Groundwater and surface-water interactions in a confined alluvial aquifer between two rivers: effects of groundwater flow dynamics on high iron anomaly

Kitchakarn Promma · Chunmiao Zheng · Pongpor Asnachinda

Abstract In a confined alluvial aquifer located between two rivers, discrete zones of anomalously high concentrations of redox species such as iron, are thought to be a result of groundwater flow dynamics rather than a chemical evolution along continuous flow paths. This new hypothesis was confirmed at a study site located between Nan and Yom rivers in Phitsanulok, Thailand, by analyzing concentrations of redox species in comparison with dynamic groundwater flow patterns. River incision into the confined alluvial aquifer and seasonally varying river stages result in truncated flow paths. The groundwater flow dynamics between two rivers has four phases that are cyclic, including: aquifer discharge into both rivers, direct flow from one river toward another, aquifer recharge from both rivers, and reverse of river-to-river flow. The resulting groundwater flow direction has a zigzag pattern and its general trend is almost parallel to the river flow. High iron anomaly appears as discrete zones in the transition areas of the confined alluvial aquifer because the lateral recharge from rivers penetrates into the aquifer only by tens of meters. The high iron anomaly, which is nearly constant in space and time, is a result of groundwater/surface-water interactions and related groundwater flow dynamics.

Received: 23 April 2005 / Accepted: 29 August 2006
Published online: 1 December 2006

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Résumé Dans un aquifère alluvial captif situé entre deux rivières, des zones discrètes présentant une anomalie élevée en concentrations d'espèces redox comme le Fer, sont supposées être le résultat de la dynamique de l'écoulement des eaux souterraines plutôt que le résultat d'une évolution chimique le long d'une ligne d'écoulement continue. Cette nouvelle hypothèse a été confirmée sur un site d'étude situé entre les rivières Nan et Yom à Phitsanulok, en Thaïlande, en analysant les concentrations des espèces redox en comparaison avec le schéma de l'écoulement dynamique des eaux souterraines. L'incision de la rivière dans l'aquifère alluvial captif et les niveaux de la rivière variant saisonnièrement engendrent des trajectoires tronquées. La dynamique de l'écoulement des eaux souterraines entre les deux rivières présente quatre phases cycliques dont : l'écoulement de l'aquifère vers les deux rivières, l'écoulement direct d'une rivière vers l'autre, la recharge de l'aquifère à partir des deux rivières, et l'écoulement inverse rivière-à-rivière. La direction résultante de l'écoulement des eaux souterraines possède une allure en zigzag et reste globalement parallèle à la rivière. L'anomalie élevée en Fer apparaît en zones discrètes dans les aires de transition de l'aquifère alluvial captif, du fait de la recharge latérale à partir des rivières pénétrant seulement sur des dizaines de mètres dans l'aquifère. L'anomalie élevée en Fer, qui est pratiquement constante dans l'espace et dans le temps, est le résultat d'interactions entre l'eau souterraine et l'eau de surface et la dynamique de l'écoulement des eaux souterraines associée.

Resumen En un acuífero aluvial confinado localizado entre dos ríos, existen zonas discretas de concentraciones anormalmente altas de especies redox, como el hierro, que se piensa son el resultado de la dinámica de flujo del agua subterránea más que el resultado de la evolución química a lo largo de líneas de flujo continuas. Esta nueva hipótesis se ha confirmado en un área de estudio localizado entre los ríos Nan y Yome Phitsanulok, Tailandia, mediante el análisis de las concentraciones de especies redox en comparación con la dinámica de las líneas de flujo del agua subterránea. La incisión del río en el acuífero aluvial confinado y las variaciones estacionales de las alturas del río dan lugar al truncamiento de las líneas de flujo. La dinámica del flujo entre los dos ríos tiene cuatro fases

 DOI 10.1007/s10040-006-0110-8

cíclicas, que incluyen: la descarga del acuífero en ambos ríos, el flujo directo de un río hacia el otro, la recarga hacia el acuífero desde ambos ríos y el flujo revertido entre un río y otro. Las direcciones de las líneas de flujo resultantes tienen un diseño en zigzag y su dirección general es casi paralela a la dirección del río. El contenido anormalmente alto en hierro aparece como una zona discreta en las áreas de transición del acuífero aluvial confinado porque la recarga lateral desde los ríos penetra en el acuífero solamente unos diez metros. La anomalía de altos contenidos en hierro, que es casi constante en el espacio y en el tiempo, es un resultado de la interacción entre el agua subterránea y el agua superficial y está relacionada con la dinámica de flujo del agua subterránea.

Keywords Groundwater and surface-water interactions · Groundwater flow · Hydrogeochemical evolution · Iron · Thailand

Introduction

The study of hydrogeochemical processes with respect to groundwater/surface-water interactions is a future direction of hydrogeology (Glynn and Plummer 2005). The groundwater/surface-water interactions have 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 systems near the stream, has 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 nature of water movements and chemical fluxes through these boundaries is critical (Dahm et al. 1998; National Research Council 2004). 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 refers to a three-dimensional body of continuously circulating groundwater bounded by a set of hydrogeologic boundaries (Tóth 1999). The groundwater flow system can be considered as either steady state or dynamic. For the steady-state concept, the groundwater flow system depends on 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 groundwater flow patterns (Freeze and Witherspoon 1967). Based on the relative lengths and positions of flow paths, Tóth (1962, 1963) classifies three types of groundwater flow systems including local, intermediate, and regional. 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. Figure 1 shows that the local groundwater flow system with steady-state, confined conditions can be classified into recharge, transition, and discharge areas. The groundwater flows from the recharge area through the transition zone to the discharge area.

