Title	RELATIONSHIP BETWEEN GEOCHEMICAL CHARACTERISTICS OF THE LATE PLEISTOCENE-HOLOCENE SEDIMENTS AND GROUND WATER QUALITY IN THE SOUTHERN AREA OF HANOI
Author(s)	Mai, Trong Nhuan; Hoang, The Anh
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RELATIONSHIP BETWEEN GEOCHEMICAL CHARACTERISTICS OF THE LATE PLEISTOCENE – HOLOCENE SEDIMENTS AND GROUND WATER QUALITY IN THE SOUTHERN AREA OF HANOI

Mai Trong Nhuan, Hoang The Anh
Department of Geology, Hanoi College of Science,334 NguyenTrai Rd. Thanh Xuan Dist. Hanoi, Vietnam;

ABSTRACT

The geologic structures, geochemical characteristics of the sediments in the study area are rather strongly differentiated in space and time. Each wellfield area in turn bears a specific feature in hydrogeological structure (with differences in composition, grain size, color and environmental geochemistry of the sediments overlying the Qp aquifer). This to some extent has affected to dynamic geochemical characteristics of the groundwater in the area. The hydrogeological system in the South of Hanoi can be divided into 3 areas: The area of Mai Dich wellfield, characterized by the overlying sediments being very thick weathered clay layers, the environmental parameters exhibiting strong oxidation, the contents of heavy metals such as Fe, Mn being low, the groundwater also showing oxidizing character with high oxidation - reduction potential (ORP), low NH4, low Fe content but with signs of elevated Mn content. On the contrary in the area of Phap Van and Ha Dinh wellfields where there are thick sediments with absolute dominance of the reducing environment, some metals such as Fe are elevated, Mn is of average content, the groundwater also exhibits the reducing character with very high increase in NH4, Fe(II), low ORP. All of these two areas are far from the Red river and are not much influence by the river. In particular in the area of Luong Yen wellfield, where the overlying sediments are characterized by an alternation between the reducing and oxidizing environments, the contents of heavy metals are moderate but the relationship between the sediments and the groundwater is unclear as the groundwater here has a rather close hydraulic and geochemical relationship with the Red river.

INTRODUCTION

Hanoi is a large economical, cultural and social center with highly concentrated and ever increasing population, which entails a considerable increase in the water demand for domestic consumption and for production, especially in the last decade.

With the geological characteristics of a delta, which bears many features similar to those of the Ginga river delta in West Belgan - India or in Bangladesh, where the people are facing serious problems related with the degradation of the groundwater quality due mainly to the process of leaching and solution of toxic elements from the sediments, similar phenomena in Hanoi are fully possible.

In recent years, many research results show that in Hanoi area (especially in the Southern area of the city on the right side of the Red river) there are indications of elevated contents of some toxic components in the groundwater such as Fe, Mn, NH_4, As... However most of these studies have been limited to the evaluation of the present status, not yet intended for explaining and looking for the causes and origins of the phenomena.

On the basis of analysis and processing of the analysis data of sediment samples from the areas of 4 large wellfields of Phap Van, Ha Dinh, Mai Dich and Luong Yen (Fig.), this paper refers to the relationship between geochemical characteristics of the sediments and the groundwater in the Southern area of Hanoi, as a contribution to the clarification of the mechanism, the development process and the origin of the above problems.

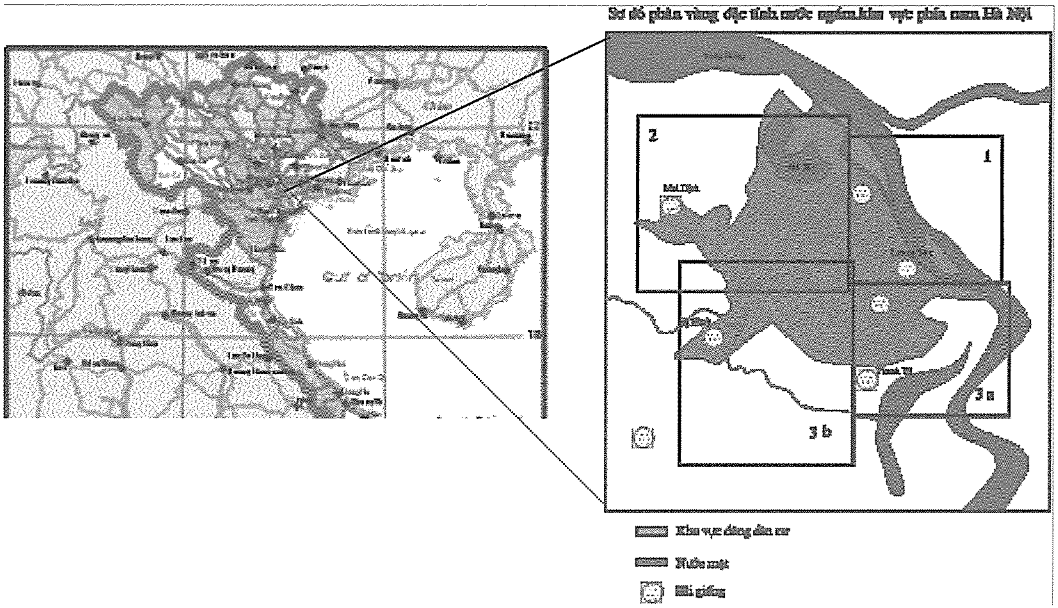

Figure 1: Schematic groundwater zoning map of the study area

MATERIAL AND METHOD

Field surveys and drilling for sampling of sediments have been carried out in the areas of 4 wellfields (Fig 1). The boreholes were designed with the depth of 40 - 50 m, where occurs the top of the cobble and gravel layer of Hanoi formation (Q_1^{2-3} *hn*) composing the main aquifer. The sediment samples collected represent sediment sequences with different compositions, structures and colors, were preserved and analyzed for various indicators (Table 1).

