conductivity is assumed to be 1/10 of the horizontal one.

The semi-permeable layer 2 consisting of silts with sands and clay of the upper parts of Vinh Phuc formation (Q_1^3vp) is existing in an area of 155.2 km^2. The layer's thickness of the layer varies from 1.1 to 32.5 m with an average of 11.4 m.

The semi-permeable layers 1 and 2 are overlying the whole area of Holocene and Pleistocene aquifers' distribution, except that along the Duong, Cau, and Ngu Huyen Khe rivers where the Holocene aquifer is exposed to the rivers' bottom, in 2.5 km in the North along the Ca Lo River and in 2 km in the North along the Cau River where the Pleistocene aquifer is exposed to the rivers' bottom.

The Pleistocene confined aquifer (qp) consists of sands, gravels, and pebbles of Vinh Phuc (aQ_1^3vp) and Ha Noi ($aQ_1^{2-3}hn$) formations. The aquifer distribution area is 312.8 km^2 (88.1% of Bac Ninh province area) from which 14.8 km^2 has the aquifer exposed to the ground surface. The aquifer particle composition as follows: (a) upper parts: very fine sands (0.05–0.1 mm)–3.9%; fine sands (0.1–0.25 mm)–13.6%, medium sands (0.25–0.5 mm)–40.9%, coarse sands (0.5–2.0 mm)–37.3% and small gravels (2–4 mm)–4.3%; (b) lower parts: small to coarse gravels and pebbles with sands. The aquifer's maximal and average thicknesses respectively are 54 and 19 m. The aquifer's transmissivity is from 101 to 2948 m^2/day, an average of 792 m^2/day, the average hydraulic conductivity is 30 m/day, and the storage coefficient is from 0.0031 to 0.038, on average 0.0248.

Under the Pleistocene aquifer is a Pre-Quaternary fractured aquifer from Vinh Bao formation (N_2vb) (Neogene) (conglomerate, sandstone, siltstone or shale) in a small area of 33.4 km^2 or Hon Gai formation (upper Triassic) (conglomerate, sandstone with siltstone or shale), or Na Khuat formation (middle Triassic) (sandstone or limestone), or Middle Permian formation (limestone). The groundwater resource of

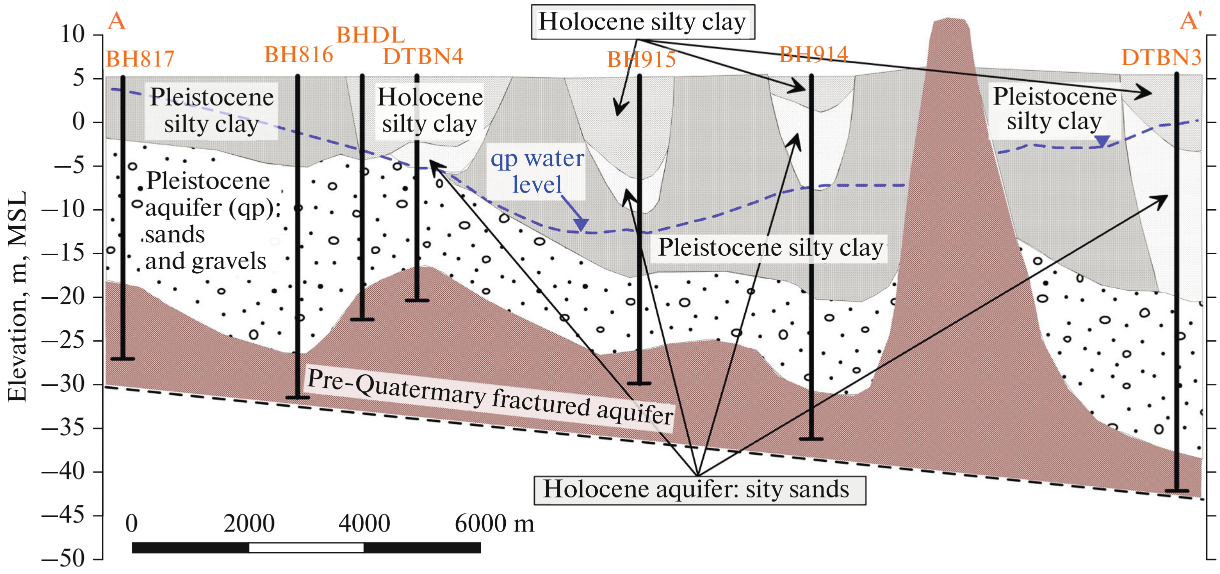


Fig. 2. Hydrogeological cross-section along line AA'.

the Pre-Quaternary fractured aquifer is much less than the Pleistocene aquifer and has only limited and scarce potential.

The hydrogeological cross-section along line AA' from North to South through Bac Ninh province is shown in Fig. 2. The cross-section AA' is shown in Fig. 3.

2.2. Groundwater Abstraction

The groundwater of the Holocene, Pleistocene, and bedrock aquifers is abstracted for different utilization purposes, mainly for domestic purposes. In Bac Ninh province, the groundwater abstraction is mostly from the Pleistocene aquifer. There are approximately 450 groundwater abstraction wells in the Pleistocene aquifer. The total groundwater abstraction is approximately 73417 m^3/day. The map of groundwater abstraction wells, centralized groundwater abstraction plants and the Pleistocene aquifer groundwater level in 2021 along with lines of hydrogeological cross sections AA' (from North to South through Bac Ninh province) and BB' (from South to North through Da Hoi craft village across the Ngu Huyen Khe river) is presented in Fig. 3.

3. RISK OF GROUNDWATER CONTAMINATION BY HEAVY METALS IN DA HOI CRAFT VILLAGE

3.1. Heavy Metals in Craft Village's Wastes, Soil, Sediments, and Surface Water

The wastes from the traditional villages are obvious man-made hazards: the environment's heavy metal contamination by the traditional craft villages. The surveys made in 2022 and 2023 [14] have an impressive feeling of the high magnitude of the negative impact of the wastes on the land environment: large areas of the thick heavy-metal rich waste dump which are highly exposed to the surrounding living and agricultural lands.

Heavy metals of waste, soil and sediment samples have been analyzed by ICP-MS system model PlasmaQuant MS produced by Analytik Jena-Germany. In this study, the waste, soil and sediment samples are of spot sample type which are taken from particular locations in accordance with Vietnam guidance on sampling techniques (TCVN 7538-2:2005 Soil quality—Sampling—Part 2: Guidance on sampling techniques). The digestion of the samples had been carried out using microwave technique (EPA 3051A—Microwave assisted acid digestion of sediments, sludge, soils, and oils). The method for the extraction of trace elements from samples uses aqua regia to produce solution is suitable for the determination of trace elements (ISO 11466:1995—Soil quality—Extraction of trace elements soluble in aqua regia).

