FINAL REPORT

EVOLUTION OF FERROUS IRON IN A LOCAL GROUNDWATER FLOW SYSTEM

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DECEMBER 2004

Contract Number TRG4580065

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EVOLUTION OF FERROUS IRON IN A LOCAL GROUNDWATER FLOW SYSTEM

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Funded by Thailand Research Fund

ACKNOWLEDGMENTS

The senior author gratefully thanks Professor Chunmiao Zheng, Ph.D., and Associate Professor Pongpor Asnachinda, Ph.D., for a chance of a lifetime to work with them and for their guidance throughout this research. We thank Thailand Research Fund for providing us financial support (TRG4580065). We also thank Roongwit Promma, Sanong Patanompee, Rath Wongnete, Prajonyuth Yimprae, and Siam Munmaung for field assistance.

บทคัดย่อ

รหัสโครงการ : TRG4580065

ชื่อโครงการ : วิวัฒนาการของเหล็กเฟอรัสในระบบการไหลของน้ำบาดาลท้องถิ่น

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การศึกษานี้เสนอสมมุติฐานใหม่ว่า ในชั้นน้ำตะกอนน้ำพาชนิดมีแรงดันซึ่งตั้งอยู่ระหว่างแม่น้ำสองสาย เขตของความเข้มข้นของสปีชีส์รีดอกซ์ที่สูงผิดปกติ เช่น เหล็ก เกิดจากกลศาสตร์ของการไหลของน้ำบาดาลมากกว่าเกิดจากวิวัฒนาการทางเคมีตามทิศทางการไหล สมมุติฐานดังกล่าวได้ผ่านการพิสูจน์แล้วว่าถูกต้อง ณ พื้นที่ศึกษาที่ตั้งอยู่ระหว่างแม่น้ำน่านและแม่น้ำยมในจังหวัดพิษณุโลก โดยการวิเคราะห์ความเข้มข้นของเหล็กเฟอรัสซึ่งเป็นดัชนีของสปีชีส์รีดอกซ์เปรียบเทียบกับรูปแบบการไหลของน้ำบาดาล การกัดเซาะของแม่น้ำที่ลึกลงไปในชั้นน้ำชนิดมีแรงดันและการเปลี่ยนแปลงตามฤดูกาลทางอุทกวิทยาที่เกี่ยวข้องทำให้แนวการไหลเกิดขึ้นอย่างไม่ต่อเนื่องและมีรูปแบบการไหลชนิดซิกแซก น้ำเติมแนวราบจากแม่น้ำแทรกซึมเข้าสู่ชั้นน้ำได้เพียงไม่เกิน 41 เมตร แม้ว่าน้ำเติมแนวดิ่งสามารถไหลซึมลงผ่านชั้นทึบน้ำซึ่งมีความหนา 13-21 เมตร โดยมีหลักฐานจากความเข้มข้นของออกซิเจนละลายน้ำที่มีค่ามาก แต่การขาดแคลนน้ำเติมแนวราบจากแม่น้ำมีอิทธิพลมากกว่าการเติมน้ำแนวดิ่งจากน้ำฝน จึงสรุปได้ว่าความเข้มข้นของสปีชีส์รีดอกซ์ที่สูงผิดปกติซึ่งปรากฏให้เห็นในแผนที่เป็นหย่อม ๆ ในชั้นน้ำชนิดมีแรงดันเกิดจากความสัมพันธ์ระหว่างน้ำบาดาลและน้ำผิวดินและกลศาสตร์ของการไหลของน้ำบาดาลที่เกี่ยวข้อง

คำหลัก : ความสัมพันธ์ระหว่างน้ำบาดาลและน้ำผิวดิน, อุทกธรณีเคมี, การไหลของน้ำบาดาล, เหล็ก

ABSTRACT

Project Code : TRG4580065

Project Title : Evolution of Ferrous Iron in a Local Groundwater Flow System

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Project Period : 1 July 2002 - 31 December 2004

This study proposes a new hypothesis that, in a confined alluvial aquifer located between two rivers, discrete zones of anomalously high concentrations of redox species, such as iron, are a result of groundwater flow dynamics rather than a chemical evolution along continuous flow paths. The hypothesis was proved correct at a study site located between Nan and Yom Rivers in Phitsanulok, Thailand, by analyzing concentrations of ferrous iron, an index of redox-sensitive species, in comparison with dynamic groundwater flow patterns. River incision into the confined aquifer and related seasonally variant hydrology result in truncated flow paths and zigzag groundwater flow patterns. The lateral recharge from rivers penetrates into the aquifer only by less than 41 m. Although vertical groundwater recharge can flow through a 13-21 m thick confining layer as indicated by high concentrations of dissolved oxygen, the absence of lateral groundwater recharge from rivers appears to play a more important role on than the presence of vertical recharge from rainfall. High anomaly of redox-sensitive species, appearing as discrete zones in a confined alluvial aquifer, is a result of groundwater/surface-water relations and related groundwater flow dynamics.

Keywords : Groundwater/surface-water relations, Hydrogeochemistry, Groundwater flow, Iron

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CHAPTER 1
INTRODUCTION

1.1 Problem and Significance

High ferrous iron (Fe^{2+}) concentrations, over 0.3 mg/L, are a common groundwater quality problem in a wide range of hydrogeologic settings. A treatment to remove the Fe^{2+} from groundwater is required in many areas, particularly in humid tropical regions. Although it is not toxic to humans or animals, the red staining and associated odor are undesirable. The United States Environmental Protection Agency (1992) set a secondary drinking water standard for Fe^{2+} at 0.3 mg/L.

The chemical composition of groundwater in a groundwater flow system varies in time and space in two ways including: (1) chemical differences between types of flow systems and (2) chemical changes within flow systems. Such variations in hydrogeochemistry are used to categorize a groundwater flow system into zones, referred to as hydrogeochemical facies. Groundwater flow influences the distribution patterns of hydrogeochemical facies because the flow reduces mixing by diffusion, carries the chemical imprints of changes from recharge areas, and leaches the aquifer system (Chebotarev 1955; Back 1966; Williams 1970; Wallick 1981; Fogg and Kreitler 1982; Sanford 1994; Ingebritsen and Sanford 1998; Stuyfzand 1999). Without the groundwater flow, less variety of groundwater compositions would exist because diffusion would reduce the difference by mixing slowly through geologic time (Volker 1961).

Within a regional groundwater flow system, patterns of high Fe^{2+} concentrations remain a controversial subject. Various observations have been presented, including: (1) no trends (Thorstenson et al. 1979), (2) discrete zones (Back and Barnes 1965; Langmuir 1969), (3) decreasing trends toward discharge areas (Champ et al. 1979), and (4) increasing trends toward discharge areas (Tóth 1999). Patterns in a local groundwater flow system are not fully understood either. Modified from Tóth (1963), a local groundwater flow system is defined as a coherent, three-dimensional unit of groundwater flow with one recharge and one or more discharge areas at depths of shallower than 100 m and along a flow path of less than 20 km. The local groundwater flow system can be classified into 3 areas including recharge, transition, and discharge by using a groundwater flow regime (Fig. 1). The groundwater flows from recharge areas through transition areas to discharge areas.

Although high Fe^{2+} concentrations are found commonly in areas far away from recharge sources, lateral patterns of high Fe^{2+} concentrations within the aquifer remain unknown. Vertically, Fe^{2+} concentrations increase toward the depths of 30-40 m but rarely increase beyond these levels (Starr and Gilham 1989; Barcelona et al. 1989; Kehew et al. 1996). An evolutionary trend may not develop along a short flow path of the local groundwater flow system.

In spite of the wide occurrence and environmental impact of the iron-contaminated groundwater, few researchers have attempted to describe causes of anomaly pattern and related evolutionary trend of iron in a confined alluvial aquifer located between two rivers. The contamination of iron in groundwater is a basic natural process but it is embarrassingly difficult to explain its occurrence and evolution.

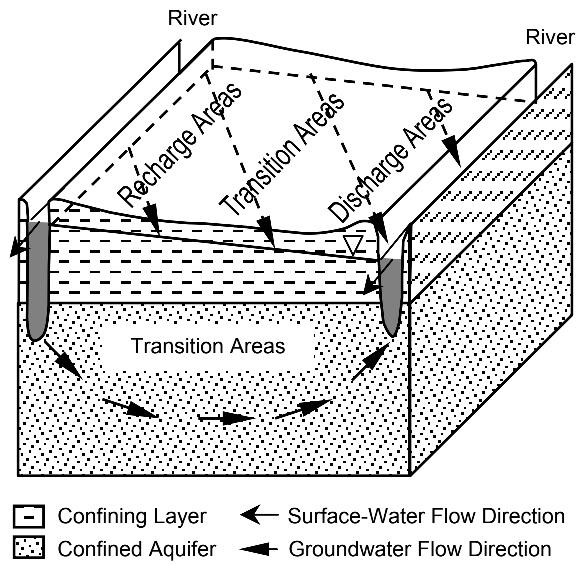

Fig. 1. A confined local groundwater flow system with static streamflows. Rivers act as a constant-head recharge and discharge. Transition areas are located between them. Continuous flow paths exist in the flow system and geochemical evolution develops.

A sequence of redox reactions has been observed during infiltration of oxic river water into the aquifer (von Gunten and Kull 1986; Jacobs et al. 1988; Lensing et al. 1994; Stuyfzand 1989; Bourg and Bertin 1993; Dousson et al. 1997; Groffman and Crossey 1999). Recently, Massmann et al. (2004) has investigated large-scale redox processes in a river recharge aquifer along the Oder River in Germany. At their site, river water permanently infiltrates into the shallow confined aquifer. Reduction processes from oxygen respiration to sulfate reduction dominate the groundwater quality about 3 km from the river. Large-scale (km-scale) redox sequences have also been reported by Lovley and

Goodwin 1988; Chapelle and Lovley 1992; Brown et al. 2000). Reduction of Fe- and Mn-hydroxides leads to high concentrations of iron and manganese.

Groundwater flow dynamics is defined herein as changes of groundwater flow patterns due to seasonal fluctuations of hydraulic heads caused by seasonal fluctuation of surface-water levels and vertical groundwater recharge. A larger-scale exchange of groundwater and surface water is controlled by: (1) the distribution and degree of hydraulic conductivities within the channel and related alluvial sediments, (2) the relation of stream stage to the adjacent groundwater level, and (3) the position and geometry of the stream channel within the alluvial plain (Woessner 2000). The flow direction of the hydrologic interactions depends on hydraulic heads.

Seasonal variant hydrology alters the hydraulic head and thus induces changes in groundwater flow direction. Brunke and Gonser (1997) summarize the interactions between groundwater and rivers. With low precipitation, baseflow in streams contributes the discharge for most of the year. On the other hand, under conditions of high precipitation, surface runoff and interflow increase slowly, causing the river to change from effluent (where groundwater drains into the stream) into influent condition (where surface water contributes to subsurface flow), infiltrating its banks, and recharging the aquifer. During flooding, the river loses water to bank infiltration. The volume of bank storage varies with duration, height, shape of the flood hydrograph, and transmissivity and storativity of the aquifer. In the dry season, the stored water is released into the river. Successive discharge and recharge of the aquifer has a buffering effect on the runoff characteristics of rivers.

This study describes a new finding that river incision into a confined alluvial aquifer results in intriguing groundwater flow dynamics which makes transition areas between two successive rivers isolate from oxygenated river water. Discrete zones of high iron concentrations in transition areas indicate the isolation. Groundwater resource developers can expect to obtain high-iron groundwater in the transition areas of a confined alluvial aquifer located between two rivers.

1.2 Objective

The objective of this research was to study causes of Fe^{2+} anomaly in comparison with groundwater flow dynamics in a local groundwater flow system, which is a confined alluvial aquifer located between two rivers. The distribution pattern of Fe^{2+} concentration anomaly was analyzed in relation to groundwater flow directions and related chemical properties.

1.3 Hypothesis

Can chemical evolution still undergo in a dynamic confined alluvial aquifer located between two rivers? Our answer is no. The hypothesis is that a continuous flow regime is truncated if two successive parallel rivers that incise partially into the confined aquifer have seasonally variant water levels. The truncated flow leads to a lack of oxygenated water from rivers in transition areas. While vertical recharge from rainfall can occur through a confining unit, a lack of lateral recharge plays a more important role. Therefore, the transition areas are isolated from oxic conditions that can be indicated by abnormally high concentrations of some redox-sensitive species such as iron. This anomaly is a result of groundwater flow dynamics rather than the slow chemical evolution.

Fig. 2 shows schematic hypothetical models mentioned above. When groundwater moves slowly from a recharge zone into the aquifer in one season, it transports dissolved oxygen only by tens of meters (Fig. 2a). After the transition into the rainy season, the groundwater and solutes move along other directions by tens of meters and the former recharge zone becomes a discharge area (Fig. 2b). Moving in a zigzag pattern in recharge-discharge areas leads to a lack of dilution-oxidation by oxygenated water from rivers in the transition areas. A lack of lateral oxygenated recharge from the river does influence redox reactions and the availability of redox-sensitive species including oxygen, nitrate, manganese, iron, sulfate, hydrogen sulfide and methane. Iron, which is highly sensitive to dissolved oxygen, is often used to indicate suboxic or anoxic conditions of the aquifer. Therefore, concentrations of dissolved iron are high in the transition areas (Fig. 2c).

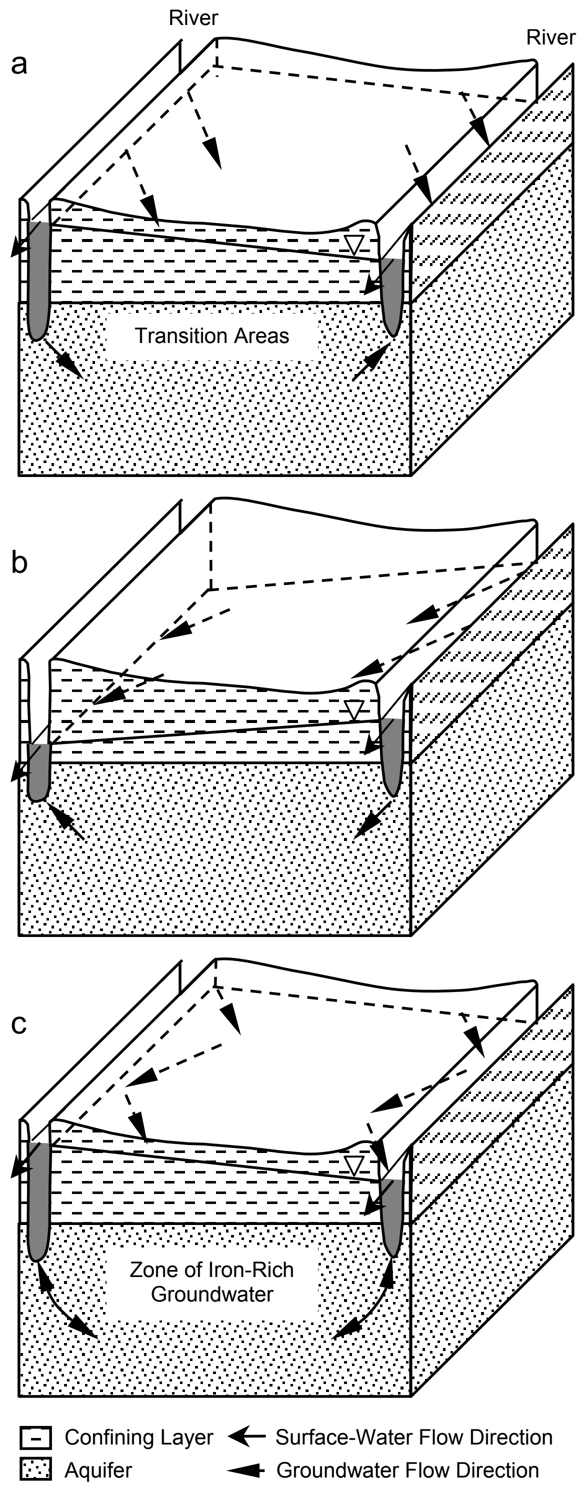
River
River
a
Transition Areas
b
c
Zone of Iron-Rich Groundwater
Confining Layer
Aquifer
Surface-Water Flow Direction
Groundwater Flow Direction

Fig. 2. Schematic hypothetical models of iron accumulation in transition areas of a confined local groundwater flow system between two dynamic streamflows. (a) When one river rises above another, groundwater levels respond quickly and begin a lateral recharge-discharge process. (b) Groundwater flow reversal follows the same process. (c) The resulting flow direction has a zigzag pattern preventing the oxygenated lateral recharge from reaching the transition areas. If vertical recharge from rainfall is less important than a lack of lateral recharge from river, anoxic conditions in the transition areas prevail and they are indicated by anomalously high concentrations of redox species such as iron. This anomaly is a result of groundwater flow dynamics rather than chemical evolution.

CHAPTER 2
LITERATURE REVIEW

2.1 Groundwater Flow Dynamics

The interaction between groundwater and surface water has been studied since the 1960s because of concerns about eutrophication and acid rain (Winter 1995). The growth in research has mushroomed during the 1990s, especially in physical and biogeochemical aspects (Stanley and Jones 2000). Recently, interest in interactions between near-channel and in-channel water, which are important for ecological system near the stream, has been increased greatly (Sophocleous 2002). The spatial and temporal dynamics of groundwater recharge and discharge along active channels in varying geomorphic settings needs further study. Quantification of the dynamic temporal changes of water movements and chemical fluxes through these boundaries is significant (Dahm et al. 1998). An understanding of interactions between groundwater and surface water as well as subsequent groundwater quality is a key for successful integrated management of water resources.

The groundwater flow system depends on hydrogeologic environment including topography, geology, and climate (Tóth 1970). Hubbert (1940) shows that, given a uniform recharge, an unconfined groundwater flow system develops and is influenced by a water table configuration, which is a subdued replica of the land surface. Hydraulic conductivity of aquifers also controls the flow patterns (Freeze and Witherspoon 1967). Groundwater moves along flow paths and form a flow system. Based on a relative position in space, Tóth (1962, 1963) classifies three types of flow systems including local, intermediate, and regional. The local groundwater flow system is defined, in this study, as a coherent, three-dimensional unit of groundwater flow with one recharge and one or more discharge areas at depths of shallower than 100 m and along a flow path of less than 20 km. Fig. 1 shows that a static local groundwater flow system can be classified, into 3 areas including recharge, transition, and discharge. The groundwater flows from recharge areas through transition areas to discharge zones.

Groundwater flow dynamics is defined herein as changes of groundwater flow patterns due to seasonal fluctuations of hydraulic heads caused by seasonal fluctuation of surface-water levels and vertical groundwater recharge. A larger-scale exchange of groundwater and surface water is controlled by: (1) the distribution and degree of hydraulic conductivities within the channel and related alluvial sediments, (2) the relation of stream stage to the adjacent groundwater level, and (3) the position and geometry of the stream channel within the alluvial plain (Woessner 2000). The flow direction of the hydrologic interactions depends on hydraulic heads.

Seasonal variant hydrology alters the hydraulic head and thus induces changes in groundwater flow direction. Brunke and Gonser (1997) summarize the interactions between groundwater and rivers. With low precipitation, baseflow in streams contributes the discharge for most of the year. On the other hand, under conditions of high precipitation, surface runoff and interflow increase slowly, causing the river to change from effluent (where groundwater drains into the stream) into influent condition (where surface water contributes to subsurface flow), infiltrating its banks, and recharging the aquifer. During flooding, the river loses water to bank infiltration. The volume of bank storage varies with duration, height, shape of the flood hydrograph, and transmissivity and storativity of the aquifer. In the dry season, the stored water is released into the river. Successive discharge and recharge of the aquifer has a buffering effect on the runoff characteristics of rivers.

2.2 Hydrogeochemistry of Iron

High concentrations of dissolved Fe^{2+} in groundwater are described in terms of equilibrium thermodynamics and microbial-involved redox reactions. The main sources of Fe^{2+} in groundwater are (1) the dissolution products of iron-bearing minerals, (2) the reduction of Fe(III) oxyhydroxides in sediments, and (3) the oxidation of Fe(III) by microorganisms (Chapelle and Lovley 1992; Appelo and Postma 1993; Chapelle 1993). Prior to 1985, most hydrogeochemists considered Fe(III) reduction to be an abiotic reaction initiated by reducing conditions (Lovley et al. 1991). Under anaerobic conditions with decreasing redox potential, thermodynamics analysis indicates that the iron occurs as Fe (III) oxyhydroxides, carbonate siderite, and ferrous sulfides (Back and Barnes 1965; Langmuir 1969; Langmuir 1997).

The iron is mobile in vadose and groundwater zones under specific conditions (Langmuir 1997). In oxidized groundwater, dissolved iron is mobile below about pH 3 to 4 as Fe^{3+} and Fe(III) inorganic complexes. Fe(III) is also mobile in many soils and groundwaters as ferric-organic (humic-fulvic) complexes up to pH 5 to 6 and as colloidal ferric oxyhydroxides between about pH 3 to 8. Under reducing conditions, the iron is soluble and mobile as Fe^{2+} below about pH 7 to 8. It usually occurs as uncomplexed Fe^{2+} ion. However, when sulfur is present and sulfate reduction is dominant, Fe^{2+} precipitates as sulfides. Therefore, the high-iron groundwater reflects the reduction of poorly soluble Fe (III) oxyhydroxides to the highly soluble ferrous state. High-iron groundwater develops only if there is little or no sulfate reduction in the aquifer because the sulfide generation tends to precipitate Fe^{2+} as iron sulfides (Berner 1969). The sulfate reduction is observed if Fe(III) oxyhydroxides in aquifer materials are depleted (Ponnamperuma 1972; Froelich et al. 1979; Reeburgh 1983). Fe(III) is usually complex, whereas Fe^{2+} occurs uncomplexed in most groundwaters.

Microorganisms also play an important role in the oxidation of Fe^{2+} and the reduction of Fe(III). The first microorganism known to reduce Fe(III) was isolated in 1987 (Lovley and Phillips 1988). For groundwater, the Fe(III)-reducing microorganisms were isolated and characterized two years later (Lovley et al. 1989). This strain was name "172", as isolated from a 172-ft-deep core. It is a short blunt rod. Another microorganism is GS-15, which is an elongated rod. Fe(III) oxyhydroxides are reduced under anaerobic conditions to Fe^{2+} by *Shewanella putrefaciens* and the Fe^{2+} is mobilized. Some Fe^{2+} enter the anaerobic portion of aquifers and remains in the groundwater.

The accumulation of dissolved iron in groundwater represents a truncation of the iron cycle (Chapelle 1993). When the Fe(III) reduction occurs at the interface of an anaerobic and anaerobic zone, there is the possibility that some Fe^{2+} produced will be cycled back to Fe(III) oxyhydroxides. In many aquifers, however, Fe(III) reduction occurs where molecular oxygen is absent and there is no possibility of reoxidation. Thus, the dissolved Fe^{2+} may accumulate in solution, causing high-iron concentrations in groundwater. The truncation of the iron cycle due to the lack of iron reoxidation is an important mechanism leading to the accumulation of iron in groundwater.

2.3 Evolution of Iron in Groundwater Flow Systems

The groundwater flow system is defined as a coherent, three-dimensional unit of groundwater flow with one recharge and one or more discharge areas (Tóth 1963; Engelen and Jones 1986). It is classified into regional, intermediate, and local using decreasing dimensions in the landscape. In this study, a local groundwater flow system is defined as a coherent, three-dimensional unit of groundwater flow with one recharge and one or more discharge areas at depths of shallower than 100 m and along a flow path of less than 20 km. During its initial stages, an aquifer is occupied by groundwater of different origins. Recharge waters displace relic groundwater and the aquifer become mature hydrogeochemically (Stuyfzand 1999).

The chemical composition of groundwater in the groundwater flow system varies in time and space in two ways including: (1) chemical differences between types of flow systems and (2) chemical changes within flow systems. Such variations in hydrogeochemistry are used to categorize a groundwater flow system into zones, or called hydrogeochemical facies. Groundwater flow influences hydrogeochemical patterns because the flow reduces mixing by diffusion, carries the chemical imprints of changes in recharge areas, and leaches the aquifer (Back 1966; Williams 1970; Galloway 1978; Wallick 1981; Fogg and Kreitler 1982; Shipovalov 1984; Back et al. 1988; Sanford 1994; Raffensperger and Garven 1995; Engelen and Kloosterman 1996; Ingebritsen and Sanford 1998). Without the groundwater flow, less variety of groundwater compositions would exist because diffusion would reduce the difference by mixing slowly through geologic time (Volker 1961; Ranganathan and Hanor 1987).

Chebotarev (1955) first recognized that groundwater tends to chemically evolve in long flow systems toward a more concentrated solution similar to the composition of sea water; that is, from bicarbonate and sulfate to chloride. These systematic changes in anion composition in aquifers are known as Chebotarev sequence. Cation evolutionary sequences are more variable than anion sequences because of ion exchange, precipitation, and other chemical processes (Kehew 2001). Later, hydrogeologists observed the evolution of hydrogeochemical patterns in the direction of groundwater flow as follows:

1. From strong to no fluctuations in water quality (Stuyfzand 1999),
2. From oxic to anoxic-methanogenic (Froelich et al. 1979; Champ et al. 1979),
3. From acidic to basic (Tóth 1999),
4. From no to significant base exchange (Stuyfzand 1999),
5. From low to high total dissolved solids (Edmunds et al. 1982), and
6. From fresh to brackish (Hardie and Eugster 1978; Jankowski and Jacobson 1989).

Complicated evolution patterns arise where groundwater is contaminated by a point source; that is, concentrations of contaminant decrease in the direction of groundwater flow. Other inversions may be as follows (Stuyfzand 1999):

1. Raised water tables in recharge areas, which convert former oxic and suboxic into anoxic conditions in the water-table domain, or

2. The deposition of clayey sediments on decalcified oxygenated aquifer in its recharge areas; therefore, restoring reducing and acid neutralizing phases that interact with shallow groundwater.

The chemical composition of groundwater in the groundwater flow system is a function of following factors (White 1957; Freeze and Cherry 1979; Palmer and Cherry 1984; Stuyfzand 1999; Kehew 2001):

1. Water origin,
2. Flow patterns,
3. Recharge composition and rate,
4. Interaction with the atmosphere, biosphere, and lithosphere,
5. Anthropogenic contamination, and
6. Temperature and pressure.

In a local groundwater flow system, lithologic heterogeneity affects an evolution of hydrogeochemistry. For uniform lithology, very little change in hydrogeochemistry may take place (Kehew 2001). Vigorous flow flushes dissolved mineral salts out of the aquifer in a relatively short period of time. As a result, the groundwater may never progress past the bicarbonate hydrogeochemical facies in the Chebotarev sequence. If carbonate minerals are present, equilibration may occur under open-system conditions in the vadose zone. Few changes occur after the water reaches the water table and moves through the aquifer to discharge areas. If the aquifer mineralogy changes, corresponding water chemistry changes will be noticed. The order of encounter of various rock types is the critical factor that controls the water quality (Palmer and Cherry 1984).

Fe^{2+} is occurred near a water table and is then transported in the aquifer. The most obvious control on Fe^{2+} concentrations in groundwater is by oxidation to Fe(III) and precipitation as Fe(III) oxyhydroxides. Above the water table, Fe^{2+} in iron-bearing minerals in soil horizons O and A is leached by infiltrating water and is accumulated as Fe (III) in the B horizon. From the B horizon to areas near the water table, infiltrating soil water and microorganisms react with Fe(III) oxyhydroxides and bring dissolved Fe^{2+} into the aquifer system. Also, bands of Fe-oxyhydroxides can form near the water table (Appelo and Postma 1993). Within the aquifer, Fe(III) oxyhydroxides may control the solubility of dissolved Fe^{2+}. However, in high Fe^{2+} groundwater, siderite may become an alternative solubility control of Fe^{2+} (Whittemore and Langmuir 1975; Nesbitt 1980; Margaritz and Luzier 1985; Morin and Cherry 1986; Morse et al. 1987). The produced Fe^{2+} may apparently be transported along groundwater flow paths (Langmuir and Whittemore 1971; Whittemore and Langmuir 1975).

The evolution of high Fe^{2+} in a groundwater flow system is ambiguous. Hydrogeologists recognize different regional patterns of groundwater composition in the regional groundwater flow system but study none in a local scale. Finding includes:

1. Trends of high Fe^{2+} concentrations may not exist (Thorstenson et al. 1979),
2. High Fe^{2+} concentrations may exist as discrete zones (Back and Barnes 1965; Langmuir 1969; Speiran 1987),
3. Fe^{2+} concentrations may decrease toward discharge areas (Champ et al. 1979),
4. Fe^{2+} concentrations may increase toward discharge areas (Tóth 1999), and

5. Fe^{2+} concentrations may increase from recharge areas to transition areas but may decrease from the transition areas to discharge areas (Chapelle and Lovley 1992; Appelo and Postma 1993).

