APPLICATION OF INVERSE MODELING TECHNIQUE TO DESCRIBE HYDROGEOCHEMICAL PROCESSES RESPONSIBLE TO SPATIAL DISTRIBUTION OF GROUNDWATER QUALITY ALONG FLOWPATH

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ABSTRACT

The main objective of this research is to define the mechanism model of chemical reactions, which are responsible to the spatial distribution of water quality along flowpath using inverse modeling technique. In addition, the Saturation Indices (SI) analysis was used to characterize the effect of geological condition toward dissolved constituent within the groundwater. Moreover, Mass Balance Modeling code was employed to describe the stoichiometry and hydrogeochemical processes along flowpath.

Field survey was carried out in order to obtain the data of hydraulic head and electrical conductivity to construct flownets and tentatively illustrate the spatial distributions of shallow groundwater quality. Next, the flow line was applied to define the sampling position of groundwater and aquifer mineral. Laboratory analysis was conducted to identify the main phases and constrains of dissolved constituent within the groundwater. Afterwards, the application of NETPATH 2.1.3 and Phreeqc Interactive 2.8 for Windows software aid to model the Mass Balance Calculation in order to account the prevailing hydrogeochemical reactions.

The result shows that firstly, the aquifer within the research area can be grouped into several aquifer systems (i.e. denudational hill, colluvial plain, alluvial plain, and beach ridges) from recharge to discharge which generally have potential groundwater resources in terms of the depth and fluctuation of groundwater table. Secondly, flownets analysis gives three flowpaths that are plausible to be modeled in order to describe their hydrogeochemical reactions. Thirdly, the Saturation Indices (SI) analysis shows that there are a positive correlation between the mineral occurrence and composition and the value of SI from recharge to discharge. In addition, The Mass Balance Model indicates that dissolution and precipitation of aquifer minerals is dominantly change the chemical composition along flowpath and the rate of the mass transfer between two wells shows a discrepancy and be certain of the percentage of the nature of aquifer mineral. Lastly, there is an interesting characteristic of mass balance chemical reaction occurs which is the entire chemical reaction shows that the sum of smallest mineral (mmol/litre) will firstly always totally be reacted.

Keywords: Groundwater, Inverse Model, Saturation Indices, Mass Balance

INTRODUCTION

The condition of groundwater quality diverges spatially depends on some influences factors such as geology, climate, vegetation, residence time as well as human activities. According to Appelo and Postma (1993), geological factor plays an essential role to change the distribution of chemical composition along the groundwater flowpath from recharge to discharge zone. Moreover, groundwater dissolves aquifer minerals during its flowing and consequences to the specific chemical constituent within the groundwater. Appelo and Postma also points out that there are some fundamental hydrogeochemical processes that accountable to modify the chemical composition along flowpath such as mineral dissolution and precipitation, cation exchange, and redox reaction.

To approach changes of chemical composition along flowpath, hydrogeochemical model is commonly be used. Jankowski (2002) reveals that hydrogeochemical models are tools that help to interpret geochemical reaction. He also defines that hydrogeochemical model can be applied for some purposes, including determination of the existing geochemical reaction along flowpath; quantification of the extent to which the reactions take place and estimation of the direction and rates of groundwater flow.

This paper will describe the research that apply inverse modeling technique to quantify and characterize hydrogeochemical processes that responsible to the spatial distribution of changing in chemical constituent along flowpath from recharge to discharge zone. Particularly, this research was conducted in some parts of Bogowonto sub-catchment, approximately 40 km away to the west from Yogyakarta city.

INVERSE MODELING

Jankowski (2002) reveals that the hydrogeochemical modeling may be divided into two general approach : (i) **inverse modeling**, which uses observed chemical groundwater constituent to assume geochemical reactions; and (ii) **forward modeling**, which uses hypothesized geochemical processes to envisage groundwater composition. In addition, there are some considerations to decide which model will be suitable for such groundwater system.

First, forward model usually be applied for systems or chemical composition as yet unstudied, where the objective is to predict the chemical composition without doing any sampling of groundwater. Additionally, this model has advantage of predicting details of thermodynamically valid reaction paths between the initial and final points. In addition, forward model probably has its greatest value in predicting the previously unidentified mass transfer and final groundwater chemical composition through hypothetical reactions models. However, this model requires the accuracy of the assumed reaction model and thermodynamic data. Furthermore, by the absence of observed water chemistry data within the initial and final points, the prediction of groundwater chemical composition may be far from reality.

On the other hand, in regional groundwater system where the data of chemical composition are available, inverse modeling is the best approach since its result always reproduces the chemistry of available samples (Jankowski, 2002). Some advantages of this model are: (a) any mass balance models found to be consistent depends on the available data of chemical composition between two sampling points; (b) all mass transfer between two points is well derived and (c) is not constrained by any thermodynamics consideration that must be checked in forward models. Next, Figure 1 illustrates the concept of inverse modeling technique to predict hydrogeochemical processes between two points.