The analysis results of metal processing slag, soil, and sediment in Man Xa craft village (6 km from Da Hoi craft village to the North) in Man Xa craft village which is specialized in alumina, lead, and zinc recycling in Van Mon commune, Yen Phong district show the following. The maximal detected concentrations along with the Vietnam technical standards permissible limits (in parentheses) of Ni, Cd, Pb, and Zn respectively are: a) 300.8 mg/kg (1400 mg/kg), 2833 mg/kg (10 mg/kg), 4410.2 mg/kg (300 mg/kg) and 7248.2 mg/kg (5000 mg/kg) in slag; (b) 18.0 mg/kg

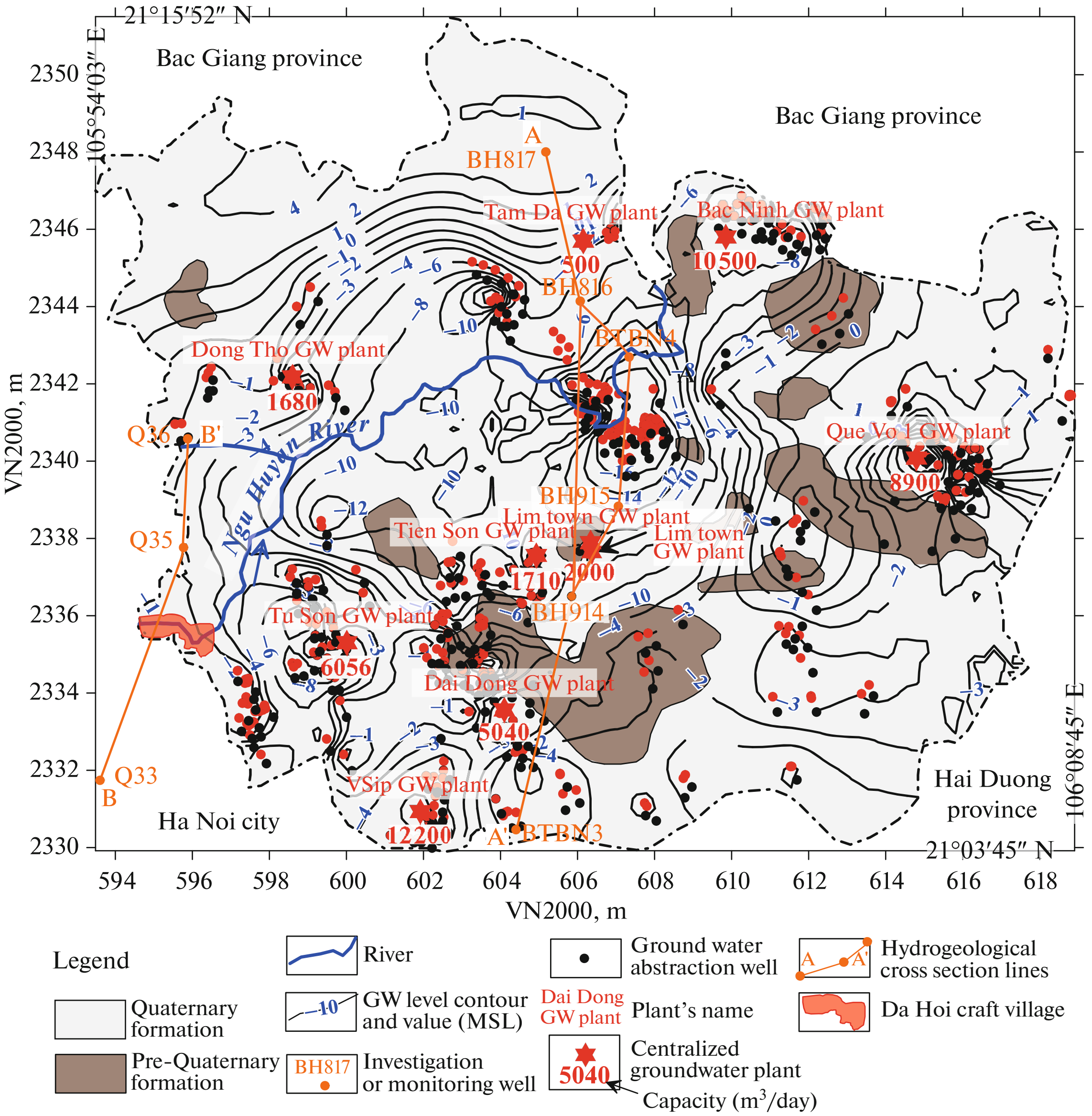


Fig. 3. Map of GW abstraction wells, qp's water level, and lines of hydrogeological cross-sections.

(21 mg/kg for freshwater sediment), 4.0 mg/kg (1.5 mg/kg), 229.3 mg/kg (70 mg/kg) and 500.2 mg/kg (200 mg/kg) in soil; (c) 87.4 mg/kg (21 mg/kg), 15.1 mg/kg (3.5 mg/kg), 433.34 mg/kg (91.3 mg/kg) and 872.6 mg/kg (315 mg/kg) in fresh lake/river sediment. In Da Hoi craft village, the maximal detected concentrations of Ni, Cd, Pb, and Zn in the lake/river sediment respectively are 15.3, 137.8, 219.8, and 6329.7 mg/kg.

The maximal concentrations of all four metals Ni, Cd, Pb, and Zn mostly are much higher than most limits specified by Vietnam's national technical regulations [16–18, 38] and Australian sediment quality guidelines [19] (Table 1).