With no explanation, Fe^{2+} shows increasing concentrations toward the depths of 30-40 m but do not increase beyond these levels (Starr and Gilham 1989; Barcelona et al. 1989; Kehew et al. 1996). Lateral evolutionary trends of high Fe^{2+} concentrations are not fully understood.

A sequence of redox reactions has been observed during infiltration of oxic river water into the aquifer (von Gunten and Kull 1986; Jacobs et al. 1988; Lensing et al. 1994; Stuyfzand 1989; Bourg and Bertin 1993; Dousson et al. 1997; Groffman and Crossey 1999). Recently, Massmann et al. (2004) has investigated large-scale redox processes in a river recharge aquifer along the Oder River in Germany. At their site, river water permanently infiltrates into the shallow confined aquifer. Reduction processes from oxygen respiration to sulfate reduction dominate the groundwater quality about 3 km from the river. Large-scale (km-scale) redox sequences have also been reported by Lovley and Goodwin 1988; Chapelle and Lovley 1992; Brown et al. 2000). Reduction of Fe- and Mn-hydroxides leads to high concentrations of iron and manganese.

2.4 Groundwater Models

Groundwater models can be classified by their application into 3 types including groundwater flow, contaminant transport, and hydrogeochemical model. The groundwater flow model, such as MODFLOW (McDonald and Harbaugh 1988), is used to determine groundwater levels and flow directions under specific scenarios. The contaminant transport model, such as MT3DMS (Zheng and Wang 1999), is used to identify concentrations of solutes in space and time. The hydrogeochemical model, for example PHREEQC (Parkhurst and Appelo 1999), is used to calculate speciation and saturation states of groundwater. Many groundwater models are reviewed and tested (Nordstrom et al. 1979; Grove and Stollenwerk 1987; Nordstrom et al. 1990; Mangold and Tsang 1991). Models used in this study include MODFLOW (McDonald and Harbaugh 1988) and MODPATH (Pollack 1994a,b) in Groundwater Vistas (Environmental Solutions Inc 2001) and PHREEQC (Parkhurst and Appelo 1999) in AquaChem (Waterloo Hydrogeologic Inc 2003).

MODFLOW, which is available at http://water.usgs.gov/software/modflow.html, is a three-dimensional, finite-difference, numerical, groundwater flow model (Harbaugh et al. 2000). It is currently the most used numerical flow model for groundwater problems. It has been developed continuously since 1984 (McDonald and Harbaugh 1988; Harbaugh and McDonald 1996a, b; Harbaugh et al. 2000). A modular structure allows it to be easily modified to adapt codes for a particular application, called package. The current version of MODFLOW-2000 has 26 packages. This code simulates steady-state and transient flow in confined, unconfined, or a combination of both aquifers. Hydraulic conductivities and storage coefficients for any layer may differ spatially. In addition to simulating groundwater flow, MODFLOW-2000 is able to incorporate related capabilities including sensitivity analysis and parameter estimation (Hill et al. 2000).

The MODFLOW code is regularly upgraded and is well documented, for example:

1. Converting no-flow cells to variable-head cells (McDonald et al. 1992),
2. Addition of alternate interblock transmissivities (Goode and Appel 1992),
3. Preconditioned conjugate gradient package (Hill 1990),
4. Streamflow-routing package (Prudic 1989),
5. Time-variant specified-head package (Leake and Prudic 1991),
6. Horizontal-flow barrier package (Hsieh and Freckleton 1993),
7. Direct solution package (Harbaugh 1995),
8. Leakage from reservoirs (Fenske et al. 1996),
9. Assignment of transient specified-flow and specified-head boundaries (Leake and Lilly 1997),
10. Advective-transport observation package (Anderman and Hill 1997, 1998),
11. Enhancing calibration (Hill 1998),
12. Extracting and processing time-series data (Hanson and Leake 1999),
13. Simulation of aquifer-system compaction (Leake and Prudic 1991),
14. Hydrogeologic-unit flow package (Anderman and Hill 2000),
15. Simulation of lake-aquifer interaction (Merritt and Konikow 2000),
16. Simulating evapotranspiration with a segmented function and drains with return flow (Banta 2000),

17. Solving matrix equations using an algebraic multigrid solver (Mehl and Hill 2001), and
18. Linkage with MT3DMS code (Zheng et al. 2001).

Groundwater Vistas (Environmental Solutions Inc 2001) is a graphic-user-interface software package that combines flow (MODFLOW) and particle tracking (MODPATH) models. MODPATH, which is available at http://water.usgs.gov/software/modpath.html, is a particle tracking post-processing program designed to work with MODFLOW (Pollock 1994a,b). Output from MODFLOW simulations was used in MODPATH to compute flow paths for imaginary particles of water moving through the simulated groundwater system. It also kept track of the time of travel for particles moving through the system. Previous versions of MODPATH are described in Pollock (1989a,b).

MODPATH is written primarily in standard Fortran 77 and can be compiled with any standard Fortran 90 compiler. The MODPATH package has been widely applied to MODFLOW-based groundwater flow simulation studies. It is useful as a visualization tool to help understand flow patterns in simulated groundwater flow systems. It also has been widely used to delineate sources of water to discharge sites and aquifers in systems simulated with MODFLOW. MODPATH has a number of limitations, which are related to (1) underlying assumptions in the particle tracking scheme, (2) discretization effects, and (3) uncertainty in parameters and boundary conditions.

MT3DMS is a numerical contaminant-transport model that consists of a comprehensive set of options and capabilities for simulating advection, hydrodynamic dispersion, and chemical reactions of contaminants in groundwater (Zheng and Wang

1999). MT3DMS stands for the Modular 3-Dimensional Transport model with Multi-Species structure. It was originally developed at SS Papadopulos & Associates Inc, and documented later for the Robert S. Kerr Environmental Research Laboratory of the US Environmental Protection Agency (Zheng 1990; Zheng and Bennett 2002). MT3DMS can be linked to MODFLOW-2000 using the LMT6 package (Zheng et al. 2001). The MT3DMS code and its predecessor have been used in many studies of contaminant transport and remediation (Johnson et al. 1994; Poeter and McKenna 1995; Hahn 1996; Hyndman and Gorelick 1996; Huang and Mayer 1997; Lessoff and Konikow 1997; Wang and Zheng 1997; Eggleston and Rojstaczer 1998; Loague et al. 1998; Sawyer and Lieuallen-Dulam 1998; Zhan and McKay 1998; Zheng and Jiao 1998; Aly and Peralta 1999a, b; Katz and Gvirtzman 1999; Lu et al. 1999; Holder et al. 2000; Hyndman et al. 2000; and Woessner 2000).

PHREEQC is a numerical hydrogeochemical model based on an ion-association aqueous model (Parkhurst and Appelo 1999). It is capable of (1) calculating activities and saturation states for a given groundwater analysis, (2) calculating how water composition changes in response to reactions or a change in temperature, and (3) testing a concept or a suite of reactions for a hydrogeochemical hypothesis (Plummer et al. 1988; Plummer et al. 1991; Plummer et al. 1994; Charlton et al. 1997). The hydrogeochemical model is developed from space-rocket science and has been used in many case studies (Smith and Missen 1982; Parkhurst and Plummer 1993; Appelo and Postma 1993; Bethke 1996). It prevents errors or violations of basic chemical laws. The mass action and mass balance relationship gives a set of non-linear equations for which a solution can be obtained using

Newton-Raphson iteration. The hydrogeochemical models have been used to study the evolution of water quality as influenced by:

1. Silicate weathering (Helgeson et al. 1970; Lichtner 1985)
2. Carbonate reactions (Plummer et al. 1983)
3. Effects of acidification and buffering reactions (Cosby et al. 1985)
4. Ore deposition and leaching of mine tailings (Garven and Freeze 1984; Liu and Narasimhan 1989)
5. Cation exchange with salt-water intrusion (Appelo and Willemsen 1987; Appelo et al. 1990)
6. Complexation of heavy metals and sorption (Felmy et al. 1984)
7. Denitrification (Postma et al. 1991).

The PHREEQC code and its predecessor have been used in many studies (Parkhurst et al. 1980; Appelo and Willemsen 1987; Mirecki and Parks 1993; Nordstrom 1996; Alpers and Nordstrom 1999; Gimeno Serrano et al. 2000; Nordstrom 2000; Welch et al. 2000).

AquaChem is another software package that interacts users with PHREEQC (Waterloo Hydrogeologic Inc 2003). It is developed for graphical display and numerical analysis and modeling of water quality data. AquaChem's data analysis capabilities include unit conversions, charge balances, sample comparison and mixing, statistical summaries, trend analysis, and relevant plotting to represent the chemical characteristics of water quality data, among others.

The plot types available in AquaChem include:

1. Correlation plots: X-Y Scatter, Ludwig-Langelier, and Wilcox
2. Summary plots: Box and Whisker, Frequency Histogram, and Schoeller
3. Trilinear plots: Piper, Durov, Ternary, and Giggenbach
4. Time-Seriesplot
5. Geothermometer plot
6. Sample plots: Radial, Stiff, and Pie
7. Thematic Map plots: Bubble, Pie, Radial and Stiff plots at sample locations

Each of these plots provides a unique interpretation of the many complex interactions between the groundwater and aquifer materials, and identifies important data trends and groupings. AquaChem also has a link to PHREEQC for calculating equilibrium concentrations (or activities) of chemical species in solution and saturation indices of solid phases in equilibrium with a solution.

CHAPTER 3
RESEARCH METHODOLOGY

3.1 Testing Site

The study area is located about 20 km from the City of Phitsanulok, lower northern Thailand. Fig. 3 shows that the site is located inside a half-graben Tertiary structure (Wongsawat and Dhanesvanich 1983). Pre-Tertiary rocks form a basement with 1-2 km deep at the bottom. The Quaternary aquifer sediments overly semi-consolidated Tertiary ones.

Fig. 4 shows a cross-section which is based on detailed hydrogeologic investigation in this study. The aquifer is continuous, heterogeneous, and confined. It is the upper part of Chao Phraya aquifer, an alluvial deposit of channel-filled sand and gravel (Department of Mineral Resources 2001). The aquifer thickness varies from 13 to 21.5 m. A continuous clay layer, 13-21 m thick, overlies the aquifer. The underlying confining layer is also continuous. There are 8 gravel lens inside the aquifer. The Nan and Yom Rivers cut through the top of the aquifer and lens of fine-grained sand that connects to the aquifer. Therefore, the groundwater is highly interactive with surface-water bodies in both rivers. The aquifer yields at least 1,056 m^3/d of groundwater. Based on Cooper and Jacob (1946), the transmissivity and storage coefficient of the aquifer, measured in this study, are 1,988 m^2/d and $3.3x10^{-4}$, respectively (Fig. 5 and Table 1).

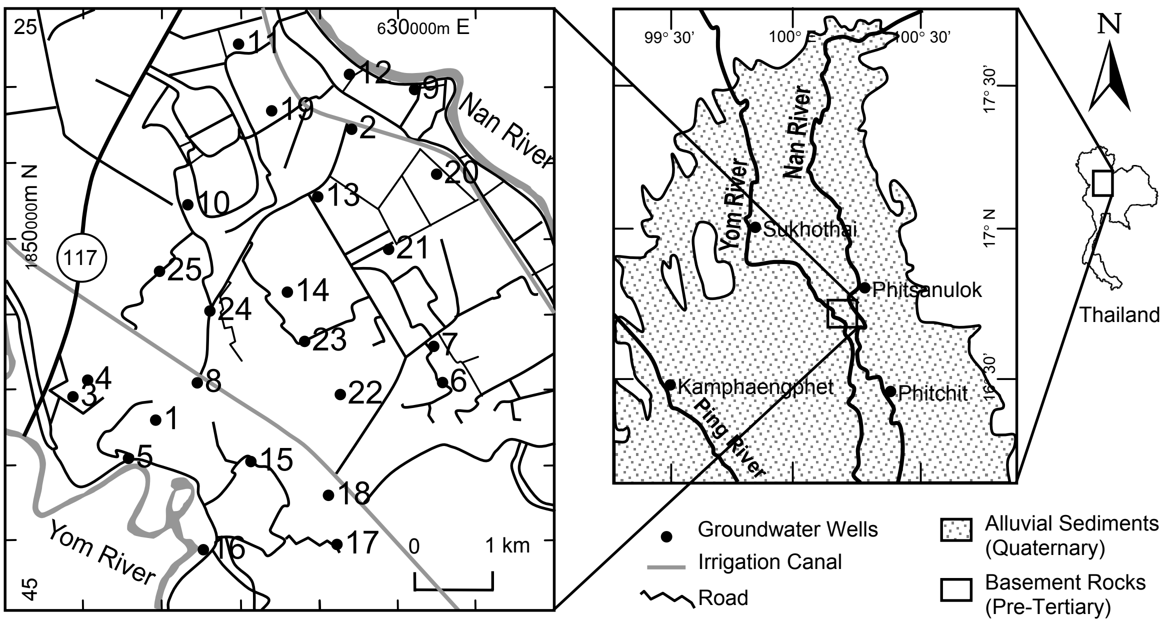

Fig. 3. Location of the study area in Phitsanulok, lower northern Thailand. The Nan River binds the aquifer in the east and the Yom River in the west. Both rivers flow southward. Wells used to test the hypothesis are sufficiently distributed between both rivers.

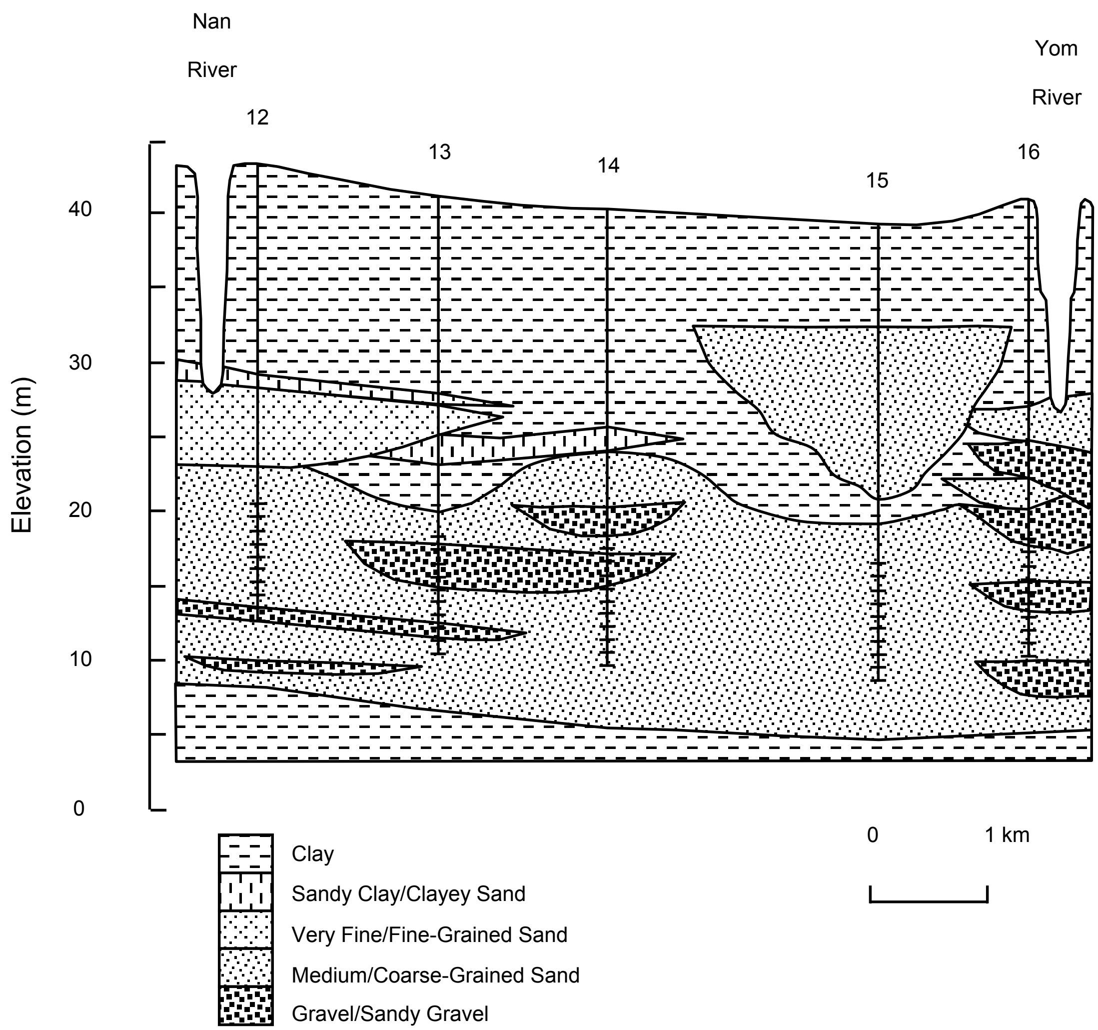

Fig. 4. Geologic cross-section. The aquifer is confined, continuous, and heterogeneous. It is bound in the top and the bottom by continuous confining units. Rivers cut through the top of the aquifer but they penetrate into it only slightly.

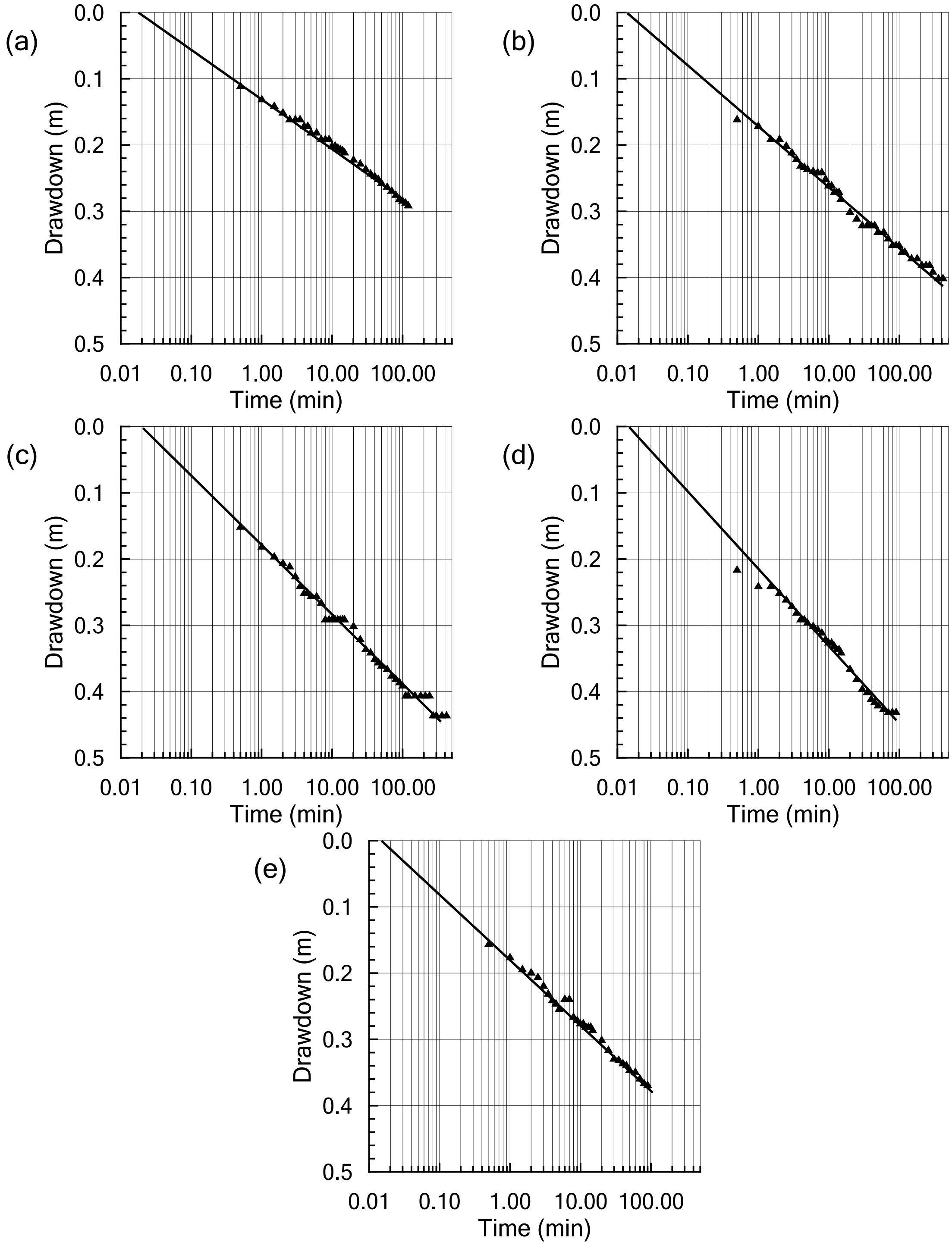

Fig. 5. Time-drawdown curves. Well 13 (b) is an observation well (11.6 m away from a pumping well). A single-well method was applied to Wells 12 (a), 14 (c), 15 (d), and 16 (e). An average transmissivity is 1,988 m^2/d. The storage coefficient is $3.3x10^{-4}$.

Table 1

Aquifer hydraulic properties

Well No.	Minimum Yield (m^3/hr)	Transmissivity (m^2/day)	Hydraulic Conductivity (m/day)	Storage Coefficient (unitless)
12	38.79	2,273	156.8	–
13	41.95	2,026	155.8	3.3×10^{-4}
14	44.37	1,931	104.4	–
15	43.98	1,790	123.4	–
16	44.13	1,920	89.3	–
Avg.	42.64	1,988	125.9	3.3×10^{-4}

Three reasons make the area ideal for testing of the hypothesis. Firstly, the flow direction of the Nan and Yom Rivers are nearly parallel, approximately southward. Secondly, the spacing between the rivers is appropriate, about 6-7 km. Finally, both rivers incise slightly into the confined alluvial aquifer. As measured at gauging stations upstream and downstream to the study area in 2002, their riverbeds are located about 12-15 m deep below the land surface or about 2-5 m of penetration (Royal Irrigation Department, unpublished data).

3.2 Groundwater Flow Dynamics

This study analyzes the groundwater from 25 wells located between the Nan and Yom Rivers (Fig. 3). The wells intersect the same aquifer at similar elevations (Fig. 4). Groundwater levels at Wells 12-16 were recorded weekly. Then, flow nets were drawn to study groundwater flow patterns, seasonal variation, and recharge-discharge relationships.

3.3 Groundwater Sampling and Analysis

Major groundwater sampling took place in the dry season (March-April 2003) with a minor follow-up sampling for iron in rainy season (September 2003). The sampling for river water was also carried out later for comparison of the iron, dissolved oxygen, and redox potential with the groundwater. A flow-cell method (Kehew 2001) was used to obtain groundwater samples and to measure field parameters including temperature (T), specific conductance (SC), dissolved oxygen (DO), pH, and redox potential (Eh). Eh was carefully measured by using the Wood Method (Wood 1976). A bottle of Zobell's solution for Eh measurements was brought to sample temperature before reading. The Eh combination electrode consists of a platinum-sensing electrode connected to a reference electrode, which is made of silver enclosed in silver-chloride solution.

The groundwater was collected and preserved by using standard procedures and methods as described by American Public Health Association et al. (1998). Quality assurance samples were collected by duplicate sampling every 10 samples. The groundwater samples were unfiltered because the flow cell helps avoid the air exposure. The samples were collected almost inline and were preserved by nitric acid immediately after filling the bottle. Filtering can cause underestimation of iron concentrations. However, the river water samples were filtered with 0.45 μm membrane filters to exclude precipitates of Fe- and Mn-oxyhydroxides, which were formed by oxidation, as well as suspended clays. Samples for cation analysis were preserved with concentrated nitric acid. Alkalinity and sulfide samples were carefully filled without air entrapment and analyzed immediately in the laboratory. The remaining samples were transported and stored at 4° C.

The chemical analysis was generally performed within one day after sampling. Table 2 shows parameters analyzed include total dissolved solids (TDS), sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), chloride (Cl^-), bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), sulfate (SO_4^{2-}), sulfide (S^{2-}), nitrate-N (NO_3^-), nitrite-N (NO_2^-), ammonia-N (NH_3), silica (SiO_2), iron (Fe^{2+}), and manganese (Mn^{2+}). Alkalinity was determined by titration. Then, HCO_3^- and CO_3^{2-} were calculated. Water samples were analyzed for Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, and Mn^{2+} by atomic adsorption spectrophotometer. The ferrous iron was then cross checked from the total iron by using a formula described by Freeze and Cherry (1979). TDS was obtained by drying at 180° C. Chloride was identified using mercuric nitrate method. Sulfate was measured using turbidimetric method. The S^{2-}, NO_3^-, and NO_2^- were analyzed by ion chromatography while NH_3 by nesslerization. Silica was analyzed by molybdosilicate method.

3.4 Interpretation of Iron Anomaly

Laboratory analyses were evaluated for reliability using charge balance (Appelo and Postma 1993) and quality assurance sample. Then, concentrations of iron and other parameters were drawn on a map and were superimposed by groundwater flow directions at the time of sampling to analyze for the effects of groundwater flow dynamics on redox conditions, particularly in transition areas. A Piper diagram was drawn to identify hydrogeochemical facies. Relationships among Fe^{2+} and other chemical species were also investigated.

Table 2

Standard methods for groundwater analysis

Parameters	Methods of Analysis
TDS	2540C[1] Dried at 180° C
Na^{+}	3500B AAS[2]
K^{+}	3500B AAS
Ca^{2+}	3500B AAS
Mg^{2+}	3500B AAS
Cl^{-}	4500C Mercuric Nitrate
HCO_3^{-}	2320B Titration
CO_3^{2-}	Calculation
SO_4^{2-}	4500E Turbidimetric
S^{2-}	4500F Iodometric
NO_3^{-}	4500E Cadmium Reduction
NO_2^{-}	4500B Colorimetric
NH_3	Nesslerization
SiO_2	4500D Molybdosilicate
Fe^{2+}	3500B AAS
Mn^{2+}	3500B AAS

[1]Code of methods in American Public Health Association et al. (1998)

[2]Atomic adsorption spectrophotometer

3.5 Speciation

PHREEQC (Parkhurst and Appelo 1999) in AquaChem version 4.0 (Waterloo Hydrogeologic Inc 2003) was used to study speciation of the groundwater. PHREEQC calculates equilibrium activities of chemical species in solution and saturation indices of solid phases in equilibrium with the groundwater. The Saturation Index (SI) of a selected mineral phase is the degree of saturation, which was used as a means to determine if certain minerals have a tendency to dissolve into or precipitate out of the groundwater in order to reach equilibrium. It is calculated as follows:

$$SI = \log(IAP/KT) \quad (1)$$

where IAP = the ion activity product for the given material, KT = the reaction constant at the given temperature

If SI > 0, then the solution is super-saturated with respect to the mineral phase, and precipitation will be likely. If SI < 0, then the solution is below saturation of the specified mineral phase and dissolution will be expected. If SI = 0, then the solution is in equilibrium with the specified mineral phase.

3.6 Simulation of Groundwater Flow Patterns

MODFLOW and MODPATH models were used to simulate transient groundwater flows between two dynamic rivers for a period from January to December 2003. Design criteria were followed those described by Anderson and Woessner (1992) and Zheng and Bennett (2002). Fig. 2 was redrawn into a simple conceptual model. Groundwater flow directions and corresponding travel times are described in Fig. 9 and Table 4. These data were used to perform model calibration and to set stress periods and subsequent time steps.

Fig. 6 shows the conceptual model of a single aquifer with a constant 15 m thickness. The domain was assumed to be homogeneous and isotropic. Rivers act as a constant head whereas the groundwater source occurs at the northwest boundary and the sink is located on the other end. Constant heads of rivers were changed in 4 scenarios to accommodate the groundwater flow dynamics. Vertical recharge from rainfall was assumed to have a constant rate over the entire domain. The bottom of the domain is a no-flow boundary.

Groundwater Vistas version 3 (Environmental Solutions Inc 2001) was used to simulate groundwater flow paths in this study. This software used a modified version of MODFLOW (McDonald and Harbaugh 1988) to solve the groundwater flow equation and used MODPATH version 3 (Pollock 1994a,b) to solve for zigzag flow paths. Output from MODFLOW simulations was used in MODPATH to compute flow paths for imaginary particles of water moving through the simulated groundwater system.