For the dynamic concept, the recharge and discharge areas can be alternated depending on seasonal groundwater flow patterns. The groundwater flow dynamics is defined as changing groundwater flow patterns as a result of seasonal variations of lateral recharge from surface water and vertical recharge from rainfall. Regional scale groundwater/surface-water interactions are controlled by: (1) the relation of stream stage to the adjacent groundwater level, (2) the position and geometry of the stream channel within the alluvial plain, and (3) the distribution and magnitude of hydraulic conductivities within the channel and surrounding alluvial sediments (Woessner 2000).

The groundwater/surface-water interactions between two rivers have seldom been studied. Seasonally varying hydrology alters the hydraulic head and thus induces changes in the groundwater flow direction. Brunke and Gonser (1997) summarize the interactions between groundwater and a single river. With low precipitation, baseflow in streams contributes to the aquifer discharge for most of the year. On the other hand, under conditions of high precipitation, surface runoff and interflow increase, causing the river to change from the effluent (where groundwater drains into the stream) to 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,

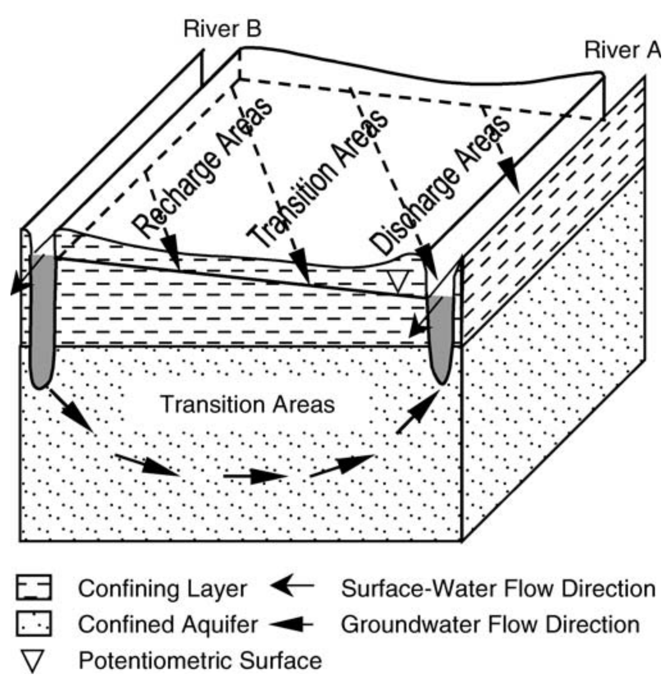

Fig. 1 Illustration of a confined alluvial aquifer between two rivers under steady-state conditions

 DOI 10.1007/s10040-006-0110-8

and transmissivity and storativity of the aquifer. In the dry season, the stored groundwater is released into the river. Successive discharge and recharge of the aquifer affect the characteristics of rivers.

The chemical composition of groundwater changes continuously through time within a groundwater flow system where recharge and discharge are relatively stable (Fig. 1). The variations in hydrogeochemistry may be used to categorize the groundwater flow system into zones, referred to as hydrochemical facies (Back 1966). The groundwater flow influences the pattern of hydrochemical facies because the groundwater flow renders the effect of diffusion less significant, 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 variation of groundwater compositions would exist because diffusion would reduce the difference by mixing slowly through geologic time (Volker 1961). A question of interest is: "Can the evolutionary patterns of hydrochemical facies 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 US Environmental Protection Agency (1992), remain a controversial subject. At a regional scale, various hypotheses have been proposed, including (1) no trend (Thorstenson et al. 1979), (2) discrete zones (Back and Barnes 1965; Langmuir 1969, 1997; Chapelle and Lovley 1992), (3) decreasing trend toward discharge areas (Champ et al. 1979), and (4) increasing trend toward discharge areas (Tóth 1999). At a 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 bank infiltration of oxic river water into the anoxic 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-recharged aquifer along the Oder River in Germany. At their site, river water consistently infiltrates into the shallow confined aquifer. Reduction processes from oxygen consumption 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), and 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 that makes the transition areas between two neighboring rivers largely isolated from oxic river water. Discrete zones of high iron concentrations in the transition areas indicate the isolation. Thus, groundwater resource developers can expect to see high iron groundwater in the transition areas of a confined alluvial aquifer located between two rivers.

Hypothesis

Can a clear trend of chemical evolution still emerge from a confined alluvial aquifer bounded by two rivers with highly dynamic fluctuations of river stages? The answer from this study appears to be no. A working hypothesis is as follows. A continuous flow regime is truncated if two successive parallel rivers that incise partially into the confined aquifer have seasonally varying water levels. The truncated flow leads to a lack of oxic 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. Consequently, the transition areas are isolated from oxic conditions that can be indicated by abnormally high concentrations of some redox species such as iron. This anomaly is a result of groundwater flow dynamics rather than the slow chemical evolution.

Figure 2 shows a schematic of conceptual models described above. There are four phases including aquifer discharge into both rivers, direct flow from one river toward another, aquifer recharge from both rivers, and reverse of river-to-river flow. In phase I, mounding groundwater in the aquifer discharges into both rivers as river stages drop (Fig. 2a). In phase II, when one river rises above the other, groundwater levels respond quickly to changing river stages and the groundwater flow direction is from river A to B (Fig. 2b). In phase III, while river A continues a recharging process, river B also rises and recharges into the aquifer (Fig. 2c). In phase IV, when river B rises above river A, the groundwater flow direction reverses itself with respect to the phase II (Fig. 2d). The four phases will repeat themselves annually. The resulting flow field has a zigzag pattern (Fig. 2e).

Moving in a zigzag pattern in recharge-discharge areas leads to little penetration of oxic river water into transition areas. The transition areas are therefore isolated and the anoxic conditions prevail. Under the anoxic conditions, redox species (oxygen, nitrate, manganese, iron, sulfate, hydrogen sulfide, and methane) plays an important role in the groundwater chemistry. In particular, the iron is usually used to indicate suboxic or anoxic conditions of the aquifer (Berner 1981). With strong anoxic conditions, the transition areas are thus characterized by elevated concentrations of dissolved ferrous iron (Fe^{2+}; Fig. 2e).