3.2. Heavy Metal Contamination Way to the Groundwater

As mentioned in paragraph 2.1 that the semi-permeable layers 1 and 2 are absent along Ngu Huyen Khe River where the Holocene aquifer is exposed to the river's bottom, heavy metals can be transported into the Holocene aquifer from the Ngu Huyen Khe River's bottom. Therefore, the specific condition which is directly related to the possible groundwater contamination by heavy metals from Da Hoi craft village is that there is absent the semi-permeable layer 1 above the Holocene aquifer and that the Holocene aquifer is directly overlying the Pleistocene aquifer along the Ngu Huyen Khe River (Fig. 4). The Ngu

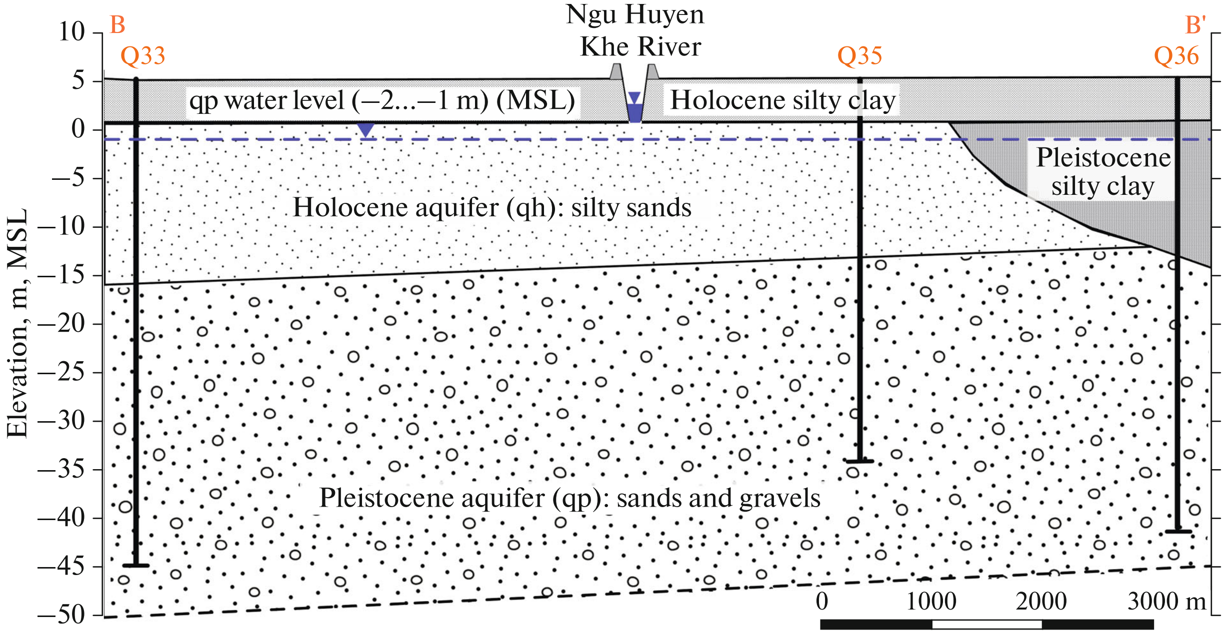
Table 1. The maximal detected concentrations and permissible concentrations of heavy metals

	Ni		Cd		Pb		Zn	
	max.	per. limit	max.	per. limit	max.	per. limit	max.	per. limit
Slag as hazardous waste, mg/kg	300.8	1400	2.833	10	4410.2	300	7248.2	5000
Agricultural soil, mg/kg	18.0	Not specified	4.0	1.5	229.3	70	500.2	200
Sediment, mg/kg	77.72	21	12.76	3.5	253.90	91.3	3869	315

Huyen Khe River's bottom sediment has an average hydraulic conductivity of 0.0174 m/day [15].

The horizontal groundwater flow velocity in Holocene and Pleistocene aquifers can be determined through the groundwater contour lines in Fig. 3. The horizontal groundwater flow in the Holocene aquifer in the study area of Da Hoi craft village has a dominant West-East flow direction with a hydraulic gradient of around 10^{-3} which gives the Darcy velocity of 0.009 m/day. While, with the water level at 2.2 m (MSL) in Ngu Huyen Khe River, the Darcy vertical water flow through the 0.2 m-thick sediment layer and Holocene aquifer is 0.0135 m/day. Therefore, along the Ngu Huyen Khe River direction, the vertical transport of heavy metals by the vertical groundwater flow from the Ngu Huyen Khe River through the Holocene aquifer into the Pleistocene aquifer would be the most predominant (Fig. 5), and the Pleistocene aquifer pos-

(a) Hydrogeological cross section



(b) Geodetic profile across the Ngu Huyen Khe River

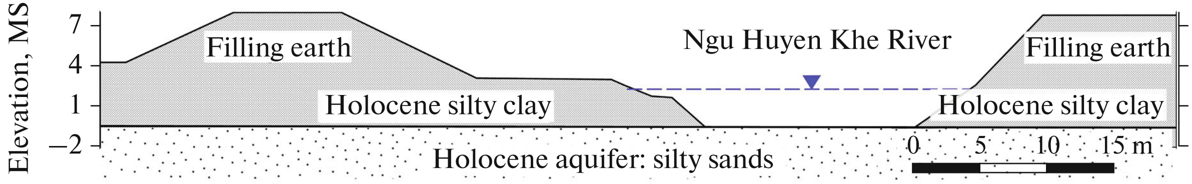


Fig. 4. Hydrogeological cross-section BB' and geodetic profile across the Ngu Huyen Khe River.

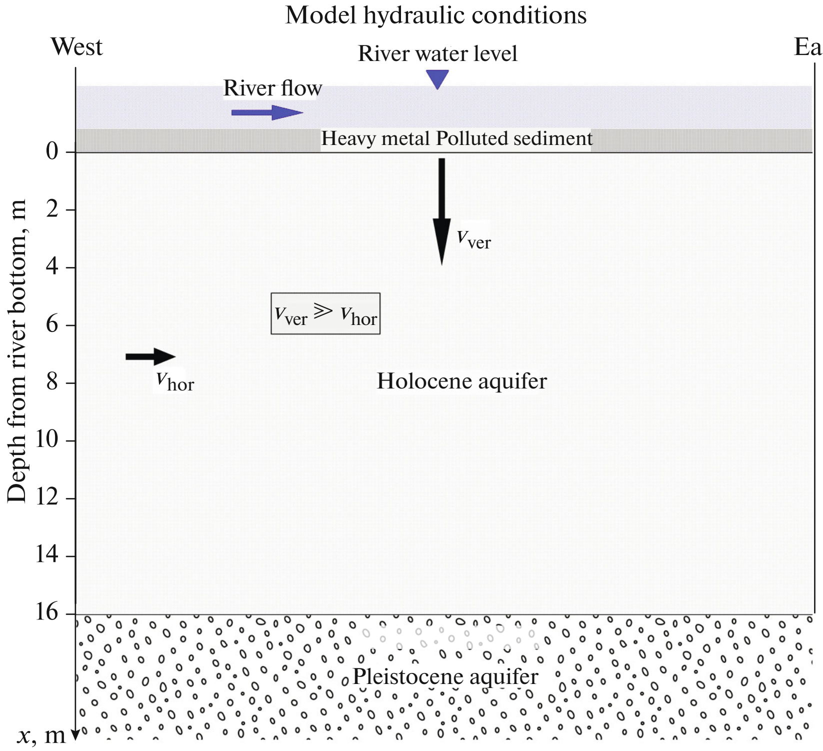


Fig. 5. Hydraulic conditions of the model domain.

sible contamination by heavy metals from the river bottom sediment can be accessed via the vertical heavy metal transport in the Holocene aquifer.