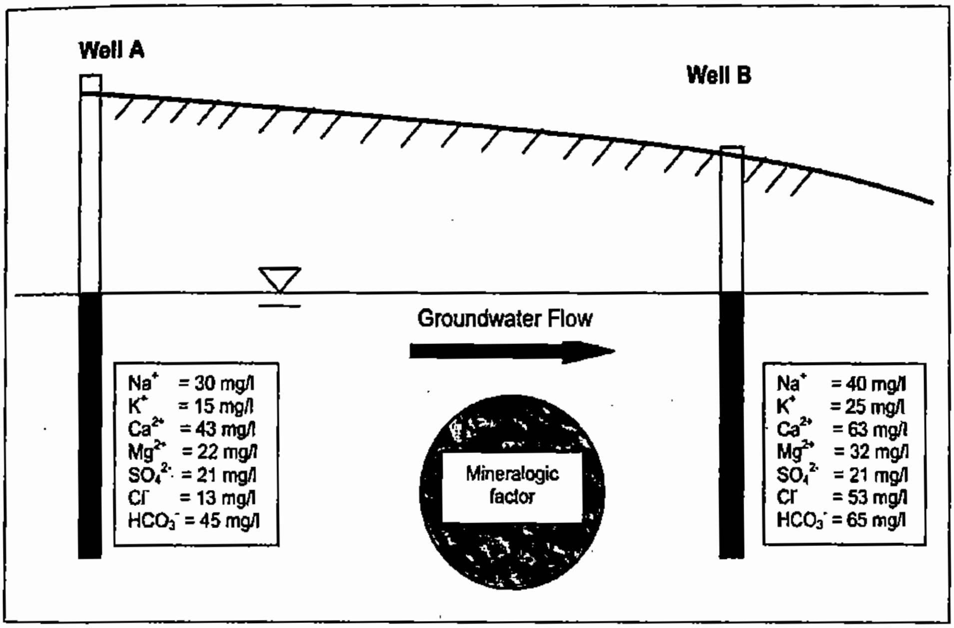

Figure 1. The concept of inverse modeling technique

According to Figure 1, it obviously seems that the chemical composition in well A and well B changes significantly along flowpath. However, there is still a question: which geochemical processes should responsible to change the chemical composition from well A to well B?. To answer this question, inverse model can be used not only to define the hydrogeochemical processes, but also to calculate the net of mass transfer as well as the rate of moles of each mineral entering or leaving the groundwater.

In addition, by looking at Figure 1, there are two main principles that must be considered consecutively to run inverse modeling, which are: (a) hydrologic consideration and (b) mineralogic factor. Firstly, hydrologic factor has a meaning that the position of initial and final point must be in one hypothetical flow system. As consequences, defining the groundwater flow system is required before running this model. Secondly, the minerals present as well as their abundances also must be observed, since mineralogy of an aquifer will strongly affect the final composition of groundwater (Appelo and Postma, 1993). Moreover, with better understanding of spatial variation in mineral condition, the geochemical reaction models will be easily to be deduced.

Shekarforoush, et al. (1998) apply inverse model to describe hydrogeochemical processes within fractured rock aquifer in Lachland Fold Belt, New South Wales, Australia. After defining the flow line, he then defines recharge and discharge zone as well as observes the mineral dominant within the aquifer. The research run the inverse model and found that the dominant hydrogeochemical reactions are redox reaction, weathering as well as dissolution of aquifer minerals. In addition, he points out that pyrite oxidation, dissolution of calcite and chlorite as well as goethite precipitation well confirmed to change the chemical composition of groundwater especially in recharge zone. Another research by Beck, et al. (1997) proposes models for hydrogeochemical reactions responsible to the changes of chemical variation within contaminated aquifer in Botany Sands Aquifer, Sydney. The inverse technique used is *mass balance modeling* approach from the source of contamination down gradient. He then summarizes that reduction and cation exchange processes are dominant within the contaminated groundwater.

SITE DESCRIPTION

The research area is part of Bogowonto sub-catchment and located administratively within Temon Sub-district, Kulon Progo Regency, DIY, and generally bounded by Serang River and Bogowonto River. Next, Figure 2 shows the detail of research area.

Geomorphologically, research area has multifaceted geomorphological unit in a short distance (6 km) from recharge to discharge zone, they are denudational hill and hillslope; alluvial plain; fluvio-marine plain; sand dune and beach ridges, respectively. This condition may be assumed that it will has a positive consequence to modify the chemical compositions of groundwater since each geomorphological unit be composed of diverse aquifer minerals. For example, denudational hill dominantly be composed of old andhesit formation while alluvium mostly found within alluvial plain. This fact suggests the different minerals within the aquifers and consequently gives the dissimilar chemical constituent of groundwater.