Besides analytical results, geological and hydrogeological data of Hanoi area have been also used, in particular the data on composition of sediments of confining layers and aquifers Qh and Qp, groundwater geochemical data of the study area, especially those concentrated in 4 wellfields of Phap Van, Ha Dinh, Mai Dich, Luong Yen.

The analytical results and the data have been processed as follows:

- Establishment of some geochemical parameters such as K2(=Fe(S)/dissolveFeII), K3(=dissolveFe(S)/FeIII), K4 (=dissolve FeII/dissolveFeIII).
- Determination of basic statistical parameters such as mean, minimum, maximum values, S (dispersion coefficient, V (variation coefficient), correlation matrix, establishment of curves showing the variation of parameters in space and time.
- Application of rapid evaluation methods for evaluating the rate of chemical weathering and the denudation rate of weathered crust in the humid tropical region (Mai Trong Nhuan, 2000), for determining the contribution and impacts of the sediment geochemistry on the groundwater geochemical characteristics, the balance of between the solid phase (sediments) and the liquid phase (groundwater), thereby to establish the weighted content coefficient (WCC) by the following formula:

$$WCC = \Sigma \, Mi.Li/Lt \quad (1)$$

Where Mi - average value of any indicator (K4, TOC, heavy metal contents) characterizing relatively homogeneous sediment layer; Li - the thickness of that sediment layer; Lt - total thickness of sediment layers. These parameters are used for considering the spatial variation of the sediment characteristics and serve as the basis for comparing them with those of the groundwater.

Table 1: Analytical indicators and number of samples analyzed

Analytical parameter	Analytical Method	Amount of sample	Analytical Equipment
Grain size	Laser diffraction	34	Master Sizer
Mineral	XRD	34	Brucker X-Ray diffractometer
Sporoplasm - pollen	Microscope	49	Microscope
Fe dissolve	Red-ox titration	53	Standard titration equipment
Sulphur	Iodine-thiosunphate titration	30	Standard titration equipment
Heavy metal	AAS	55	AAS-Mark II, Nippon Jarell AAS

RESULT AND DISCUSSION

Sediment characteristics

Based on the analytical results of grainsize distribution, mineral, sporoplasm-pollen composition, and environmental indicators (Table 2), with correlation with the stratigraphic sections of previous studies, we have developed the comprehensive structural sections for 4 boreholes in the study area (Figure 2**Figure 2**).

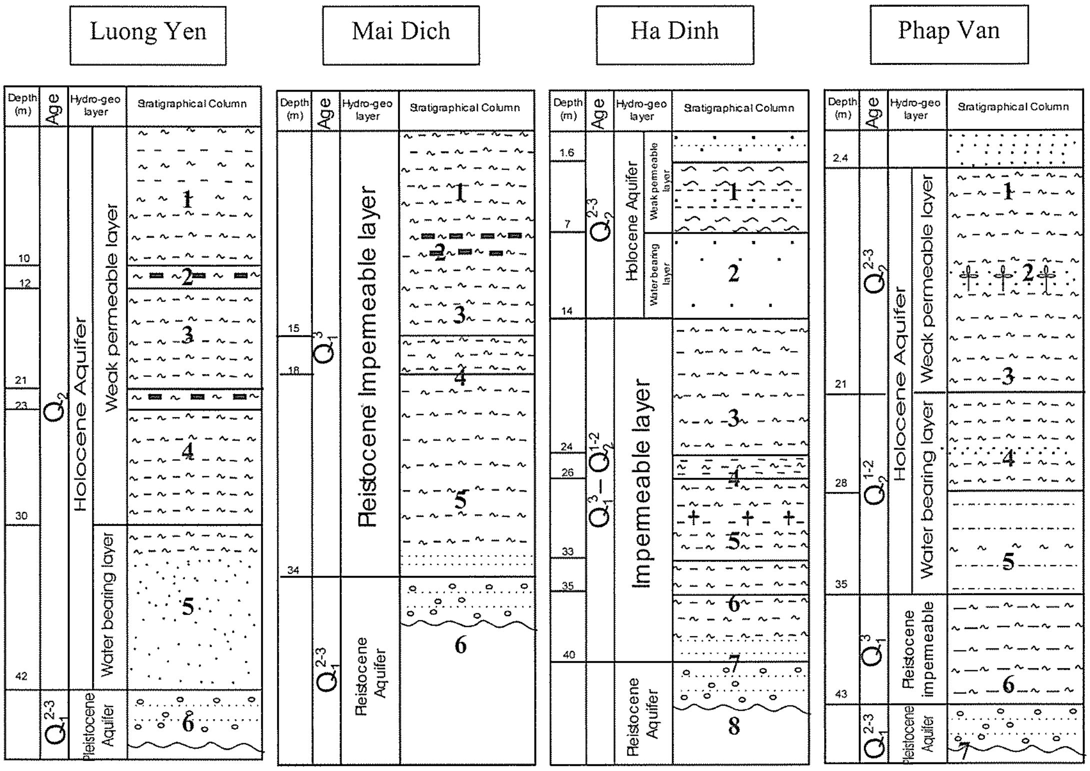

Figure 2: The comprehensive structural sections of the 4 boreholes in Luong Yen, Mai Dich, Ha Dinh and Phap Van area

Luong Yen borehole: silty clay of black grey color and silt clay of light brown color; 2- Claycy silt and black bearing peat; 3-Claycy silt of green grey color, bearing sand with organic thin layer and claycy silt of brown grey; 4-Claycy silt of black grey color in the upper and claycy silt of red brown and brow grey color in the lower; 5-Claycy silt of brown grey color (in the upper) and sandy silt of grey color in the lower; 6- the lowest part of well are cobbles, gravels and coarse sand.