4. MODELLING OF HEAVY METAL TRANSPORT IN SOIL BY GROUNDWATER MOVEMENT

4.1. Theory of Heavy Metal Advection-Dispersion Transport with Adsorption by the Soil

The one-dimensional general transport equation for a contaminant plume is given by (Jacob and Arnold) [20]:

$$D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} = \frac{1-n}{n}\rho_s\frac{\partial q_e}{\partial t} + \frac{\partial C}{\partial t}, \qquad (1)$$

where t is time, D is the diffusion-dispersion coefficient (m^2/d), x is the distance (m), v is the seepage velocity (m/d), ρ_s is the solid particle density (note that $\rho_d = \rho_s(1-n)$ in which ρ_d is the unit weight of the dry soil), n is porosity and the other terms are as already defined. The first, second, and third terms respectively represent diffusion, advection, and adsorption.

Solid particles are capable of adsorption of dissolved ions of heavy metals in the soil pore water. The two most common models used to represent the adsorption isotherm are the Freundlich and Langmuir [21]. The Freundlich isotherm is the most common isotherm model, used to describe physical adsorption in a solid-liquid system [22]. Freundlich's adsorption isotherm is used in this study and is described as follows [23, 24]:

$$q_e = K_F C^{1/\eta}, \qquad (2)$$

where q_e is the mass adsorbed per adsorbent mass (mg/g); C is the concentration in solution at equilibrium (mg/L); K_F and $1/\eta$ are fitting constants: K_F is termed as the Freundlich coefficient (adsorption coefficient) [(mg/g)(l/mg)$^{1/\eta}$] and $1/\eta$ is adsorption intensity (dimensionless). The distribution coefficient K_d in terms of K_F and $1/\eta$ is:

$$\frac{dq_e}{dC} = K_F\frac{1}{\eta}C^{\frac{1-\eta}{\eta}} = K_d. \qquad (4)$$

The adsorption intensity $1/\eta$ depends on the linearity of the isotherm and varies between 0 and 1. Only when $1/\eta = 1$ the isotherm is linear does $K_F = K_d$.

From (4) the source term $\frac{\rho_s}{n}\frac{\partial q_e}{\partial t}$ in (1) is:

$$\frac{1-n}{n}\rho_s\frac{\partial q_e}{\partial t} = \frac{1-n}{n}\rho_s K_F\frac{1}{\eta}C^{\frac{1-\eta}{\eta}}\frac{\partial C}{\partial t}. \qquad (5)$$

Therefore, the equation (1) may be written in the following form:

$$D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} = \left(1 + \frac{1-n}{n}\rho_s K_F \frac{1}{\eta} C^{\frac{1-\eta}{\eta}}\right)\frac{\partial C}{\partial t}. \quad (6)$$

The so-called coefficient of retardation (retardation factor) R is also used:

$$R = 1 + \frac{1-n}{n}\rho K_F \frac{1}{\eta} C^{\frac{1}{\eta}-1} = 1 + \frac{1-n}{n}\rho K_d, \quad (7)$$

$$D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} = R\frac{\partial C}{\partial t}. \quad (8)$$

The retardation factor (dimensionless) is greater or equal to 1 and is equal to 1 when $1/\eta = 1$ which gives $K_F = K_d$.

The equation is subject to initial and boundary conditions for a particular problem in reality over a certain domain and only has an analytical solution for simple domain configuration with unchanged boundary conditions and spatial and temporal constant values of parameters, i.e., D, v, and R. Among the transport parameters, the retardation factor is the most sensitive and variable value in time and space as it is a non-linear function of the heavy metal concentration. This issue needs to always be kept in mind in numerical simulation of solute transport in groundwater in a medium with adsorption ability. Numerical methods are capable of solving the equation for any domain configuration, spatial and temporal changing boundary conditions, and parameters' values. The finite element method (FEM) is used in this study.

Due to the adsorption isotherm, to more accurately estimate retardation and contaminant transport other than the use of a single value is required by the relationship in Eq. (7). However, defining transport in terms of a retardation coefficient based on nonlinear adsorption could be complicated. Therefore, Coles [25] examined how the Freundlich model can be used to predict retardation by presenting a simpler way of accounting for nonlinear adsorption and by employing a more appropriate parameter than the Freundlich constant. The linear distribution coefficient K_d was used by the author to calculate the retardation factor R. Based on the results the author concluded that the actual ratio of adsorbate to adsorbent may be smaller by a factor of about 10 at higher contaminant concentrations, it could be safer and more accurate to make use of the unified sorption variable K_F to calculate R. Since K_F changes constantly with C and using a constantly changing K_F would be complicated, one solution is to select a small number of discrete values of K_F that can be used to approximate and slightly underestimate the actual values of K_F and each of these values can be used to calculate R over the range of contaminant concentrations that they are applicable.

4.2. FEM of the Heavy Metal Advection-Dispersion Transport with Adsorption by Aquifer Formation

Dividing the model area $0 - L$ into M finite elements with $M + 1$ nodes and applying the Galerkin FEM with linear shape functions and central time scheme with time step Δt [26]. The following system of linear equations can be obtained.

Dividing the model area $0 - L$ into M finite elements with $M + 1$ nodes and applying the Galerkin FEM with certain shape functions N. The term $C_m(t)$ is the approximate concentration at node m in time t. All unknown variables that need to be solved for are $C_1, C_2, \ldots, C_{M+1}$. The FEM algorithm results in the following matrix form:

$$\mathbf{K}C + \mathbf{E}\frac{dC}{dt} = \mathbf{F}, \quad (9)$$

in which:

$$\mathbf{K} = \sum_{m=1}^{M+1}\left[\int_{x_0}^{x_L}\left(vN_\ell \frac{dN_m}{dx} + D\frac{dN_\ell}{dx}\frac{dN_m}{dx}\right)dx\right], \quad (10)$$

$$\mathbf{E} = \sum_{m=1}^{M+1}\left[\int_{x_0}^{x_L} RN_\ell N_m dx\right], \quad (11)$$

$$\mathbf{F} = \left[DN_\ell \frac{\partial C}{\partial x}\right]_{x_0}^{x_L}; \quad (1 \le \ell \le M+1). \quad (12)$$

Note that at the global the matrices are **K**, **E**, and **F** (bold letter), and at the element level, the element matrix are K, E, and F (not bold letter).