Study area

The study area is located about 20 km from the City of Phitsanulok, lower northern Thailand (Fig. 3). Based on observations from this study, there are two major seasons in the study area. In 2003, the dry season lasted from 1 November to 31 May whereas the rainy season occurred

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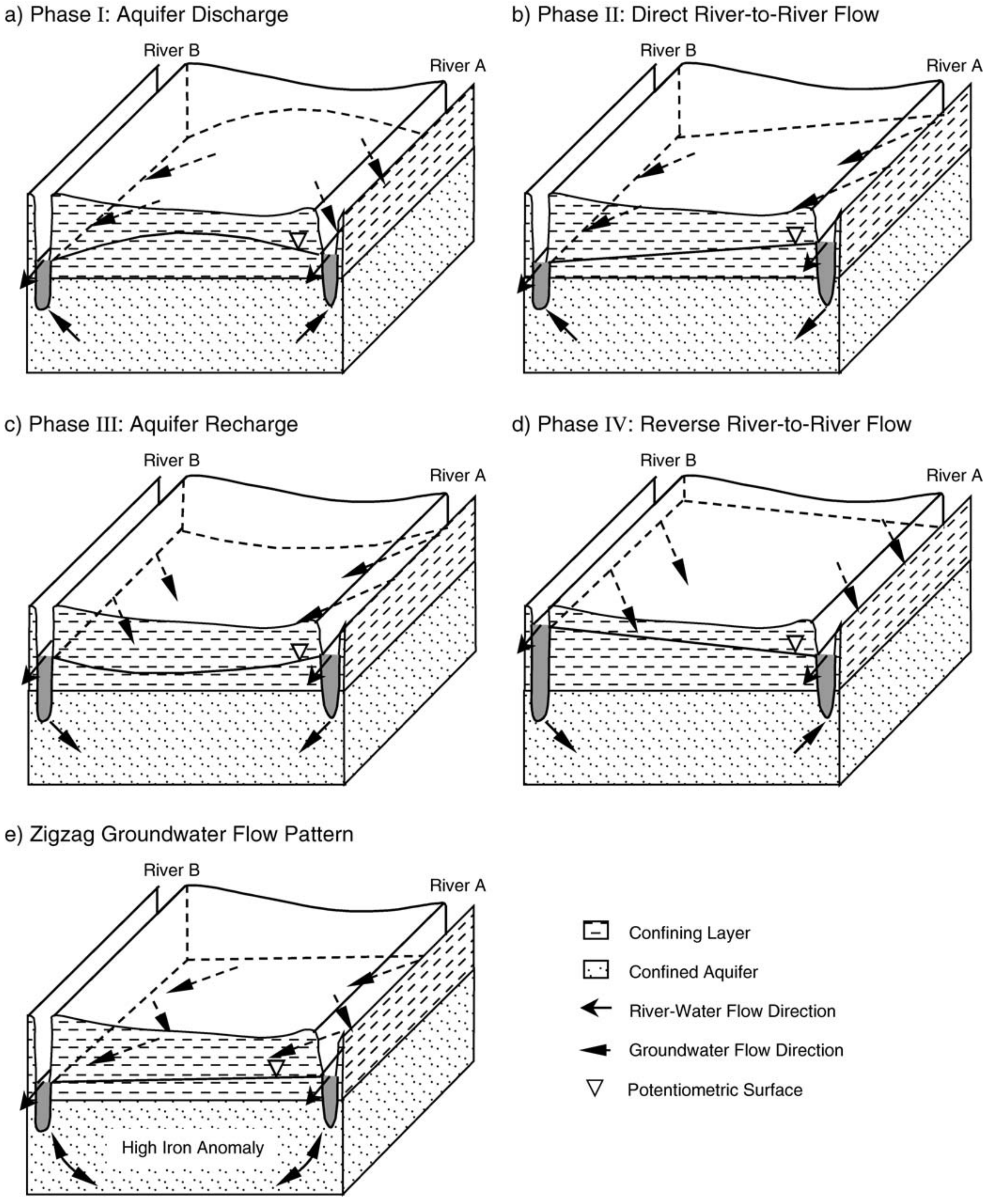

Fig. 2 Schematic of conceptual models of iron accumulation in transition areas of a confined alluvial aquifer between two rivers under dynamic conditions: **a** groundwater recharges into both rivers; **b** groundwater flows from one river (*A*) to another (*B*); **c** both rivers recharge into the aquifer; and **d** groundwater reverses its river-to-river flow direction. The resulting groundwater flow has a zigzag pattern **e** preventing the oxic lateral recharge from reaching the transition areas