Table 2: Grainsize, mineralogical composition, heavy metal and organic matter contents in sediment of boreholes in the southern area of Hanoi

Depth (m)	TOC (%)	% grain size			mineral(%)					Heavy metal (ppm)					
		sand	silt	clay	Q	ilit	clor	kal	anb	Zn	Pb	Co	Ni	Mn	Cu
Phap Van Well field															
2.45-2.50	1.563121	2.77	55.26	41.97	28	28	18	15	4	128	97	39	59	653	129
9.2-10	8.107032	10.8	68.12	21.08	34	26	15	15	6	118	25	29	52	133	78
20.7-20.75	3.073254	2.84	59.99	37.16	34	27	15	13	6	133	56	36	60	462	90
23.6-23.8	1.192211	4.58	61.34	34.09	43	22	15	8	7	95	56	32	49	388	63
23.95-24	0.688833	8.73	60.99	30.29	51	8	7	4	31	68	56	20	31	441	28
27.4-27.5	2.463902	4.52	64.11	31.36	39	31	7	15	6	95	56	29	46	887	47
31.4-31.5	-	13.36	62.48	24.16	52	2	42	2	2	-	-	-	-	-	-
37.2-37.4	0.355014	1.76	60.15	38.08	38	30	13	10	8	95	45	29	51	536	59
Ha Dinh Wellfield															
2-2.4	0.768314	0	43.2	56.8	49	18	9	13	6	128	87	41	66	249	98
4-4.5	0.609352	0.26	50.3	49.44	60	13	8	10	6	103	66	32	44	388	55
6.8-7	0.768314	0	43	57	45	20	15	12	4	120	66	39	60	207	78
14-14.5	3.073254	4.1	65.9	30	38	22	19	14	5	90	45	25	44	653	40
23.5-23.6	2.808318	3.14	61.63	35.23	26	30	21	14	5	123	45	36	56	728	78
23.6-23.7	6.278976	3.71	58.22	38.07	32	23	18	14	7	125	87	38	55	685	82
23.8-23.85	1.775069	5.22	64.5	30.27	68	13	10	5	3	95	66	27	41	441	36
27.6-27.85	1.642601	0	54.18	45.82	26	26	24	15	4	133	87	39	60	164	71
32.55-32.65	3.788581	1.23	43.65	55.11	20	28	25	16	4	130	97	39	63	249	71
32.8-33	1.997615	2.97	62.2	34.83	48	14	11	6	21	125	66	39	56	1025	59
39-40	3.550138	1.45	53.72	44.83	73	6	10	5	5	143	138	39	63	101	55
Mai Dich Well field															
3.35-3.4	0.241041	0.42	60.91	38.66	29	21	30	10	4	128	76	39	60	674	71
7.7-7.8	0.63805	3.69	70.33	25.99	18	27	28	15	2	128	66	35	56	164	90
15-15.4	0.25522	0	48.45	51.55	38	27	21	0	5	75	45	16	56	526	59
16.15-16.4	0.226862	0.38	52.16	47.46	32	27	21	10	3	100	66	33	55	356	75
20.4-20.45	0.538797	3.15	59.78	37.07	29	24	28	13	2	93	45	29	48	504	71
Luong Yen Well field															
3.25-3.4	0.831898	0.12	43.29	56.6	31	31	16	15	4	130	76	41	60	643	63
7.9-8.1	0.646443	0.19	57.37	42.43	33	28	19	13	3	105	87	45	52	866	55
9.7-9.8	2.077096	0.72	59.57	39.71	33	26	22	15	5	128	56	35	60	175	55
12.8-12.9	3.59	9.06	68.04	22.9	38	25	17	14	6	115	66	35	56	122	59
19.65-19.8	2.898397	1.24	62.69	36.06	37	27	18	13	5	-	-	-	-	-	-
23-23.05	-	5.53	56.94	37.73	56	19	13	8	4	118	97	36	53	409	47
23.25-23.3	1.865147	4.45	53.73	45.97	53	23	11	11	0	103	107	33	49	345	59
26.15-26.3	0.672937	4.5	59.3	40.38	43	28	13	13	3	83	76	33	45	1354	51
29.85-30	0.381507	2.47	60.47	37.06	79	8	7	3	3	90	66	22	45	717	36
34.9-35	-	24.11	55.72	20.17	90	5	0	0	5	-	-	-	-	-	-

Note: Q - quartz, ilit - illite, clor - clorite; kal - kaolinite; anb - anbite

Mai Dich borehole: 1- Claycy silt consolidated, weathered with various color in the upper, Under is there ductile claycy silt of black color; 2-claycy silt of black color bearing peat; 3-

Claycy silt of various color (brown, green grey, dark brown); 4-Silty clay of various color and claycy silt of brown color; 5- Claycy silt of black color interbeds with clay of green grey in the upper and silty clay and ductile and black color in the lower. 0n the depth of 34 m apperances sand; 6-cobbles, gravels and coarse sand.

Ha Dinh borehole: 1- silty clay of light brown color with thin sand layer in the middle; 2- black grey sand increasing grain size on the depth; 3-Claycy silt of black color; 4-Silt of green grey color interbeded with silty clay of black grey color; 5-Black grey claycy silt with plant remains; 6- Dark brown claycy silt and silty clay with leave; 7-Brown grey claycy silt in the upper, fine and coarse sand in the lower; 8-Cobbles, gravels and coarse sand.