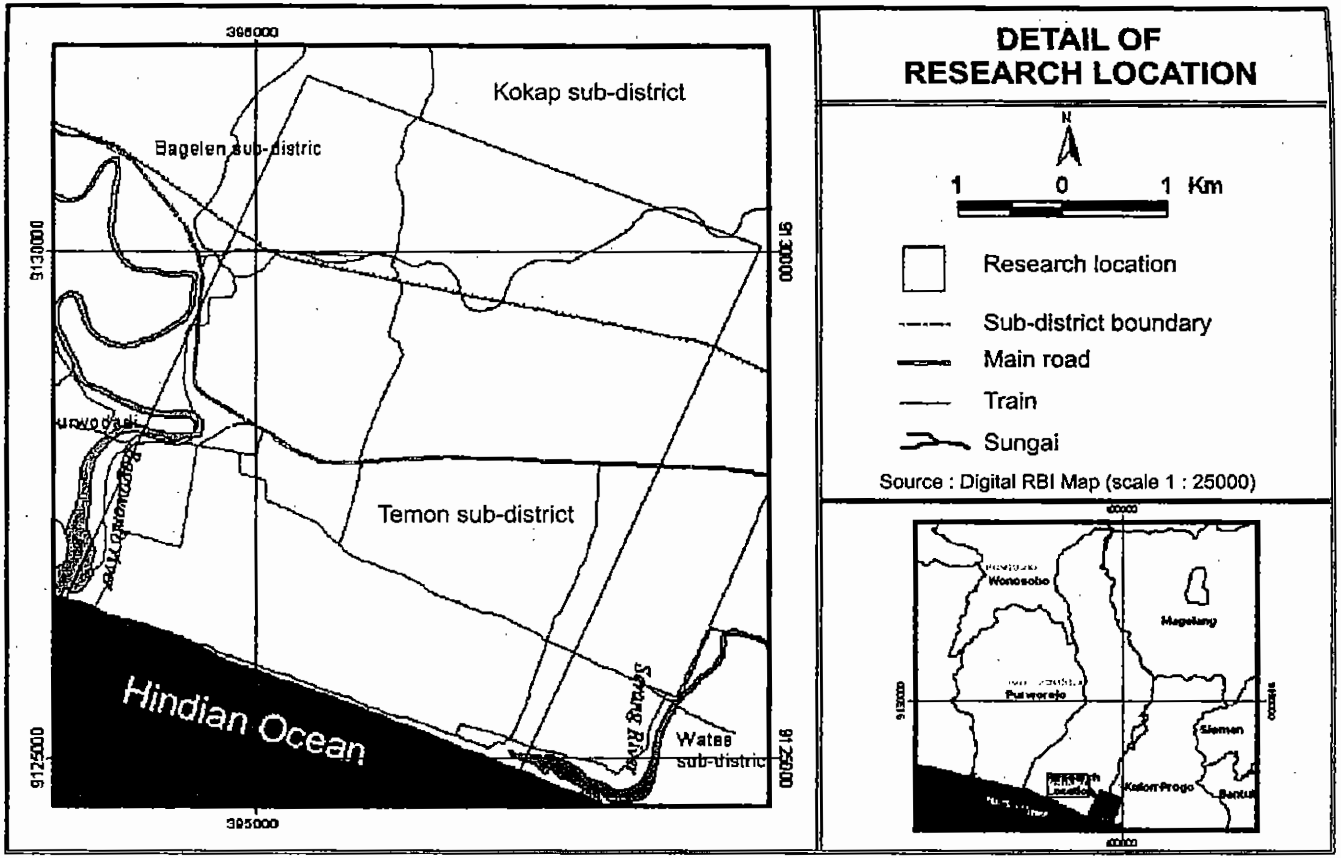

Figure 2. Detail of Research Location

METHODS

To locate the position of groundwater and mineral samples, flownets construction within the research area is necessity. First, 96 dug-wells were sampled to measure the hydraulic head, and then interpolation was conducted to produce equipotential line and its flowline. Afterwards, the position of groundwater and mineral samples were defined according to the direction of groundwater flowline from recharge to discharge. Figure 3 illustrates the flownets as well as the position of mineral and groundwater samples.

Thirteen groundwater and mineral samples were collected to analyze their properties in terms of chemical compositions in laboratory. To evaluate the accuracy of groundwater laboratory analysis, charge balance error analysis was used in particular to identify the deviation of chemical reaction balance within cation and anion in meq/litre. This analysis implies that the sample which has deviation more than 5% can not be used.

Next, after laboratory analysis presents the chemical composition of the samples, Saturation Indices (SI) with respect to aquifer minerals calculation (using Phreeqc Interactive 2.8 for Windows) was used to describe the stage of chemical reaction from recharge to discharge in terms of their dissolution or precipitation processes. According to this SI, the stage of chemical reaction will be define i.e. $SI < 0$ denotes that dissolution processes occur, $SI=0$ equivalent to equilibrium stage and $SI>0$ represents that mineral precipitation processes dominant. In addition, to preliminary predict the geochemical processes along flowpath, some analysis were conducted including bivariate plot and ratio ion as well as classification of chemical type using Szczukariew-Priklonski (Alekin, 1970). Lastly, mass balance modeling calculation was guidance by interactive code NETPATH 2.1.3 (Plummer et al, 1991) and the results subsequently are used to define the chemical reaction consistent with the minerals present and the net of mass transfer.

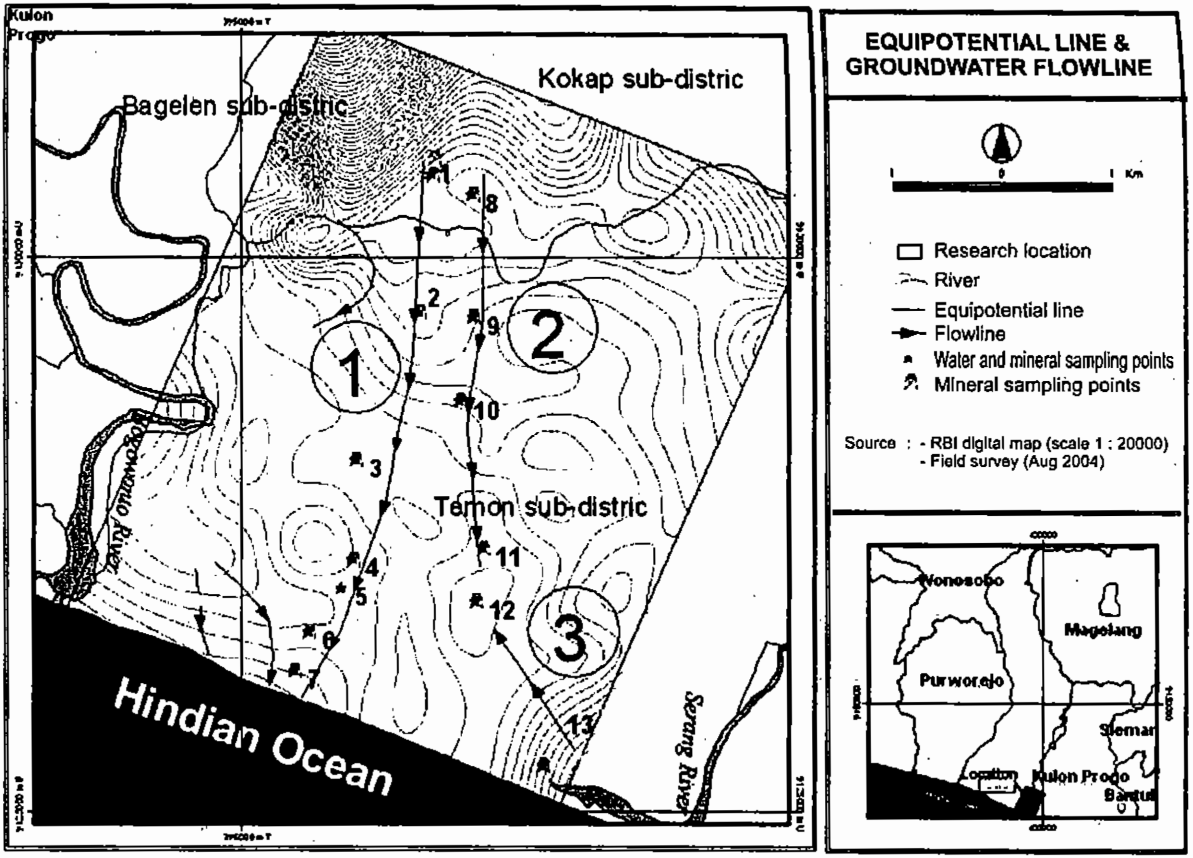

Figure 3. Three Flowpaths Occur Within Research Area (1, 2 & 3)