A regularly spaced, finite-difference model grid was constructed and rotated so that the x-axis would roughly parallel the principal direction of groundwater flow (Fig. 7). Each cell is 200 m × 200 m in the horizontal plane. The grid consists of 50 rows and 35 columns. The rotation angle from the North is clockwise 73 degrees. The model rows are

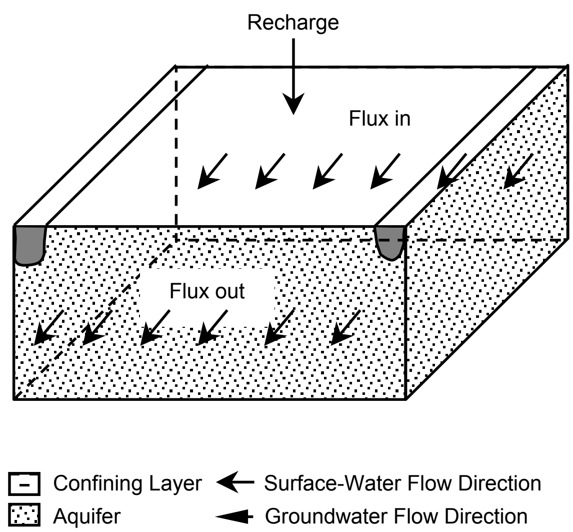

Fig. 6. Conceptual model. The model has a single aquifer with a constant 15 m thickness. The domain is assumed to be homogeneous and isotropic. Rivers act as a constant head whereas the groundwater source occurs at the northwest boundary and the sink is located on the other end. Vertical recharge from rainfall was assumed to have a constant rate over the entire domain. The bottom of the domain is a no-flow boundary.

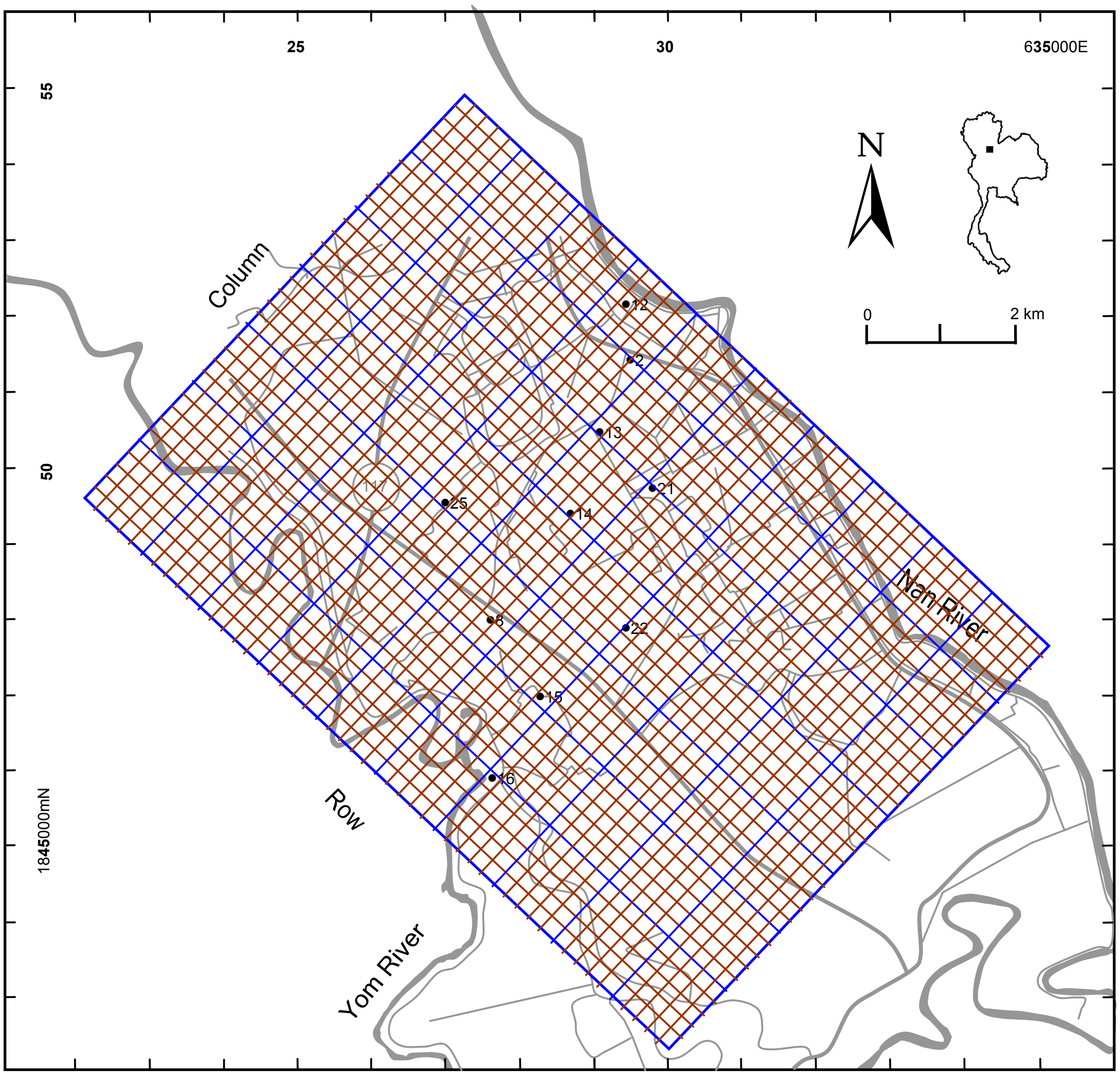

Fig. 7. Grid design and boundary conditions. A regularly spaced, finite-difference model grid was constructed and rotated so that the x-axis would roughly parallel the principal direction of ground-water flow. Each cell is 200 m × 200 m in the horizontal plane. The grid consists of 50 rows, 35 columns, and 4 layers. Rivers are located in the first layer.

aligned with the principal direction of groundwater flow. A simulation stress period of one year was discretized into 4 scenarios. For each scenario, parameters are assumed to be constant. Each stress period is divided into time steps, the lengths of which are determined by Groundwater Vistas to meet specified criteria related to solving the governing equation. About 20 time steps were required for each stress period. Parameters were assigned to the model as simply as possible to minimize complexity and runtimes. Table 3 shows these parameters.

Table 3

Assignment of model parameters

Scenarios and Parameters	Values
Simulation Type	Transient
Aquifer Type	Confined, Homogeneous, Isotropic
Number of Cells	7,000
Number of Layers	4
Number of Rows	50
Number of Columns	35
Spacing along Rows (DELR) (m)	200
Spacing along Columns (DELC) (m)	200
Aquifer Thickness (m)	15
Bottom Elevation (m)	7 (Flat)
Hydraulic Conductivity (m/day)	133
Storage Coefficient (dimensionless)	0.00033
Boundary Conditions	
1. No Flow	All boundaries except rivers and top
2. Constant Head	Rivers (Varied),
3. Variable Head	All others
Initial Head (m)	100
Recharge Flux (m/day)	1.4×10^{-6}

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Groundwater Flow Dynamics

Fluctuation of groundwater levels depends on surface-water levels. Fig. 8 illustrates that groundwater levels near the Nan River (Well 12) are highly fluctuated. They are fairly stable in dry season and slightly increase in rainy season. In contrast, groundwater levels near the Yom River (Wells 16) drop in dry season but rapidly rise in rainy season. This feature responds to river-water levels. In transition areas (Wells 13, 14 and 15), groundwater levels, however, change slowly indicating that the role of river flow dynamics is less significant. Groundwater levels in all areas reach their peaks by the end of rainy season in late September-early October.

Seasonally variant hydraulic head in rivers is a predominant factor that controls the groundwater flow directions of the confined alluvial aquifer. Potentiometric surface is not a subdued replica of the land surface at all time. River flow dynamics changes groundwater flow directions continuously, particularly in areas near the rivers. Fig. 9 shows that the Nan and Yom Rivers flow southeastward. From January 27 (mid dry season) to June 3 (early rainy season), groundwater has flown continuously from the Nan River to the Yom River along 17° SW with a flow path of 15.2 m (Figs. 8a and 9a). From June 4 to October 4 (early dry season), the Yom River has begun to recharge into the aquifer along 80° NE with a flow path of 35 m while the Nan River is still recharging the

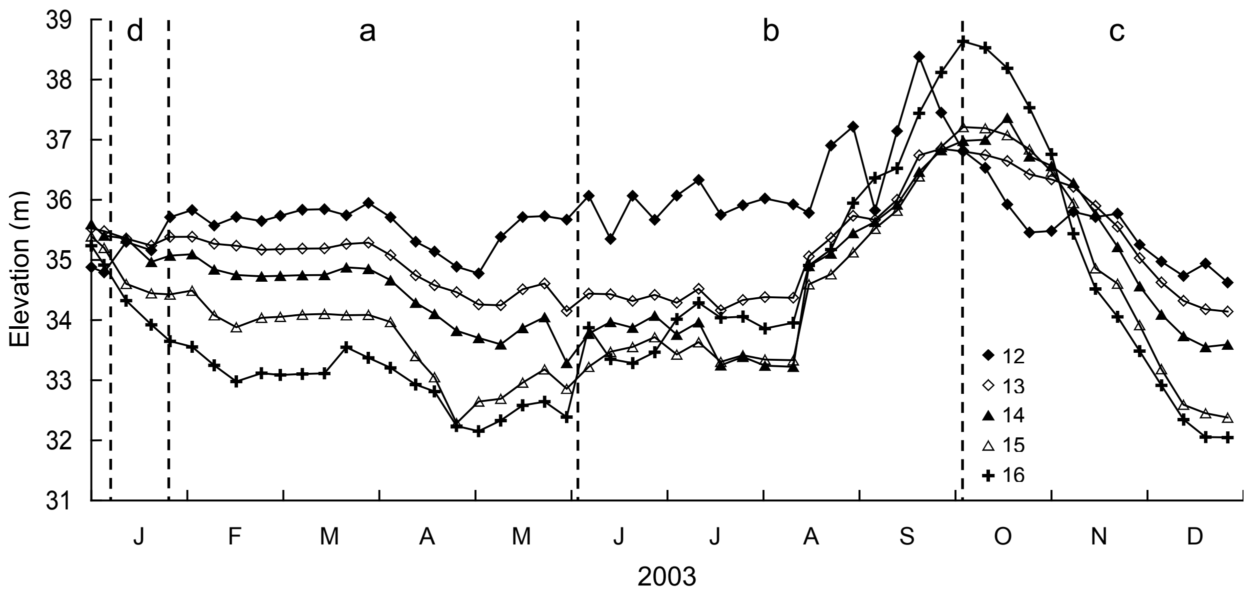

Fig. 8. Seasonal fluctuation of groundwater levels. (a) In the mid-late dry season, groundwater levels near the Yom River decline rapidly and the aquifer discharges into the Yom River. (b) The Yom River begins to recharge into the aquifer in the rainy season. (c) After groundwater levels approach their peaks in the late rainy season, the aquifer discharges into the Nan River. (d) Finally, groundwater mounds in transition areas recharge both rivers.

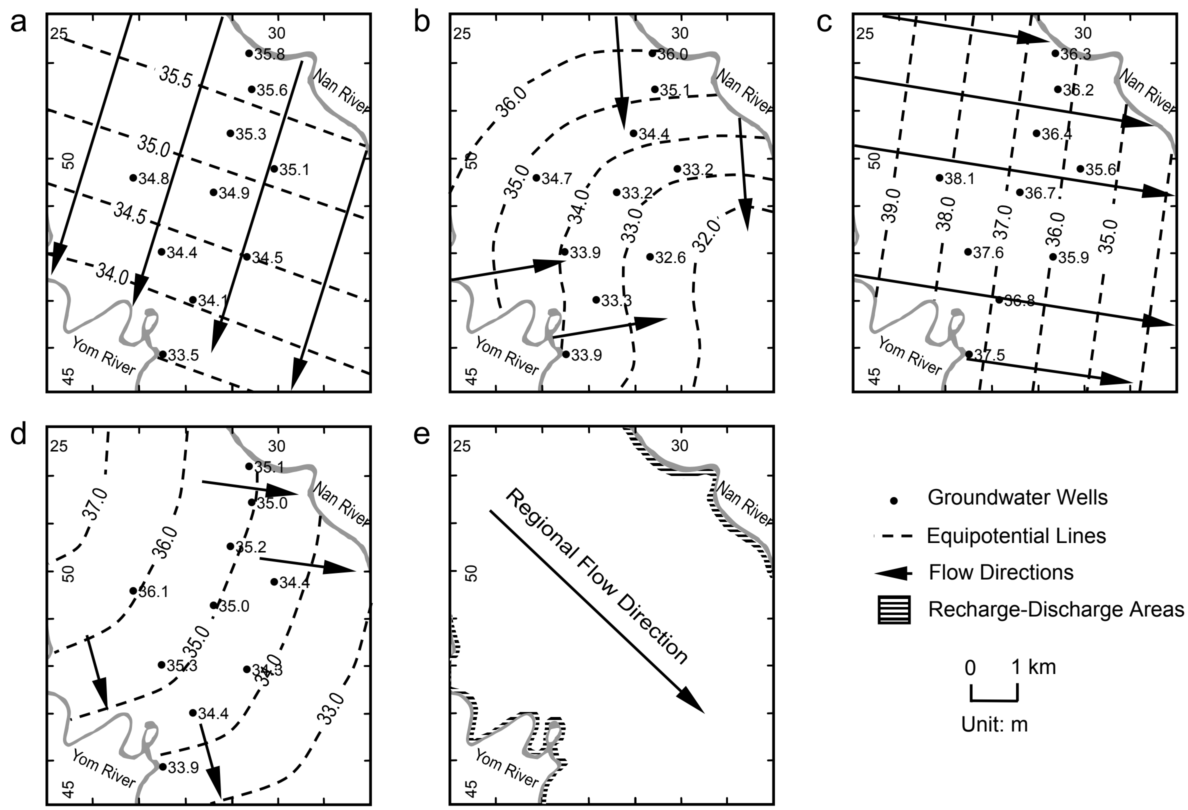

Fig. 9. Groundwater flow dynamics. The groundwater flow regime can be classified into 4 phases, including (a) uniform flow from Nan River to Yom River, (b) recharge from both rivers into the aquifer, (c) uniform flow from Yom River to Nan River, and (d) discharge from mounds to rivers. The regional flow direction is shown in (e). See Fig. 8 for weekly groundwater levels.

system along 5° SE with a flow path of 40.3 m (Figs. 8b and 9b). From October 5 to January 7 (mid dry season), groundwater flows continuously from the Yom River toward the Nan River along 81° SE with a flow path of 34.7 m while the Nan River becomes a discharge area (Figs. 8c and 9c). From January 8 to 26, groundwater mounds in transition areas discharge into both Nan (82° SE) and Yom Rivers (15° SE) with flow paths of 4.5 m (Figs. 8d and 9d). The regional groundwater flow direction is toward 62° SE (Fig. 9e).

Our results are opposite to those done by Brunke and Gonser (1997) and Massmann et al. (2004), who consider water exchange processes at a single river. Obviously in this study, at a particular moment in time, one river is effluent but another is influent. The baseflow from the aquifer into the stream does not always occur in the dry season but it occurs at both rivers only in about 2 weeks. For infiltration into the river bank, hydraulic heads in nearby rivers must be carefully considered. Classification of effluent and influent condition requires a through understanding of groundwater flow system in three dimensions.

Flow paths of oxygenated lateral recharge have, therefore, a zigzag pattern near recharge-discharge areas rather than a continuous curvilinear one across the entire flow system. Our study site does not conform to the conceptual model of a continuous flow regime across the entire system (i.e., Tóth 1963; Mayboom 1966, 1967; Winter 1976, 1999). Table 4 shows that lateral groundwater recharge from rivers does not penetrate into transition areas. Groundwater flow paths in each time period are very short in comparison

Table 4

Distances of flow paths

Figure	No. Days	Distance (m)	
		Nan to Yom	Yom to Nan
5a	128	15.2	-
5b	123	40.3	35.0
5c	95	-	34.7
5d	19	4.5	4.5

with the distance of 6-7 km between both rivers. In general, the groundwater flow direction in transition areas has a similar zigzag pattern while flowing toward the SE. A generalized regional groundwater flow direction in transition areas is nearly parallel to the rivers.

As the works of Mayboom et al. (1966), Mayboom (1966, 1967), Winter (1976), Winter et al. (1999), Tóth (1962, 1963, 1999), and others have shown, flow paths between groundwater and surface water are two-dimensional and static but this research shows the dynamic one. The spatial distribution of flow systems influences groundwater discharge. Groundwater discharge is not only confined along stream channel but also extends throughout discharge areas. Lakes and rivers are dynamic bodies, and the movement of groundwater in their vicinity is not static (Domenico 1972). A set of hydraulic-head measurements gives information only at a particular moment in time. The groundwater flow regime indeed requires a three-dimensional point-of-view consideration (Sophocleous et al. 1988; Sophocleous 1991; Harvey and Bencala 1993; Wondzell and Swanson 1996; Woessner 2000; Sophocleous 2002).

The general groundwater flow direction, toward the southeast, is nearly parallel to that of the river (Fig. 9e). This observation is coherent to what Larkin and Sharp (1992) calls the "underflow-component dominated stream-aquifer system," which the groundwater flux moves parallel to the river and in the same direction as the streamflow. The underflow component is predominant in fluvial systems of mixed-load to bed-loaded character and in systems with large channel gradients, small sinuosities, large width-to-depth ratios, and low river penetrations.

4.2 Interpretation of Iron Anomaly

Table 5 shows results of groundwater analysis. Using the flow cell method, an exposure of groundwater to the atmosphere is negligible. Average change balance is 3.66%, which indicates that the chemical analysis is reliable. Quality assurance samples meet the standard duplicated criteria. As plotted in the Eh-pH diagram, Fe^{2+} is the stable phase. Hydrochemical properties of major ions are identified as homogeneous, mainly Ca^{2+}-Mg^{2+}-HCO_3^- facies, by using the Piper's diagram.

4.2.1 Effects of Lateral Recharge

Fig. 10 shows that iron-rich groundwater exists in transition areas. It is mostly likely that a lack of oxygenated lateral recharge in transition areas has led to this anomaly. This evidence has proved that our hypothesis is correct. The zigzag flow pattern and the

Table 5

Groundwater quality across a confined alluvial aquifer between two rivers

Well	T	SC	DO	pH	Eh	TDS	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	CO_3^{2-}	SO_4^{2-}	S^{2-}	NO_3^-	NO_2^-	NH_3	SiO_2	Fe^{2+}	Mn^{2+}	CB	Depth
1	27.99	276	0.71	6.38	148.2	171	21.1	1.78	23.4	5.9	2	135.39	0.02	7.5	<0.01	<0.01	<0.01	0.80	24	8.11	0.44	3.65	28
2	28.59	238	1.57	6.72	146.0	145	8.5	1.04	27.5	7.0	7	113.40	0.03	<0.1	<0.01	<0.01	<0.01	0.94	25	9.25	0.40	6.53	33
3	28.44	294	1.38	6.53	169.0	179	24.4	1.79	22.4	5.1	2	150.01	0.03	4.5	<0.01	<0.01	<0.01	0.72	26	10.33	0.35	0.67	28
4	28.64	297	0.59	6.54	182.3	181	26.6	1.68	22.0	5.0	2	148.79	0.03	5.8	<0.01	<0.01	<0.01	1.04	25	10.14	0.36	1.74	26
5	28.76	310	0.51	6.50	173.9	188	15.9	1.72	26.8	5.7	12	113.42	0.02	12.5	<0.01	<0.01	<0.01	0.32	21	8.70	0.78	1.67	28
6	28.46	269	1.61	6.46	183.1	164	7.0	1.19	29.5	8.2	8	103.67	0.01	7.0	<0.01	<0.01	<0.01	0.58	21	18.02	0.55	9.03	32
7	26.37	324	1.47	6.77	155.0	205	16.2	1.57	33.7	6.2	3	143.88	0.04	<0.1	<0.01	<0.01	<0.01	0.98	28	23.09	0.62	9.16	30
8	27.77	329	0.52	6.52	245.4	203	20.8	1.54	30.0	7.2	2	146.35	0.02	14.0	<0.01	0.03	<0.01	0.87	22	14.92	0.48	4.96	30
9	28.37	137	2.28	6.66	146.1	84	4.6	0.99	11.1	5.1	4	64.63	0.01	<0.1	<0.01	<0.01	<0.01	1.46	22	4.67	0.29	1.12	38
10	28.11	310	1.06	6.55	135.2	191	24.4	1.91	24.2	5.5	2	153.67	0.03	1.0	<0.01	<0.01	<0.01	1.20	28	11.85	0.09	3.24	36
11	28.75	268	1.78	6.77	126.0	162	14.4	0.91	28.9	7.6	3	134.12	0.04	<0.1	<0.01	<0.01	<0.01	0.62	31	11.42	0.05	8.66	30
12	28.85	423	1.30	6.85	97.7	256	9.1	1.79	40.3	11.7	20	168.24	0.06	13.0	<0.01	<0.01	<0.01	4.30	20	8.68	0.11	-2.55	30
13	28.39	383	1.64	6.60	118.4	233	22.0	1.32	33.3	9.1	4	189.02	0.04	<0.1	<0.01	<0.01	<0.01	1.58	21	19.41	0.10	2.86	30
14	28.06	291	2.82	6.75	132.8	179	23.9	1.28	28.9	5.2	3	163.39	0.05	2.0	<0.01	<0.01	<0.01	0.80	24	16.93	0.05	2.38	30
15	28.00	318	0.88	7.24	141.2	196	19.1	1.42	49.0	2.7	5	181.46	0.16	<0.1	<0.01	<0.01	<0.01	0.46	21	1.29	0.01	6.22	30
16	28.72	247	0.73	6.81	130.0	150	13.3	1.76	31.6	4.6	3	129.24	0.04	4.0	<0.01	<0.01	<0.01	0.52	20	9.50	0.18	5.99	30
17	27.65	301	0.72	6.46	89.9	186	14.7	1.31	25.6	8.0	3	156.11	0.01	2.5	<0.01	<0.01	<0.01	0.84	22	10.19	0.47	-1.64	28
18	27.11	320	0.97	6.46	130.6	200	19.7	1.00	24.6	7.6	1	162.21	0.01	5.5	<0.01	<0.01	<0.01	1.10	22	11.28	0.66	-1.19	20
19	26.92	319	2.27	6.61	131.7	200	18.6	1.15	24.3	8.0	5	171.95	0.02	<0.1	<0.01	<0.01	<0.01	0.70	24	8.85	0.11	-4.42	30
20	24.41	357	1.26	6.68	107.8	235	32.3	0.26	31.4	11.7	4	190.23	0.03	<0.1	<0.01	<0.01	<0.01	2.36	24	14.33	0.47	9.89	26
21	28.17	250	1.85	6.58	118.3	153	16.0	0.30	17.6	5.9	3	119.51	0.01	1.5	<0.01	<0.01	<0.01	0.62	20	19.64	0.68	-0.18	26
22	27.65	378	1.31	6.70	119.6	234	26.9	0.29	38.6	8.1	3	189.01	0.03	0.5	<0.01	<0.01	<0.01	0.70	18	14.86	0.55	8.28	30
23	27.69	328	0.87	6.69	112.7	203	21.7	0.27	22.9	7.1	2	152.43	0.03	<0.1	<0.01	<0.01	<0.01	0.76	19	17.59	0.38	2.33	30
24	27.12	298	1.19	6.73	115.4	186	20.0	0.31	17.7	6.7	3	117.06	0.03	1.5	<0.01	<0.01	<0.01	0.89	20	15.26	0.24	6.37	30
25	27.05	386	0.76	6.67	108.1	241	32.7	2.17	20.4	6.8	4	146.33	0.03	7.5	<0.01	<0.01	<0.01	0.87	20	21.30	0.47	6.77	30
Ave	27.84	306	1.28	6.65	138.6	189	19.0	1.23	27.4	6.9	4.4	145.74	0.03	3.6	<0.01	<0.01	<0.01	1.04	22.7	12.78	0.36	3.66	27.6
SD	0.98	57.6	0.60	0.18	33.3	36.5	7.2	0.58	7.9	2.0	4.0	29.92	0.03	4.4	0.00	0.01	0.00	0.80	3.2	5.29	0.22	3.98	6

All parameters in mg/L except T (°C), SC (µS/cm), Eh (mV), CB (%), and depth (m); Ave = average value; SD = standard deviation.

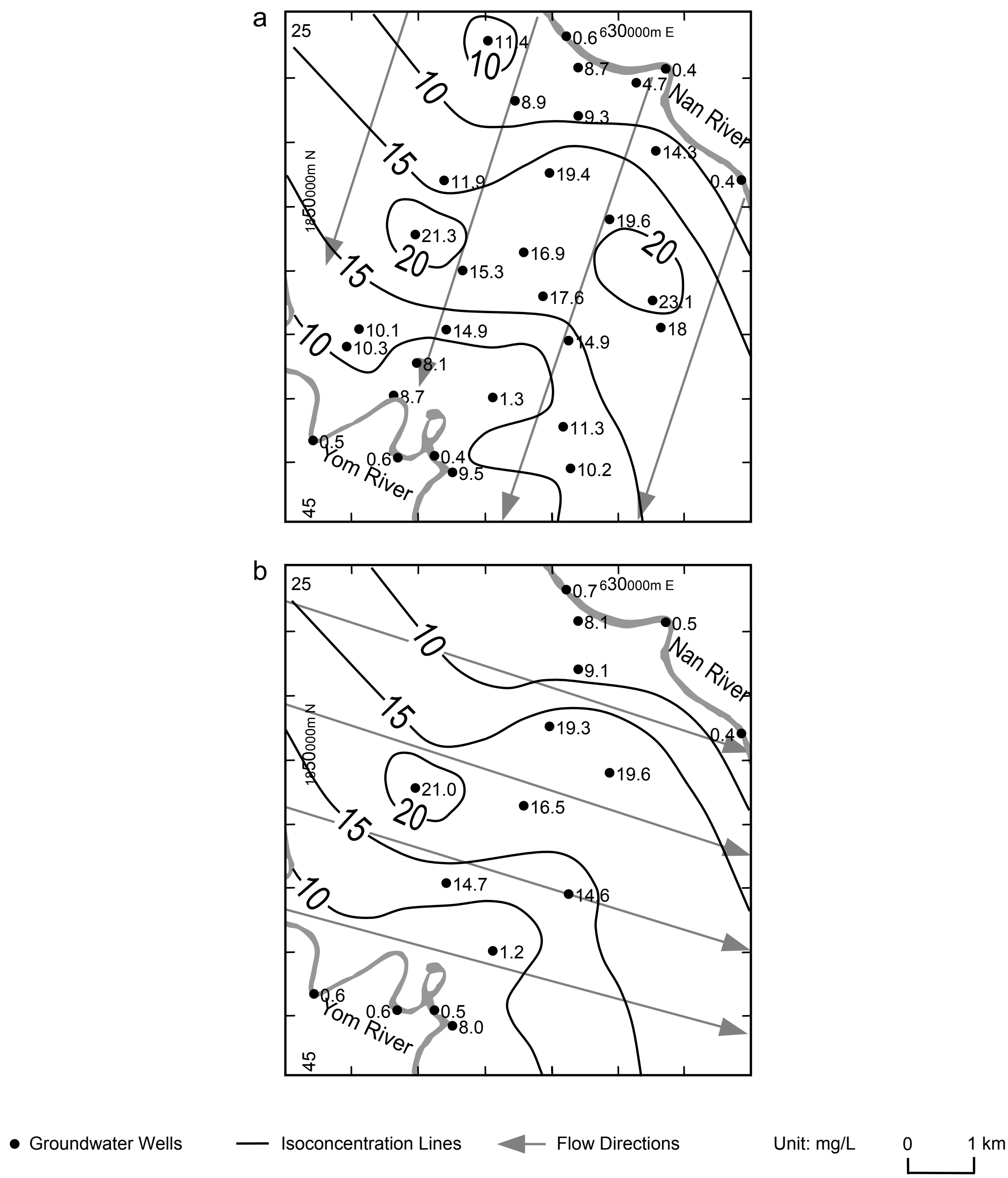

Fig. 10. Iron-rich groundwater in transition areas of the aquifer. High Fe^{2+} concentrations appear obviously in transition areas in both (a) dry and (b) rainy seasons. The hydrogeochemistry in transition areas is fairly constant in space and time.

low penetration from the rivers leave the transition areas lack of dilution and oxidation by oxygenated river water, which influences redox reactions and the availability of redox-sensitive species, particularly iron. Therefore, concentrations of dissolved iron are high in the transition areas.