Phap Van borehole: 1-Claycy silt of red brown, color on the depth of 5m there is claycy silt of green grey color; 2- percent of sand grain increases on the depth of 10 m, and the sediment is rich in plant remain; 3-In the lower there is mainly claycy silt of black grey, black brown and green grey color; 4- Claycy silt of dark brown color interbeds with thin sand layer of black color; 5-Silt sandy and claycy of black grey color, rich in organic matter; 6-Claycy silt of various color (brown, green grey, greenish yellow..); 7- Cobbles, gravels, coarse sands.

Table 3: Average grain size and mineral composition of sediment layers with different times of formation

Age	N°	Sediment	Grain size (%)			Mineral (%)				
			sand	silt	clay	Q	ilit	clorit	kaolinit	fenspat
Q_2^{2-3}	9	silty clay	0.56	48.74	50.71	41.00	23.00	14.17	13.00	4.50
	8	claycy silt	2.04	61.34	36.61	35.50	27.00	16.50	13.00	5.50
	7	coarse sand								
Q_2^{1-2}	6	claycy silt containing sand	4.63	60.65	35.50	48.00	20.64	12.82	9.91	6.73
	5	claycy silt	1.40	53.34	45.25	31.33	22.67	20.00	12.33	9.67
	4	silty sand	18.74	59.10	22.17	71.00	3.50	21.00	1.00	3.50
Q_1^3	3	claycy silt	0.80	55.08	44.12	42.00	22.20	19.00	7.00	5.00
	2	claycy silt containing sand	3.15	59.78	37.07	29.00	24.00	28.00	13.00	2.00
Q_1^{2-3}	1	cobbles, coarse gravel								

The sediments here are characterized by a complicated differentiation in space and in time of formation (Table 3). In the same sediment layer at different borehole locations the thickness and the red-ox characteristics of the depositional environment are different. Typically in the boreholes drilled in the areas of Phap Van and Ha Dinh wellfields, the sediments are composed of layers of silt and clay, sandy silt and clay formed in strongly reducing environment (the indicators K4, TOC are very high) but in the borehole drilled in the area of Mai Dich wellfield the sediments are characterized by the predominance of motley weathered silt and clay formed in an oxidizing environment. The same layer of weathered silt and clay aged Q_1^{2-3} in the borehole drilled in Mai Dich wellfield has very large thickness, with environmental indicators showing oxidizing characteristics much stronger than in the borehole drilled in Phap Van wellfield (Figure 4).

Table 4: Correlation matrix of sediment parameters

	sand	*silt*	*clay*	*Q*	*ilit*	*clorit*	*kaolinit*	*anbit*	*Zn*	*Pb*	*Co*	*Ni*	*Mn*	*Cu*	*K2*	*K3*	*K4*	*%TOC*
sand	1.00																	
silt	0.37	1.00																
clay	**-0.73**	**-0.89**	1.00															
Q	**0.47**	-0.05	-0.18	1.00														
ilit	**-0.48**	-0.02	0.26	-0.81	1.00													
clorit	-0.18	0.12	-0.01	**-0.63**	0.22	1.00												
kaolinit	**-0.42**	0.01	0.20	**-0.75**	**0.76**	0.23	1.00											
anbit	0.13	0.13	-0.18	0.09	-0.28	-0.33	-0.26	1.00										
Zn	-0.26	-0.18	0.19	**-0.46**	0.30	0.37	**0.60**	-0.25	1.00									
Pb	-0.29	**-0.45**	**0.47**	0.05	-0.04	0.00	0.16	-0.22	0.36	1.00								
Co	-0.34	-0.28	0.32	**-0.42**	0.33	0.27	**0.63**	-0.23	**0.81**	**0.56**	1.00							
Ni	**-0.50**	**-0.43**	**0.46**	**-0.54**	**0.48**	**0.49**	**0.44**	-0.37	**0.82**	0.30	**0.68**	1.00						
Mn	-0.08	0.13	-0.04	0.12	0.05	-0.21	-0.14	0.12	-0.30	0.04	-0.01	-0.28	1.00					
Cu	-0.24	-0.23	0.23	**-0.56**	**0.43**	0.39	**0.50**	-0.28	**0.64**	0.21	**0.53**	**0.69**	-0.21	1.00				
K2	**0.51**	0.35	**-0.44**	-0.10	0.13	-0.03	0.20	0.00	0.10	-0.27	-0.05	0.06	-0.36	0.07	1.00			
K3	**0.52**	0.34	-0.44	-0.09	0.11	-0.05	0.21	0.01	0.10	-0.39	-0.08	0.01	-0.33	0.09	**0.89**	1.00		
K4	**0.52**	**0.47**	**-0.53**	-0.16	0.15	-0.10	0.30	0.13	0.12	-0.34	-0.06	-0.12	-0.09	0.01	**0.55**	**0.69**	1.00	
%TOC	0.34	0.27	-0.33	-0.15	0.15	-0.11	0.38	0.02	0.32	-0.17	0.08	0.10	-0.18	0.17	**0.55**	**0.66**	**0.90**	1.00

Except Fe, Mn, trace metal elements such as Cu, Pb, Zn, Co (which are closely related with each other) do not show any correlation with the red-ox characteristics of the sedimentary environment (Table 4). The Fe (III), Mn contents in the sediments in oxidation environment are usually high. On the contrary Fe (II) is only elevated in the reducing sediments. Besides, most of trace metals tend to be accumulated in (directly correlated with) clay-rich sediments (potential confining layers), while major metals such as Fe, Mn tend to increase in silt sediments (potential aquitards). This is a rather important characteristic which will be much related with the possibility of dissolution and leaching of these elements from the sediments into the groundwater. The weighted contents calculated for K4 and TOC. The sediment characteristics and composition show a rather clear spatial variation of the red-ox degrees of the depositional environment with the tendency of decreasing the reducing characteristics from Phap Van through Ha Dinh to Luong Yen and Mai Dich (Figure 3).