RESULT AND DISCUSSION

Depth to water table and flownets

Depth to water table based on field measurement (96 dug-wells) gives values range from 1 m to 9.36 m. Spatially, in the upper part of the research area, the depth to water table generally be found above 7 meter whereas in discharge zone it varies between 1 and 6 meter. Next, flownets construction gives 3 (three) main flowpaths from recharge to discharge. Afterwards, these three flowpaths are used to define the sampling position of water quality and mineral. Figure 3 shows three flowpaths occurred and sampling points position. Flowpath 1 represents the hydrogeochemical evolution from denudational hill to beach ridge (samples no. 1-2-3-4-5-6-7), Flowpath 2, denudational hill to alluvial plain represented by samples no. 8-9-10-11, and Flowpath 3 from beach ridges to alluvial plains represented by samples no 13-12.

Groundwater Quality and Its Hydrochemical Type

To define the chemical and physical characteristics of groundwater within research area, 13 wells were sampled and analyzed in laboratory. Next, Table 1 shows the result of field and laboratory samples analysis.

As described in Table 1, physical characteristic of groundwater may be discussed by looking at the result of electrical conductivity (EC) value as measured in 96 wells within research area. Spatially, the value of EC varies from 200 to 500 µmhos/cm found in hilly area as also found a little bit lower in marine and aeolian landform (200-300 µmhos/cm). Meanwhile, in the centre part of research area (alluvial plain) the value of EC shows a discrepancy from 300 to 1300 µmhos/cm.

Table 1. The result of field and laboratory analysis of groundwater samples

Samples	Unit	1	2	3	4	5	6	7	8	9	10	11	12	13
Ca^{2+}	mg/l	78,8	95,1	67,2	88,1	62,6	69,6	76,5	44	53,3	132	58	69,8	34
Mg^{2+}	mg/l	49,3	19,7	36,7	29,6	33,6	35,2	14	30	42,2	46,6	40,8	18,1	54,9
Na^{+}	mg/l	17	11,7	20,8	15,1	10,9	10,3	13,3	15,9	31,3	25,1	17,2	12,5	12
K^{+}	mg/l	4,7	5,4	3,5	6	8,3	4,9	5,1	2,7	8,4	7,4	2	5,4	7,3
Cl^{-}	mg/l	23,2	48,7	34,8	44	44	25,5	32,4	23,2	95,1	90,4	34,8	27,8	67,2
SO_4^{2-}	mg/l	22,5	24	34,8	23,7	11,2	26,2	42,5	17,5	60	37,5	31,5	35	31,6
HCO_3^{-}	mg/l	194	241	315	298	185	73,4	90,7	216	354	444	142	155	155
Fe(tot)	mg/l	0,06	0,04	2,4	0,02	0,02	0,04	0	0,06	0,02	0,04	2	0	0
SiO_2	mg/l	105	96,8	133	122	153	128	0,02	120	95,8	98,6	115	133	114
Al^{2+}	mg/l	0	0	0,39	0,32	0,38	0,22	0,19	0,11	0,28	0,32	0,2	0,09	0,12
NH_4^{+}	mg/l	0	0	0	0	0	0	0	0	0	0	0	0	0
NO_3^{-}	mg/l	0,6	2	0	3	0	3,8	0	0	0	0	0	0	0
PO_4^{3-}	mg/l	0,01	0,01	0	0	0,07	0	0	0	0	0	0,16	0	0
CO_2	mg/l	0	10	0	0	0	12	8	6	10	8	10	14	12
O_2	mg/l	6,2	6,1	6,4	6,1	6,3	6,2	6,3	6,1	6,2	6	5,9	5,8	5,8
pH		7,78	6,88	6,96	7,12	7,6	7,33	7,82	6,68	6,64	6,97	6,58	6,56	7,5
EC	µmhos/cm	328	370	489	255	220	266	266	365	794	686	305	333	248
Eh	mV	-90	-51	-71	-70	-73	-68	-59	-23	-21	-14	-12	-33	-50

Source: Field measurement and laboratory analysis (September, 2004)

Next, the chemical constituent of major cation and anion shows a variation of values within the three main flowpath from recharge to discharge. Moreover, the minor elements such as ammonia, nitrate, and phosphate analyzed in this research do not perform any value that in excess of the maximum value of Water Standard for Drinking (Class A) as commence by Jogjakarta Special Province (DIY) Governor nr. 214/KPTS/1991. Note, this research does not deal with the biological parameters such as coli bacteria.

Hydrochemical Type of groundwater may figure out the evolution and hydrogeochemical processes occur within the groundwater system (Jankowski, 2001). Here, the hydrochemical type is defined by using Szczukariew-Priklonski classification as shown in Table 2. According to Table 2, it appears that the most dominant anion in all flowpath is bicarbonate (HCO_3^-), followed by chloride (Cl-), and then sulfate (SO_4^{2-}). In flowpath 1, the most dominant cation is calcium (Ca^{2+}) except in sample 1 as dominated by magnesium (Mg^{2+}). The dissimilar condition presents in flowpaths 2 and 3 when dominant cation is magnesium while within sample 10 and 12 is dominated by calcium.