During mid dry season and early rainy season (January 27-June 3), the groundwater moves slowly from the Nan River (recharge zone) through the aquifer to the Yom River. It transports dissolved oxygen, which oxidizes ferrous iron immediately, by 15.2 m. In the rainy season (June 4-October 4), both rivers recharge the aquifer with the penetration ranging from 35-40.3 m from the rivers. In early to mid dry season (October 5-January 7), the Yom River continues to infiltrate the aquifer by 34.7 m whereas the groundwater drains into the Nan River. Baseflow into both rivers occurs only in two weeks (January 8-26) with a flow path of 4.5 m.

Reduction processes at our study site take place less than 100 m from both rivers whereas Massmann et al. (2004) finds the affected area of about 3 km from the river and tens of km by Lovley and Goodwin (1988). Difference in spacing between successive rivers may explain the contradiction. The short distance of 6-7 km between Nan and Yom Rivers causes the groundwater flow regime more dynamic.

Despite the fact that, based on isotope analyses in nearby aquifers, the groundwater at shallow depths of up to 50 m is likely to be less than 10 yrs old and that the groundwater recharge is almost entirely from rainfall (Howard Humphreys 1986), the seasonal changes of groundwater flow regime do not significantly affect the Fe^{2+} distribution in transition areas. Fe^{2+} concentrations in dry season (March-April) (Fig. 10a) decrease slightly in rainy season (September) (Fig. 10b) with larger discrepancy near the rivers. The anomaly is nearly constant in space.

Sophocleous (2002) points out that hydraulics properties of stream and lake beds control interactions between surface water and groundwater but these properties are difficult to measure directly. The limitation is the difficulty of spatially defining the hydraulic properties and spatial heterogeneities of those beds. Subsurface flow through the aquifer is slowly. The mechanisms that groundwater flow into streams quickly enough to contribute to streamflow responses to each rainstorm inputs is not fully understood. With better understanding of this process, effects of the lateral recharge on hydrogeochemistry of the aquifer will be clearly understood.

4.2.2 Effects of Vertical Recharge

At the study area, vertical recharge from rainfall flows through a confining layer as indicated by a high average DO concentration of 1.3 mg/L. Recharge is focused initially where the vadose zone is thin with respect to adjacent areas. It then progresses laterally over time to areas that have thicker unsaturated zones (Winter 1983). The changing volumes and distribution of recharge results in flow dynamics of groundwater flow systems directly adjacent to surface water, which causes highly variable discharge near the surface-water bodies. The infiltrating water is subject to physical and biogeochemical changes when entering the aquifer. Oxygen depletion occurs from the oxidation of iron bearing minerals in the aquifer sediments.

Groundwater recharge from canals is negligible. Only a few field investigations detail the pathways of water infiltration from stream channels or from canals to the water table (Stephens 1996). The aquifer in this study is too deep from the surface to have groundwater mound rising through the vadose zone to intersect the channel. This fact is always true even if the flow duration are sufficiently long for the vadose zone to reach steady-state moisture distribution, as long as the aquifer can transmit the recharging water away from the area (Bouwer and Maddock 1997). The aquifer becomes hydraulically disconnected from the canal.

It is uncommon to detect high concentrations of dissolved oxygen in a confined aquifer (Champ et al. 1979; Berner 1981). The oxygenated water of vertical recharge affects redox conditions of most unconfined aquifers (i.e., Rose and Long 1988) rather than confined systems. We suspect that preferential flow through sandy parts of the confining unit leads to the above phenomenon. Nevertheless, a few researchers obtained results similar to ours (Edmunds et al. 1987; Groffman and Crossey 1999; Massmann et al. 2004). Winograd and Robertson (1982) found that 10,000-yr old groundwater, that traveled for 80 km from recharge areas, is still rich in DO (>7 mg/L). The presence of vertical recharge is, however, less important than the absence of lateral recharge, as evident by the high-iron anomaly in transition areas (Fig. 10).

4.2.3 Evolutionary Pattern

The evolutionary pattern of high iron concentrations along the general groundwater flow direction does not exist. Along the general groundwater direction, the anomaly is constant in the transition areas. This feature supports the hypothesis of discrete hydrogeochemical zones (Back and Barnes 1965; Langmuir 1969, 1997; Chapelle and Lovley 1992). Additional understanding of the aquifer mineralogy plus vertical redox conditions inside the aquifer will enhance our understanding about the anomaly present.

4.3 Relationship of Iron with other Chemical Species

Fig. 11 shows that, Fe^{2+} is stable thermodynamically and hydrogeochemical properties are homogeneous in the aquifer. Fe^{2+} is directly related to Mn^{2+} but is inversely related to Eh and DO (Figs. 12 and 13). High Fe^{2+} concentrations are associated with high Mn^{2+} concentrations (Fig. 12a). This relationship is, however, varied widely. The linear upper boundary is written in Eq. 2 and the lower boundary in Eq. 3:

$$Fe = 22.9Mn+11 \tag{2}$$

$$Fe = 22.9Mn-0.6 \tag{3}$$

where Fe = Fe^{2+} concentrations (mg/L); Mn = Mn^{2+} concentrations (mg/L).

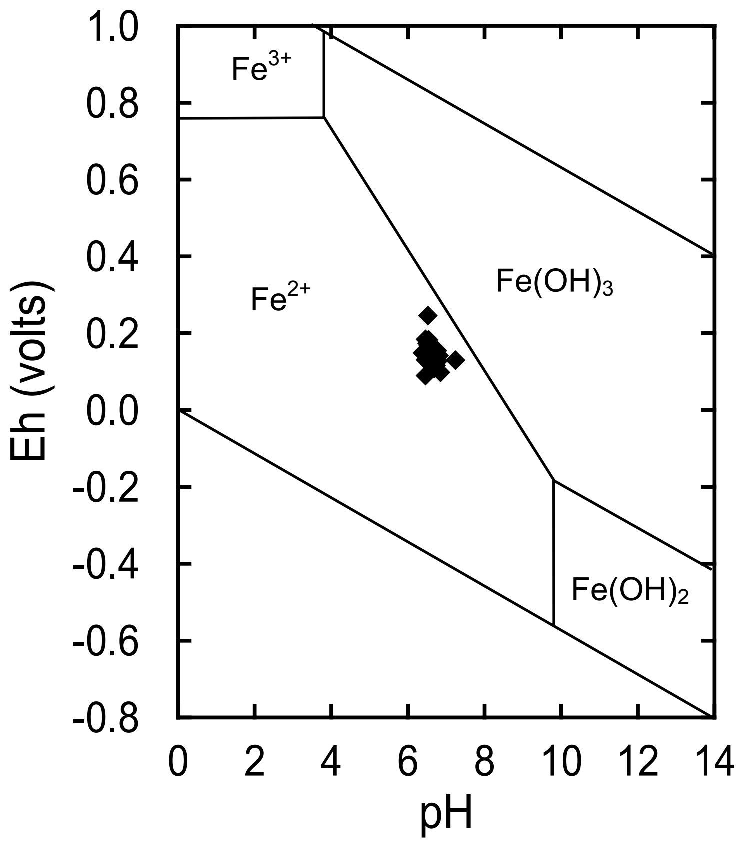

Fig. 11. Eh-pH diagram of the Fe-O_2-H_2O system. The upper and lower lines on the field represent the oxidation of water to O_2 and the reduction of water to H_2. The groundwater is homogeneous containing stable Fe^{2+} in the system.

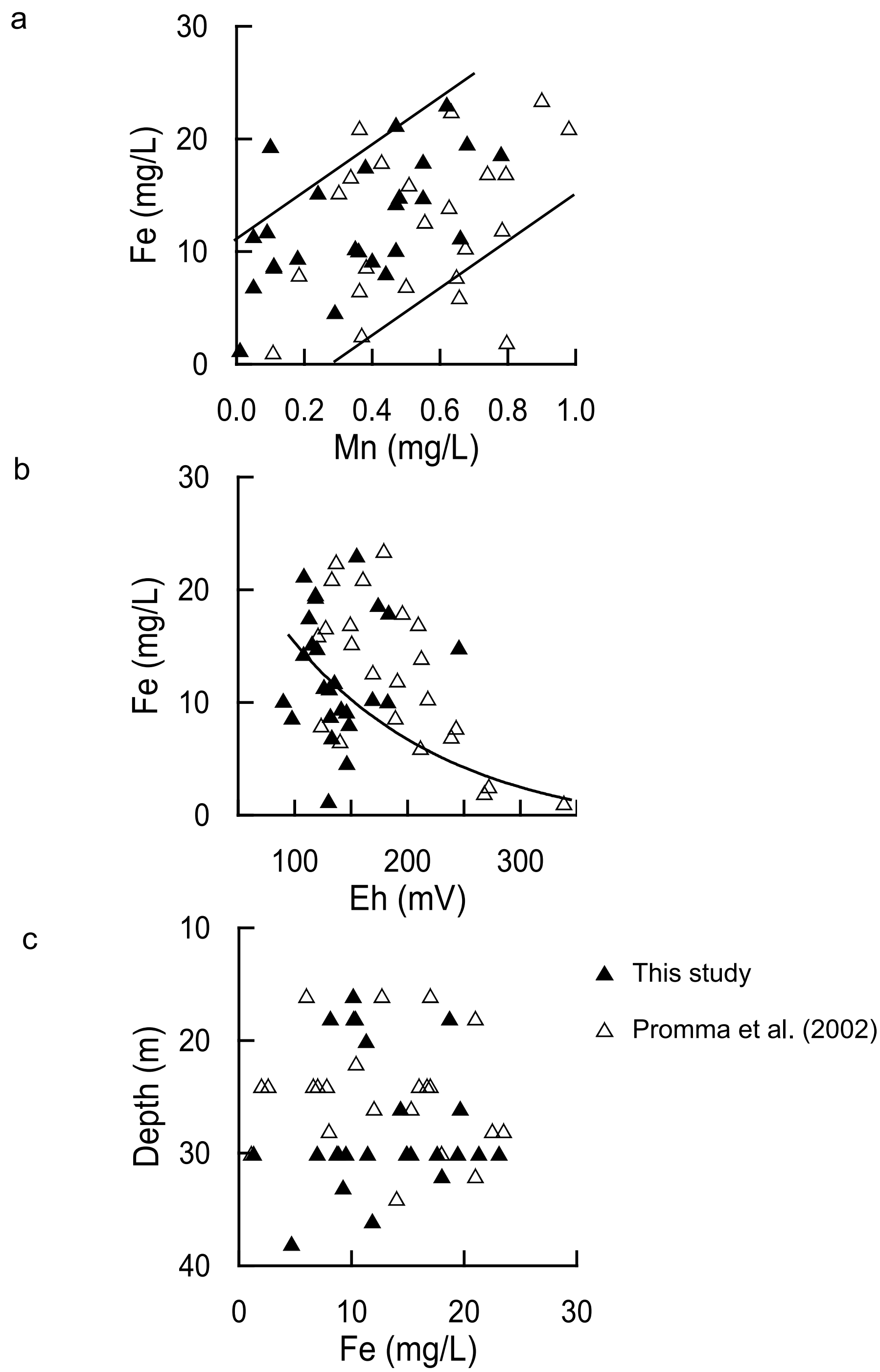

Fig. 12. Relationship between Fe^{2+} and other chemical species. Fe^{2+} is directly related to Mn^{2+} (a) but is inversely related to Eh (b). In a confined alluvial aquifer, Fe^{2+} is independent of screen depth (c). Fe^{2+} has no relationship with major ions, pH, T, or TDS. See correlation equations in text.

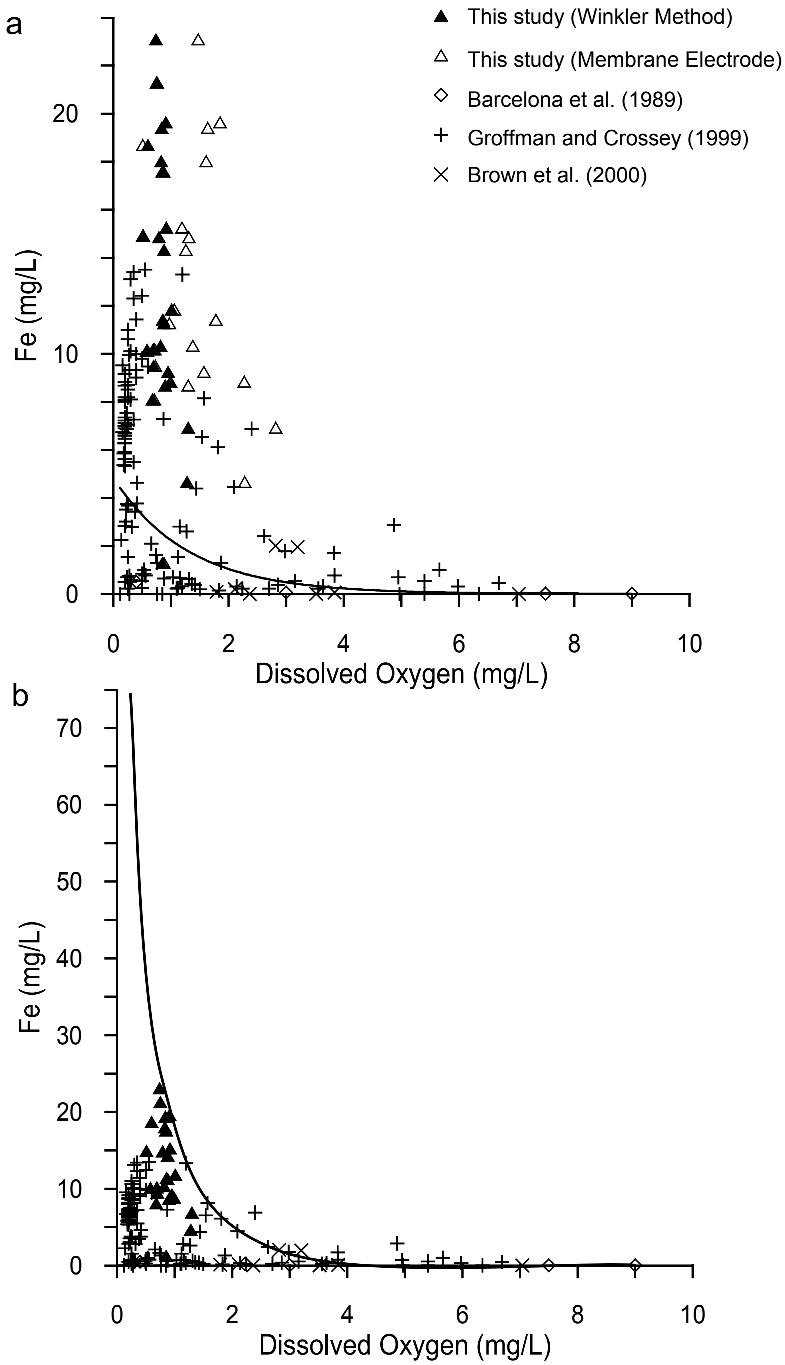

Fig. 13. Relationship between Fe^{2+} and DO. (a) Fe^{2+} decreases exponentially as DO increases. See correlation equations in text. (b) With compressed y-axis, an envelope line indicates that no groundwater has Fe^{2+} concentrations over 75 mg/L when DO is absent. Fe^{2+} will be unstable if DO is over 4-5 mg/L.

Fe^{2+} decreases exponentially as Eh increases (Fig. 12b). It is noteworthy that Eh is qualitative. The correlation equation, with a coefficient of determination of 0.26, is as follows:

$$Fe = 30.53e^{-0.0065Eh} \tag{4}$$

where Eh = redox potential (mV). The presence of Fe^{2+} in a confined alluvial aquifer is independent of screen depth (Fig. 12c).

Overall, the Fe^{2+} concentration decreases exponentially as DO increases (Fig. 13). The best fit is written in Eq. 5 with the coefficient of determination of 0.30 (Fig. 13a). With compressed y-axis, an envelope line (Eq. 6) indicates that no groundwater has Fe^{2+} concentrations over 75 mg/L when DO is absent (Fig. 13b). Fig. 13 also shows that Fe^{2+} will be unstable if DO is over 4-5 mg/L.

$$Fe = 4.88e^{-0.77DO} \tag{5}$$

$$Fe = 75e^{-1.57DO} \tag{6}$$

where DO = concentrations of dissolved oxygen (mg/L).

4.4 Speciation

Table 6 shows dominant ion activities and saturation indices with respect to particular minerals in aquifer materials. The average activity of ferrous iron is similar to other cations except manganese, which has a lower activity of about two orders of magnitude. Minerals that have a tendency to dissolve into the groundwater include aragonite, calcite, dolomite, anhydrite, gypsum, halite, talc, and pyrite. Minerals that have

Table 6

Ion activities and saturation indices with respect to minerals

Well	log Ca^{2+}	log Cl^{-}	log Fe^{2+}	log Mg^{2+}	log Mn^{2+}	log Na^{+}	log SO_4^{2-}	SI Ara	SI Cal	SI Dol	SI Anh	SI Gyp	SI Hal	SI Tal	SI Pyr	SI Goe	SI Hem	SI Sid	SI Qtz	SI Cha
1	-3.38	-4.28	-4.09	-3.76	-5.34	-3.07	-4.28	-1.34	-1.20	-2.61	-3.29	-3.08	-8.94	-7.65	-64.65	5.69	13.40	0.50	0.54	0.12
2	-3.30	-3.74	-4.01	-3.67	-5.37	-3.46	-6.16	-0.99	-0.85	-1.90	-5.08	-4.88	-8.79	-5.22	-73.37	6.78	15.58	0.85	0.55	0.13
3	-3.40	-4.28	-4.00	-3.83	-5.46	-3.01	-4.50	-1.16	-1.02	-2.30	-3.53	-3.32	-8.88	-6.76	-72.36	6.60	15.22	0.79	0.57	0.15
4	-3.41	-4.28	-4.01	-3.83	-5.45	-2.97	-4.39	-1.16	-1.02	-2.29	-3.42	-3.22	-8.84	-6.78	-75.45	6.85	15.72	0.79	0.55	0.13
5	-3.32	-3.50	-4.04	-3.77	-5.08	-3.19	-4.06	-1.23	-1.09	-2.45	-3.00	-2.80	-8.29	-7.12	-72.26	6.56	15.15	0.60	0.47	0.05
6	-3.28	-3.68	-3.72	-3.61	-5.22	-3.55	-4.33	-1.27	-1.13	-2.42	-3.23	-3.02	-8.82	-6.91	-73.92	6.91	15.84	0.84	0.47	0.06
7	-3.23	-4.11	-3.65	-3.74	-5.22	-3.19	-6.18	-0.81	-0.66	-1.69	-5.04	-4.83	-8.88	-5.17	-75.53	7.33	16.68	1.33	0.63	0.20
8	-3.29	-4.28	-3.86	-3.69	-5.33	-3.08	-4.03	-1.08	-0.94	-2.12	-2.94	-2.73	-8.95	-6.76	-88.91	7.96	17.94	0.90	0.50	0.08
9	-3.66	-3.97	-4.24	-3.78	-5.44	-3.72	-6.11	-1.64	-1.50	-2.95	-5.39	-5.18	-9.28	-6.13	-72.53	6.36	14.75	0.33	0.49	0.08
10	-3.37	-4.28	-3.94	-3.79	-6.05	-3.01	-5.16	-1.11	-0.96	-2.18	-4.15	-3.95	-8.88	-6.45	-65.96	6.13	14.29	0.87	0.60	0.18
11	-3.29	-4.11	-3.94	-3.65	-6.30	-3.24	-6.17	-0.85	-0.71	-1.61	-5.08	-4.87	-8.93	-4.44	-69.49	6.67	15.37	1.04	0.64	0.22
12	-3.17	-3.29	-4.11	-3.49	-6.01	-3.44	-4.08	-0.56	-0.42	-0.98	-2.87	-2.67	-8.32	-4.23	-60.18	6.28	14.59	1.05	0.45	0.03
13	-3.25	-3.98	-3.76	-3.59	-6.04	-3.06	-6.19	-0.85	-0.71	-1.59	-5.06	-4.86	-8.63	-6.01	-64.77	6.20	14.42	1.19	0.48	0.06
14	-3.30	-4.11	-3.80	-3.82	-6.33	-3.02	-4.87	-0.81	-0.67	-1.70	-3.79	-3.59	-8.71	-5.61	-67.88	6.83	15.69	1.24	0.54	0.12
15	-3.08	-3.89	-4.97	-4.12	-7.09	-3.12	-6.18	-0.06	0.09	-0.70	-4.89	-4.68	-8.59	-3.79	-81.45	7.27	16.56	0.61	0.48	0.06
16	-3.25	-4.10	-4.02	-3.87	-5.74	-3.27	-4.56	-0.79	-0.65	-1.74	-3.43	-3.23	-8.97	-5.63	-67.90	6.78	15.58	0.99	0.45	0.03
17	-3.35	-4.11	-4.01	-3.63	-5.33	-3.23	-4.77	-1.17	-1.03	-2.18	-3.74	-3.53	-8.92	-6.97	-53.09	5.02	12.05	0.72	0.51	0.08
18	-3.37	-4.58	-3.97	-3.66	-5.19	-3.10	-4.43	-1.19	-1.04	-2.22	-3.42	-3.21	-9.27	-7.12	-61.78	5.70	13.43	0.76	0.51	0.09
19	-3.37	-3.88	-4.09	-3.63	-5.98	-3.13	-6.16	-1.02	-0.87	-1.86	-5.17	-4.96	-8.60	-6.02	-67.99	6.05	14.12	0.82	0.55	0.13
20	-3.27	-3.99	-3.90	-3.48	-5.38	-2.89	-6.19	-0.85	-0.71	-1.50	-5.11	-4.88	-8.46	-5.43	-62.76	5.91	13.83	1.08	0.59	0.16
21	-3.49	-4.10	-3.69	-3.75	-5.14	-3.19	-4.98	-1.31	-1.17	-2.42	-4.09	-3.89	-8.88	-6.72	-61.87	6.20	14.42	1.05	0.46	0.04
22	-3.19	-4.11	-3.88	-3.64	-5.31	-2.97	-5.49	-0.69	-0.55	-1.40	-4.31	-4.10	-8.67	-5.91	-65.22	6.36	14.74	1.16	0.42	0.00
23	-3.39	-4.28	-3.77	-3.68	-5.43	-3.06	-7.17	-1.00	-0.86	-1.85	-6.19	-5.98	-8.93	-6.00	-66.67	6.33	14.67	1.17	0.44	0.02
24	-3.49	-4.10	-3.80	-3.69	-5.60	-3.09	-4.97	-1.18	-1.04	-2.12	-4.09	-3.88	-8.78	-5.77	-63.45	6.43	14.89	1.07	0.47	0.05
25	-3.45	-3.98	-3.69	-3.71	-5.34	-2.88	-4.29	-1.11	-0.96	-2.03	-3.37	-3.16	-8.45	-6.17	-59.30	6.24	14.50	1.21	0.47	0.05
Ave	-3.33	-4.04	-3.96	-3.72	-5.61	-3.16	-5.19	-1.01	-0.87	-1.95	-4.15	-3.94	-8.79	-6.03	-68.35	6.46	14.94	0.92	0.51	0.09
SD	0.12	0.28	0.26	0.13	0.48	0.20	0.92	0.31	0.31	0.50	0.92	0.92	0.25	0.95	7.56	0.60	1.19	0.25	0.06	0.06

SI = saturation index; Ara = aragonite; Cal = calcite; Dol = dolomite; Anh = anhydrite; Gyp = gypsum; Hal = halite, Tal = talc; Pyr = pyrite; Goe = goethite; Hem = hematite; Sid = siderite; Qtz = quartz; Cha = chalcedony; Ave = average value; SD = standard deviation.

a tendency to precipitate out of the groundwater include goethite, hematite, siderite, quartz, and chalcedony.

For carbonate group, calcite and aragonite have marginal saturation indices to an equilibrium but bicarbonate-rich groundwater indicates that the mineral dissolution is highly likely. In addition, aquifer materials are fairly uniform so that very little change in hydrogeochemistry takes place in transition areas. As a result, the groundwater does not progress past the bicarbonate facies in the Chebotarev sequence. For silicate group, quartz and chalcedony are very close to equilibrium, which is coherent to our observation that they are a majority of aquifer materials. For sulfur group, anhydrite and gypsum dissolve into the groundwater as shown by sulfate appearance. Sulfate reduction is, however, not dominant.

For iron species, pyrite is completely reduced and ferrous iron is released into the groundwater. On the other hand, goethite, hematite, and siderite are stable in the aquifer. Under a range of pH 6.38-7.24, the ferrous iron occurs as uncomplexed Fe^{2+} ion (Fig. 11). Fe(III) is also mobile in the groundwater as ferric-organic (humic-fulvic) complexes and as colloidal ferric oxyhydroxides (Langmuir 1997).

Besides Fe(III) oxyhydroxides, siderite and sulfate reduction control the solubility of dissolved Fe^{2+}. Since sulfate reduction is not dominant, Fe^{2+} does not precipitate as sulfides. Coherent to Berner (1969), high-iron groundwater develops only if there is little or no sulfate reduction in the aquifer because the sulfide generation tends to precipitate Fe^{2+} as iron sulfides. The sulfate reduction is observed if Fe(III) oxyhydroxides in aquifer materials are depleted (Ponnamperuma 1972; Froelich et al. 1979; Reeburgh 1983). Therefore, the high-iron groundwater reflects the reduction of poorly soluble Fe(III) oxyhydroxides and pyrite to the highly soluble ferrous state. The above finding is coherent to Whittemore and Langmuir (1975) and Morse et al. (1987).

In this study, Fe(III) reduction occurs in transition areas where molecular oxygen is absent with no possibility of reoxidation. The dissolved Fe^{2+} thus accumulates in the groundwater causing high-iron concentrations. The accumulation of dissolved iron in groundwater represents a truncation of the iron cycle (Chapelle 1993).

4.5 Simulation of Groundwater Flow Patterns

The simulation of groundwater flow patterns was considered satisfactory (well matched to those observed in the field). Fig. 14 shows simulated equipotential lines in comparison with Fig. 9. The calibration was a trial-and-error process. Calibration targets were defined as measured heads ± 0.5 m. This error was based on our subjective judgment. The recharge flux was considered optimal when the root mean squared difference reaches the lowest value. There is no perfect method used to estimate a recharge flux. The recharge flux for modeling was obtained from calibration rather than from water budget analysis. Initial heads are important in transient simulations. The potentiometric surface in the past model controls the shape of predicted surface.

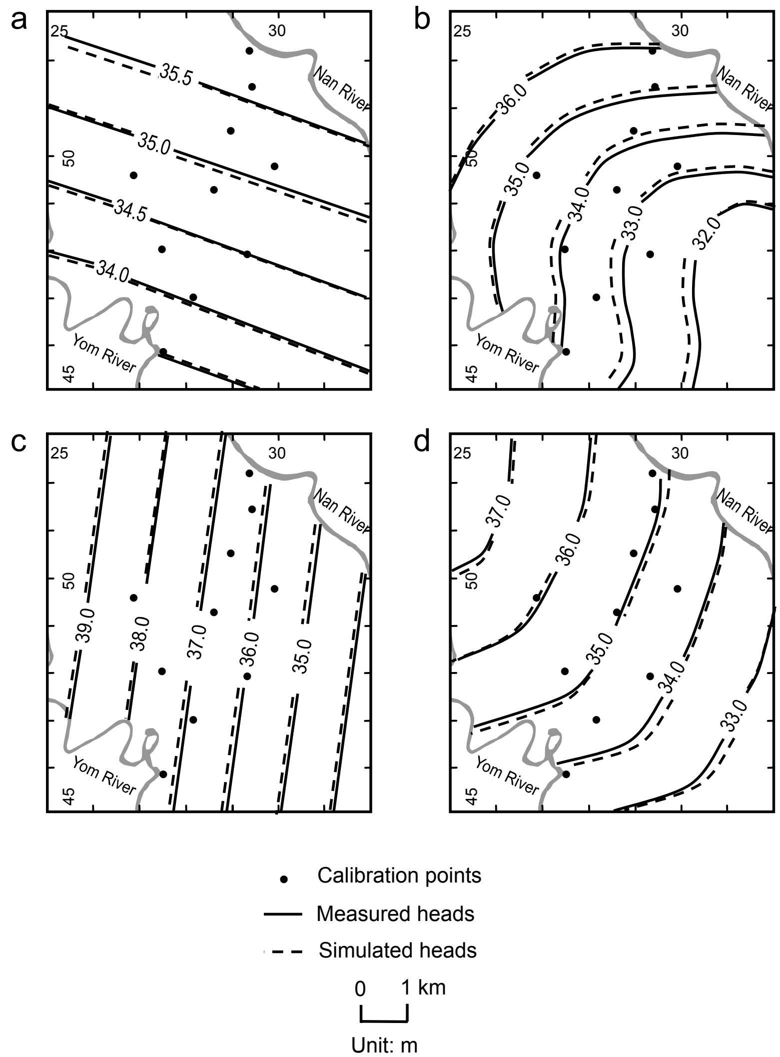

Fig. 14. Simulated flow patterns. Simulated groundwater flow patterns are well matched to those observed in the field. The groundwater flow regime includes: (a) uniform flow from Nan River to Yom River, (b) recharge from both rivers into the aquifer, (c) uniform flow from Yom River to Nan River, and (d) discharge from mounds to rivers.