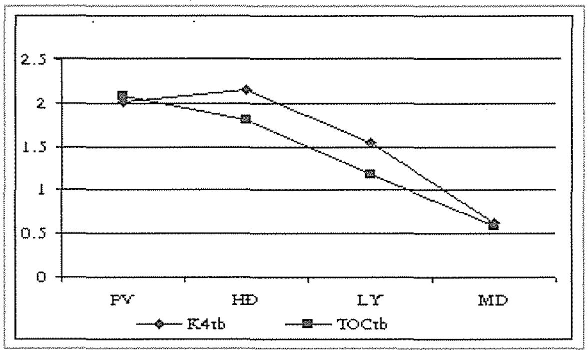

Figure 3: Spatial variation of weighted contents coefficient of K4 and TOC in 4 boreholes

Hydrogeological characteristics

The strong differentiation in space and time of sediments layers aged Late Pleistocene - Holocene has created distinct features in the hydrogeological structure system in each wellfield area (For the designation of sediments layers see Note)*Note: Q - quartz, ilit - illite, clor - clorite; kal - kaolinite; anb - anbite*

Mai Dich borehole: 1- Claycy silt consolidated, weathered with various color in the upper, Under is there ductile claycy silt of black color; 2-claycy silt of black color bearing peat; 3-Claycy silt of various color (brown, green grey, dark brown); 4-Silty clay of various color and claycy silt of brown color; 5- Claycy silt of black color interbeds with clay of green grey in the upper and silty clay and ductile and black color in the lower. 0n the depth of 34 m apperances sand; 6-cobbles, gravels and coarse sand.

Ha Dinh borehole: 1- silty clay of light brown color with thin sand layer in the middle; 2- black grey sand increasing grain size on the depth; 3-Claycy silt of black color; 4-Silt of green grey color interbeded with silty clay of black grey color; 5-Black grey claycy silt with plant remains; 6- Dark brown claycy silt and silty clay with leave; 7-Brown grey claycy silt in the upper, fine and coarse sand in the lower; 8-Cobbles, gravels and coarse sand.

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Table 3In the Luong Yen wellfield area, the Holocene confining layer is about 29 m thick (from 2m to 31m), composed mainly of black clay, silty clay containing much organic matter, is a good potential confining layer. Besides, in this confining layer there are also peat layers 2 m thick, showing that here the reducing environment was predominant. Down below is the Holocene aquifer composed of black gray, fine to medium grained sand with a thickness of about 12 m, with high permeability. At the depth of 42 m, this layer passes directly into the cobble and gravel layer of the main aquifer (Qp).

In the area of Phap Van wellfield the Holocene-confining layer is about 14m thick (at the depth 2 - 16m), composed mainly of clayey silt, in some places containing sand. Although it is of good confining characteristics, in some places it is absent, forming potential hydraulic windows. The Holocene weak aquifer is about 14m thick (at the depth 21-35m), its grain size increases with depth, composed mainly of clayey silt mixed with sand passing into sand, with potentially high permeability. The Pleistocene confining layer is 8m thick (with depth 35-43m), composed mainly of altered and weathered clay and clayey silt, with good confining characteristics. At the depth of about 40m occurs the main Pleistocene aquifer, composed mainly of the cobbles, gravel and coarse sand.

In the area of Ha Dinh wellfield, the Middle-Upper Holocene confining layer is about 5.4m thick, composed mainly of clay, clayey silt (with particle size >50μm accounting for about 0-1%), with good confining characteristics. Down below is the Middle - Upper Holocene aquifer which is 7m thick (with depth 7 - 14m), composed mainly of black gray sand, with grain size increasing with the depth, with high permeability. The Upper Pleistocene- Lower Holocene confining layer is composed mainly of clayey silt, clayey silt mixed with sand (with particle size >50μm accounting for about 4-5%), with low permeability. The Lower - Middle Pleistocene aquifer is met at the depth of about 40m, composed of cobbles, gravel, sand...

In the area of Mai Dich wellfield, the confining layer consisting of sequences 2 and 3, is about 32m thick (at the depth 2-34m), composed mainly of silty clay, clayey silt, in some places containing sand, having been altered and weathered, with particle size > 50μm accounting for 3-4%, with good confining characteristics. The Lower - Middle Pleistocene aquifer is met in the borehole at the depth of about 34 m, composed mainly of cobble, gravel, sand. The hydrogeological system in this area is rather simple, consisting of a very thick confining layer overlying directly the aquifer. Besides, this area is far from the river, therefore the groundwater here has the least hydraulic relationship with the surface water.