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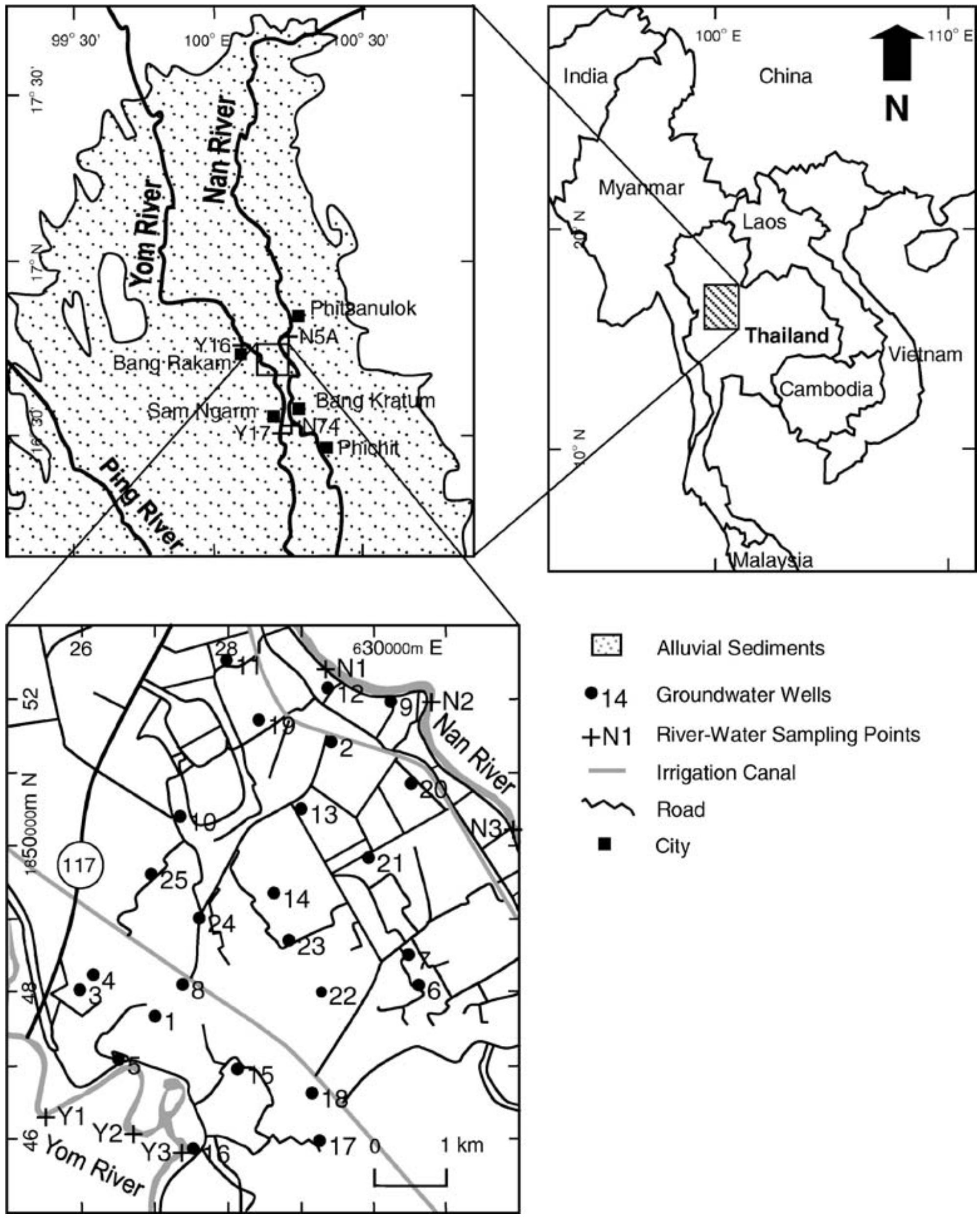

Fig. 3 Location of the study area and sampling points of groundwater and surface water, Phitsanulok, Thailand. Representative river stages in the *Nan River* are located at *N1* and the *Yom River* at *Y3*. Upstream and downstream stations with respect to the study area in the *Nan River* are located at *N5A* and *N74*, and in the *Yom River* at *Y16* and *Y17*, respectively

between 1 Jun and 31 October. Monsoon rains and tropical storms contributed most of the precipitation to the area.

Figure 4 shows a geologic 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 the Chao Phraya aquifer (Wongsawat and Dhanesvanich 1983; 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 eight gravel lenses inside the aquifer. The Nan and Yom rivers cut through the top of the aquifer and a lens of fine-grained sand that connects to the aquifer. Therefore, the groundwater is highly interactive with surface-water bodies in both rivers. The transmissivity and storage coefficient were measured in this study using the Cooper-Jacob straight-line method (Cooper and Jacob 1946). Their values are 1,988 m^2/d and 3.3×10^{-4}, respectively. Based on an average aquifer thickness of 16 m, the hydraulic conductivity is 124.3 m/d. Effective porosity is estimated to be 0.3.

The aquifer consists of Quaternary alluvial deposits of channel-filled sands and gravels. Major compositions of the aquifer are made of quartz (about 95% of the aquifer materials). No iron-rich sands were observed. Minor iron-bearing minerals include hematite, pyrite, siderite, biotite, amphibole, and pyroxene.

Three reasons make the area ideal for testing of the proposed hypothesis. Firstly, the flow directions 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

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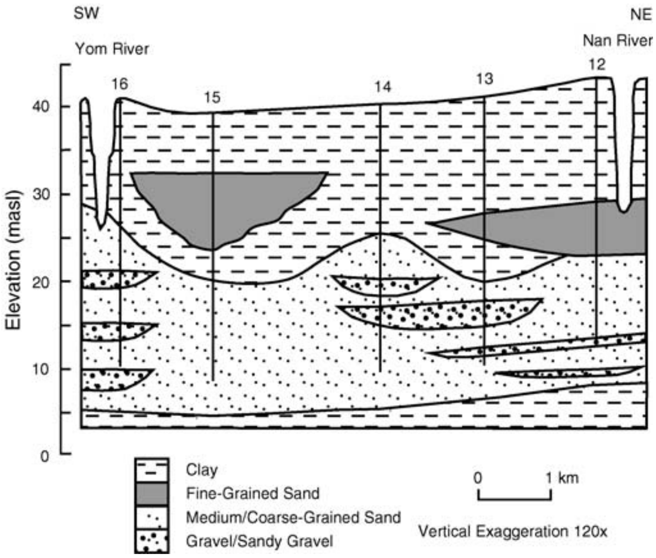


Fig. 4 Geologic cross-section. The rivers cut through the top of the aquifer, but they penetrate into it only slightly. The well screen, 8-m long at the bottom, is located in the middle of the aquifer in order to obtain depth-integrated groundwater samples. See Fig. 3 for the location of numbered wells

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 below the land surface or about 2–5 m of penetration (Royal Irrigation Department, unpublished data, 2003).