Table 2. Hydrochemical type by Szczukariew-Priklonski classification

Flowpath 1 (Denudational Hill – Alluvial Plain – Beach Ridges)		
No	**Geomorphology**	**Hydrochemical Type**
1	Denudational Hill	HCO_3-Mg-Ca
2	Alluvial Plain	HCO_3-Cl-Ca-Mg
3	Alluvial Plain	HCO_3-Ca-Mg
4	Old beach ridge	HCO_3-Ca-Mg
5	Old beach ridge	HCO_3-Cl-Ca-Mg
6	Mature Beach ridge	HCO_3-Cl-SO_4-Ca-Mg
7	Complex of young beach ridge and sand dune	HCO_3-Cl-SO_4-Ca-Mg
Flowpath 2 (Denudational Hill – Alluvial Plain)		
No	**Geomorphology**	**Hydrochemical Type**
8	Colluvial Plain	HCO_3-Cl-SO_4-Mg-Ca
9	Alluvial Plain	HCO_3-Cl-Mg-Ca
10	Alluvial Plain	HCO_3-Cl-Ca-Mg
11	Alluvial Plain	HCO_3-Cl-Mg-Ca
Flowpath 3 (Beach Ridges - Alluvial Plain)		
No	**Geomorphology**	**Hydrochemical Type**
13	Mature beach ridge	HCO_3-Cl-Mg-Ca
12	Old beach ridge	HCO_3-Ca-Mg

Source : Laboratory analysis (September 2004)

Ratio of Ion

Ratio of ion analysis will give preliminary understanding of hydrogeochmeical processes occur within the groundwater system. Next, Table 3 shows the ration of ion in all samples.

Table 3. Ratio of ion

Samples	Na : Cl	Ca : Mg	Ca : SO_4	Na : K
	meq/l	meq/l	meq/l	meq/l
1	1.14	0.97	0.88	6.17
2	0.37	2.93	5.37	3.64
3	0.92	1.11	3.27	10.00
4	0.53	1.80	7.52	4.40
5	0.38	1.13	13.19	2.24
6	0.63	1.20	9.60	3.46
7	0.64	3.32	10.98	4.46
8	0.07	1.06	0.89	6.11
9	0.21	0.51	0.77	2.13
10	0.19	0.43	1.72	8.45
11	15.00	0.77	0.86	4.38
12	0.69	2.34	4.77	3.86
13	0.27	0.38	2.58	2.74

Source : Laboratory analysis (September 2004)

According to Table 3, most ratio ion of Na : K and Ca : Mg are higher than 1 with maximum value is 20 in ration of Na : K within flowpath 1 and 2. This phenomenon might designate that in the research area, potassium has already absorbed theoretically by plant activities or exchanged to sodium. This fact, according to Jankowski (2001) frequently occurs within the system dominated by clay mineral as present in the alluvial plains. In addition, the value of ratio ion of Ca : SO_4 that mostly found above 1 indicates that dissolution or even precipitation of minerals contain calcium has already occurred. Next, ratio ion of Na : Cl will be above 1 if dissolution of minerals contain silica as well as cation exchanged has already occurred within the groundwater. In the research area, the possibility as described above might be come about since most minerals founds contain of silica in addition to the present of clay mineral in the alluvial plains (the centre part of research area).

Saturation Indices Analysis

To define the spatial distribution of Saturation Indices (SI) within the samples, we need to understand the mineralogy condition. Next, analysis of mineralogy within aquifers gives aquifer distribution in each lithological unit as shown in Table 4. Generally, there are 3 main lithological complex within research area: (1) complex of old andhesit formation consists of mineralogy plagioclase, hornblende, pyroxene, and quartz; (2) complex of alluvial plains dominated by clay mineral and still consists as minerals described in (1); (3) complex of marine and aeolin dominated by plagioclase, hornblende, pyroxene, quartz and clay. In this research, not all of the minerals present within the aquifer are analyzed by SI method, but only mineral dominant of (a) CO_2 (gas), quartz, and glass; (b) albite and anorthite; and (c) clay. The complete value of SI analysis with respect to all minerals was done by Netpath software.

Table 4. Distribution of mineralogy dominant

Old Andhesite Formation

Lithology	Mineral	Chemical Composition	Ion
Andhesit – breccias	Amphibole	$Ca,Mg,Fe,Al(SiO_3)$	Ca^{2+},Mg^{2+},Al^{3+}, SiO_2
	Pyroxene	$CaMg(SiO_3)_2$	Ca^{2+},Mg^{2+}, SiO_2
		$CaFe(SiO_3)_2$	Ca^{2+},Fe^{2+}, SiO_2
	Augite	$CaMg(SiO_3)_2$	Ca^{2+},Mg^{2+}
	Hornblende	$(Ca_2Na(Mg,Fe)_4(Al,Fe)((Si,Al)_4O_{11})_2(OH)_2$	Ca^{2+},Mg^{2+},Al^{3+}, SiO_2, Fe^{2+}, OH^- OH^-
Tuff	Augite	$Ca,Mg(SiO_3)_2$	Ca^{2+},Mg^{2+}
		SiO_2	SiO_2
	Feldspar	$KAlSi_3O_8$	K^{2+},AL^{3+},SiO_2
		$NaAlSi_3O_8$	Na^{2+},AL^{3+},SiO_2
		$CaAlSi_3O_8$	Ca^{2+},AL^{3+},SiO_2
Lava Andesite	Pyroxene	$CaMg(SiO_3)_2$	Ca^{2+},Mg^{2+}, SiO_2
		$CaFe(SiO_3)_2$	Ca^{2+},Fe^{2+}, SiO_2
	Augite	$CaMg(SiO_3)_2$	Ca^{2+},Mg^{2+}
Lapili Tuff	Chlorite	(Mg Fe dan Al)	Mg^{2+}, Fe^{2+}, Al^{3+}, SiO_2
	Serpentine	$CH_4(Mg,Fe)_3(SiO_3)_2$	Mg^{2+}, Fe^{2+}, Al^{3+},OH^-