The time discretization in the above equation dC/dt may also be carried out by finite element procedure [26] and the following results:

$$\left(\theta K + \frac{E}{\Delta t}\right)C^{t+\Delta t} = \left(-(1-\theta)K + \frac{E}{\Delta t}\right)C^t + \frac{1}{2}\left(F^t + F^{t+\Delta t}\right); \quad \mathbf{0} \le \theta \le 1. \quad (13)$$

The FEM code used in this work had been compiled from the work of Nguyen Van Hoang [27].

4.3. Soil Heavy Metal Adsorption Parameters

It is widely known that the adsorption capacities of heavy metals change with pH values [28]. Since the soil and soil water in our study have a more or less neutral condition (the average pH is 6.85), we will deal with the heavy metal adsorption capacity at neutral pH.

The temperature affects the adsorption of heavy metals, e.g., He et al. [29] showed an increase in the adsorption capacities of HMs in the soil material with the increase in temperature. In our work, the isotherm adsorption coefficients are determined for the temperature of 25°C.

Table 2. The Freundlich isotherm parameters' K_F (mg/g)(l/mg)$^{1/\eta}$ and $1/\eta$ values

	Pb		Cd		Ni		Zn	
	K_F	$1/\eta$	K_F	$1/\eta$	K_F	$1/\eta$	K_F	$1/\eta$
Aquifer's clay	20.330	0.362	1.480	0.276	2.935	0.580	9.595	0.267
Aquifer	0.862		0.042		0.083		0.367	

The Freundlich isotherm parameters of the Holocene aquifer under the study are determined based on that of illite from the related studies and the clay content of the Holocene formation of 2.8%. From the experiment results of Ali Sdiriet al. [30], the Freundlich isotherms of the Holocene aquifer formation for Pb and Zn are $K_F = 0.862$ (mg/g) (l/mg)$^{1/\eta}$, $1/\eta = 0.362$ for Pb and $K_F = 0.367$(mg/g) (l/mg)$^{1/\eta}$, $1/\eta = 0.267$ for Zn, from that of the work of Abbou Brahim et al. (2021) [31] $K_F = 0.042$ (mg/g) (l/mg)$^{1/\eta}$, $1/\eta = 0.276$ for Cd, and from that of the work of Echeverrıa et al. (2003) [32] $K_F = 0.083$ (mg/g) (l/mg)$^{1/\eta}$, $1/\eta = 0.580$ for Ni. It is worthwhile to note that in the numerical modeling, the equilibrium concentrations of Cd and Ni in groundwater C_e are corresponding to the adsorption q_e of the illite clay in the Holocene aquifer formation.

The Freundlich isotherms K_F and $1/\eta$ of the Holocene aquifer under this study are determined and given in Table 2.

4.4. Dispersion Parameters

The coefficient of longitudinal hydrodynamic dispersion D_L in the water flow direction which is the coefficient of hydrodynamic dispersion coefficient D in the equation (1) consists of two components: the coefficient of mechanical dispersion D' and the coefficient of molecular diffusion in a porous medium D_d^*, i.e., $D_L = D' + D_d^*$ [20].

The coefficient of mechanical dispersion D' depends upon the microstructure of the soil, the seepage velocity, and molecular dispersion in water which by Jacob and Arnold [20] is as follows:

$$D'_{ij} = a_L v f(\mathrm{Pe},\xi); \quad \mathrm{Pe} = \frac{Lv}{D_d}, \tag{14}$$

in which: v is the seepage velocity (m/d); Pe is the Peclet number; L is the characteristic length of the pores (m); D_d is the molecular dispersion in water; ξ is the ratio between the pores' size and the characteristic length through the pores; $f(\mathrm{Pe}, \xi) = \mathrm{Pe}/(\mathrm{Pe} + 2 + 4\xi^2)$ is a function which is expressing the transport of the heavy metals or solutes via molecular dispersion between the neighboring flow streams at the macro scale, and in most cases $f(\mathrm{Pe}, \xi) \cong 1$; a_L is the longitudinal dispersivity.

For a one-directional groundwater flow, the coefficient of mechanical dispersion D' is the multiplication of longitudinal dispersivity (a_L) and seepage velocity (Jacob and Arnold, 1987). The longitudinal dispersivity is of the order of the average soil particle [20], e.g., particle size d_{50}. However, taking the field-scale dispersion due to the influence of different degrees of aquifer heterogeneity at different sites recommended by Gelhar et al. [33], the practical longitudinal dispersivity for our case may be selected. The obtained longitudinal dispersivities of the tracer tests in porous media presented by Gelhar et al. [33] show that for a 15–20 m field scale, the longitudinal dispersivity is around 1 m. Therefore, the vertical Darcy velocity of the model domain of 0.0135 m/day (paragraph 3.2) and the effective porosity of 0.145 [15] give the seepage velocity equal to 0.093 m/day and the coefficient of mechanical dispersion D' equal to 0.093 m^2/day.

The coefficient of molecular diffusion in a porous medium D_d^* is as follows (Ghislain de Marsily, 1986) [34]:

$$D_d^* = \frac{D_d}{nF_\mathrm{R}}, \tag{15}$$

in which: n is the formation porosity and F_R is the formation factor which is specified by the geophysicists as the ratio between soil resistivity and water resistivity.

The Holocene aquifer porosity is 0.48 [35], and the formation factor F_R is taken to be 0.7 as the aquifer consists of sand [13]. The coefficient of molecular diffusion in water D_d may be found in Henry's book (1994) [36]: Ni—0.61×10^{-5} m^2/day; Zn—0.61×10^{-5} m^2/day; Pb—0.82×10^{-5} m^2/day; Cd—0.62×10^{-5} m^2/day, the coefficients of molecular diffusion in a porous medium D_d^* are: Ni, Zn – 1.82×10^{-5} m^2/day; Pb – 2.44×10^{-5} m^2/day; Cd – 1.85×10^{-5} m^2/day. In our case, the mechanical dispersion is thousands of times greater than the molecular diffusion of the heavy metals in the Holocene porous aquifer.