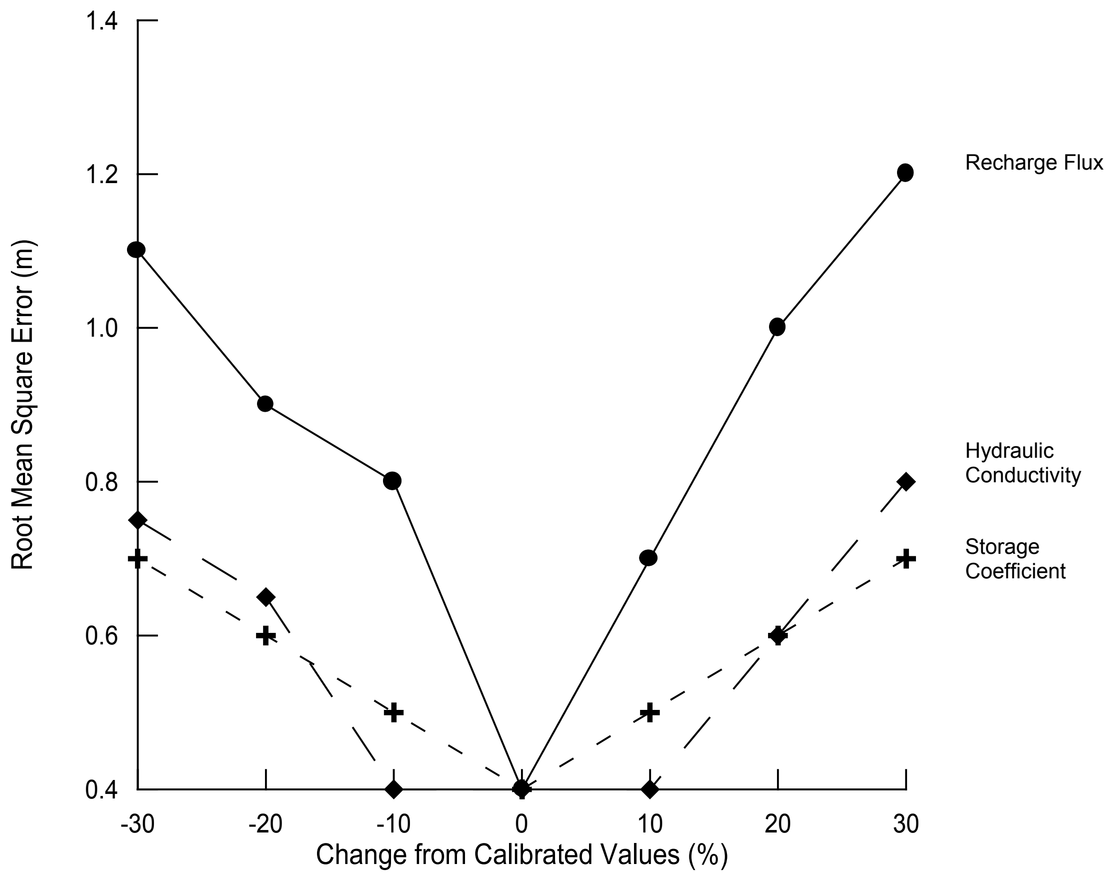

Fig. 15. Sensitivity analysis. Recharge flux is the most sensitive parameter followed by hydraulic conductivity and storage coefficient, respectively.

CHAPTER 5
CONCLUSIONS AND FUTURE RESEARCH

Nature is dynamic. The interactions of surface water with groundwater of a confined alluvial aquifer located between two rivers are governed by the positions of surface-water bodies with respect to geologic characteristics of the aquifer and climatic settings. Subsequent groundwater flow dynamics is controlled by channel slope, river sinuosity, degree of river incision into the aquifer, characteristics of depositional system, and, most importantly, the seasonal fluctuation of surface-water levels. Interactions between surface water and groundwater occur by vertical recharge through the unsaturated zone and by infiltration into or exfiltration from the aquifer. These interactions affect redox conditions of the groundwater flow system.

This study shows an interesting situation where two rivers partially cut into a confined aquifer and seasonally variant heads lead to groundwater flow dynamics. Groundwater flow reversal occurs when heads in both rivers change. Seasonal reversals of groundwater flow path yield a zigzag flow pattern rather than a continuous curvilinear one. Transition areas are thus isolated from oxygenated recharge water. The absence of lateral groundwater recharge from the rivers appears to play a more important role on than the presence of vertical recharge through the confining unit. The above mechanism explains the occurrence of discrete zones of high redox constituents such as iron in groundwater better than the hypothesis of chemical evolution. An evolutionary trend does not develop along short flow paths particularly in a river-bound local groundwater flow system whose flow paths are truncated. Redox conditions and patterns of redox-sensitive species are controlled by the groundwater and surface water flow patterns. This process is typical for a confined alluvial aquifer located between two rivers, particularly in tropical regions.

Future research includes:

1. Streams and aquifers exchange water horizontally and vertically but most studies have used one- or two-dimensional models. A detailed three-dimensional study is needed for a better comprehension of the surface water-groundwater interactions. As Sophocleous (2002) notes, the present inability to characterize subsurface heterogeneity causes an upscaling problem and leads to uncertainties in data analysis and interpretation. Groundwater-surface water interactions must be quantified using multidisciplinary and multiscale approach including field observation, geographic information system, remote sensing, numerical modeling, and statistical analysis. The construction of alluvial-plain and stream cross-sections to show groundwater flow and quality along flow paths to the stream requires careful consideration.
2. The spacing between the bounded rivers is important. At our study site, the Nan and Yom Rivers are about 6-7 km apart. Fluctuation of the river water levels at different periods leads to the zigzag groundwater flow pattern. It is of interest to study the effect of this factor on the groundwater flow regime and related hydrogeochemical pattern.
3. Microorganisms, particularly *Shewanella putrefaciens*, also play an important role in the reduction of Fe(III). It reduces Fe(III) oxyhydroxides under anaerobic conditions to Fe^{2+}. Some Fe^{2+} remain in the groundwater. Future research should characterize its role in the presence of iron anomaly.

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OUTPUT

Project Code : TRG4580065

Project Title : Evolution of Ferrous Iron in a Local Groundwater Flow System

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Project Period : 1 July 2002 - 31 December 2004

1. Publication in international journal. We attempted to publish our first paper in *Ground Water* in 2003 but, unfortunately, the manuscript was refused. We are preparing it anew for publication in *Hydrogeology Journal* (Appendix A). The second paper (Appendix B) will be submitted to *Hydrogeology Journal* as well after our peer revision in early 2005. Upon publication, we will send Thailand Research Fund a hard copy of them. Research outcome has never been published anywhere or presented in an international conference to follow a copyright rule set by the publisher.
2. Application of research. Research outcome has been used to teach graduate and undergraduate students at Naresuan University in several topics related to groundwater and the environment. Graduate students who assisted us in the field had learned techniques and skills of field hydrogeology.

APPENDIX A

Manuscript 1

Effects of Groundwater Flow Dynamics on Redox-Sensitive Species in a Confined Alluvial Aquifer Located between Two Rivers

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Abstract

This paper proposes a new hypothesis that, in a confined alluvial aquifer located between two rivers, discrete zones of anomalously high concentrations of redox species, such as iron, are a result of groundwater flow dynamics rather than a chemical evolution along continuous flow paths. The hypothesis was proved correct at a study site located between Nan and Yom Rivers in Phitsanulok, Thailand, by analyzing concentrations of redox-sensitive species in comparison with dynamic groundwater flow patterns. River incision into the confined aquifer and related seasonally variant hydrology result in truncated flow paths and zigzag groundwater flow patterns. The lateral recharge from rivers penetrates into the aquifer only by tens of meters. Although vertical groundwater recharge can flow through a 13-21 m thick confining layer as indicated by high concentrations of dissolved oxygen, the absence of lateral groundwater recharge from rivers appears to play a more important role on than the presence of vertical recharge from rainfall. High anomaly of redox-sensitive species, appearing as discrete zones in a confined alluvial aquifer, is a result of groundwater/surface-water relations and related groundwater flow dynamics.

(180 words)

Keywords

Groundwater/surface-water relations, Hydrochemistry, Groundwater flow, Iron, Thailand

Introduction

The interaction between groundwater and surface water has been studied since the 1960s because of concerns about eutrophication and acid rain (Winter 1995). The growth in research has mushroomed during the 1990s, especially in physical and biogeochemical aspects (Stanley and Jones 2000). Recently, interest in interactions between near-channel and in-channel water, which are important for ecological system near the stream, has been increased greatly (Sophocleous 2002). The spatial and temporal dynamics of groundwater recharge and discharge along active channels in varying geomorphic settings needs further study. Quantification of the dynamic temporal changes of water movements and chemical fluxes through these boundaries is significant (Dahm et al. 1998). An understanding of interactions between groundwater and surface water as well as subsequent groundwater quality is a key for successful integrated management of water resources.

The groundwater flow system depends on hydrogeologic environment including topography, geology, and climate (Tóth 1970). Hubbert (1940) shows that, given a uniform recharge, an unconfined groundwater flow system develops and is influenced by a water table configuration, which is a subdued replica of the land surface. Hydraulic conductivity of aquifers also controls the flow patterns (Freeze and Witherspoon 1967). Groundwater moves along flow paths and form a flow system. Based on a relative position in space, Tóth (1962, 1963) classifies three types of flow systems including local, intermediate, and regional. The local groundwater flow system is defined, in this study, as a coherent, three-dimensional unit of groundwater flow with one recharge and one or more discharge areas at depths of shallower than 100 m and along a flow path of less than 20 km. Fig. 1 shows that a static local groundwater flow system can be classified, into 3 areas including recharge, transition, and discharge. The groundwater flows from recharge areas through transition areas to discharge zones.

Groundwater flow dynamics is defined herein as changes of groundwater flow patterns due to seasonal fluctuations of hydraulic heads caused by seasonal fluctuation of surface-water levels and vertical groundwater recharge. A larger-scale exchange of groundwater and surface water is controlled by: (1) the distribution and degree of hydraulic conductivities within the channel and related alluvial sediments, (2) the relation of stream stage to the adjacent groundwater level, and (3) the position and geometry of the stream channel within the alluvial plain (Woessner 2000). The flow direction of the hydrologic interactions depends in hydraulic heads.

Seasonal variant hydrology alters the hydraulic head and thus induces changes in groundwater flow direction. Brunke and Gonser (1997) summarize the interactions between groundwater and rivers. With low precipitation, baseflow in streams contributes the discharge for most of the year. On the other hand, under conditions of high precipitation, surface runoff and interflow increase slowly, causing the river to change from effluent (where groundwater drains into the stream) into influent condition (where surface water contributes to subsurface flow), infiltrating its banks, and recharging the aquifer. During flooding, the river loses water to bank infiltration. The volume of bank storage varies with duration, height, shape of the flood hydrograph, and transmissivity and storativity of the aquifer. In the dry season, the stored water is released into the river. Successive discharge and recharge of the aquifer has a buffering effect on the runoff characteristics of rivers.

The chemical composition of groundwater changes through geologic time within a continuous flow system where recharge and discharge are static (Fig. 1). Such variations in hydrogeochemistry are used to categorize the groundwater flow system into zones, referred to as hydrogeochemical facies. Groundwater flow influences the distribution patterns of the facies because the flow reduces mixing by diffusion, carries the chemical imprints of changes from recharge areas, and leaches the aquifer (Chebotarev 1955; Back 1966; Williams 1970; Wallick 1981; Fogg and Kreitler 1982; Sanford 1994; Ingebritsen and Sanford 1998; Tóth 1999; Stuyfzand 1999). Without the groundwater flow, less variety of groundwater compositions would exist because diffusion would reduce the difference by mixing slowly through geologic time (Volker 1961). Can chemical composition patterns of groundwater develop in a dynamic confined alluvial aquifer located between two rivers?

For iron, evolutionary patterns of concentrations higher than 0.3 mg/L, a secondary drinking water standard set by the United States Environmental Protection Agency (1992), remain a controversial subject. At regional scale, various hypotheses have been presented, including: (1) no trend (Thorstenson et al. 1979), (2) discrete zones (Back and Barnes 1965; Langmuir 1969; Chapelle and Lovley 1992), (3) decreasing trend toward discharge areas (Champ et al. 1979), and (4) increasing trend toward discharge areas (Tóth 1999). At local scale, lateral evolutionary patterns of the iron remain unknown whereas the vertical pattern shows that iron concentrations increase toward the depths of 30-40 m but rarely increase beyond these levels (Starr and Gilham 1989; Barcelona et al. 1989; Barcelona and Holm 1991; Kehew et al. 1996; Kehew 2001).

A sequence of redox reactions has been observed during infiltration of oxic river water into the aquifer (von Gunten and Kull 1986; Jacobs et al. 1988; Lensing et al. 1994; Stuyfzand 1989; Bourg and Bertin 1993; Dousson et al. 1997; Groffman and Crossey 1999). Recently, Massmann et al. (2004) has investigated large-scale redox processes in a river recharge aquifer along the Oder River in Germany. At their site, river water permanently infiltrates into the shallow confined aquifer. Reduction processes from oxygen respiration to sulfate reduction dominate the groundwater quality about 3 km from the river. Large-scale (km-scale) redox sequences have also been reported by Lovley and Goodwin 1988; Chapelle and Lovley 1992; Brown et al. 2000). Reduction of Fe- and Mn-hydroxides leads to high concentrations of iron and manganese.

This paper describes a new finding that river incision into a confined alluvial aquifer results in intriguing groundwater flow dynamics which makes transition areas between two successive rivers isolate from oxygenated river water. Discrete zones of high iron concentrations in transition areas indicate the isolation. Groundwater resource developers can expect to obtain high-iron groundwater in the transition areas of a confined alluvial aquifer located between two rivers.

Hypothesis

Can chemical evolution still undergo in a dynamic confined alluvial aquifer located between two rivers? Our answer is no. The hypothesis is that a continuous flow regime is truncated if two successive parallel rivers that incise partially into the confined aquifer have seasonally variant water levels. The truncated flow leads to a lack of oxygenated water from rivers in transition areas. While vertical recharge from rainfall can occur through a confining unit, a lack of lateral recharge plays a more important role. Therefore, the transition areas are isolated from oxic conditions that can be indicated by abnormally high concentrations of some redox-sensitive species such as iron. This anomaly is a result of groundwater flow dynamics rather than the slow chemical evolution.

Fig. 2 shows schematic hypothetical models mentioned above. When groundwater moves slowly from a recharge zone into the aquifer in one season, it transports dissolved oxygen only by tens of meters (Fig. 2a). After the transition into the rainy season, the groundwater and solutes move along other directions by tens of meters and the former recharge zone becomes a discharge area (Fig. 2b). Moving in a zigzag pattern in recharge-discharge areas leads to a lack of dilution-oxidation by oxygenated water from rivers in the transition areas. A lack of lateral oxygenated recharge from the river does influence redox reactions and the availability of redox-sensitive species including oxygen, nitrate, manganese, iron, sulfate, hydrogen sulfide and methane. Iron, which is highly sensitive to dissolved oxygen, is often used to indicate suboxic or anoxic conditions of the aquifer. Therefore, concentrations of dissolved iron are high in the transition areas (Fig. 2c).

Testing Site

The study area is located about 20 km from the City of Phitsanulok, lower northern Thailand. Fig. 3 shows that the site is located inside a half-graben Tertiary structure (Wongsawat and Dhanesvanich 1983). Pre-Tertiary rocks form a basement with 1-2 km deep at the bottom. The Quaternary aquifer sediments overly semi-consolidated Tertiary ones.

Fig. 4 shows a cross-section which is based on detailed hydrogeologic investigation in this study. The aquifer is continuous, heterogeneous, and confined. It is the upper part of Chao Phraya aquifer, an alluvial deposit of channel-filled sand and gravel (Department of Mineral Resources 2001). The aquifer thickness varies from 13 to 21.5 m. A continuous clay layer, 13-21 m thick, overlies the aquifer. The underlying confining layer is also continuous. There are 8 gravel lens inside the aquifer. The Nan and Yom Rivers cut through the top of the aquifer and lens of fine-grained sand that connects to the aquifer. Therefore, the groundwater is highly interactive with surface-water bodies in both rivers. The aquifer yields at least 1,056 m^3/d of groundwater. The transmissivity and storage coefficient of the aquifer, measured in this study, are 1,988 m^2/d and 3.3×10^{-4}, respectively.

Three reasons make the area ideal for testing of the hypothesis. Firstly, the flow direction of the Nan and Yom Rivers are nearly parallel, approximately southward. Secondly, the spacing between the rivers is appropriate, about 6-7 km. Finally, both rivers incise slightly into the confined alluvial aquifer. As measured at gauging stations upstream and downstream to the study area in 2002, their riverbeds are located about 12-15 m deep below the land surface or about 2-5 m of penetration (Royal Irrigation Department, unpublished data).

Methodology

This study analyzes the groundwater from 25 wells located between the Nan and Yom Rivers (Fig. 3). The wells intersect the same aquifer at similar elevations (Fig. 4). Elevations of the land surface and the well's top were measured using standard surveying methods. Groundwater levels at Wells 12-16 were recorded weekly. Then, flow nets were drawn to study groundwater flow patterns, fluctuations, seasonal variation, and recharge-discharge relationships. Then, concentrations of iron and other parameters were drawn on a map and were superimposed by groundwater flow directions at the time of sampling to analyze for the effects of groundwater flow dynamics on redox conditions, particularly in transition areas.

Sampling

Major groundwater sampling took place in the dry season (March-April 2003) with a minor follow-up sampling for iron in rainy season (September 2003). The sampling for river water was also carried out later for comparison of the iron, dissolved oxygen, and redox potential with the groundwater. A flow-cell method (Kehew 2001) was used to obtain groundwater samples and to measure field parameters including temperature (T), specific conductance (SC), dissolved oxygen (DO), pH, and redox potential (Eh). Eh was carefully measured by using the Wood Method (Wood 1976). A bottle of Zobell's solution for Eh measurements was brought to sample temperature before reading. The Eh combination electrode consists of a platinum-sensing electrode connected to a reference electrode, which is made of silver enclosed in silver-chloride solution.

The groundwater was collected and preserved by using standard procedures and methods as described by American Public Health Association et al. (1998). Quality assurance samples were collected by duplicate sampling every 10 samples. The groundwater samples were unfiltered because the flow cell helps avoid the air exposure. The samples were collected almost inline and were preserved by nitric acid immediately after filling the bottle. Filtering can cause underestimation of iron concentrations. However, the river water samples were filtered with 0.45 μm membrane filters to exclude precipitates of Fe- and Mn-oxyhydroxides, which were formed by oxidation, as well as suspended clays. Samples for cation analysis were preserved with concentrated nitric acid. Alkalinity and sulfide samples were carefully filled without air entrapment and analyzed immediately in the laboratory. The remaining samples were transported and stored at 4° C.

Chemical Analysis

The chemical analysis was generally performed within one day after sampling. Parameters analyzed include total dissolved solids (TDS), sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), chloride (Cl^-), bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), sulfate (SO_4^{2-}), sulfide (S^{2-}), nitrate-N (NO_3^-), nitrite-N (NO_2^-), ammonia-N (NH_3), silica (SiO_2), iron (Fe^{2+}), and manganese (Mn^{2+}). Results were evaluated for their reliability using charge balance (Appelo and Postma 1993).

Alkalinity was determined by titration. Then, HCO_3^- and CO_3^{2-} were calculated. Water samples were analyzed for Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, and Mn^{2+} by atomic adsorption spectrophotometer. The ferrous iron was then calculated from the total iron by using a formula described by Freeze and Cherry (1979). TDS was obtained by drying at 180° C. Chloride was identified using mercuric nitrate method. Sulfate was measured using turbidimetric method. The S^{2-}, NO_3^-, and NO_2^- were analyzed by ion chromatography while NH_3 by nesslerization. Silica was analyzed by molybdosilicate method.

Results and Discussion

Groundwater Flow Dynamics

Fluctuation of groundwater levels depends on surface-water levels. Fig. 5 illustrates that groundwater levels near the Nan River (Well 12) are highly fluctuated. They are fairly stable in dry season and slightly increase in rainy season. In contrast, groundwater levels near the Yom River (Wells 16) drop in dry season but rapidly rise in rainy season. This feature responds to river-water levels. In transition areas (Wells 13, 14 and 15), groundwater levels, however, change slowly indicating that the role of river flow dynamics is less significant. Groundwater levels in all areas reach their peaks by the end of rainy season in late September-early October.

Seasonally variant hydraulic head in rivers is a predominant factor that controls the groundwater flow directions of the confined alluvial aquifer. Potentiometric surface is not a subdued replica of the land surface at all time. River flow dynamics changes groundwater flow directions continuously, particularly in areas near the rivers. Fig. 6 shows that the Nan and Yom Rivers flow southeastward. From January 27 (mid dry season) to June 3 (early rainy season), groundwater has flown continuously from the Nan River to the Yom River along 17°SW with a flow path of 15.2 m (Figs. 5a and 6a). From June 4 to October 4 (early dry season), the Yom River has begun to recharge into the aquifer along 80°NE with a flow path of 35 m while the Nan River is still recharging the system along 5°SE with a flow path of 40.3 m (Figs. 5b and 6b). From October 5 to January 7 (mid dry season), groundwater flows continuously from the Yom River toward the Nan River along 81°SE with a flow path of 34.7 m while the Nan River becomes a discharge area (Figs. 5c and 6c). Finally, from January 8 to 26, groundwater mounds in transition areas discharge into both Nan (82°SE) and Yom Rivers (15°SE) with flow paths of 4.5 m (Figs. 5d and 6d). The regional groundwater flow direction is toward 62°SE (Fig. 6e).

Our results are opposite to those done by Brunke and Gonser (1997) and Massmann et al. (2004), who consider water exchange processes at a single river. Obviously in this paper, at a particular moment in time, one river is effluent but another is influent. The baseflow from the aquifer into the stream does not always occur in the dry season but it occurs at both rivers only in about 2 weeks. For infiltration into the river bank, hydraulic heads in nearby rivers must be carefully considered. Classification of effluent and influent condition requires a through understanding of groundwater flow system in three dimensions.

Flow paths of oxygenated lateral recharge have, therefore, a zigzag pattern near recharge-discharge areas rather than a continuous curvilinear one across the entire flow system. Our study site does not conform to the conceptual model of a continuous flow regime across the entire system (i.e., Tóth 1963; Mayboom 1966, 1967; Winter 1976, 1999). Fig. 7 shows that lateral groundwater recharge from rivers does not penetrate into transition areas. Groundwater flow paths in each time period are very short in comparison with the distance of 6-7 km between both rivers. In general, the groundwater flow direction in transition areas has a similar zigzag pattern while flowing toward the SE. A generalized regional groundwater flow direction in transition areas is nearly parallel to the rivers.

As the works of Mayboom et al. (1966), Mayboom (1966, 1967), Winter (1976), Winter et al. (1999), Tóth (1962, 1963, 1999), and others have shown, flow paths between groundwater and surface water are two-dimensional and static but this paper shows the dynamic one. The spatial distribution of flow systems influences groundwater discharge. Groundwater discharge is not only confined along stream channel but also extends throughout discharge areas. Lakes and rivers are dynamic bodies, and the movement of groundwater in their vicinity is not static (Domenico 1972). A set of hydraulic-head measurements gives information only at a particular moment in time. The groundwater flow regime indeed requires a three-dimensional point-of-view consideration (Sophocleous et al. 1988; Sophocleous 1991; Harvey and Bencala 1993; Wondzell and Swanson 1996; Woessner 2000; Sophocleous 2002).

The general groundwater flow direction, toward the southeast, is nearly parallel to that of the river (Fig. 6e). This observation is coherent to what Larkin and Sharp (1992) calls the "underflow-component dominated stream-aquifer system," which the groundwater flux moves parallel to the river and in the same direction as the streamflow. The underflow component is predominant in fluvial systems of mixed-load to bed-loaded character and in systems with large channel gradients, small sinuosities, large width-to-depth ratios, and low river penetrations.

Evaluation of Chemical Analysis

Table 1 shows results of groundwater analysis. Using the flow cell method, an exposure of groundwater to the atmosphere is negligible. Average change balance is 3.66%, which indicates that the chemical analysis is reliable. Quality assurance samples meet the standard duplicated criteria. As plotted in the Eh-pH diagram, Fe^{2+} is the stable phase. Hydrochemical properties of major ions are identified as homogeneous, mainly Ca^{2+}-Mg^{2+}-HCO_3^- facies, by using the Piper's diagram.

Effects of Lateral Recharge

Fig. 7 shows that iron-rich groundwater exists in transition areas. It is mostly likely that a lack of oxygenated lateral recharge in transition areas has led to this anomaly. This evidence has proved that our hypothesis is correct. The zigzag flow pattern and the low penetration from the rivers leave the transition areas lack of dilution and oxidation by oxygenated river water, which influences redox reactions and the availability of redox-sensitive species, particularly iron. Therefore, concentrations of dissolved iron are high in the transition areas.

During mid dry season and early rainy season (January 27-June 3), the groundwater moves slowly from the Nan River (recharge zone) through the aquifer to the Yom River. It transports dissolved oxygen, which oxidizes ferrous iron immediately, by 15.2 m. In the rainy season (June 4-October 4), both rivers recharge the aquifer with the penetration ranging from 35-40.3 m from the rivers. In early to mid dry season (October 5-January 7), the Yom River continues to infiltrate the aquifer by 34.7 m whereas the groundwater drains into the Nan River. Baseflow into both rivers occurs only in two weeks (January 8-26) with a flow path of 4.5 m.

Reduction processes at our study site take place less than 100 m from both rivers whereas Massmann et al. (2004) finds the affected area of about 3 km from the river and tens of km by Lovley and Goodwin (1988). Difference in spacing between successive rivers may explain the contradiction. The short distance of 6-7 km between Nan and Yom Rivers causes the groundwater flow regime more dynamic.

Despite the fact that, based on isotope analyses in nearby aquifers, the groundwater at shallow depths of up to 50 m is likely to be less than 10 yrs old and that the groundwater recharge is almost entirely from rainfall (Howard Humphreys 1986), the seasonal changes of groundwater flow regime do not significantly affect the Fe^{2+} distribution in transition areas. Fe^{2+} concentrations in dry season (March-April) (Fig. 7a) decrease slightly in rainy season (September) (Fig. 7b) with larger discrepancy near the rivers. The anomaly is nearly constant in space.

Sophocleous (2002) points out that hydraulics properties of stream and lake beds control interactions between surface water and groundwater but these properties are difficult to measure directly. The limitation is the difficulty of spatially defining the hydraulic properties and spatial heterogeneities of those beds. Subsurface flow through the aquifer is slowly. The mechanisms that groundwater flow into streams quickly enough to contribute to streamflow responses to each rainstorm inputs is not fully understood. With better understanding of this process, effects of the lateral recharge on hydrogeochemistry of the aquifer will be clearly understood.

Effects of Vertical Recharge

At the study area, vertical recharge from rainfall flows through a confining layer as indicated by a high average DO concentration of 1.3 mg/L. Recharge is focused initially where the vadose zone is thin with respect to adjacent areas. It then progresses laterally over time to areas that have thicker unsaturated zones (Winter 1983). The changing volumes and distribution of recharge results in flow dynamics of groundwater flow systems directly adjacent to surface water, which causes highly variable discharge near the surface-water bodies. The infiltrating water is subject to physical and biogeochemical changes when entering the aquifer. Oxygen depletion occurs from the oxidation of iron bearing minerals in the aquifer sediments.

Groundwater recharge from canals is negligible. Only a few field investigations detail the pathways of water infiltration from stream channels or from canals to the water table (Stephens 1996). The aquifer in this study is too deep from the surface to have groundwater mound rising through the vadose zone to intersect the channel. This fact is always true even if the flow duration are sufficiently long for the vadose zone to reach steady-state moisture distribution, as long as the aquifer can transmit the recharging water away from the area (Bouwer and Maddock 1997). The aquifer becomes hydraulically disconnected from the canal.