Alluvial Plain

Lithology	Mineral	Chemical Composition	Ion
Clay	Amphibole	$Ca,Mg,Fe,Al(SiO_3)$	Ca^{2+},Mg^{2+},Al^{3+}, SiO_2
	Pyroxene	$CaMg(SiO_3)_2$	Ca^{2+},Mg^{2+}, SiO_2
		$CaFe(SiO_3)_2$	Ca^{2+},Fe^{2+}, SiO_2
	Plagioclase	$CaAl_2Si_3O_8$	Ca^{2+}, Al^{3+}, SiO_2
		$NaAl_2Si_3O_8$	Na^{2+},Al^{3+}, SiO_2
	Augite	$CaMg(SiO_3)_2$	Ca^{2+},Mg^{2+}
	Clay	Al_2O_3 ,$2SiO_2$,$2H_2O$	Al^{2+},SiO_2,H_2O
	Hornblende	$(Ca_2Na(Mg,Fe)_4(Al,Fe)((Si,Al)_4O_{11})_2(OH)_2$	Ca^{2+},Mg^{2+},Al^{3+}, SiO_2, Fe^{2+}, OH^- OH^-

Marine and Aeolin

Lithology	Mineral	Chemical Composition	Ion
Quartz sand	Amphibole	$Ca,Mg,Fe,Al(SiO_3)$	Ca^{2+},Mg^{2+},Al^{3+}, SiO_2
	Pyroxene	$CaMg(SiO_3)_2$	Ca^{2+},Mg^{2+}, SiO_2
		$CaFe(SiO_3)_2$	Ca^{2+},Fe^{2+}, SiO_2
	Plagioclase	$CaAl_2Si_3O_8$	Ca^{2+}, Al^{3+}, SiO_2
		$NaAl_2Si_3O_8$	Na^{2+},Al^{3+}, SiO_2
	Augite	$CaMg(SiO_3)_2$	Ca^{2+},Mg^{2+}
	Clay	Al_2O_3 ,$2SiO_2$,$2H_2O$	Al^{2+},SiO_2,H_2O
	Quartz	SiO_2	SiO_2
	Hornblende	$(Ca_2Na(Mg,Fe)_4(Al,Fe)((Si,Al)_4O_{11})_2(OH)_2$	Ca^{2+},Mg^{2+},Al^{3+}, SiO_2, Fe^{2+}, OH^- OH^-

Source : Widayatto (1990) and laboratory analysis (2004)

CO_2 (gas) is not a mineral but it is a very important phase to determine the hydrogeochemical reactions within the groundwater, while quartz and glass are minerals with the same chemical composition but differ in terms of their genesis. Laboratory analysis of minerals gives understanding that aquifers contain quartz and glass in relatively high percentage (above 25%) from the total minerals occurs (sample no. 1, 2, 3, 4). In addition, quartz is distributed less than 5% in recharge area and shows a moderate increasing to the coast (discharge). SI analysis with respect to CO_2 (gas), quartz, and glass confirms that the rate of dissolution pattern follows the fluctuation of CO_2 (gas) saturation indices, and indicates that the dominant process is dissolution strongly controlled by CO_2 (gas) content. Generally, in three flowpaths, analysis SI with respect to quartz demonstrates the nearly equilibrium stage, whereas analysis of SI with respect to glass confirms the under-saturated stage.

Next, albite and anorthite that include in mineral group of plagioclase is almost found in all samples. Albite ($NaAlSi_3O_8$) will significantly increase the sodium (Na^+) content in under-saturated stage and it will decrease sodium content of groundwater in super-saturated condition. Meanwhile, anorthite ($CaAl_2Si_2O_8$) will affect the chemical constituent mainly to decrease or increase the calcium (Ca^{2+}) content. Besides that, anorthite and albite will also affect the value of aluminum and silica in groundwater. According to SI analysis in flowpath 1, the two mineral has already in super-saturated condition means that precipitation process to occur. In flowpath 2, SI analysis gives value slightly below 0 points toward that dissolution process might be to occur but it has already in nearly equilibrium, while flowpath 3 confirms that SI value has already in super-saturated condition. In general, it seems that the value of SI with respect to albite is always lower than anorthite. To sum up, this condition may be a sign of the field condition that dominated by calcium.

SI analysis with respect to clay mineral is represented by K-feldspar ($KAlSi_3O_8$) and kaolinite ($Al_2Si_2O_5(OH)_4$) that mostly found in alluvial plain aquifer. In flowpath 1, the two minerals show an increasing value of SI to nearly equilibrium stage, while in flowpath 2 it fluctuated depend on the clay content along flowpath. In addition, flowpath 3 gives SI value above 0 (super-saturated) with increasing pattern, since clay content in sample 12 is higher than in sample 13.

Mass Balance Model

Mass balance modeling attempts to determine the nature and extent of geochemical reaction that are occurring in a groundwater system by identifying the minerals that are reacting and to establish the amounts of these minerals that dissolve or precipitate (Jankowski, 2002). The aim of mass balance modeling is to define the net masses of minerals dissolved or precipitated along flowpath downgradient.

In this research, mass balance modeling is conducted in all three flowpath between each well (sample), for instance: sample 1 to sample 2, 2 - 3, 3 – 4, and so on until flowpath 3 from sample 13 to 12. To model in each flowpath between samples, the chemical composition of groundwater and aquifer minerals present is not always the same, depends on the aquifer condition. Therefore, the model defined is the best model that has already matched to the minerals condition and spatial distribution of SI values as described above. Tables 5, 6, and 7 hereunder put forward examples of models chosen represent the three flowpaths occur within research area.