4.5. Initial and Boundary Conditions

The initial concentrations of the heavy metals of the Holocene aquifer are taken as the minimal value of the analyzed samples and are as follows: Pb—0.0012 mg/L, Cd—0.0006 mg/L, Ni—0.0014 mg/L and Zn—0.0002 mg/L.

Table 3. Heavy metal concentrations of the aquifer formation (q_c) and aquifer water (C_c) in the top boundary

Heavy metals:	Pb	Cd	Ni	Zn
Aquifer formation (mg/g) (q_c)	0.2539	0.01276	0.7772	3.869
Aquifer water (mg/L) (C_c)	0.034	0.014	0.893	8.107
Permissible limits (mg/L) [38]	0.01	0.005	0.02	3.0

The boundary condition of the upper end, i.e., at the bottom of the river sediment and the surface of the Holocene aquifer is assumed to be the Dirichlet boundary with specified concentrations of heavy metals. The concentrations of the heavy metals in the soil on the surface (q_c) of the Holocene aquifer are the maximal concentrations from the analyzed sediment samples, while the concentrations of the heavy metals in the water on the surface (C_c) of the Holocene aquifer are determined by the Freundlich isotherm parameters in Table 2 and the sediment maximal concentrations (Table 3). For the sake of convenience, permissible concentration limits in groundwater by Vietnam technical standards [38] are attached in Table 3.

The boundary condition of the lower end, i.e., at the bottom of the Holocene aquifer and the surface of the Pleistocene aquifer is set to be the Cauchi boundary through which fluxes of advected and dispersed heavy metals are specified, which are determined using the vertical groundwater flow rate, the hydrodynamic dispersion and the concentration gradient. The fluxes of heavy metals at the simulation time step t are calculated through the concentrations of the heavy metals at the previous simulation time step $t-1$.

4.6. The FEM Results

The element sizes and time step need to be selected based on the following criteria via the Peclet and Courant numbers (Huyakorn and Pinder, 1983) [37]:

$$\text{Peclet number: } P_d = \frac{v_x \Delta x}{D_x} \leq 2 \Rightarrow \Delta x \leq \frac{2D_x}{v_x}, \quad (17)$$

$$\text{Courant number: } C_r = \frac{v_x \Delta t}{\Delta x} \leq 1 \Rightarrow \Delta t \leq \frac{2\Delta x}{v_x}. \quad (18)$$

In which: Δx is the element size (m) and Δt is the time step (days).

With the hydrodynamic dispersion coefficient determined based on the above-described values of the coefficient of molecular diffusion, the soil porosity, and the formation factor, the element size needs to be not greater than 2 m. An element size of 0.1 m and a time step of 1 day are used in this modeling for better modeling accuracy.

FEM simulations for heavy metal Pb had been carried out for 30 years while for Cd, Ni, and Zn had been carried out for six years and the model outputs of year-intervals (for Pb with 0.25- and 0.5-years) and quarter-year-intervals (for Cd, Ni, and Zn) are graphically presented.

The heavy metal concentration breakthrough curves are presented in Fig. 6 which can be summarized as follows.

The Pb concentrations in the Holocene aquifer water and aquifer formation slowly increase with time and 0.5 times the concentration of the upper boundary, i.e., $0.5C_c = 0.017$ mg/L and $0.5q_c = 0.127$ mg/g reached the bottom of the Holocene aquifer, i.e., the surface of the Pleistocene aquifer after about 20 years and $0.9\boldsymbol{C_c}$ and $0.9\boldsymbol{q_c}$ reached the surface of the Pleistocene aquifer after about 27 years (Figs. 6.a1 and 6.a2).

The Zn concentrations in the Holocene aquifer water and aquifer formation of $0.5C_c = 4.054$ mg/L and $0.5q_c = 1.935$ mg/g reached the surface of the Pleistocene aquifer after about 2.3 years and $0.9C_c$ and $0.9q_c$ reached the surface of the Pleistocene aquifer after about 4 years (Figs. 6.b1 and 6.b2).

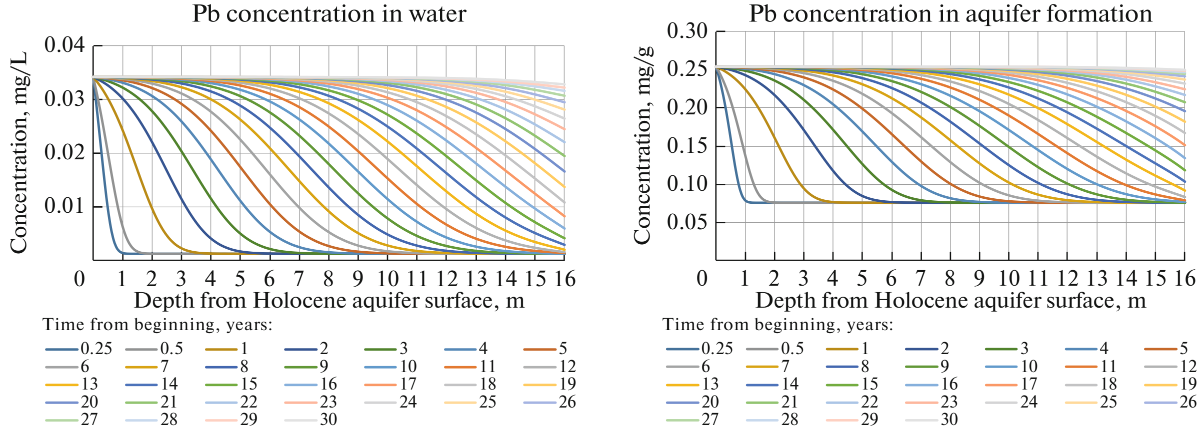
The Cd concentrations in the Holocene aquifer water and aquifer formation of $0.5C_c = 0.007$ mg/L and $0.5q_c = 0.00638$ mg/g reached the surface of the Pleistocene aquifer after about 1.8 years and $0.9C_c$ and $0.9q_c$ reached the surface of the Pleistocene aquifer after about 2.4 years (Figs. 6.c1 and 6.c2).

The Ni concentrations in the Holocene aquifer water and aquifer formation of $0.5C_c = 0.447$ mg/L and $0.5q_c = 0.3886$ mg/g reached the surface of the Pleistocene aquifer after about 1.4 years and $0.9C_c$ and $0.9q_c$ reached the surface of the Pleistocene aquifer after about 1.9 years (Figs. 6.d1 and 6.d2).