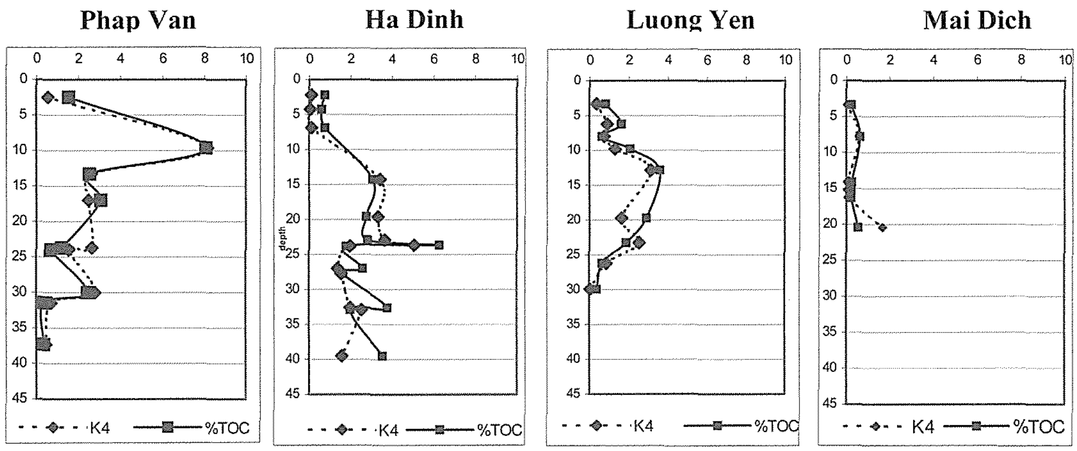

Figure 4: Variation of the coefficient K4 and TOC values in the sediments with depth

Geochemical characteristics of the groundwater

For the groundwater in the Southern area of Hanoi, the biggest problem at present is the high content of NH_4, Fe, Mn, As (Table 5). Their behavior depends much on the red-ox characteristics of the groundwater. The contents of other trace metals in general have not exceeded the permissible limit of the Environment Standards of Vietnam.

The results of previous studies, especially those of the most recent research by Tran Thi Viet Nga (2002) show that according to the geochemical characteristics, the Southern area of Hanoi can be divided into 3 areas with distinct characteristics, especially the difference in groundwater quality.

Table 5: Contents of heavy metals (ppm) and NH4 in the groundwater at 4 main wellfields (HLTB: average content, Ttc: Contamination coefficient)

Wellfield	Index	Cd	Cu	Fe	Mn	Ni	Hg	Pb	As	Co	NH_4(mg/l)
Luong Yen	HLTB	2.25	13.07	2149	366	5.77	0.67	28.34	60.37	0.52	0.71
	Ttc	*0.25*	*0.13*	*2.15*	*0.73*	*0.06*	*0.67*	*0.57*	*1.21*	*0.10*	*1.42*
Ha Dinh	HLTB	1.96	8.79	8329	128	7.15	1.43	28.85	263.87	0.54	9
	Ttc	*0.20*	*0.09*	*8.33*	*0.26*	*0.07*	*1.43*	*0.58*	*5.28*	*0.11*	*18*
Phap Van	HLTB	1.57	5.49	4496	112	5.29	1.21	43.35	342.17	0.99	16
	Ttc	*0.16*	*0.05*	*4.5*	*0.22*	*0.05*	*1.21*	*0.87*	*6.84*	*0.20*	*32*
Mai Dich	HLTB	1.62	4.66	300	951	5.40	0.86	28.81	36.25	0.18	0.07
	Ttc	*0.16*	*0.05*	*0.3*	*1.90*	*0.05*	*0.86*	*0.58*	*0.73*	*0.04*	*0.14*
Vietnam standard 1995	*(µ/l)*	10.00	100	1000	500	100	1.00	50.00	50.00	5.00	0.5

Area I: Luong Yen - Yen Phu (located near the river): The contents of the main ions are similar to those of the river water samples: The contents of NH_4, Fe^{2+}, COD are low, that of Mn is at average level, but the ORP index measured is very low (-162,4), showing that there are many agents originating from the river that affect the geochemical characteristics of the groundwater here.

Area 2: Mai Dich (located farthest from the river): The elements characterizing the reducing environment such as NH_4, Fe (II) are of very low contents, in the mean time the DO, Mn, ORP index values are very high. Besides, the occurrence of NO_2, shows the high oxidizing characteristics of the groundwater.

Area 3: Phap Van, Ha Dinh: The groundwater environment is of strong reducing characteristics, especially with high accumulation of NH_4, Fe(II), COD. In more detail this area may be divided into 2 sub-areas: 3a (Ha Dinh) and 3b (Phap Van), where the groundwater in the Phap Van sub-area is of slightly higher reducing characteristics in comparison with the Ha Dinh sub-area in the shallow aquifer (Qh) and lower in the deep aquifer (Qp).

Especially in the areas where groundwater is rich in NH_4 (such as in Phap Van, Ha Dinh) the SO_4^{2-} content is usually very low. This proves that the groundwater here is of strong reducing characteristics and the sulfate reducing process has occurred. More over, the heavy metals in the groundwater in the study area are usually closely related with the contents of NH_4-N, and the variation in the content of this component can be considered as that of the red-ox characteristics of the groundwater.

Geochemical relationship between the sediments and the groundwater

The geochemical relationship between the sediments and the groundwater is expressed in the red-ox characteristics and heavy metal contents.

The red-ox characteristics of the sediments are rather closely related with those of the groundwater. The comparison of the weighted content of the K4 and TOC values in the sediments with the NH_4, ORP contents in the groundwater shows that the relationship between them is rather close (Figure 5).