Table 5. Result of Mass Balance Modeling from sample 1 to sample 2 (Flowpath 1)

Constrains including	Phases including	Model result (- = precipitation) Unit = mmol/lt
C Ca Al Mg Na K SiO2 Fe	1. Hornblenda : $Ca_2Na(Mg,Fe)_4(Al,Fe)((Si,Al)_4O_{11})_2(OH)_2$ 2. Quartz : SiO_2 4. K-Feldspar : $KAlSi_3O_8$ 5. Kaolinite : $Al_2Si_2O_5(OH)_4$ 6. Anorthite : $CaAl_2Si_2O_8$ 7. Albite : $NaAlSi_3O_8$ 8. Air : H2O 9. Carbondioxide gas :CO2 gas 10. Cation exchange 11. Augite : $CaMg(SiO_3)_2$	MODEL 4 HORNBLND + -1.21807 CO2 GAS 1.72863 EXCHANGE -0.83353 K-SPAR + 0.01792 KAOLINIT -0.90969 ALBITE + 1.43643 ANORTH + 0.78155 MODEL 5 HORNBLND + 0.73036 CO2 GAS 1.72863 EXCHANGE -0.65087 K-SPAR + 0.01792 KAOLINIT -0.86614 ALBITE + 1.07110 AUGITE + -2.43553

Table 6. Result of Mass Balance Modeling from sample 9 to sample 10 (Flowpath 2)

Constrains including	Phases including	Model result (- = precipitation) Unit = mmol/lt
C Ca Al Na K SiO2 Mg Fe	1. Quartz : SiO_2 2. K-Feldspar : $KAlSi_3O_8$ 3. Air : CH2O 4. Carbondioxide gas :CO2 gas 5. Anorthite : $CaAl_2Si_2O_8$ 6. Albite : $NaAlSi_3O_8$ 7. Augite : $CaMg(SiO_3)_2$ 8. Kaolinite : $Al_2Si_2O_5(OH)_4$ 9. Cation Exchange	MODEL 1 ALBITE + 3.48814 AUGITE 0.21644 EXCHANGE -1.87893 K-SPAR + -0.02556 KAOLINIT -1.75219 CO2 GAS + 0.35755 SiO2 + -7.24771 MODEL 2 ANORTH + 1.74407 AUGITE 0.21644 EXCHANGE -0.13487 K-SPAR + -0.02556 KAOLINIT -1.75219 Co2 GAS + 0.35755 SiO2 + -0.27143

Table 7. Result of Mass Balance Modeling from sample 13 to sample 12 (Flowpath 3)

Constrains including	Phases including	Model result (- = precipitation) Unit = mmol/lt
C	1. Quartz : SiO_2	MODEL 1 ALBITE + 3.48814 AUGITE 0.21644 EXCHANGE -1.87893 K-SPAR + -0.02556 KAOLINIT -1.75219 CO2 GAS + 0.35755 SIO2 + -7.24771
Ca	2. K-Feldspar : $KAlSi_3O_8$	
Al	3. Air : CH2O	
Na	4. Carbondioxide gas:CO2 gas	
K	5. Anorthite : $CaAl_2Si_2O_8$	
SiO2	6. Albite : $NaAlSi_3O_8$	
Mg	7. Augite : $CaMg(SiO_3)_2$	
Fe	8. Kaolinit : $Al_2Si_2O_5(OH)_4$	
	9. Cation Exchange	MODEL 2 ANORTH + 1.74407 AUGITE 0.21644 EXCHANGE -0.13487 K-SPAR + -0.02556 KAOLINIT -1.75219 Co2 GAS + 0.35755 SiO2 + -0.27143

By looking at Table 5 (for example), we can see that in model 4 (above), approximately 1.72 mmol/litre CO_2 (gas), 0.018 mmol/litre K-feldspar, 1.44 mmol/litre albite, and 0.79 mmol/litre anorthite are dissolved. On the other hand, there are some minerals precipitated such as 1.21 mmol/litre hornblende and 0.9 mmol/litre kaolinite. This model also finds that 0.13 mmol/litre cation exchange has already occurred within the system as already clarified by ratio ion analysis above. Generally, two dominant processes in all models are dissolution and precipitation by the different rate and minerals including. Hereunder, there are two examples of hydrogeochemical processes that occur to change the chemical composition along flowpath 1 from sample 1 to sample 2 and model 1 along sample 9 to 10 (flowpath 2).

1. Model 4 (as described in Table 5, above) from sample 1 to sample 2, flowpath 1

Minerals occur within the system in this model: Hornblende, CO_2 gas, K-Feldspar, Kaolinite, Albite and Anorthite, with the most dominant reactions are dissolution and precipitation.

a. Dissolution reaction

There are some minerals dissolved in this section i.e. K-Feldspar, Albite, Anorthite dan CO_2 gas, and the chemical reaction are describe hereunder:

- **K-feldspar dissolution**

$0.018\ KAlSi_3O_8 + 0.018\ CO_2 + 0.027\ H_2O \rightarrow\ 0.009\ Al_2Si_2O_5(OH)_4 + 0.018\ HCO_3 + 0.018\ K^+ + 0.036\ SiO_2$

K-feldspar kaolinite

Accordingly, to dissolve 0.018 mmol/litre of K-Feldspar needs 0.018 mmol/litre of CO_2.

- **Anorthite dissolution**

$0.791\ CaAl_2Si_2O_8 + 1.582\ H_2CO_3 + 7.746H_2O \rightarrow 1.582\ Al(OH)_3 + 0.791Ca^{+2} + 1.582HCO_3^- + 1.582H_4SiO_4$

anorthite gibbsite

Accordingly, the dissolution process of 0.791 mmol/litre anorthite needs 1.582 mmol/litre of CO_2.

- **Albite dissolution**

$0.717NaAlSi_3O_8 + 1.434H_2CO_3 + 6.453H_2O \rightarrow 0.717Al_2Si_2O_5(OH)_4 + 1.143Na^+ + 1.434HCO_3^- + 2.868H_4SiO_4$

albite kaolinite

Accordingly, the dissolution of 0.717 mmol/litre albite needs 1.434 mmol/litre of CO_2.