Methodology

Water levels

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. At wells 12–16, groundwater levels were recorded weekly in 2003.

Weekly river stages in 2003 were obtained from four automatic gauging stations (Fig. 3). Since no gauging station is available within the study site, data from the upstream and downstream gauging stations were linearly averaged using Eq. 1.

$$R(x) = R_u - \left(\frac{R_u - R_d}{d_{ud}}\right) d(x) \quad (1)$$

where R(x) is the river stage at position x along the river from the upstream station (L), R_u is the river stage measured at the upstream gauging station (L), R_d is the river stage measured at the downstream gauging station (L), d_{ud} is the distance between the upstream and downstream gauging stations (L), and d(x) is the distance from the upstream gauging station to the position x along the river (L).

In this study, the river stages were calculated for the sampling station N1, which is next to well 12 in the Nan River, and Y3, which is close to well 16 in the Yom River. The upstream station to N1 is N5A in the Phitsanulok City and the downstream station is N74 in Bang Kratum (close to Phichit). For N1, d_{ud} is equal to 50 km and d(x) is equal to 15.4 km. The upstream station to Y3 is Y16 in Bang Rakam and the downstream station is Y17 in Sam Ngarm, Phichit. For Y3, d_{ud} is equal to 46.5 km and d(x) is equal to 16.15 km.

Then, fluctuations of groundwater levels and river stages were drawn as a function of time and were used with flow nets to study groundwater flow patterns, seasonal variation, and recharge-discharge relationships. Firstly, stages of the Nan River were compared with groundwater levels in well 12, and those of the Yom River with heads in well 16. Secondly, groundwater levels in all wells were analyzed. The groundwater flow dynamics was then classified into phases following the concept presented in Fig. 2. The corresponding flow nets were drawn to illuminate the classification and interpretation. In addition, flow paths were calculated using Darcy's Law, flow nets, and traveled time in individual phases.

Water sampling

Although the groundwater flow regime was divided into four phases, the groundwater and river water samplings were carried out primarily in phases II and III. The main reason is that the groundwater chemistry is rather constant throughout the year and phases I and IV are on transitional changes with a short time scale. Detailed groundwater sampling activities were conducted in the dry season or phase II (March–April 2003 and February 2006). The groundwater sampling in the rainy season or phase III (September 2003) focused on wells along the cross-section (Figs. 3 and 4). The river water was also sampled in the same period.

Field parameters including pH, specific conductance (SC), temperature (T), and dissolved oxygen (DO) were measured immediately after purging by lowering multiple probes (YSI 556 MPS) into wells. The DO was measured using a membrane electrode whose detection limit is 0.2 mg/L (Rose and Long 1988). In addition, oxidation-reduction (redox) potential (Eh) was carefully measured by using the Wood Method (Wood 1976; Kehew 2001). A bottle of Zobell's solution (YSI 3682) 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 and river water were collected and preserved by using standard methods as described by American Public Health Association et al. (1998). After purging, the groundwater samples were collected using a closed flow-through cell with an inline filter. The groundwater samples were filtered by 0.45-μm filters for the analysis of dissolved metals (Puls and Barcelona 1989). Unfiltered groundwater samples were also collected to determine the total iron and manganese. The river water samples were filtered using 0.45-μm filters to

 DOI 10.1007/s10040-006-0110-8

exclude suspended clays and Fe- and Mn-oxyhydroxides. Quality-assurance samples were collected by duplicate sampling once every ten samples.

The groundwater samples for the analysis of dissolved Fe^{2+} were preserved by 20 mL concentrated HCl per liter of water and other metals by 10 mL concentrated HNO_3 per liter of water. The preservation was done immediately after filling the bottle. Sulfide samples were carefully filled without air entrapment and preserved by 4 drops of 2N zinc acetate solution per 100 mL sample. The remaining samples were stored at 4°C and transported to the laboratory.

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), total iron (Fe_{total}), ferrous iron (Fe^{2+}), and total manganese (Mn_{total}). Results were evaluated for their reliability using charge balance (CB) or electroneutrality of less than 5% (Appelo and Postma 1993).

The ferric iron (Fe^{3+}) was calculated using Eq. 2 (Puls and Barcelona 1989).

$$Fe^{3+} = Fe_{total} - Fe^{2+} \tag{2}$$

where Fe^{3+} is ferric iron (mg/L), Fe_{total} is total mobile iron (mg/L), and Fe^{2+} is dissolved ferrous iron (mg/L).

The water samples were analyzed by following standard methods (American Public Health Association et al. 1998). Alkalinity was determined by titration onsite. The HCO_3^- and CO_3^{2-} were calculated using the alkalinity. The atomic adsorption spectrophotometer was used to analyze Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe_{total}, and Mn_{total}. TDS was obtained by drying at 180°C. Cl^- was identified by using mercuric nitrate method, SO_4^{2-} by turbidimetric method, S^{2-} by iodometric method, and SiO_2 by molybdosilicate method. The NO_3^- and NO_2^- were analyzed by ion chromatography while NH_3 by nesslerization.