It is uncommon to detect high concentrations of dissolved oxygen in a confined aquifer (Champ et al. 1979; Berner 1981). The oxygenated vertical recharge water affects redox conditions of most unconfined aquifers (i.e., Rose and Long 1988) rather than confined systems. We suspect that preferential flow through sandy parts of the confining unit leads to the above phenomenon. Nevertheless, a few researchers obtained results similar to ours (Edmunds et al. 1987; Groffman and Crossey 1999; Massmann et al. 2004). Winograd and Robertson (1982) found that 10,000-yr old groundwater, that traveled for 80 km from recharge areas, is still rich in DO (>7 mg/L). The presence of vertical recharge is, however, less important than the absence of lateral recharge, as evident by the high-iron anomaly in transition areas (Fig. 7).

Evolutionary Pattern

The evolutionary pattern of high iron concentrations along the general groundwater flow direction does not exist. Along the general groundwater direction, the anomaly is constant in the transition areas. This feature supports the hypothesis of discrete hydrogeochemical zones (Back and Barnes 1965; Langmuir 1969, 1997; Chapelle and Lovley 1992). Additional understanding of the aquifer mineralogy plus vertical redox conditions inside the aquifer will enhance our understanding about the anomaly present.

CONCLUSIONS AND NEEDED RESEARCH

Nature is dynamic. The interactions of surface water with groundwater of a confined alluvial aquifer located between two rivers are governed by the positions of surface-water bodies with respect to geologic characteristics of the aquifer and climatic settings. Subsequent groundwater flow dynamics is controlled by channel slope, river sinuosity, degree of river incision into the aquifer, characteristics of depositional system, and, most importantly, the seasonal fluctuation of surface-water levels. Interactions between surface water and groundwater occur by vertical recharge through the unsaturated zone and by infiltration into or exfiltration from the aquifer. These interactions affect redox conditions of the groundwater flow system.

This paper shows an interesting situation where two rivers partially cut into a confined aquifer and seasonally variant heads lead to groundwater flow dynamics. Groundwater flow reversal occurs when heads in both rivers change. Seasonal reversals of groundwater flow path yield a zigzag flow pattern rather than a continuous curvilinear one. Transition areas are thus isolated from oxygenated recharge water. The absence of lateral groundwater recharge from the rivers appears to play a more important role on than the presence of vertical recharge through the confining unit. The above mechanism explains the occurrence of discrete zones of high redox constituents such as iron in groundwater better than the hypothesis of chemical evolution. An evolutionary trend does not develop along short flow paths particularly in a river-bound local groundwater flow system whose flow paths are truncated. Redox conditions and patterns of redox-sensitive species are controlled by the groundwater and surface water flow patterns. This process is typical for a confined alluvial aquifer located between two rivers, particularly in tropical regions.

The spacing between the bounded rivers is important. At our study site, the Nan and Yom Rivers are about 6-7 km apart. Fluctuation of the river water levels at different periods leads to the zigzag groundwater flow pattern. It is of interest to study the effect of this factor on the groundwater flow regime and related hydrogeochemical pattern.

Streams and aquifers exchange water horizontally and vertically but most studies have used one- or two-dimensional models. A detailed three-dimensional study is needed for a better comprehension of the surface water-groundwater interactions. As Sophocleous (2002) notes, the present inability to characterize subsurface heterogeneity causes an upscaling problem and leads to uncertainties in data analysis and interpretation. Groundwater-surface water interactions must be quantified using multidisciplinary and multiscale approach including field observation, geographic information system, remote sensing, numerical modeling, and statistical analysis. The construction of alluvial-plain and stream cross-sections to show groundwater flow and quality along flow paths to the stream requires careful consideration.

Acknowledgements: Thailand Research Fund provided financial support (TRG4580065). We thank Roongwit Promma, Sanong Patanompee, Rath Wongnete, Prajonyuth Yimprae, and Siam Munmaung for field assistance.

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Table 1

Groundwater Quality across a Confined Alluvial Aquifer between Two Rivers[1]

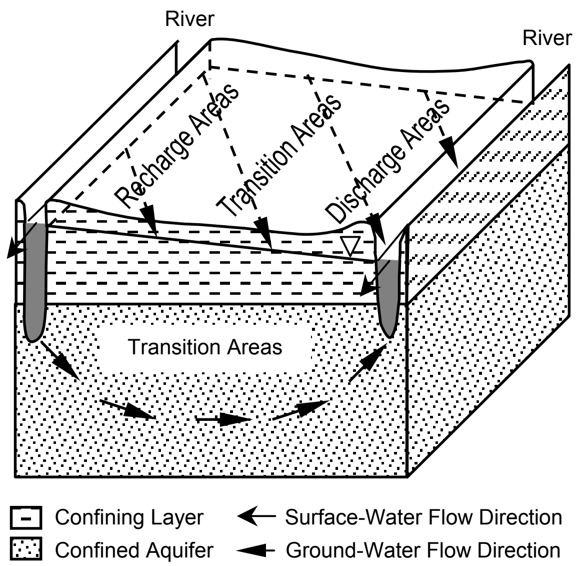
Well	T	SC	DO	pH	Eh	TDS	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	CO_3^{2-}	SO_4^{2-}	S^{2-}	NO_3^-	NO_2^-	NH_3	SiO_2	Fe^{2+}	Mn^{2+}	CB	Depth
1	27.99	276	0.71	6.38	148.2	171	21.1	1.78	23.4	5.9	2	135.39	0.02	7.5	<0.01	<0.01	<0.01	0.80	24	8.11	0.44	3.65	28
2	28.59	238	1.57	6.72	146.0	145	8.5	1.04	27.5	7.0	7	113.40	0.03	<0.1	<0.01	<0.01	<0.01	0.94	25	9.25	0.40	6.53	33
3	28.44	294	1.38	6.53	169.0	179	24.4	1.79	22.4	5.1	2	150.01	0.03	4.5	<0.01	<0.01	<0.01	0.72	26	10.33	0.35	0.67	28
4	28.64	297	0.59	6.54	182.3	181	26.6	1.68	22.0	5.0	2	148.79	0.03	5.8	<0.01	<0.01	<0.01	1.04	25	10.14	0.36	1.74	26
5	28.76	310	0.51	6.50	173.9	188	15.9	1.72	26.8	5.7	12	113.42	0.02	12.5	<0.01	<0.01	<0.01	0.32	21	8.70	0.78	1.67	28
6	28.46	269	1.61	6.46	183.1	164	7.0	1.19	29.5	8.2	8	103.67	0.01	7.0	<0.01	<0.01	<0.01	0.58	21	18.02	0.55	9.03	32
7	26.37	324	1.47	6.77	155.0	205	16.2	1.57	33.7	6.2	3	143.88	0.04	<0.1	<0.01	<0.01	<0.01	0.98	28	23.09	0.62	9.16	30
8	27.77	329	0.52	6.52	245.4	203	20.8	1.54	30.0	7.2	2	146.35	0.02	14.0	<0.01	0.03	<0.01	0.87	22	14.92	0.48	4.96	30
9	28.37	137	2.28	6.66	146.1	84	4.6	0.99	11.1	5.1	4	64.63	0.01	<0.1	<0.01	<0.01	<0.01	1.46	22	4.67	0.29	1.12	38
10	28.11	310	1.06	6.55	135.2	191	24.4	1.91	24.2	5.5	2	153.67	0.03	1.0	<0.01	<0.01	<0.01	1.20	28	11.85	0.09	3.24	36
11	28.75	268	1.78	6.77	126.0	162	14.4	0.91	28.9	7.6	3	134.12	0.04	<0.1	<0.01	<0.01	<0.01	0.62	31	11.42	0.05	8.66	30
12	28.85	423	1.30	6.85	97.7	256	9.1	1.79	40.3	11.7	20	168.24	0.06	13.0	<0.01	<0.01	<0.01	4.30	20	8.68	0.11	-2.55	30
13	28.39	383	1.64	6.60	118.4	233	22.0	1.32	33.3	9.1	4	189.02	0.04	<0.1	<0.01	<0.01	<0.01	1.58	21	19.41	0.10	2.86	30
14	28.06	291	2.82	6.75	132.8	179	23.9	1.28	28.9	5.2	3	163.39	0.05	2.0	<0.01	<0.01	<0.01	0.80	24	16.93	0.05	2.38	30
15	28.00	318	0.88	7.24	141.2	196	19.1	1.42	49.0	2.7	5	181.46	0.16	<0.1	<0.01	<0.01	<0.01	0.46	21	1.29	0.01	6.22	30
16	28.72	247	0.73	6.81	130.0	150	13.3	1.76	31.6	4.6	3	129.24	0.04	4.0	<0.01	<0.01	<0.01	0.52	20	9.50	0.18	5.99	30
17	27.65	301	0.72	6.46	89.9	186	14.7	1.31	25.6	8.0	3	156.11	0.01	2.5	<0.01	<0.01	<0.01	0.84	22	10.19	0.47	-1.64	28
18	27.11	320	0.97	6.46	130.6	200	19.7	1.00	24.6	7.6	1	162.21	0.01	5.5	<0.01	<0.01	<0.01	1.10	22	11.28	0.66	-1.19	20
19	26.92	319	2.27	6.61	131.7	200	18.6	1.15	24.3	8.0	5	171.95	0.02	<0.1	<0.01	<0.01	<0.01	0.70	24	8.85	0.11	-4.42	30
20	24.41	357	1.26	6.68	107.8	235	32.3	0.26	31.4	11.7	4	190.23	0.03	<0.1	<0.01	<0.01	<0.01	2.36	24	14.33	0.47	9.89	26
21	28.17	250	1.85	6.58	118.3	153	16.0	0.30	17.6	5.9	3	119.51	0.01	1.5	<0.01	<0.01	<0.01	0.62	20	19.64	0.68	-0.18	26
22	27.65	378	1.31	6.70	119.6	234	26.9	0.29	38.6	8.1	3	189.01	0.03	0.5	<0.01	<0.01	<0.01	0.70	18	14.86	0.55	8.28	30
23	27.69	328	0.87	6.69	112.7	203	21.7	0.27	22.9	7.1	2	152.43	0.03	<0.1	<0.01	<0.01	<0.01	0.76	19	17.59	0.38	2.33	30
24	27.12	298	1.19	6.73	115.4	186	20.0	0.31	17.7	6.7	3	117.06	0.03	1.5	<0.01	<0.01	<0.01	0.89	20	15.26	0.24	6.37	30
25	27.05	386	0.76	6.67	108.1	241	32.7	2.17	20.4	6.8	4	146.33	0.03	7.5	<0.01	<0.01	<0.01	0.87	20	21.30	0.47	6.77	30
Ave	27.84	306	1.28	6.65	138.6	189	19.0	1.23	27.4	6.9	4.4	145.74	0.03	3.6	<0.01	<0.01	<0.01	1.04	22.7	12.78	0.36	3.66	27.6
SD	0.98	57.6	0.60	0.18	33.3	36.5	7.2	0.58	7.9	2.0	4.0	29.92	0.03	4.4	0.00	0.01	0.00	0.80	3.2	5.29	0.22	3.98	6

All parameters in mg/L except T (°C), SC (μS/cm), Eh (mV), CB (%), and depth (m); Ave = average value; SD = standard deviation

LIST OF FIGURE LEGENDS

Fig. 7. Iron-rich groundwater in transition areas of the aquifer. High Fe^{2+} concentrations appear obviously in transition areas in both (a) dry and (b) rainy seasons. The hydrogeochemistry in transition areas is fairly constant in space and time.

Figure 1



River
River
Recharge Areas
Transition Areas
Discharge Areas
Transition Areas
Confining Layer
Confined Aquifer
Surface-Water Flow Direction
Ground-Water Flow Direction

Figure 2

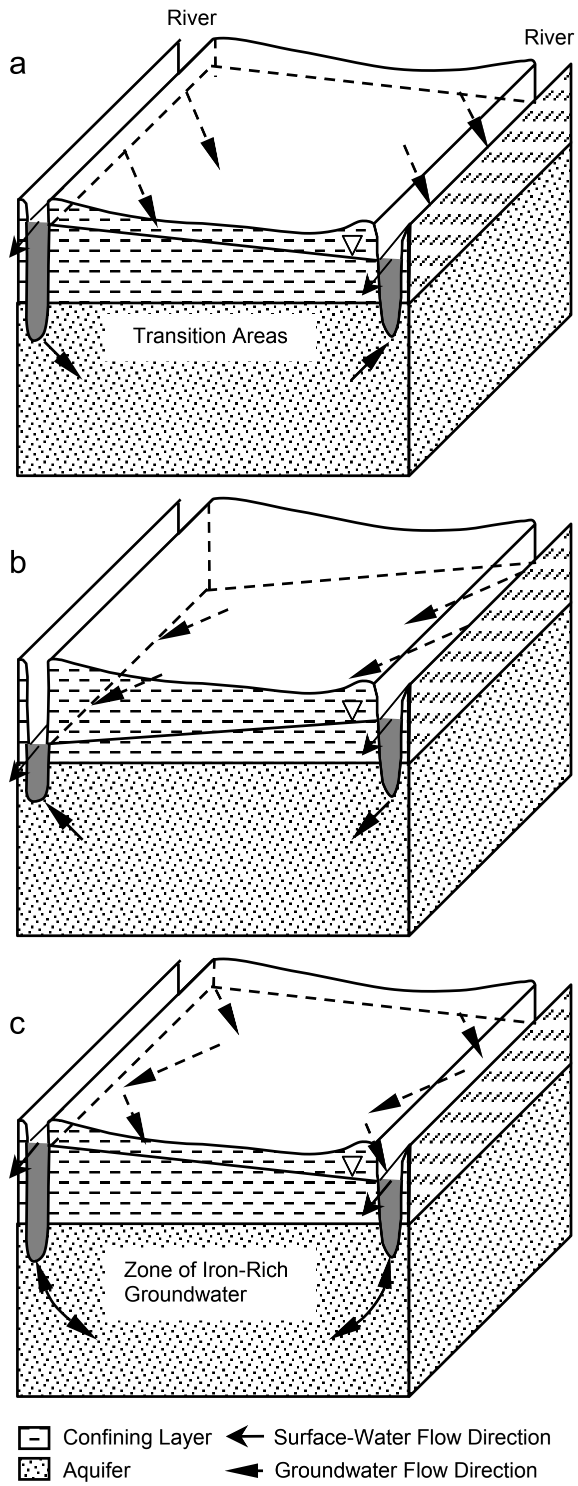

River
River
a
Transition Areas
b
c
Zone of Iron-Rich
Groundwater
Confining Layer
Aquifer
Surface-Water Flow Direction
Groundwater Flow Direction

Figure 3

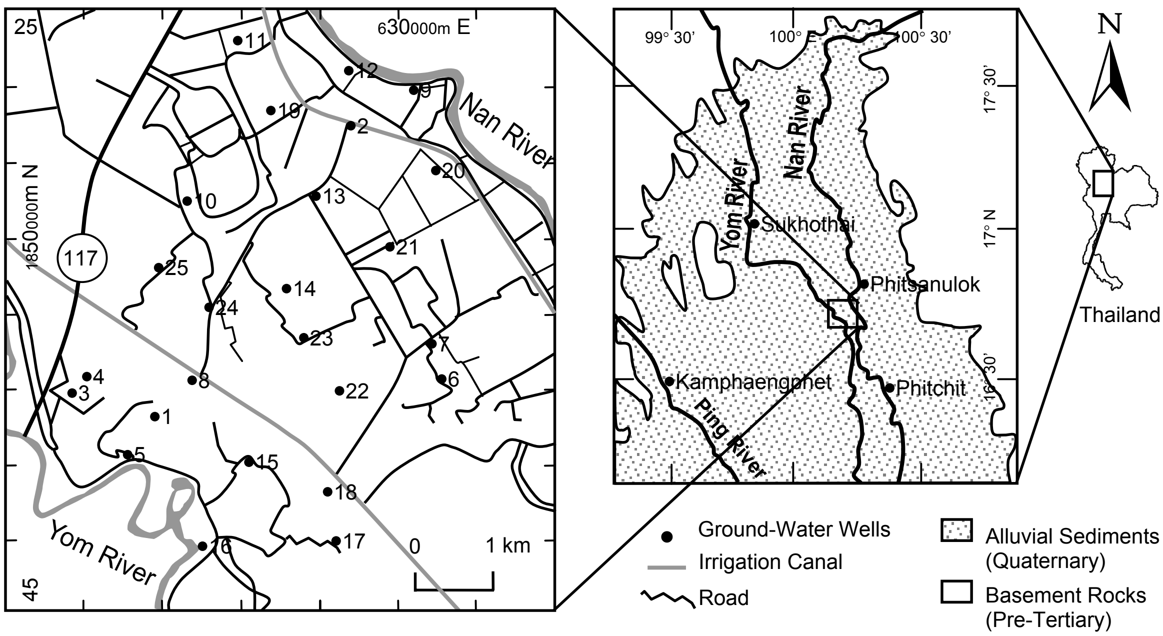

25
630000m E
1850000m N
45
117
Nan River
Yom River
0
1 km
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
99° 30'
100° E
100° 30'
17° 30'
17° N
16° 30'
Yom River
Nan River
Sukhothai
Phitsanulok
Kamphaengphet
Phitchit
Ping River
N
Thailand
Ground-Water Wells
Irrigation Canal
Road
Alluvial Sediments (Quaternary)
Basement Rocks (Pre-Tertiary)

Figure 4

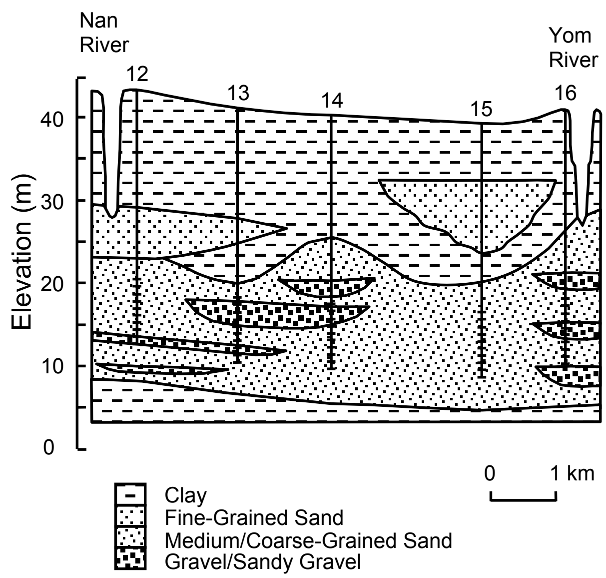
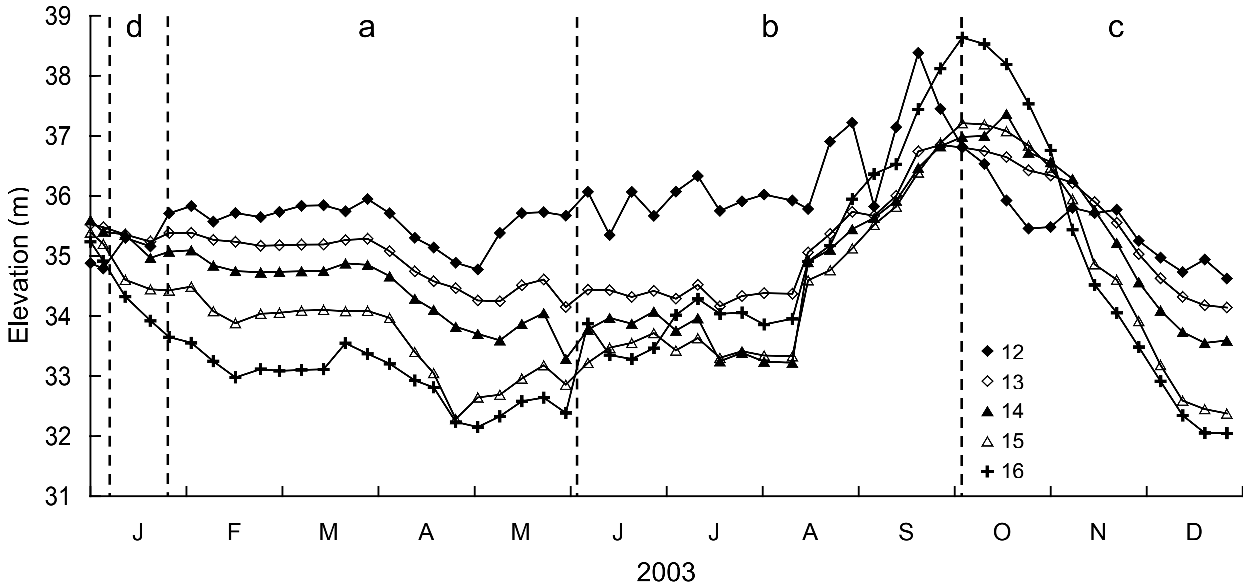

Nan
River
Yom
River
12
13
14
15
16
40
30
20
10
0
Elevation (m)
0
1 km
Clay
Fine-Grained Sand
Medium/Coarse-Grained Sand
Gravel/Sandy Gravel

Figure 5



39
38
37
36
35
34
33
32
31
Elevation (m)
d
a
b
c
12
13
14
15
16
J
F
M
A
M
J
J
A
S
O
N
D
2003

Figure 6

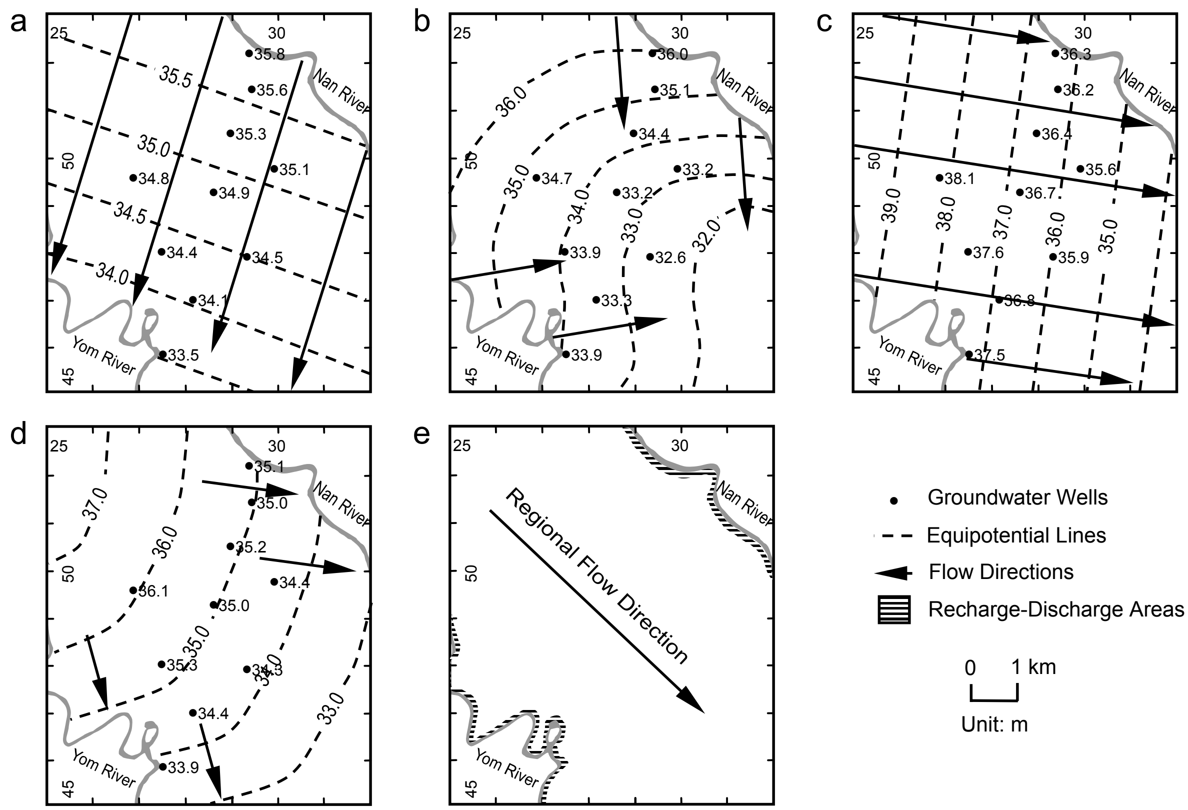
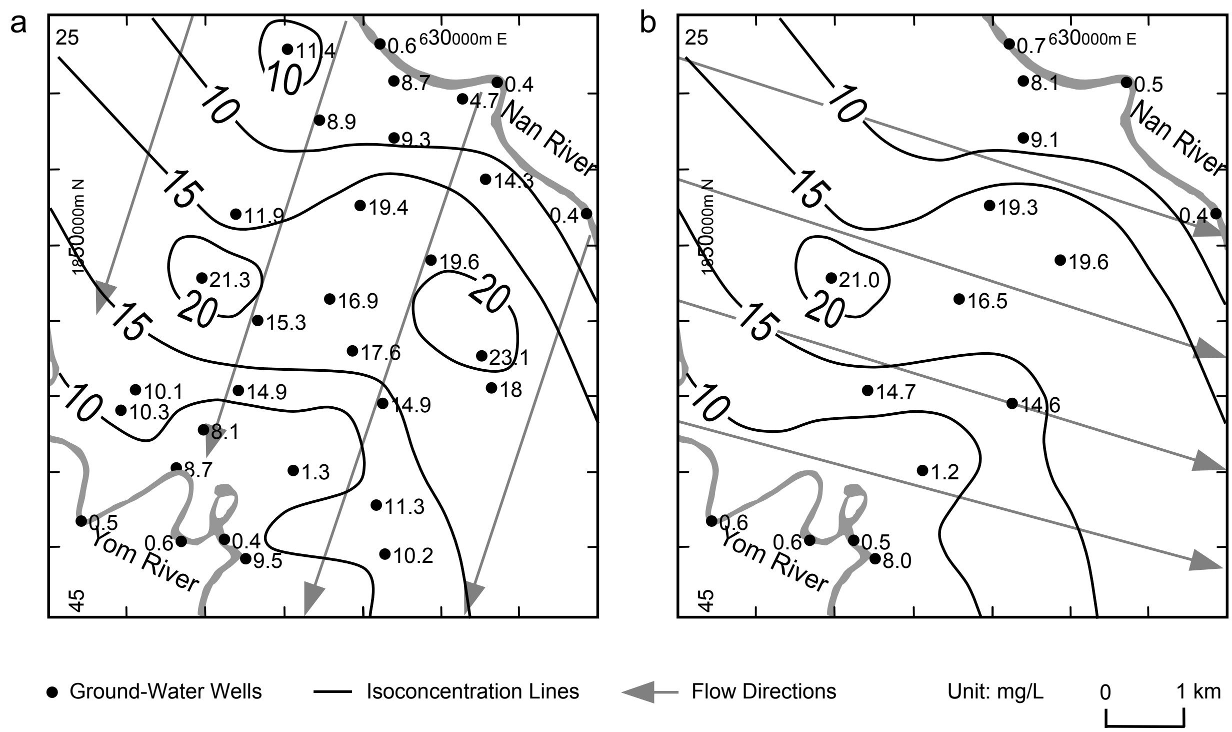

a
b
c
d
e
Nan River
Yom River
Regional Flow Direction
Groundwater Wells
Equipotential Lines
Flow Directions
Recharge-Discharge Areas
0 1 km
Unit: m

Figure 7


a
b
25
630000m E
1850000m N
45
Nan River
Yom River
10
15
20
11.4
0.6
8.7
0.4
4.7
8.9
9.3
14.3
11.9
19.4
0.4
19.6
21.3
16.9
15.3
17.6
23.1
18
10.1
10.3
14.9
14.9
8.1
8.7
1.3
11.3
0.5
0.6
0.4
9.5
10.2
0.7
8.1
0.5
9.1
19.3
0.4
19.6
21.0
16.5
14.7
14.6
1.2
0.6
0.6
0.5
8.0
Ground-Water Wells
Isoconcentration Lines
Flow Directions
Unit: mg/L
0
1 km

APPENDIX B

Manuscript 2

Simulation of Groundwater Flow Dynamics and Traces of Redox-Sensitive Species in a Confined Alluvial Aquifer Located between Two Rivers

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Abstract

This paper demonstrates a simulation of particle tracing of redox-sensitive species, mainly iron, in a dynamic confined alluvial aquifer located between two rivers. In this groundwater flow system, discrete zones of anomalously high concentrations of redox species are a result of groundwater flow dynamics. At a study site located between Nan and Yom Rivers in Phitsanulok, Thailand, a river incision into the confined aquifer and related seasonally variant hydrology result in truncated flow paths and zigzag groundwater flow patterns. In a conceptual model, the lateral recharge from rivers penetrates into the aquifer only by tens of meters. Because the absence of lateral groundwater recharge from rivers appears to play a more important role on than the presence of vertical recharge from rainfall, a low recharge rate was set uniform over the domain. Simulated flow patterns match observed ones very well. The vertical recharge rate is the most sensitive parameter. Transient flow modeling can simulate groundwater flow dynamics and traces of redox-sensitive species in a confined alluvial aquifer located between two rivers.