Figures 7a–7d present the retardation factors of the advection and dispersion transport in the Holocene aquifer for the four metals, which are highly non-linear and very much varying in time and space as had been described in paragraph 4.1. The greatest retardation factor is for Pb the maximal value of which is more than 66. The maximal values of retardation factors for Zn, Cd, and Zn are about 12, 5, and 6, respectively. The minimal retardation factor value of around 8.7, 2.0, 1.7, and 1.1 for Pb, Zn, Cd, and Ni, respectively, reached after about 28 years (for Pb) and from 4 to 2 years for Zn, Cd, and Ni which means the constant heavy metal transport through the Holocene aquifer into the top of the Pleistocene aquifer.

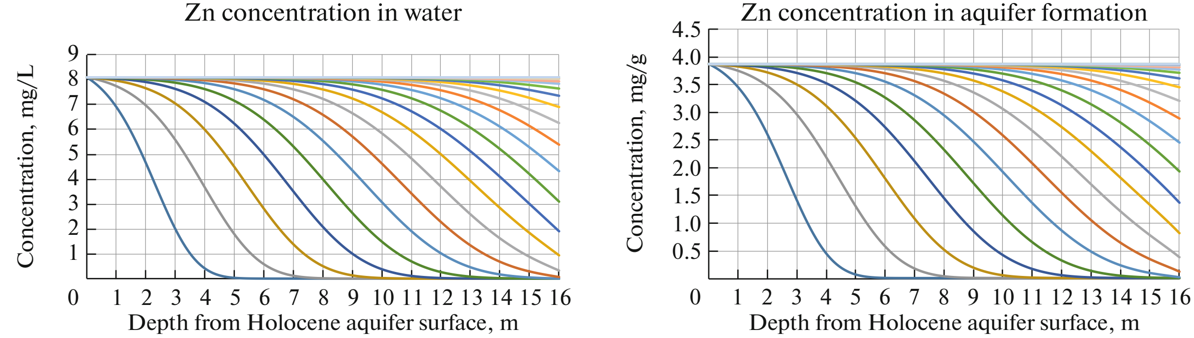
(a1) Lead in water

(a2) Lead in aquifer formation



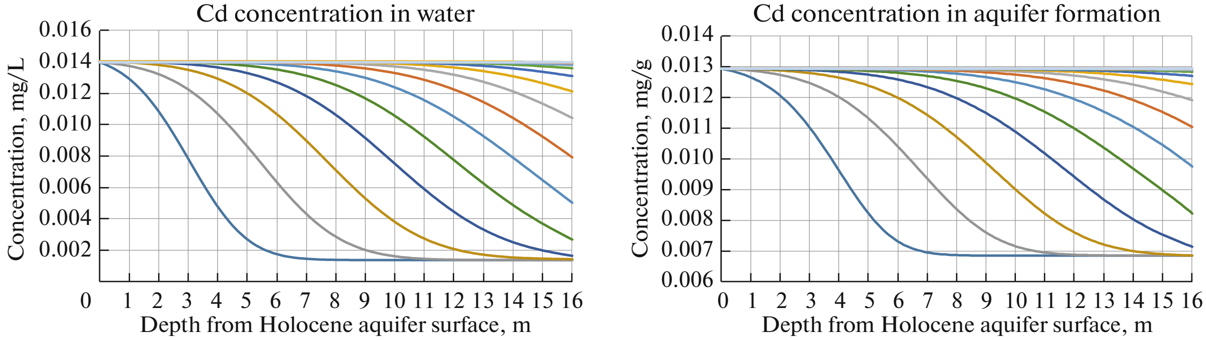
(b1) Zinc in water

(b2) Zinc in aquifer formation



(c1) Cadmium in water

(c2) Cadmium in aquifer formation



(d1) Nickel in soil

(d2) Nickel in aquifer formation

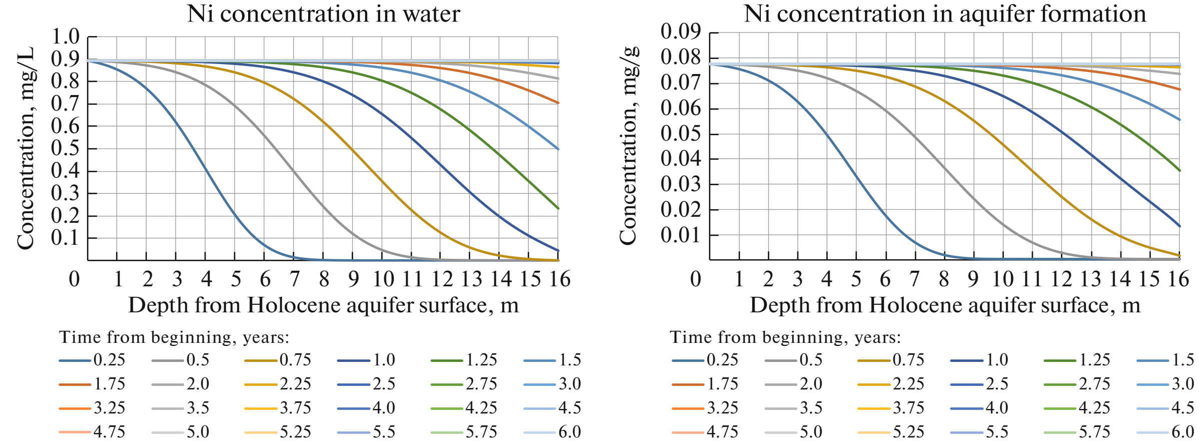
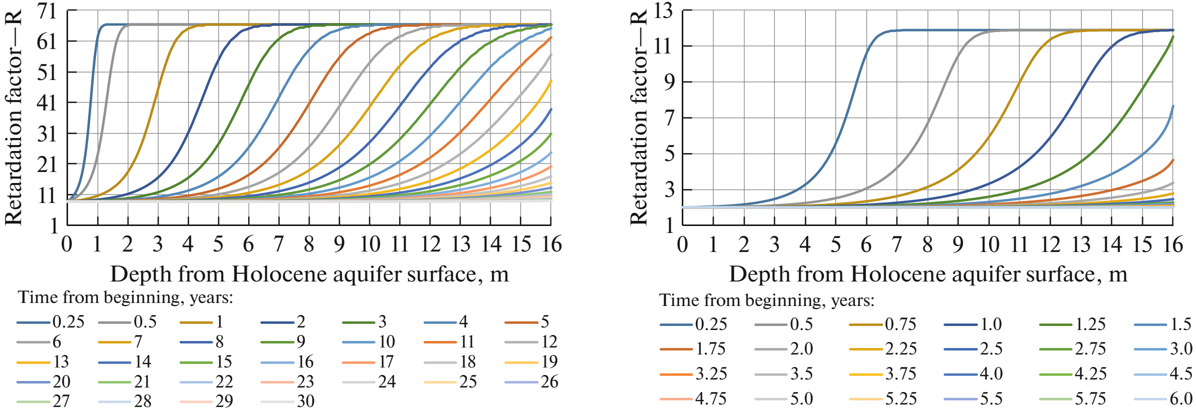
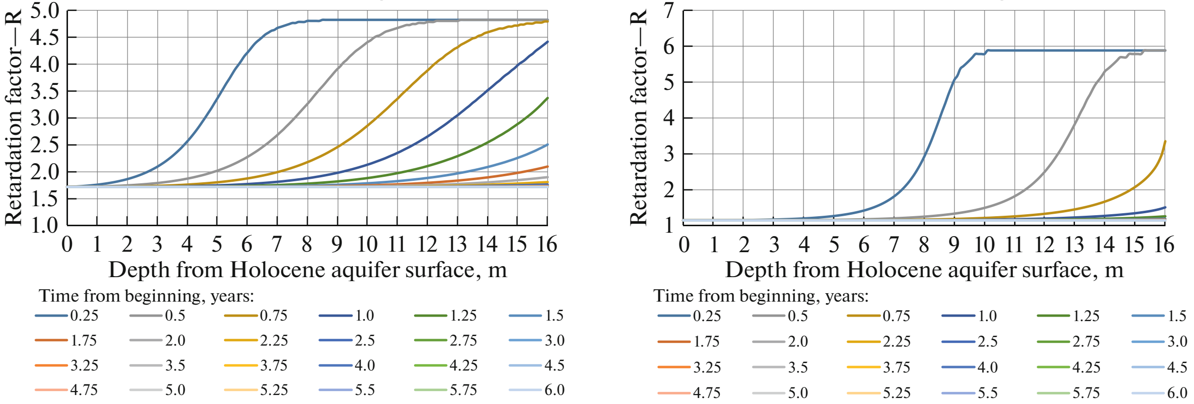