Interpretation of iron anomaly

Concentrations of iron and other parameters were drawn on maps and were superimposed not only by groundwater

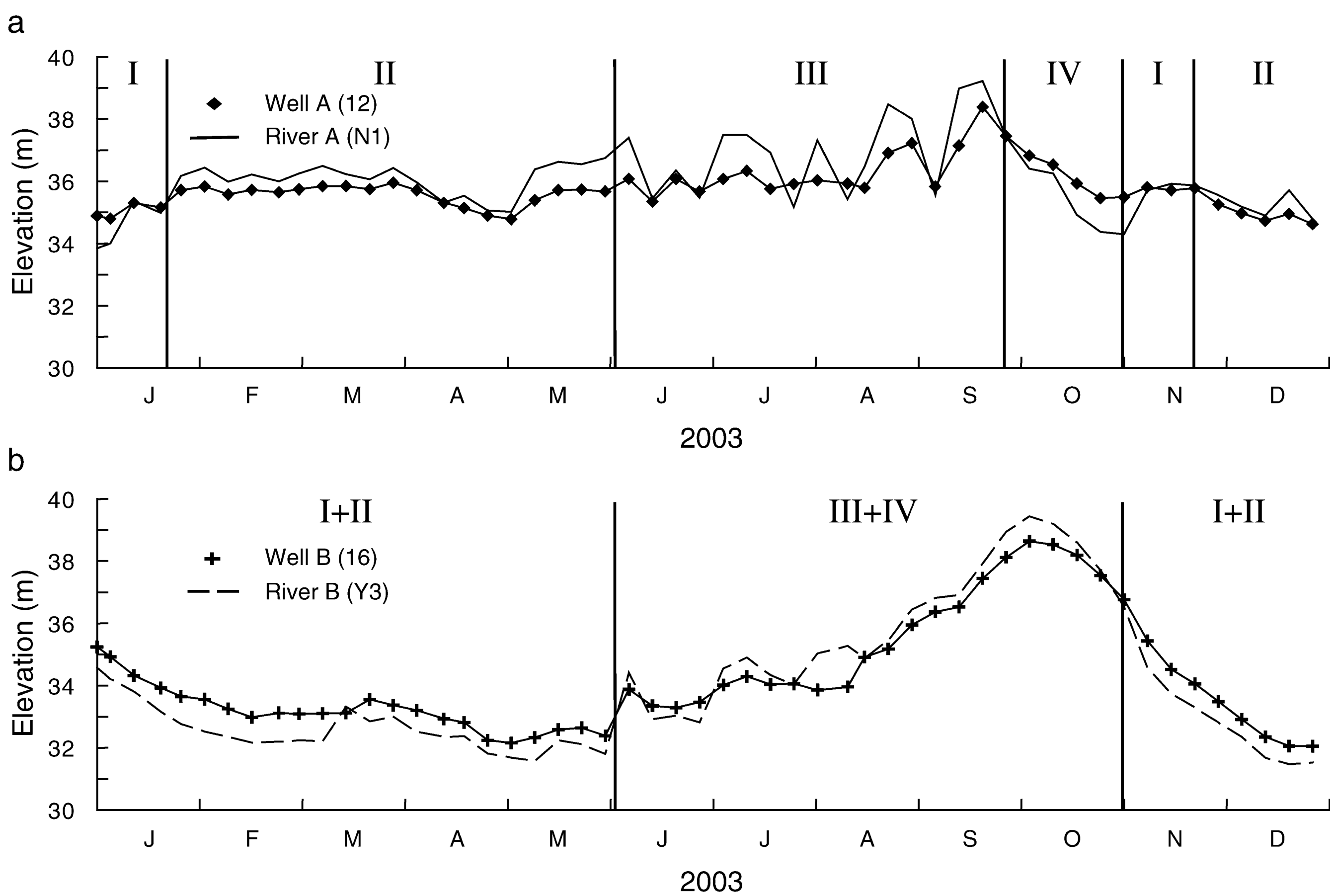


Fig. 5 Groundwater levels (wells *12* and *16*) and river stages (*N1* and *Y3*) near the groundwater/surface-water interface during phases *I* to *IV*: **a** the Nan River mainly recharges the aquifer from January to September (phases *II* and *III*) with groundwater discharges in phases *I* and *IV* and **b** the Yom River responds directly to seasonal changes with effluent condition in the dry season (phases *I* and *II*) and influent condition in the rainy season (phases *III* and *IV*)

DOI 10.1007/s10040-006-0110-8

flow patterns at the time of sampling but also by the overall zigzag groundwater flow pattern. Then, the effects of groundwater flow dynamics on redox conditions and high iron anomaly, particularly in the transition areas, were analyzed. The high iron anomaly in the transition areas was also evaluated for its consistency in space and time with respect to the zigzag groundwater flow pattern.

Results and discussion

Groundwater flow dynamics

Groundwater flow dynamics depends on river stages from both sides of the aquifer. The groundwater/surface-water interactions near the Nan River are more complex than the Yom River. Figure 5a indicates that phase I occurred in the shortest period of time, about 3 weeks. It occurred twice in 1 year. The interaction in phase II was fairly stable in the dry season but that in phase III was highly interactive in the rainy season. Phase IV started when river stages dropped below the groundwater levels and ended when river stages began to rise. Phase IV was also short, about 5 weeks. Figure 2 shows the conceptual models corresponding to each of the four phases.

In Fig. 5b, groundwater levels near the Yom River show simple interactions but exhibit significant fluctuations between 32–39 masl within a year. Both groundwater levels and river stages dropped dramatically in the dry season. When river stages were below groundwater levels in well 16, the aquifer discharged groundwater into the Yom River. This event was concurrent with phases I and II in the Nan River (Fig. 5a). When the rainy season began in June and the river stages rose above groundwater levels, the Yom River recharged into the aquifer. This event, occurring simultaneously to phases III and IV in the Nan River (Fig. 5a), ended in November.