- **Release of Hydrogen**

$1.729\ CO_2 + 1.729\ H_2O \rightarrow 1.729\ H^+ + 1.729\ HCO_3^-$

According to above reaction, to release 1.729 mmol/litre hydrogen, it needs 1.729 mmol/litre of CO_2.

b. Precipitation reactions

There are 2 minerals precipitated, Hornblende and Kaolinite, and the geochemical reaction are describe hereunder:

- **Precipitation of hornblende that produce kaolinite into the water**

$1.218(CaNa(Mg.Fe)_4(Al.Fe)(Si.Al)_4O_{11})_2(OH)_2 + 12.18H_2CO_3 + 17.052O_2 + 30.45H_2O \rightarrow$

hornblenda

$3.658Al_2Si_2O_5(OH)_4 + 4.872Na^+ + 9.744Ca^{+2} + 4.872Mg^{+2} + 12.18HCO_3 + 12.18Fe(OH)_3 + 4.872Al(OH)_3 + 2.436H_4SiO_4$

kaolinite

According to above reaction, to produce 3.658 mmol/l $Al_2Si_2O_5(OH)_4$, 12.18 mmol/l $Fe(OH)_3$ and 4.872 mmol/l $Al(OH)_3$ needs 1.218 mmol/l mineral of Hornblende.

- **Precipitation of kaolinite to produce gibbsite into the water**

$0.666\ Al_2Si_2O_5(OH)_4 + 3.33\ H_2O \rightarrow 1.332\ Al(OH)_3 + 1.332\ H_4SiO_4$

kaolinite gibbsite

According to above reaction, to produce 1.332 mmol/l $Al(OH)_3$ needs 0.666 mmol/l mineral of Kaolinite.

2. Model 1 (as described in Table 6, above) from sample 9 to sample 10, flowpath 2

Minerals occur within the system in this model: CO_2 gas, K-Feldspar, Kaolinite, Albite, SiO_2 dan Augite .

a. Dissolution reactions

- **Dissolution of Albite**

$0,67\ NaAlSi_3O_8 + 0,67\ H_2CO_3 + 3,015H_2O \rightarrow 0,335Al_2Si_2O_5(OH)_4 + 0,67\ Na^+ + 0,67\ HCO_3^- + 01,34H_4SiO_4$

albite kaolinite

From the above reaction, to dissove 0.67 mmol/l Albite needs 0.67 mmol/l CO_2

- **Dissolution of Augite**

$0.875CaMg(SiO_3)_2 + 3.5H_2CO_3 + 1.75H_2O \rightarrow 0.875Ca^{+2} + 0.875Mg^{+2} + 3.5HCO_3 + 1.75H_2SiO_4$
augite

From the above reaction, to dissove 0.875 mmol/l Augite needs 3,5 mmol/l CO_2.

- **Release of Hydrogen**

$1.729\ CO_2 + 1.729\ H_2O \rightarrow 1.729\ H^+ + 1.729\ HCO_3^-$

According to above reaction, to release 1.729 mmol/litre hydrogen, it needs 1.729 mmol/litre of CO_2.

h. Precipitation reactions

There are 3 minerals precipitated: K-Feldspar, SiO_2 dan Kaolinite, and the geochemical reaction are describe hereunder:

- **Precipitation of K-feldspar to produce Gibbsite**

$0.049\ KalSi_3O_8 + 0.343\ H_2O \rightarrow 0.049\ Al(OH)_2 + 0.049\ K^+ + 0.147\ H_4SiO_4$
K-feldspar gibbsite

According to above reaction, to produce 0.049 mmol/l of Gibbsite needs 0.49 mmol/l of K-Feldspar.

- **Precipitation of Kaolinite to produce Gibbsite**

$0.889\ Al_2Si_2O_5(OH)_4 + 4.445\ H_2O \rightarrow 1.778\ Al(OH)_3 + 1.778\ H_4SiO_4$
kaolinite gibbsite

According to above reaction, to produce 1.778 mmol/l of $Al(OH)_3$ needs 0.889 mmol/l of Kaolinite.

- **Precipitation of SiO2**

$1.788\ SiO_2 + 3{,}576\ H_2O \rightarrow 1.788\ H_4SiO_4$

According to above reaction, to precipitate 1.788mmol/l quartz needs 3.576 mmol/l of H_2O.

CONCLUDING REMARKS

As clarified above, there are three flowpaths found within the research area that across several geomorphological unit (i.e. denudational hill, colluvial plain, alluvial plain, and beach ridges) from recharge to discharge. Therefore, the inverse modeling has run in the three flowpaths.

In general, physically and chemically, groundwater condition in all samples meets the requirement of water drinking standard. Next, the analysis of chemical type and ionic ratio of groundwater shows the variation of chemical compositions of groundwater from recharge to discharge. This fact is also found in minerals present within the aquifers that demonstrates variation in terms of distribution and composition along flowpath. For that reason, it can be deduced that mineral condition strongly affects the chemical constituent of groundwater. In addition, the result of SI analysis gives indication that the values of SI measured in every sample are controlled by the composition and distribution of mineral present. The result shows that generally, groundwater condition is still aggressive with respect to carbondioxide gas, glass, albite and anorthite. Meanwhile, all samples especially occur in alluvial plains have super-saturated condition with respect to clay minerals.

The result of mass balance modeling in each flowpath confirms that precipitation and dissolution processes strongly be in charge of the spatial distribution of groundwater quality along flowpath beside cation exchanged that also contribute to change the chemical constituent of groundwater. In addition, most models found that the entire chemical reaction shows that the sum of smallest mineral (mmol/litre) will firstly always totally be reacted.

Lastly, even tough this research found some hydrogeochmical reactions as well as their stoichiometry, the accuracy of these models needs to be verified by conducting another modeling in different flowpath in the same area. Additionally, the description of minerals occurs must be clarified by analysis of element carried out in mineral laboratory.

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