In Phap Van and Ha Dinh wellfields, where the sediment layer overlying the Qp aquifer is composed mainly of clayey silt formed in the reducing environment rich in organic matter (high K4 coefficient and TOC content), the groundwater also demonstrate also a reducing environment with very low ORP and high NH_4 content. In the mean time, in Luong Yen, where the overlying confining layer is composed of complicated intercalation of silty clay sequences rich in organic matter and motley weathered clay sequences, the reducing characteristics of the groundwater seems to decrease but this is not quite clear. This may be explained by the possible hydraulic relationship between the groundwater here and the Red river. Especially, as shown by analyses, while the confining layer in the Mai Dich wellfield consisting of a single thick weathered clay layer has very low K4 and TOC values, the groundwater here also shows a very clear oxidizing characteristics with high ORP (> 0), very low NH_4 and apparition of NO_2.

A rather close geochemical relationship between the sediments and the groundwater in the shallow aquifer (20m) is expressed rather clearly in 2 wellfields Phap Van and Ha Dinh (which have similar hydrogeological structure). The sediments within the upper 20 m in the Phap Van borehole has more strong reducing characteristics tan that of Ha Dinh borehole. When passing from the Qh aquifer to Qp aquifer, the Fe(II) content in the groundwater in both Phap Van and Ha Dinh increases, however the increase in Ha Dinh is higher than in Phap Van. This may be explained by the presence of a 8 m thick weathered clay layer in Phap Van which diminishes the reducing characteristics of the whole sediment column.

In particular for the Luong Yen borehole, besides the reducing sediments, there are also 2 peat layers with thickness of 2 m, creating a high reducing potential. But the reducing characteristics of the groundwater here is not high respectively due to the strong influence of the Red river water.

The above-mentioned red-ox characteristics of the sediments and the groundwater affect the distribution and behavior of the metals, especially those with changing valence.

The fine sediments (rich in silt, clay) are characterized by high metal contents. The ratio between the contents of elements in the sediments and the same in the related groundwater varies within the range of 0.1-0.97, mostly >0,6 (Table 6). Figure 6 also shows a similar variation of the metal contents in the sediments and the related groundwater. Thus the contents of elements in the sediments and the related groundwater are closely related. This to some extent proves the sedimentary origin of the elements in the groundwater.

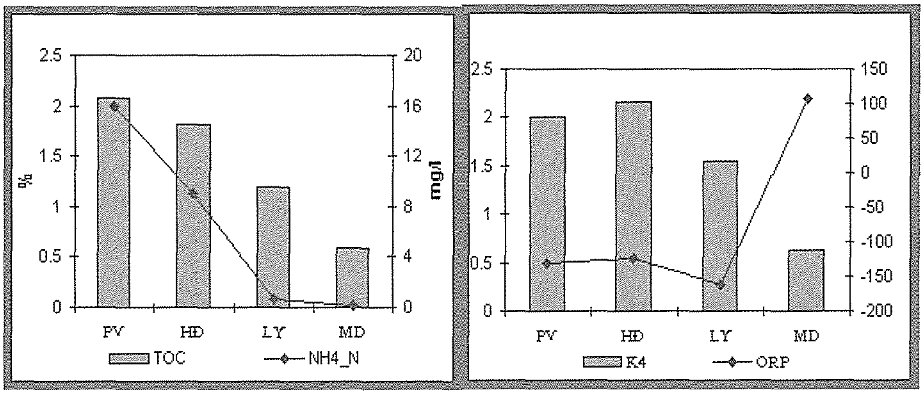

Figure 5: Relationship between the WCC of K4 and TOC in the sediments and the NH4, ORP in the groundwater in 4 boreholes

Table 6: Correlation matrix between the content of heavy metals in the groundwater and their weighted contents coefficient of heavy metals in the sediments

	Fe(III)	Fe(II)	Fe(total)	Cr	Co	Ni	Pb	Cu	Mn	As
Fe(II)tt	**0.60**	**0.65**	**0.62**	**0.50**	**-0.84**	-0.24	0.11	-0.34	**-0.97**	**0.75**
Fe(III)tt	**-0.82**	**-0.88**	**-0.84**	-0.44	**0.55**	-0.19	-0.25	0.01	**0.87**	**-0.93**
Zntt	0.19	0.24	0.20	**-0.54**	**0.78**	**0.82**	-0.10	0.46	0.42	0.14
Pbtt	-0.12	0.00	-0.09	**-0.52**	-0.19	-0.29	**-0.77**	**-0.72**	-0.26	0.08
Cott	-0.24	-0.15	-0.22	**-0.88**	**0.68**	0.37	**-0.63**	-0.09	0.48	-0.19
Nitt	-0.39	-0.38	0.39	**-0.72**	1.00	**0.54**	-0.24	0.38	**0.91**	**-0.49**
Mntt	**-0.65**	**-0.74**	**-0.67**	0.08	-0.02	**-0.54**	0.01	-0.13	0.41	**-0.73**