Figure 6 confirms that groundwater flow dynamics is a cycle consisting of four phases including: (1) phase I-aquifer discharge, (2) phase II-direct river-to-river flow, (3) phase III-aquifer recharge, and (4) phase IV-reversed river-to-river flow. The periodicity of the cycle may be less than a year depending on precipitation events and subsequent river runoff. Phase I is short because the groundwater/surface-water interactions are on transitional changes, with the mounding groundwater discharging into both rivers. In phase II, the aquifer has a groundwater flow pattern directly from the Nan River to the Yom River. Phases I and II also repeat by the end of the year. In phase III, both rivers recharge the aquifer during the rainy season. Phase IV also shows a groundwater flow pattern from one river to another, but with a direction reversed from that of phase II. Table 1 shows raw data of Fig. 6. Groundwater levels in the transition areas (wells 13, 14 and 15) change slowly, indicating that the role of river flow dynamics is less significant in this zone. It should be pointed out that even though the classification of dynamic flow regimes is based on a 1-year data set, it is applicable to other times due to repetition of seasonal flow cycles.

Based on the data in Fig. 6, Fig. 7 shows a generalized relationship between river stages and groundwater levels in

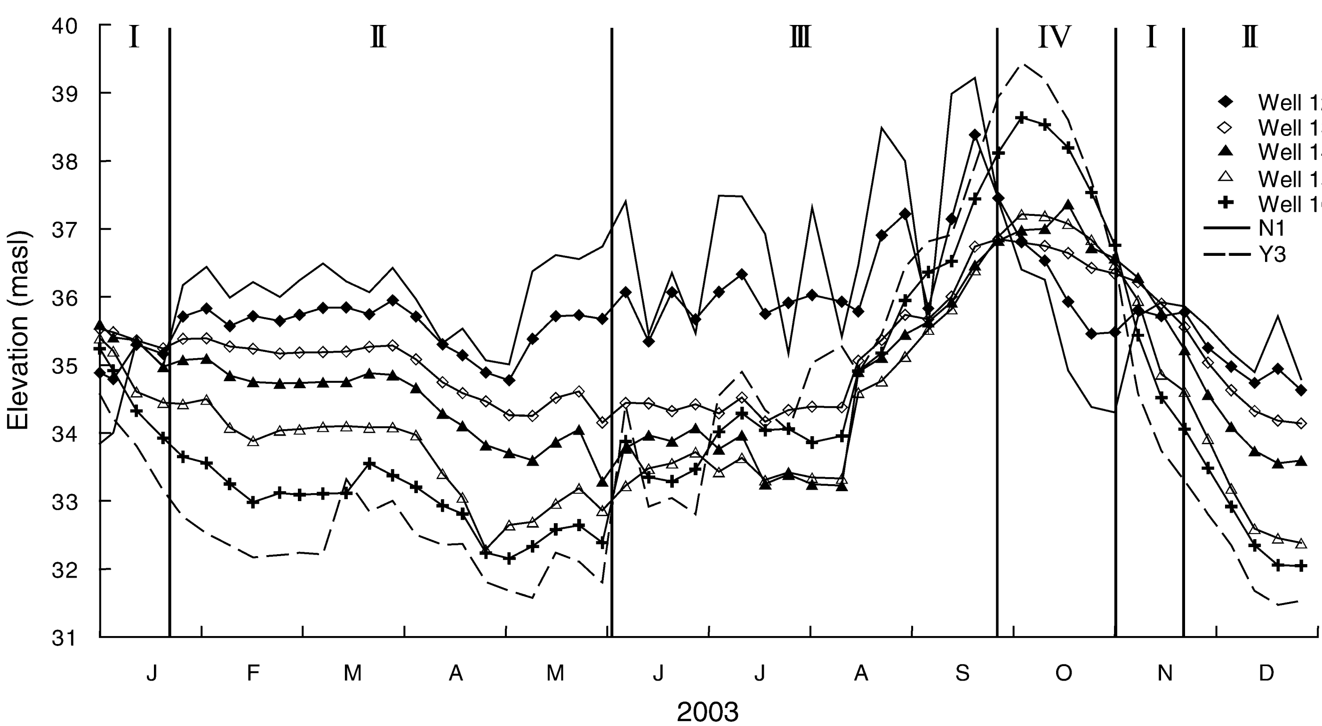


Fig. 6 Seasonal fluctuation of groundwater levels and river stages (*N1* and *Y3*). Two main phases of groundwater flow dynamics are direct flow from Nan River toward Yom River in the dry season (phase *II*) and aquifer recharge in the rainy season (phase *III*). Other two phases (phases *I* and *IV*) occur during transitional changes. In phase *I*, the aquifer discharges into both rivers. In phase *IV*, the aquifer has a reversed groundwater flow direction with respect to phase *II*