Fig. 6. Heavy metal concentrations by FEM for 6 years.



(a) In regard to Lead
Retardation factor in regard to Pb

(b) In regard to Zinc
Retardation factor in regard to Zn



(c) In regard to Cadmium
Retardation factor in regard to Cd

(d) In regard to Nickel
Retardation factor in regard to Ni

Fig. 7. Retardation factors in regard to modeled heavy metals.

CONCLUDING REMARKS AND RECOMMENDATIONS

Although the traditional craft villages in Vietnam in general and in Bac Ninh province, in particular, have been contributing significantly to economic development, they have been exposing many negative impacts on the environment. The heavy metal-rich wastes from the metal recycling casting craft villages in the field of metal recycling and metal casting are causing severe heavy metal pollution not only to the air, soils, and sediments but also to the groundwater resources. In despite of that in most areas in Bac Ninh province the Holocene aquifer is underlying a thick silty and clay layer and is well protected from contaminated from surface contaminants, but in Da Hoi iron recycling craft village in Chau Khe ward, Tu Son town, the Holocene aquifer is exposed to the Ngu Huyen Khe river into which arbitrary dispose of heavy metal rich wastes takes place, the aquifer is contaminated.

The results of this work's FE modeling of heavy metal transport with Freundlich isotherm parameters which result in high temporal and spatial varying retardation factors provide valuable quantitative heavy metals' distribution in depth and time. Due to the relatively not high concentrations of Ni and Cd, but much higher permissible limits, in the river sediment and low Freundlich adsorption constant K_F, the heavy metal transport in the Holocene aquifer is very fast and the entire aquifer thickness has equilibrium aquifer formation and aquifer water heavy concentrations after around 2–2.5 years, while for heavy metal Zn, the time is around 4 years. Since the heavy metal Pb adsorption capacity of the aquifer formation is significantly high, the equilibrium time is much longer, i.e., around 27 years. The heavy metals' fluxes from the Holocene aquifer to the Pleistocene aquifer are maximal and more or less constant from the equilibrium time and therefore cause server contamination of the Pleistocene aquifer from which there are some water wells are exploiting the aquifer. The heavy metal adsorption capacity of the Pleistocene aquifer would be insignificant because the formation consists mostly of coarse sands and gravels which helps fast contaminant transport. Besides, the Pleistocene aquifer's dispersivity, especially longitudinal dispersivity, is much greater than that of the Holocene aquifer plus much greater seepage velocity thanks to high hydraulic conductivity and a greater horizontal hydraulic gradient, the heavy metal transport within the Pleistocene aquifer would be expected very fast.

From the status of high concentrations of heavy metal in the craft villages' wastes, in the soils and sediments, and the results of the heavy metal transport simulation, some recommendations for supporting the protection and management of the Pleistocene aquifer groundwater quality in the study area are as follows.

— Carry out a system of monitoring of the heavy metals in groundwater in both the Holocene and the Pleistocene aquifers downstream of the Ngu Huyen Khe River's portion of the Chau Khe craft village to have needed contamination prevention actions.

— Carry out HM adsorption experiments for estimation of the Pleistocene aquifer isotherm adsorption parameters for HMs under concern in the HMs' concentrations;

— Carry out field tracer experiments of the Pleistocene aquifer to determine the aquifer dispersivity to support modeling transport of the heavy metals within the Pleistocene aquifer by the temporal fluxes of the heavy metals from the Holocene aquifer. The specific interesting methodology of the tracer experiment with tracer injection well and pumping out well would be that recommended by Nguyen Van Hoang [39].

— Carry out a 2- or 3-dimensional heavy metal transport model for the Pleistocene aquifer to determine the picture of heavy metals contamination in space and time and to identify the contamination risk to the near groundwater abstraction fields in the Pleistocene aquifer downstream of the Ngu Huyen Khe river's portion the Da Hoi (Chau Khe ward, Tu Son town) craft village.

ACKNOWLEDGMENTS

This paper has been completed within the research project DTDLCN.86/21. Using the opportunity, the authors would like to express sincere thanks to the Ministry of Science and Technology of Vietnam for the approval of the research project DTDLCN.86/21.

FUNDING

This work was supported by funding from Ministry of Science and Technology of Vietnam. The paper has been completed also as part of Russian governmental program 124022100078-7.

CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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