(171 words)

Keywords

Groundwater/surface-water relations, Numerical modeling, Groundwater flow, Particle tracking, Thailand

INTRODUCTION

Groundwater/Surface-Water Relations

The interaction between groundwater and surface water has been studied since the 1960s because of concerns about eutrophication and acid rain (Winter 1995). The growth in research has mushroomed during the 1990s, especially in physical and biogeochemical aspects (Stanley and Jones 2000). Recently, interest in interactions between near-channel and in-channel water, which are important for ecological system near the stream, has been increased greatly (Sophocleous 2002). The spatial and temporal dynamics of groundwater recharge and discharge along active channels in varying geomorphic settings needs further study. Quantification of the dynamic temporal changes of water movements and chemical fluxes through these boundaries is significant (Dahm et al. 1998). An understanding of interactions between groundwater and surface water as well as subsequent groundwater quality is a key for successful integrated management of water resources.

The groundwater flow system depends on hydrogeologic environment including topography, geology, and climate (Tóth 1970). Hubbert (1940) shows that, given a uniform recharge, an unconfined groundwater flow system develops and is influenced by a water table configuration, which is a subdued replica of the land surface. Hydraulic conductivity of aquifers also controls the flow patterns (Freeze and Witherspoon 1967). Groundwater moves along flow paths and form a flow system. Based on a relative position in space, Tó th (1962, 1963) classifies three types of flow systems including local, intermediate, and regional. The local groundwater flow system is defined, in this study, as a coherent, three-dimensional unit of groundwater flow with one recharge and one or more discharge areas at depths of shallower than 100 m and along a flow path of less than 20 km. Fig. 1 shows that a static local groundwater flow system can be classified, into 3 areas including recharge, transition, and discharge. The groundwater flows from recharge areas through transition areas to discharge zones.

Groundwater flow dynamics is defined herein as changes of groundwater flow patterns due to seasonal fluctuations of hydraulic heads caused by seasonal fluctuation of surface-water levels and vertical groundwater recharge. A larger-scale exchange of groundwater and surface water is controlled by: (1) the distribution and degree of hydraulic conductivities within the channel and related alluvial sediments, (2) the relation of stream stage to the adjacent groundwater level, and (3) the position and geometry of the stream channel within the alluvial plain (Woessner 2000). The flow direction of the hydrologic interactions depends in hydraulic heads.

Seasonal variant hydrology alters the hydraulic head and thus induces changes in groundwater flow direction. Brunke and Gonser (1997) summarize the interactions between groundwater and rivers. With low precipitation, baseflow in streams contributes the discharge for most of the year. On the other hand, under conditions of high precipitation, surface runoff and interflow increase slowly, causing the river to change from effluent (where groundwater drains into the stream) into influent condition (where surface water contributes to subsurface flow), infiltrating its banks, and recharging the aquifer. During flooding, the river loses water to bank infiltration. The volume of bank storage varies with duration, height, shape of the flood hydrograph, and transmissivity and storativity of the aquifer. In the dry season, the stored water is released into the river. Successive discharge and recharge of the aquifer has a buffering effect on the runoff characteristics of rivers.

A sequence of redox reactions has been observed during infiltration of oxic river water into the aquifer (von Gunten and Kull 1986; Jacobs et al. 1988; Lensing et al. 1994; Stuyfzand 1989; Bourg and Bertin 1993; Dousson et al. 1997; Groffman and Crossey 1999). Recently, Massmann et al. (2004) has investigated large-scale redox processes in a river recharge aquifer along the Oder River in Germany. At their site, river water permanently infiltrates into the shallow confined aquifer. Reduction processes from oxygen respiration to sulfate reduction dominate the groundwater quality about 3 km from the river. Large-scale (km-scale) redox sequences have also been reported by Lovley and Goodwin 1988;

Chapelle and Lovley 1992; Brown et al. 2000). Reduction of Fe- and Mn-hydroxides leads to high concentrations of iron and manganese.

Groundwater Models

Groundwater models can be classified by their application into 3 types including groundwater flow, contaminant transport, and hydrogeochemical model. The groundwater flow model, such as MODFLOW (McDonald and Harbaugh 1988), is used to determine groundwater levels and flow directions under specific scenarios. The contaminant transport model, such as MT3DMS (Zheng and Wang 1999), is used to identify concentrations of solutes in space and time. The hydrogeochemical model, for example PHREEQC (Parkhurst and Appelo 1999), is used to calculate speciation and saturation states of groundwater. Many groundwater models are reviewed and tested (Nordstrom et al. 1979; Grove and Stollenwerk 1987; Nordstrom et al. 1990; Mangold and Tsang 1991). Models used in this study include MODFLOW (McDonald and Harbaugh 1988) and MODPATH (Pollack 1994a,b) in Groundwater Vistas (Environmental Solutions Inc 2001) and PHREEQC (Parkhurst and Appelo 1999) in AquaChem (Waterloo Hydrogeologic Inc 2003).

MODFLOW, which is available at http://water.usgs.gov/software/modflow.html, is a three-dimensional, finite-difference, numerical, groundwater flow model (Harbaugh et al. 2000). It is currently the most used numerical flow model for groundwater problems. It has been developed continuously since 1984 (McDonald and Harbaugh 1988; Harbaugh and McDonald 1996a, b; Harbaugh et al. 2000). A modular structure allows it to be easily modified to adapt codes for a particular application, called package. The current version of MODFLOW-2000 has 26 packages. This code simulates steady-state and transient flow in confined, unconfined, or a combination of both aquifers. Hydraulic conductivities and storage coefficients for any layer may differ spatially. In addition to simulating groundwater flow, MODFLOW-2000 is able to incorporate related capabilities including sensitivity analysis and parameter estimation (Hill et al. 2000).

The MODFLOW code is regularly upgraded and is well documented, for example:

1. Converting no-flow cells to variable-head cells (McDonald et al. 1992),
2. Addition of alternate interblock transmissivities (Goode and Appel 1992),
3. Preconditioned conjugate gradient package (Hill 1990),
4. Streamflow-routing package (Prudic 1989),
5. Time-variant specified-head package (Leake and Prudic 1991),
6. Horizontal-flow barrier package (Hsieh and Freckleton 1993),
7. Direct solution package (Harbaugh 1995),
8. Leakage from reservoirs (Fenske et al. 1996),
9. Assignment of transient specified-flow and specified-head boundaries (Leake and Lilly 1997),
10. Advective-transport observation package (Anderman and Hill 1997, 1998),

11. Enhancing calibration (Hill 1998),
12. Extracting and processing time-series data (Hanson and Leake 1999),
13. Simulation of aquifer-system compaction (Leake and Prudic 1991),
14. Hydrogeologic-unit flow package (Anderman and Hill 2000),
15. Simulation of lake-aquifer interaction (Merritt and Konikow 2000),
16. Simulating evapotranspiration with a segmented function and drains with return flow (Banta 2000),
17. Solving matrix equations using an algebraic multigrid solver (Mehl and Hill 2001), and
18. Linkage with MT3DMS code (Zheng et al. 2001).

Groundwater Vistas (Environmental Solutions Inc 2001) is a graphic-user-interface software package that combines flow (MODFLOW) and particle tracking (MODPATH) models. MODPATH, which is available at http://water.usgs.gov/software/modpath.html, is a particle tracking post-processing program designed to work with MODFLOW (Pollock 1994a,b). Output from MODFLOW simulations was used in MODPATH to compute flow paths for imaginary particles of water moving through the simulated groundwater system. It also kept track of the time of travel for particles moving through the system. Previous versions of MODPATH are described in Pollock (1989a,b).

MODPATH is written primarily in standard Fortran 77 and can be compiled with any standard Fortran 90 compiler. The MODPATH package has been widely applied to MODFLOW-based groundwater flow simulation studies. It is useful as a visualization tool to help understand flow patterns in simulated groundwater flow systems. It also has been widely used to delineate sources of water to discharge sites and aquifers in systems simulated with MODFLOW. MODPATH has a number of limitations, which are related to (1) underlying assumptions in the particle tracking scheme, (2) discretization effects, and (3) uncertainty in parameters and boundary conditions.

PHREEQC is a numerical hydrogeochemical model based on an ion-association aqueous model (Parkhurst and Appelo 1999). It is capable of (1) calculating activities and saturation states for a given groundwater analysis, (2) calculating how water composition changes in response to reactions or a change in temperature, and (3) testing a concept or a suite of reactions for a hydrogeochemical hypothesis (Plummer et al. 1988; Plummer et al. 1991; Plummer et al. 1994; Charlton et al. 1997). The hydrogeochemical model is developed from space-rocket science and has been used in many case studies (Smith and Missen 1982; Parkhurst and Plummer 1993; Appelo and Postma 1993; Bethke 1996). It prevents errors or violations of basic chemical laws. The mass action and mass balance relationship gives a set of non-linear equations for which a solution can be obtained using Newton-Raphson iteration. The hydrogeochemical models have been used to study the evolution of water quality as influenced by:

1. Silicate weathering (Helgeson et al. 1970; Lichtner 1985)
2. Carbonate reactions (Plummer et al. 1983)
3. Effects of acidification and buffering reactions (Cosby et al. 1985)

4. Ore deposition and leaching of mine tailings (Garven and Freeze 1984; Liu and Narasimhan 1989)
5. Cation exchange with salt-water intrusion (Appelo and Willemsen 1987; Appelo et al. 1990)
6. Complexation of heavy metals and sorption (Felmy et al. 1984)
7. Denitrification (Postma et al. 1991).

The PHREEQC code and its predecessor have been used in many studies (Parkhurst et al. 1980; Appelo and Willemsen 1987; Mirecki and Parks 1993; Nordstrom 1996; Alpers and Nordstrom 1999; Gimeno Serrano et al. 2000; Nordstrom 2000; Welch et al. 2000).

AquaChem is another software package that interacts users with PHREEQC (Waterloo Hydrogeologic Inc 2003). It is developed for graphical display and numerical analysis and modeling of water quality data. AquaChem's data analysis capabilities include unit conversions, charge balances, sample comparison and mixing, statistical summaries, trend analysis, and relevant plotting to represent the chemical characteristics of water quality data, among others.

The plot types available in AquaChem include:

1. Correlation plots: X-Y Scatter, Ludwig-Langelier, and Wilcox
2. Summary plots: Box and Whisker, Frequency Histogram, and Schoeller
3. Trilinear plots: Piper, Durov, Ternary, and Giggenbach
4. Time-Seriesplot
5. Geothermometer plot
6. Sample plots: Radial, Stiff, and Pie
7. Thematic Map plots: Bubble, Pie, Radial and Stiff plots at sample locations

Each of these plots provides a unique interpretation of the many complex interactions between the groundwater and aquifer materials, and identifies important data trends and groupings. AquaChem also has a link to PHREEQC for calculating equilibrium concentrations (or activities) of chemical species in solution and saturation indices of solid phases in equilibrium with a solution.

This paper describes the model development and application of the Groundwater Vistas code (Environmental Simulations Inc. 2001), a combined user-interface version of MODFLOW and MODPATH, for the purpose of simulating zigzag flow paths in a confined alluvial aquifer. The zigzag flow paths are a result of river incision into a confined alluvial aquifer and related intriguing groundwater flow dynamics.

Hydrogeologic Setting

The study area is located about 20 km from the City of Phitsanulok, lower northern Thailand. Fig. 1 shows that the site is located inside a half-graben Tertiary structure (Wongsawat and Dhanesvanich 1983). Pre-Tertiary rocks form a basement with 1-2 km deep at the bottom. The Quaternary aquifer sediments overly semi-consolidated Tertiary ones.

Fig. 2 shows a cross-section which is based on detailed hydrogeologic investigation in this study. The aquifer is continuous, heterogeneous, and confined. It is the upper part of Chao Phraya aquifer, an alluvial deposit of channel-filled sand and gravel (Department of Mineral Resources 2001). The aquifer thickness varies from 13 to 21.5 m. A continuous clay layer, 13-21 m thick, overlies the aquifer. The underlying confining layer is also continuous. There are 8 gravel lens inside the aquifer. The Nan and Yom Rivers cut through the top of the aquifer and lens of fine-grained sand that connects to the aquifer. Therefore, the groundwater is highly interactive with surface-water bodies in both rivers. The aquifer yields at least 1,056 m^3/d of groundwater. The transmissivity and storage coefficient of the aquifer, measured in this study, are 1,988 m^2/d and 3.3×10^{-4}, respectively.

The flow direction of the Nan and Yom Rivers are nearly parallel, approximately southward. The spacing between the rivers is appropriate, about 6-7 km. Both rivers incise slightly into the confined alluvial aquifer. As measured at gauging stations upstream and downstream to the study area in 2002, their riverbeds are located about 12-15 m deep below the land surface or about 2-5 m of penetration (Royal Irrigation Department, unpublished data).

Groundwater Flow Dynamics

According to Promma et al. (xxx), fluctuation of groundwater levels depends on surface-water levels. Fig. 3 illustrates that groundwater levels near the Nan River (Well 12) are highly fluctuated. They are fairly stable in dry season and slightly increase in rainy season. In contrast, groundwater levels near the Yom River (Wells 16) drop in dry season but rapidly rise in rainy season. This feature responds to river-water levels. In transition areas (Wells 13, 14 and 15), groundwater levels, however, change slowly indicating that the role of river flow dynamics is less significant. Groundwater levels in all areas reach their peaks by the end of rainy season in late September-early October.

Seasonally variant hydraulic head in rivers is a predominant factor that controls the groundwater flow directions of the confined alluvial aquifer. Potentiometric surface is not a subdued replica of the land surface at all time. River flow dynamics changes groundwater flow directions continuously, particularly in areas near the rivers. Fig. 4 shows that the Nan and Yom Rivers flow southeastward. From January 27 (mid dry season) to June 3 (early rainy season), groundwater has flown continuously from the Nan River to the Yom River along 17°SW with a flow path of 15.2 m (Figs. 3a and 4a). From June 4 to October 4 (early dry season), the Yom River has begun to recharge into the aquifer along 80°NE with a flow path of 35 m while the Nan River is still recharging the system along 5°SE with a flow path of 40.3 m (Figs. 3b and 4b). From October 5 to January 7 (mid dry season), groundwater flows continuously from the Yom River toward the Nan River along 81°SE with a flow path of 34.7 m while the Nan River becomes a discharge area (Figs. 3c and 4c). Finally, from January 8 to 26, groundwater mounds in transition areas discharge into both Nan (82°SE) and Yom Rivers (15°SE) with flow paths of 4.5 m (Figs. 3d and 4d). The regional groundwater flow direction is toward 62°SE (Fig. 4e).

Flow paths of oxygenated lateral recharge have, therefore, a zigzag pattern near recharge-discharge areas rather than a continuous curvilinear one across the entire flow system. Our study site does not conform to the conceptual model of a continuous flow regime across the entire system (i.e., Tóth 1963; Mayboom 1966, 1967; Winter 1976, 1999). Fig. 5 shows that lateral groundwater recharge from rivers does not penetrate into transition areas. Groundwater flow paths in each time period are very short in comparison with the distance of 6-7 km between both rivers. In general, the groundwater flow direction in transition areas has a similar zigzag pattern while flowing toward the SE. A generalized regional groundwater flow direction in transition areas is nearly parallel to the rivers.

As the works of Mayboom et al. (1966), Mayboom (1966, 1967), Winter (1976), Winter et al. (1999), Tóth (1962, 1963, 1999), and others have shown, flow paths between groundwater and surface water are two-dimensional and static but this paper shows the dynamic one. The spatial distribution of flow systems influences groundwater discharge. Groundwater discharge is not only confined along stream channel but also extends throughout discharge areas. Lakes and rivers are dynamic bodies, and the movement of groundwater in their vicinity is not static (Domenico 1972). A set of hydraulic-head measurements gives information only at a particular moment in time. The groundwater flow regime indeed requires a three-dimensional point-of-view consideration (Sophocleous et al. 1988; Sophocleous 1991; Harvey and Bencala 1993; Wondzell and Swanson 1996; Woessner 2000; Sophocleous 2002).

The general groundwater flow direction, toward the southeast, is nearly parallel to that of the river (Fig. 4e). This observation is coherent to what Larkin and Sharp (1992) calls the "underflow-component dominated stream-aquifer system," which the groundwater flux moves parallel to the river and in the same direction as the streamflow. The underflow component is predominant in fluvial systems of mixed-load to bed-loaded character and in systems with large channel gradients, small sinuosities, large width-to-depth ratios, and low river penetrations.

MODEL DEVELOPMENT

MODFLOW and MODPATH models were used to simulate transient groundwater flows between two dynamic rivers for a period from January to December 2003. Design criteria were followed those described by Anderson and Woessner (1992) and Zheng and Bennett (2002). Fig. 6 was redrawn into a simple conceptual model (Fig. 7). These data were used to perform model calibration and to set stress periods and subsequent time steps.

Fig. 7 shows the conceptual model of a single aquifer with a constant 15 m thickness. The domain was assumed to be homogeneous and isotropic. Rivers act as a constant head whereas the groundwater source occurs at the northwest boundary and the sink is located on the other end. Constant heads of rivers were changed in 4 scenarios to accommodate the groundwater flow dynamics. Vertical recharge from rainfall was assumed to have a constant rate over the entire domain. The bottom of the domain is a no-flow boundary.

Groundwater Vistas version 3 (Environmental Solutions Inc 2001) was used to simulate groundwater flow paths in this study. It used a modified version of MODFLOW (McDonald and Harbaugh 1988) to solve the groundwater flow equation and used MODPATH version 3 (Pollock 1994a,b) to solve for zigzag flow paths. Output from MODFLOW simulations was used in MODPATH to compute flow paths for imaginary particles of water moving through the simulated groundwater system.

A regularly spaced, finite-difference model grid was constructed and rotated so that the x-axis would roughly parallel the principal direction of groundwater flow (Fig. 8). Each cell is 200 m x 200 m in the horizontal plane. The grid consists of 50 rows and 35 columns. The rotation angle from the North is anticlockwise 46 degrees. The model rows are aligned with the principal direction of groundwater flow. A simulation stress period of one year was discretized into 4 scenarios. For each scenario, parameters are assumed to be constant. Each stress period is divided into time steps, the lengths of which are determined by Groundwater Vistas to meet specified criteria related to solving the governing equation. About 20 time steps were required for each stress period.

SIMULATED FLOW PATTERNS

Simulated groundwater flow patterns matched observed ones very well (Fig. 9). During mid dry season and early rainy season (January 27-June 3), the groundwater moves slowly from the Nan River (recharge zone) through the aquifer to the Yom River. It transports dissolved oxygen, which oxidizes ferrous iron immediately, by 15.2 m. In the rainy season (June 4-October 4), both rivers recharge the aquifer with the penetration ranging from 35-40.3 m from the rivers. In early to mid dry season (October 5-January 7), the Yom River continues to infiltrate the aquifer by 34.7 m whereas the groundwater drains into the Nan River. Baseflow into both rivers occurs only in two weeks (January 8-26) with a flow path of 4.5 m.

Sophocleous (2002) points out that hydraulics properties of stream and lake beds control interactions between surface water and groundwater but these properties are difficult to measure directly. The limitation is the difficulty of spatially defining the hydraulic properties and spatial heterogeneities of those beds. Subsurface flow through the aquifer is slowly. The mechanisms that groundwater flow into streams quickly enough to contribute to streamflow responses to each rainstorm inputs is not fully understood. With better understanding of this process, effects of the lateral recharge on hydrogeochemistry of the aquifer will be clearly understood.

CONCLUSIONS

Dynamic groundwater flow can be simulated using transient mode. Nature is dynamic. The interactions of surface water with groundwater of a confined alluvial aquifer located between two rivers are governed by the positions of surface-water bodies with respect to geologic characteristics of the aquifer and climatic settings. Subsequent groundwater flow dynamics is controlled by channel slope, river sinuosity, degree of river incision into the aquifer, characteristics of depositional system, and, most importantly, the seasonal fluctuation of surface-water levels. Interactions between surface water and groundwater occur by vertical recharge through the unsaturated zone and by infiltration into or exfiltration from the aquifer. These interactions affect redox conditions of the groundwater flow system.

Acknowledgements: Thailand Research Fund provided financial support (TRG4580065). We thank Roongwit Promma, Sanong Patanompee, Rath Wongnete, Prajonyuth Yimprae, and Siam Munmaung for field assistance.

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LIST OF FIGURE LEGENDS

Fig. 1. Location of the study area in Phitsanulok, lower northern Thailand (Promma et al. xxx). The Nan River binds the aquifer in the east and the Yom River in the west. Both rivers flow southward. Wells used to test the hypothesis are sufficiently distributed between both rivers.

Fig. 2. Geologic cross-section (Promma et al. xxx). The aquifer is confined, continuous, and heterogeneous. It is bound in the top and the bottom by continuous confining units. Rivers cut through the top of the aquifer but they penetrate into it only slightly.

Fig. 3. Seasonal fluctuation of groundwater levels and flow dynamics (Promma et al. xxx). (a) In the mid-late dry season, groundwater levels near the Yom River decline rapidly and the aquifer discharges into the Yom River. (b) Then, the Yom River begins to recharge into the aquifer in the rainy season. (c) After groundwater levels approach their peaks in the late rainy season, the aquifer discharges into the Nan River. (d) Finally, groundwater mounds in transition areas recharge both rivers.

Fig. 4. Groundwater flow dynamics (Promma et al. xxx). The groundwater flow regime can be classified into 4 phases, including (a) uniform flow from Nan River to Yom River, (b) recharge from both rivers into the aquifer, (c) uniform flow from Yom River to Nan River, and (d) discharge from mounds to rivers. The regional flow direction is shown in (e). See Fig. 5 for weekly groundwater levels.

Fig. 5. Iron-rich groundwater in transition areas of the aquifer (Promma et al. xxx). High Fe^{2+} concentrations appear obviously in transition areas in both (a) dry and (b) rainy seasons. The hydrogeochemistry in transition areas is fairly constant in space and time.

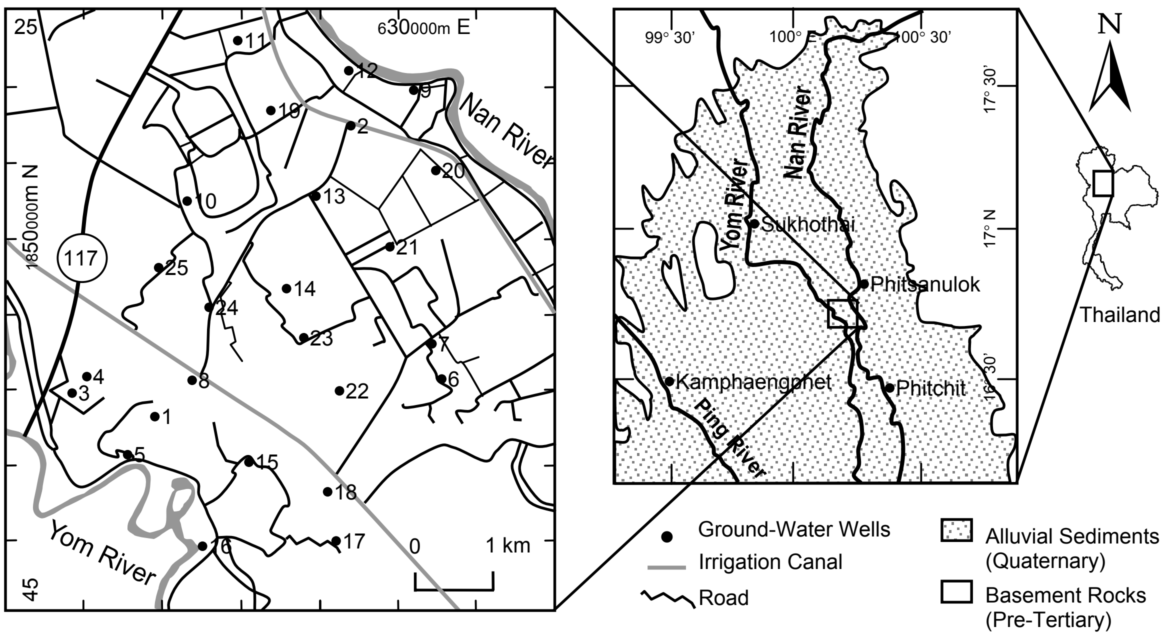
Fig. 6. Schematic hypothetical models of iron accumulation in transition areas of a confined local groundwater flow system between two dynamic streamflows (Promma et al. xxx). (a) When one river rises above another, groundwater levels respond quickly and begin a lateral recharge-discharge process. (b) Groundwater flow reversal follows the same process. (c) The resulting flow direction has a zigzag pattern preventing the oxygenated lateral recharge from reaching the transition areas. If vertical recharge from rainfall is less important than a lack of lateral recharge from river, anoxic conditions in the transition areas prevail and they are indicated by anomalously high concentrations of redox species such as iron. This anomaly is a result of groundwater flow dynamics rather than chemical evolution.

Fig. 7. Conceptual model. The model has a single aquifer with a constant 15 m thick. The domain is assumed to be homogeneous and isotropic. Rivers act as a constant head whereas the groundwater source occurs at the northwest boundary and the sink is located on the other end. Constant heads of rivers were changed in 4 scenarios to accommodate the groundwater flow dynamics. Vertical recharge from rainfall was assumed to have a constant rate over the entire domain. The bottom of the domain is a no flow boundary.

Fig. 8. Grid design and boundary conditions. A regularly spaced, finite-difference model grid was constructed and rotated so that the x-axis would roughly parallel the principal direction of ground-water flow. Each cell is 200 m x 200 m in the horizontal plane. The grid consists of 50 rows and 35 columns.

Fig. 9. Simulated flow paths. Simulated groundwater flow patterns are well matched to those observed in the field. The groundwater flow regime includes: (a) uniform flow from Nan River to Yom River, (b) recharge from both rivers into the aquifer, (c) uniform flow from Yom River to Nan River, and (d) discharge from mounds to rivers. All regimes result in a zigzag flow pattern along a general groundwater flow direction (e).