Note: Mtt-content of metal in sediment

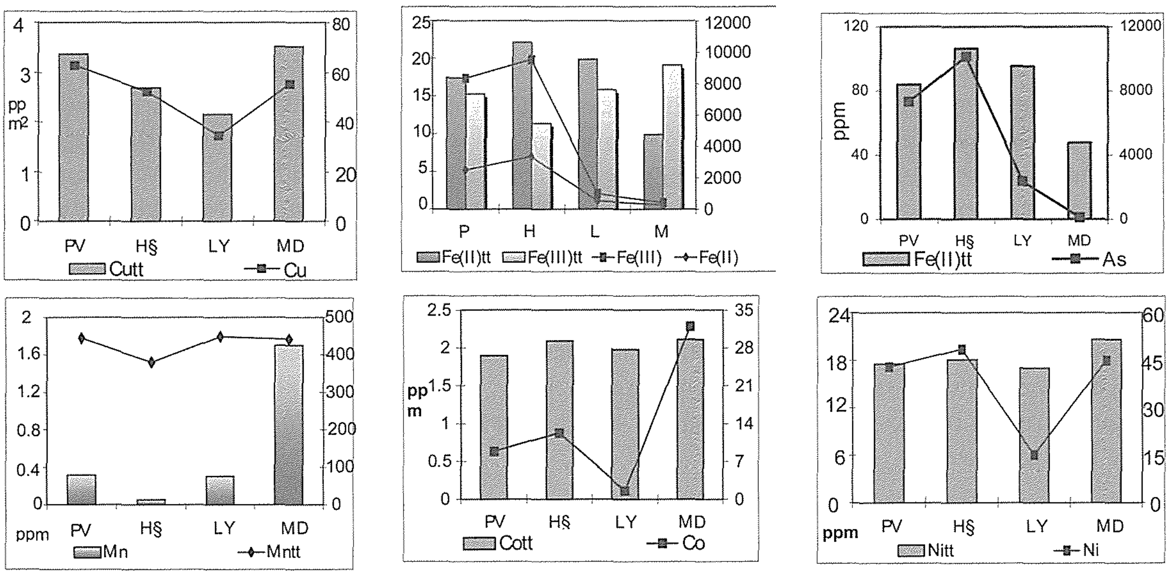

Figure 6: Variation of weighted content coefficient of heavy metals in the sediments and their average contents in the related groundwater of the 4 boreholes areas

The fine sediments (rich in silt, clay) are characterized by high metal contents. The ratio between the contents of elements in the sediments and the same in the related groundwater varies within the range of 0.1-0.97, mostly >0,6 (Table 6). Figure 6 also shows a similar variation of the metal contents in the sediments and the related groundwater. Thus the contents of elements in the sediments and the related groundwater are closely related. This to some extent proves the sedimentary origin of the elements in the groundwater.

Reduction theory equation

$$FeOOH + CH_2O + H_2CO_3 \xrightarrow[\text{Organic matter}]{\text{Bacteria}} 4Fe^{2+} + 6HCO_3^- + 6H_2O$$

The relatively close relationship between the sediments and the related groundwater is also clearly expressed in the variation of contents of metals such as Fe, Mn whose behavior depends much on the red-ox regime. In the case of the overlying sediments formed in the reducing environment with high Fe(II) content, the total Fe content in the groundwater is also high (Phap Van, Ha Dinh). Whereas, where the overlying sediments were formed in the oxidizing environment with high Fe(III) content and poor in organic matter, the groundwater has high Mn content.

In particular for As, which is a very toxic element and has the indication of being elevated in some countries (and is usually met in the Qp aquifer more than in the Qh aquifer), occurs mainly in the inorganic form (Tran Thi Viet Nga et al., 2001). The previous analytical results of sediment samples from the boreholes also show that between As and Fe(II) in the sediments there is also a close correlation. The high content of As is explained by the "Reduction theory " (Pham Hung Viet and et al., 2001).

As shown by the subsequent analyses of Tran Thi Viet Nga, while As is of high content and much concentrated in the area of Phap Van, Ha Dinh wellfields, the Fe(II), HCO_3^- contents in the groundwater there are also elevated. This and especially the high NH4 content have consolidated this reduction theory. The analytical results in 4 wellfield areas in terms of environmental, permeability, confining and red-ox and other characteristics show that the geochemical behavior and mechanism of As (when it has entered into the groundwater) are in accordance with the "Reduction theory". As generally remarked, within the last 10 years, the intensive groundwater extraction has caused the formation of cones of depression, typically in Phap Van, Ha Dinh; and many hydraulic windows. This has resulted in the air circulation in the aquifers, whereby O_2 and DO have the possibility to enter the deep aquifers, activating the bacteria which facilitate the reducing process. Between the sediment layers rich in organic matter and the intercalating ones rich in accumulation of adsorbed FeOOH and As a geochemical process (the reducing process) is formed and breaks this connection.

Besides, it is remarked that the trace metals accumulated in the clay-rich sediments are of low content, with no indication of pollution in the groundwater. In the mean time the contents of metals such as Mn, Fe (and often accompanying As) which tend to increase in clayey silt sediments (with coarser particle size) are also elevated in the groundwater. This proves that the permeability plays a very important role in the geochemical balance between the sediments and the related groundwater, greatly affecting the solution and leaching of components from the sediments into the groundwater.

CONCLUSION

- The differentiation of geological structure, geochemical characteristics of the sediment lead to the differences in hydrological feature of the study area.
- The relationship between geochemical characteristics of the late Pleistocene - Holocene sediments and groundwater quality in the study area is rather closed, as follows:
  - Concentration of Fe, Mn, As, NH_4, in the groundwater closely depends on the geochemical sediment environment: their (except Mn) high concentration in the area with clay and argilite sediments rich in organic matters (Phap Van and Ha Dinh wellfields).

- The weathered sediment poor in organic matter has high concentration of Mn (Mai Dich area)
- Concentration of Cu, Pb, Co, Ni in both aquifer sediments and the groundwater is low, especially in the Luong Yen wellfield.
- The oxidation - reduction condition of sediment strongly influence of the geochemistry of the related water

▪ The aquifer sediments could be considered as a source of chemical elements geochemical environment for the related groundwater

▪ River deltas in Southeast Asia countries have some similarities in geology, geochemistry, hydrogeochemistry and pollution of groundwater so it is very important to establish and realize the joint projects concerning cooperation research of sediment geochemistry and hydrogeochemistry of the big river delta.

▪ Exchanging data of groundwater monitoring systems in river deltas of ASEAN is very useful and should be in priority of the cooperation in groundwater investigation.

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