Figure 1



630000m E
1850000m N
25
45
117
Nan River
Yom River
0
1 km
99° 30'
100° E
100° 30'
17° 30'
17° N
16° 30'
Yom River
Nan River
Sukhothai
Phitsanulok
Kamphaengphet
Phitchit
Ping River
N
Thailand
Ground-Water Wells
Irrigation Canal
Road
Alluvial Sediments (Quaternary)
Basement Rocks (Pre-Tertiary)

Figure 2

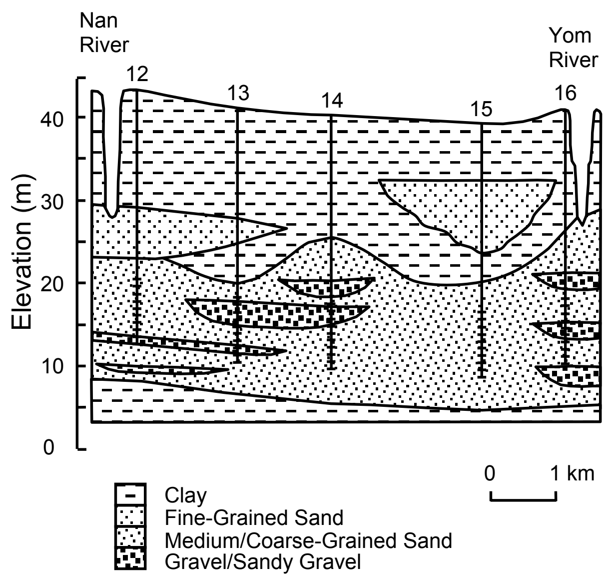

Nan River
Yom River
12
13
14
15
16
Elevation (m)
40
30
20
10
0
0
1 km
Clay
Fine-Grained Sand
Medium/Coarse-Grained Sand
Gravel/Sandy Gravel

Figure 3

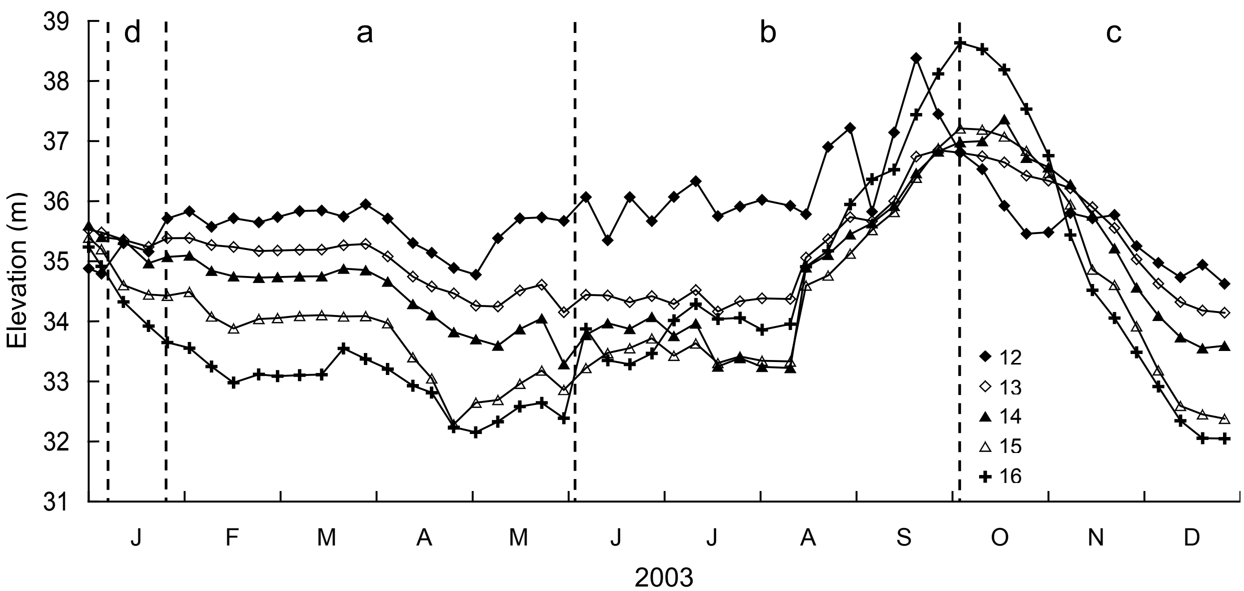

39
38
37
36
35
34
33
32
31
Elevation (m)
d
a
b
c
12
13
14
15
16
J
F
M
A
M
J
J
A
S
O
N
D
2003

Figure 4

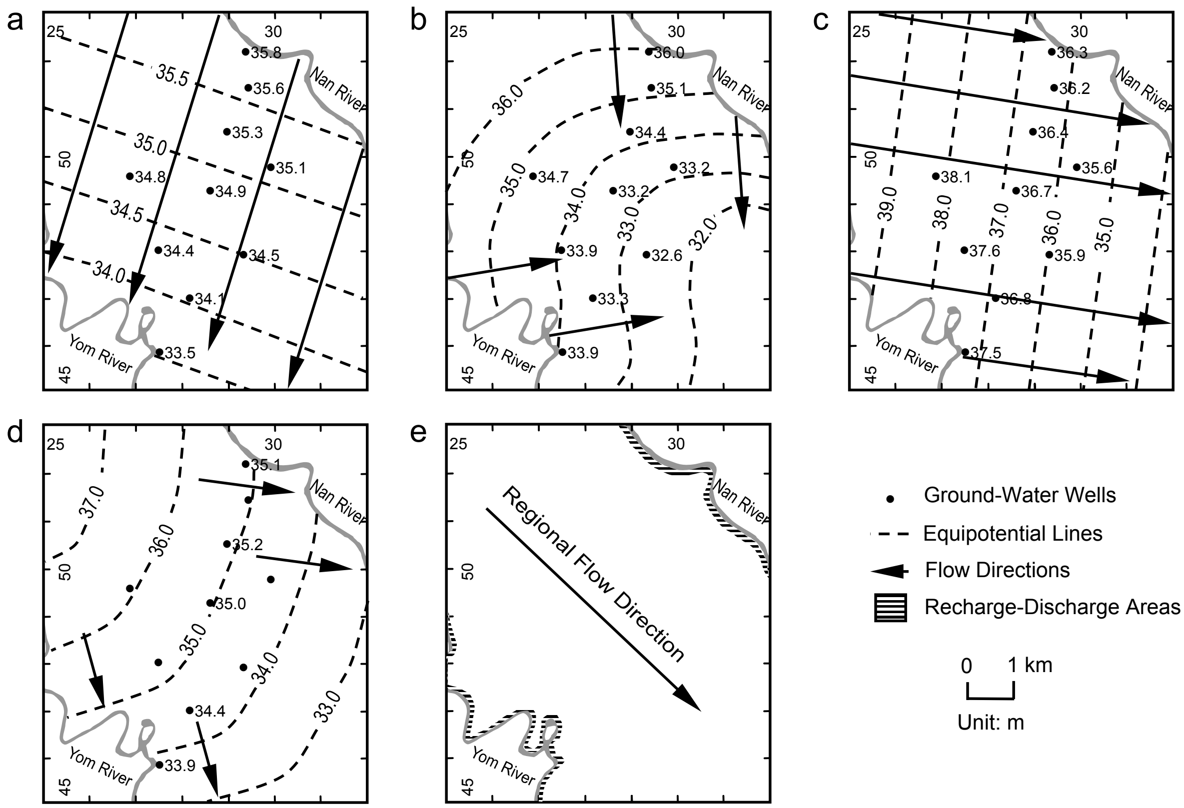

a
b
c
d
e
Nan River
Yom River
Regional Flow Direction
Ground-Water Wells
Equipotential Lines
Flow Directions
Recharge-Discharge Areas
0 1 km
Unit: m

Figure 5

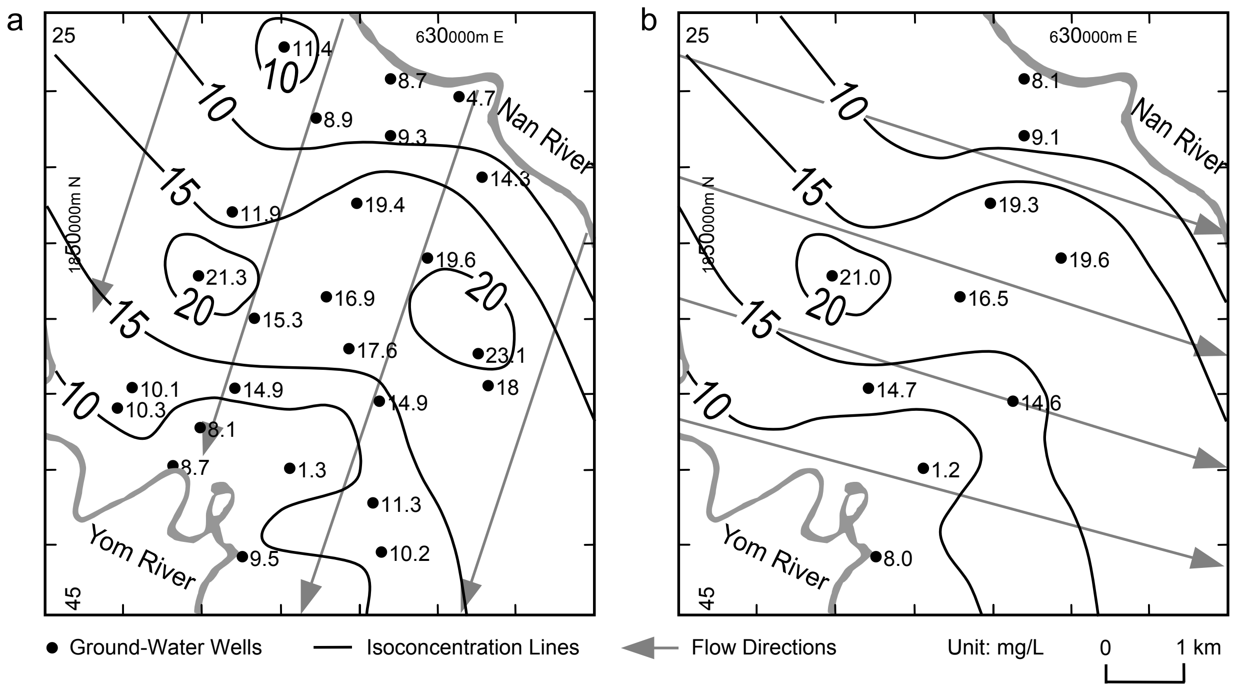

a
25
630000m E
1850000m N
45
11.4
10
8.7
4.7
8.9
9.3
Nan River
14.3
15
11.9
19.4
19.6
21.3
20
16.9
15.3
15
17.6
23.1
18
10.1
10.3
10
14.9
14.9
8.1
8.7
1.3
11.3
Yom River
9.5
10.2
b
25
630000m E
8.1
10
9.1
Nan River
15
19.3
19.6
21.0
16.5
20
15
14.7
14.6
10
1.2
Yom River
8.0
45
Ground-Water Wells
Isoconcentration Lines
Flow Directions
Unit: mg/L
0
1 km

Figure 6

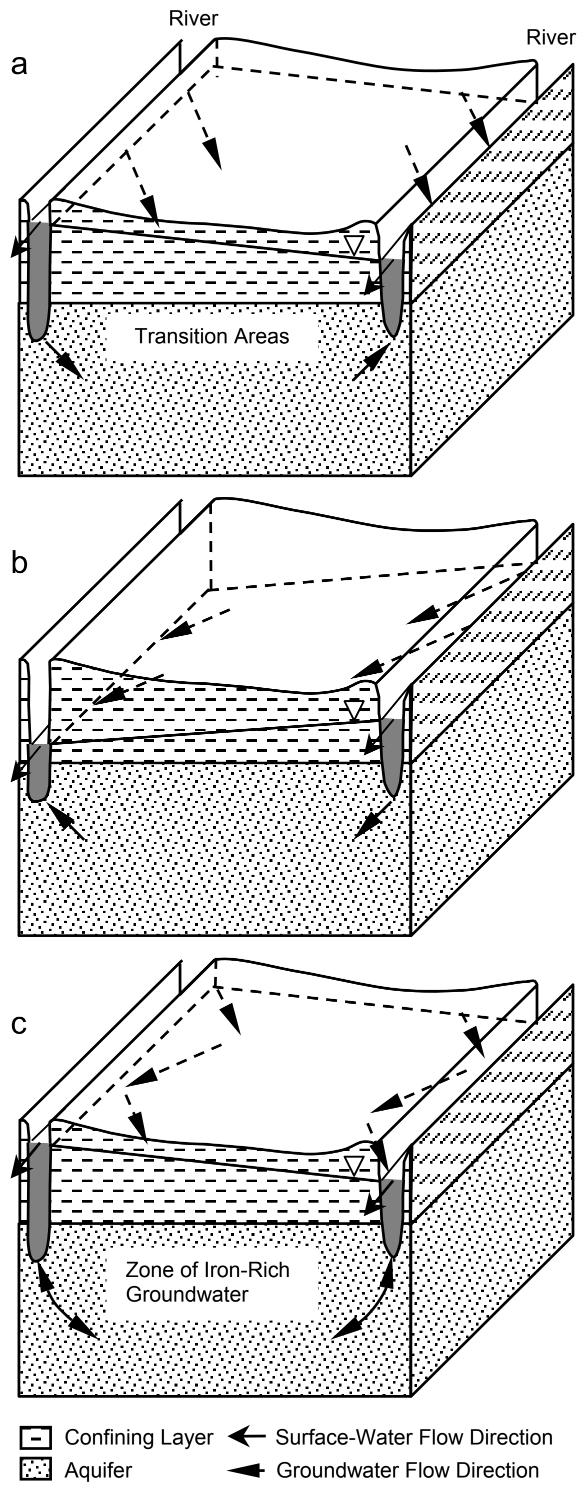

River
River
a
Transition Areas
b
c
Zone of Iron-Rich
Groundwater
Confining Layer
Aquifer
Surface-Water Flow Direction
Groundwater Flow Direction

Figure 7

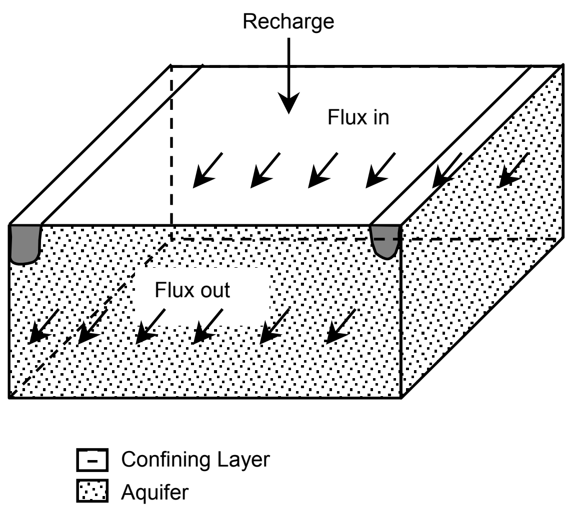


Figure 8

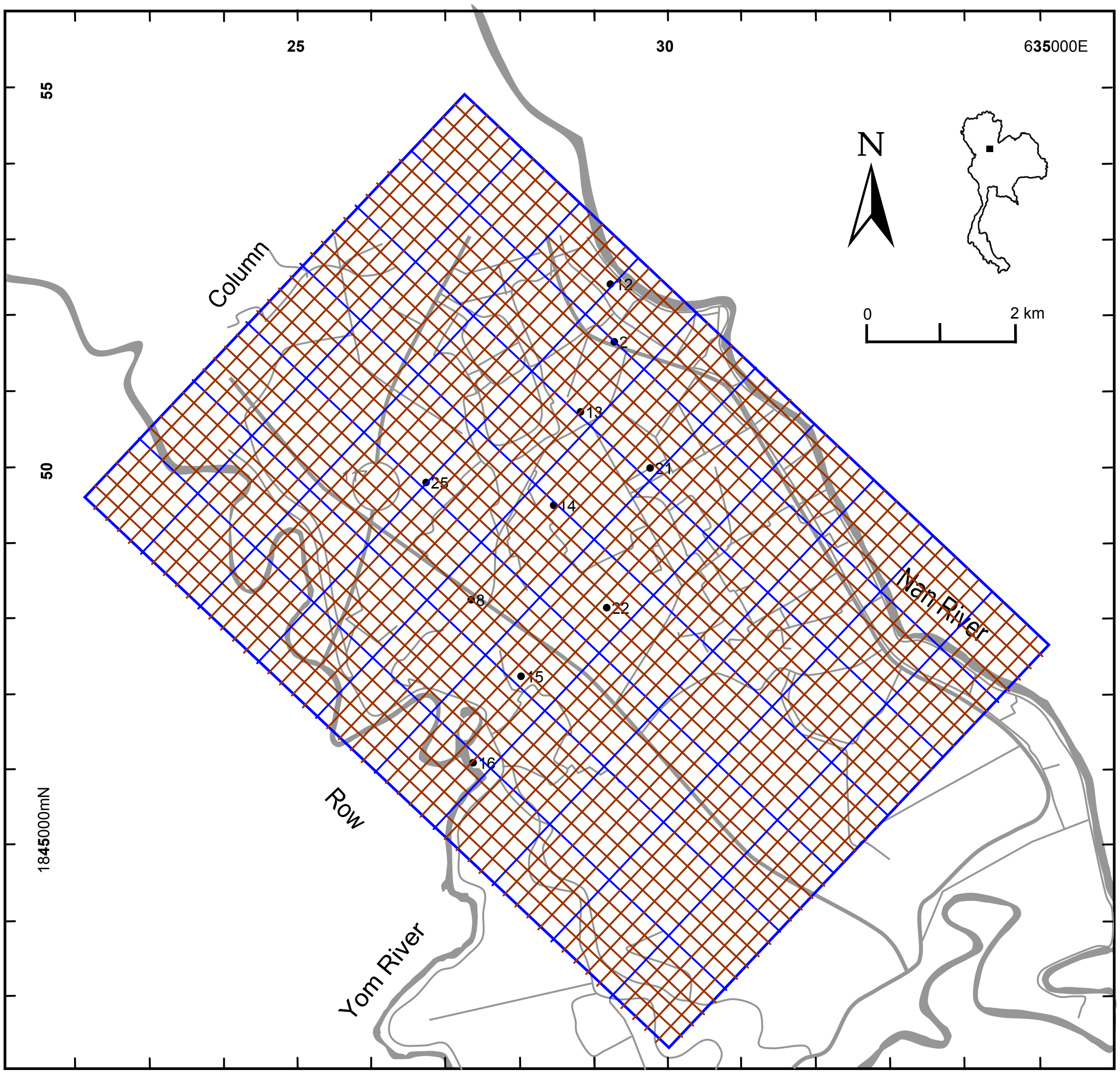
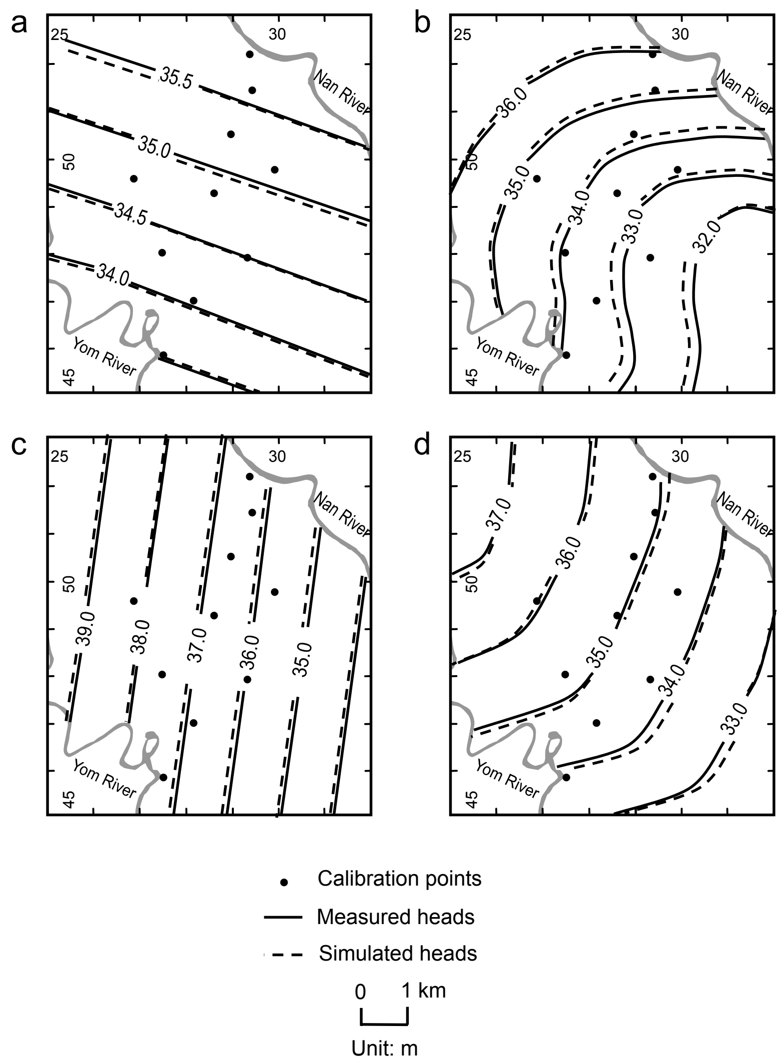

25
30
635000E
55
50
1845000mN
N
0
2 km
Column
Row
Nan River
Yom River
12
2
13
21
25
14
8
22
15
16

Figure 9


a
b
c
d
25
30
50
45
Nan River
Yom River
35.5
35.0
34.5
34.0
36.0
33.0
32.0
39.0
38.0
37.0
Calibration points
Measured heads
Simulated heads
0 1 km
Unit: m

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Expertise Environmental Hydrogeology

Publication

Promma K. 2004. Urban growth into problematic shallow groundwater resources. In: Daniell T. (ed) Proceedings of the 2004 International Conference on Water Sensitive Urban Design, Adelaide, Australia: 418-427.

Hatheway AW, Y Kanaori, T Cheema, J Griffiths, **K Promma**. 2004. 9th Annual Report on the International Status of Engineering Geology-Year 2003-2004: Encompassing Hydrogeology, Environmental Geology, and the Applied Geoscience. Engineering Geology 74: 1-31 (Impact Factor = 0.516)

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Education

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1984 Postgraduate work (Geology and Applied Mathematics), Chengdu Institute of Geology (now Chengdu University of Technology), China
1983 B.S. (Geology), Chengdu Institute of Geology, China

Professional Honors

1999 Fellow, Geological Society of America
1998 Recipient of the John Hem Excellence in Science and Engineering Award, National Ground Water Association (NGWA)

Expertise and Research Interests

New innovative approaches and computer software for contaminant transport simulation and remediation design optimization; Field, laboratory, and theoretical studies of contaminant transport in heterogeneous subsurface media; Coupling of physical transport processes with biological and geochemical reactions for evaluation of bioremediation systems and radioactive waste disposal; Investigation of abnormal fluid pressures in large sedimentary basins

Professional Experience

2002-Present Professor, University of Alabama
1997-2002 Associate Professor, University of Alabama
1993-1997 Assistant Professor, University of Alabama
Summer 2001 Visiting Fellow, University of Sheffield, UK
2000 Visiting Faculty, Stanford University

	Visiting Scientist, US Geological Survey-Menlo Park
1995	Visiting Fellow, Australian Nuclear Science and Technology Organization
1988-1993	Senior Hydrogeologist and Director of Software Development, S. S. Papadopulos & Associates, Inc.
1991	Assistant Professional Lecturer, George Washington University
1986-1988	Research Assistant, University of Wisconsin-Madison and Wisconsin Geological and Natural History Survey

Recent Professional Activities

2003	Organization Committee, "MODFLOW and More 2003", an international conference on groundwater modeling, International Ground Water Modeling Center, Golden, CO
2003-present	Associate Editor, Hydrogeology Journal
2002	Review Panelist, Global Water Cycle Research Program, NSF
2002	Invited Speaker, Special Session on “Use Groundwater Models to Guide Field Data Collection”, AGU 2002 Fall Meeting, San Francisco
2002-present	Standing Committee on Hydrologic Information Systems, Consortium of Universities for the Advancement of Hydrologic Science, Inc. (CUAHSI)
2002-present	Software Editor, Ground Water
2002	Invited Seminar Speaker, Institute of Applied Geology, University of T□ bingen, Germany
2001-2003	Instructor, Short course on “Reactive Transport Modeling”, University of Sheffield, Sheffield, UK
2001	Scientific Advisory Committee Member and Keynote Speaker, Groundwater Quality 2001: 3rd International Conference on Groundwater Quality, University of Sheffield, Sheffield, UK
2001	Organizing Committee and Keynote Speaker, "MODFLOW 2001 and Other Modeling Odysseys", International Conference on Groundwater Modeling, Colorado School of Mines, CO
2000	Invited Speaker, International Symposium on Groundwater Contamination, sponsored by Japanese Association of Groundwater Hydrology, Tokyo, Japan
2000	Guest Lecturer, Mass Transport in Groundwater, Freiberg University of Mining and Technology, Freiberg, Germany
1999	Seminar Speaker, Department of Geological and Environmental Sciences, Stanford University
1999	Graduate Fellowship Grant Application Review Panel, U.S. Environmental Protection Agency, Washington, DC
1999	Invited Speaker, American Geophysical Union (AGU) 1999 Spring Meeting, Boston, MA
1998-present	Associate Editor, Ground Water
1998	Colloquium Speaker, Department of Geology and Geophysics, Texas A & M University

1998	Member, Optimization Initiative Project Review Panel, U.S. Environmental Protection Agency, Washington, DC
1998	Co-chairman, MODFLOW'98 – An International Conference on Groundwater Modeling, Colorado School of Mines, Golden, Colorado
1998	Co-instructor, short course on "Computer Modeling of Natural Attenuation and Bioremediation Systems", sponsored by National Ground Water Association
1998	Co-instructor, short course on "Groundwater Modeling", sponsored by the University of Hong Kong, Hong Kong, China
1998-2001	Visiting Professor, Chengdu University of Technology, China
1997	Invited speaker, A Workshop on Reactive Transport Modeling, held at the Pacific Northwest National Laboratory, Richland, Washington
1997	Invited speaker, International Conference on Advances in Groundwater Hydrology – A Decade of Progress, American Institute of Hydrology, Tampa, Florida
1997	Co-Instructor, Workshop on Coupling of Contaminant Transport with Geochemistry, University of Technology, Sydney, Australia
1996-present	Member, Groundwater Committee, American Geophysical Union (AGU)

Books and Edited Work

Zheng, C., and G. D. Bennett, 2002, Applied Contaminant Transport Modeling. 2nd Edition, Wiley, New York, 621 pp.

Zheng, C., and G. D. Bennett, 1995, Applied Contaminant Transport Modeling: Theory and Practice. Van Nostrand Reinhold (now Wiley), New York, 440 pp.

Chien, C.C., M.A. Medina, Jr., G.F. Pinder, D.R. Reible, B.E. Sleep, **C. Zheng**, eds., 2002, Environmental Modeling and Management, Theory, Practice, and Future Directions, A Research Monograph Prepared under the auspices of DuPont Company, Wilmington, DE.

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Ouyang, Y. and **C. Zheng**, 2000, Surficial processes and CO2 flux in soil ecosystem, J. Hydrology, 234: 54-70.

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Jiao J.J., and **C. Zheng**. 1998. Abnormal fluid pressures caused by erosion and subsidence of sedimentary basins. *Journal of Hydrology* 204, 124-137.

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Research Experience

1978 Tin mineralization in the Burmese-Malayan Penisula: a plate tectonic model (Project leader)
1978 Tin mineralization and petrochemistry relationship of the Thai granitoids (Project leader)
1981 The stibnite-bearing deposits of northern Thailand (Project leader)
1982 Relationship of fracture patterns and epigenetic ore deposits of northern Thailand (Project leader)
1982 Identification of ore minerals using their electrical resistance (Project leader)
1983 Electrical resistance of galena, pyrite and chalcopyrite from deposits of diverse origin (Project leader)
1984 Regional control of hydrothermal ore localization in northern Thailand (Project leader)
1986 Geology of magnesite and chromite deposits at Amphoe Na Noi, Changwat Nan (Co-investigator)
1987 Preparing and cataloging heavy mineral specimens from alluvial tin ores of Thailand (Project leader)
1988 Geochemical and sedimentological characteristics of Hong Hoi Formation, near Lampang (Co-investigator)
1988 Geochemistry of niobium-tantalum in tin-tungsten deposits at Ban Rai, Uthai Thani, Thailand (Co-investigator)

1990 Preliminary investigation of radon and radon daughter concentration in dwelling close to certain fluorite mines in northern Thailand (Co-investigator)
1991 Uranium exploration in the vicinity of Doi Pae Po Mak, Ban Doi Tao, Changwat Chiang Mai (Co-investigator)
1993 Characterization and uses of upgraded barytes (Co-investigator)
1994 Geochemistry of groundwater of the Chiang Mai Basin (Project leader)
1994 Geology and hydrogeology of the Muang Paeng geothermal area, Amphoe Pai, Changwat Mae Hong Son (Project leader)
1995 Hydrogeochemistry of Chiang Mai Basin, northern Thailand (Project leader)
1995 Keng Tung Geothermal Field, eastern Shan State, Myanmar (Project leader)
1996 Geochemical characterization of natural waters of the Chiang Mai Basin using principal component analysis (Project leader)
1996 Microbial activities and nitrate content in shallow groundwater at Ban Na Kob, Amphoe Chom Thong, Changwat Chiang Mai (Project leader)
1996 Water quality monitoring of Ping and Kuang rivers in 1995 (Project leader)
1997 Water quality monitoring of Ping and Kuang rivers in 1996 (Project leader)
1998 Relationship between fluorotoxicosis and excess fluoride activity in some domestic groundwater supplies of the Chiang Mai Basin (Project leader)
1999 Preliminary investigation of some main wetlands in the Chiang Mai-Lamphun Basin I (Project leader)
1999 Preliminary investigation of some main wetlands in the Chiang Mai-Lamphun Basin II (Project leader)
1999 Biodiversity of some main wetlands in the Chiang Mai-Lamphun Basin (Project leader)
1999 Investigation of the hydrology of the Fang geothermal system by isotope and geochemical tools (Project leader)
2000 Geology of Pai District, Mae Hong Son Province (Project leader)

Publication

Asnachinda, P., Praserdvigai, S., and Ramingwong, T., 2001, Development and Utilization of Low Temperature Geothermal Systems in Northern Thailand, Presented at the combined IAEA Workshop RAS/8/092 and INT/0/060 on Isotopic and Geochemical Techniques in Geothermal Exploration and Reservoir management, March 12-17, Manila and Cebu City, the Philippines

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