DOI 10.1007/s10040-006-0110-8

Table 1 Groundwater levels and river stages in 2003, Phitsanulok, Thailand

Date (M/D/Y)	Groundwater levels (masl)					River stages (masl)					
	Well 12	Well 13	Well 14	Well 15	Well 16	N5A	N74	Y16	Y17	N1	Y3
12/28/02	34.88	35.53	35.60	35.39	35.24	35.19	30.81	34.89	33.96	33.84	34.57
01/04/03	34.79	35.48	35.41	35.20	34.91	35.38	30.89	34.58	33.52	34.00	34.21
01/11/03	35.30	35.36	35.36	34.60	34.32	36.71	32.29	34.13	33.20	35.35	33.81
01/19/03	35.14	35.24	35.10	34.44	33.92	36.35	31.91	33.31	32.86	34.98	33.15
01/25/03	35.71	35.38	35.07	34.43	33.65	37.54	33.09	32.90	32.51	36.17	32.76
02/01/03	35.83	35.39	35.09	34.49	33.55	37.78	33.42	32.65	32.29	36.44	32.52
02/08/03	35.57	35.27	34.84	34.08	33.25	37.37	32.87	32.48	32.09	35.98	32.34
02/15/03	35.71	35.23	34.75	33.88	32.98	37.59	33.12	32.14	32.22	36.21	32.17
02/23/03	35.64	35.17	34.73	34.04	33.12	37.34	32.98	32.18	32.24	36.00	32.20
03/01/03	35.73	35.18	34.74	34.05	33.09	37.61	33.17	32.21	32.29	36.24	32.24
03/08/03	35.83	35.19	34.75	34.09	33.10	37.87	33.39	32.10	32.41	36.49	32.21
03/15/03	35.84	35.19	34.75	34.10	33.11	37.58	33.19	33.55	32.88	36.23	33.32
03/22/03	35.75	35.26	34.88	34.08	33.54	37.36	33.15	33.01	32.54	36.06	32.85
03/29/03	35.95	35.29	34.85	34.09	33.37	37.79	33.36	33.09	32.82	36.43	33.00
04/05/03	35.71	35.08	34.66	33.97	33.21	37.30	32.96	32.44	32.62	35.96	32.50
04/13/03	35.30	34.74	34.29	33.40	32.93	36.73	32.14	32.33	32.39	35.32	32.35
04/19/03	35.14	34.58	34.10	33.05	32.81	36.93	32.40	32.42	32.27	35.53	32.37
04/26/03	34.89	34.47	33.82	32.29	32.24	36.48	31.88	31.96	31.52	35.06	31.81
05/03/03	34.77	34.26	33.70	32.65	32.15	36.40	31.88	31.98	31.10	35.01	31.67
05/10/03	35.38	34.25	33.60	32.69	32.33	37.78	33.23	31.96	30.86	36.38	31.58
05/17/03	35.71	34.51	33.87	32.96	32.58	37.96	33.59	32.36	32.01	36.61	32.24
05/24/03	35.73	34.61	34.05	33.18	32.64	37.93	33.46	32.10	32.12	36.55	32.11
05/31/03	35.67	34.15	33.29	32.86	32.39	38.14	33.59	31.90	31.61	36.74	31.80
06/07/03	36.07	34.44	33.77	33.22	33.88	38.85	34.14	34.63	33.99	37.40	34.41
06/14/03	35.35	34.43	33.97	33.47	33.35	36.72	32.58	32.98	32.79	35.44	32.91
06/21/03	36.07	34.32	33.87	33.55	33.28	37.73	33.24	33.16	32.82	36.35	33.04
06/28/03	35.67	34.42	34.08	33.72	33.47	36.75	32.57	32.92	32.60	35.46	32.81
07/05/03	36.07	34.29	33.76	33.43	34.02	38.88	34.34	34.99	33.71	37.48	34.55
07/12/03	36.33	34.52	33.97	33.63	34.29	38.93	34.21	35.37	34.01	37.48	34.90
07/19/03	35.75	34.16	33.25	33.31	34.04	38.26	33.91	34.67	33.70	36.92	34.33
07/26/03	35.91	34.33	33.39	33.42	34.06	36.36	32.48	34.34	33.46	35.16	34.03
08/02/03	36.02	34.38	33.24	33.34	33.86	38.76	34.05	35.41	34.30	37.31	35.02
08/11/03	35.92	34.37	33.22	33.33	33.95	36.66	32.62	35.71	34.45	35.42	35.27
08/16/03	35.78	35.06	34.90	34.59	34.91	37.90	33.23	35.29	34.10	36.46	34.88
08/23/03	36.90	35.37	35.11	34.76	35.17	40.09	34.85	35.95	34.52	38.48	35.45
08/30/03	37.22	35.73	35.45	35.13	35.95	39.44	34.76	37.01	35.38	38.00	36.44
09/06/03	35.83	35.67	35.63	35.52	36.36	36.85	32.64	37.41	35.69	35.55	36.81
09/13/03	37.14	36.00	35.92	35.82	36.52	40.71	35.11	37.55	35.71	38.99	36.91
09/20/03	38.38	36.74	36.47	36.39	37.44	40.47	36.41	38.68	36.48	39.22	37.92
09/27/03	37.45	36.85	36.83	36.88	38.12	38.40	35.22	40.10	36.76	37.42	38.94
10/04/03	36.82	36.80	36.98	37.21	38.64	37.27	34.45	40.69	37.08	36.40	39.44
10/11/03	36.53	36.75	37.00	37.19	38.53	37.28	33.94	40.30	37.12	36.25	39.20
10/18/03	35.92	36.64	37.36	37.07	38.19	36.00	32.47	39.47	36.96	34.91	38.60
10/25/03	35.46	36.42	36.72	36.84	37.53	35.50	31.86	38.36	36.47	34.38	37.70
11/01/03	35.48	36.34	36.56	36.47	36.76	35.35	31.94	37.02	35.60	34.30	36.53
11/08/03	35.80	36.21	36.28	35.95	35.44	37.05	32.70	34.92	33.93	35.71	34.58
11/15/03	35.71	35.90	35.76	34.86	34.52	37.22	32.99	33.96	33.32	35.92	33.74
11/22/03	35.77	35.55	35.22	34.60	34.06	37.14	32.98	33.50	32.90	35.86	33.29
11/29/03	35.25	35.03	34.56	33.92	33.48	36.86	32.62	32.94	32.56	35.55	32.81
12/06/03	34.97	34.63	34.09	33.18	32.92	36.49	32.24	32.37	32.31	35.18	32.35
12/13/03	34.73	34.32	33.74	32.59	32.35	36.26	31.81	31.89	31.27	34.89	31.67
12/20/03	34.94	34.18	33.55	32.45	32.05	37.03	32.75	31.82	30.82	35.71	31.47
12/27/03	34.63	34.14	33.59	32.38	32.05	36.12	31.78	31.82	30.98	34.78	31.53

a confined alluvial aquifer between two rivers. In Fig. 7, the rivers A and B refer to the Nan (N1) and Yom (Y3) rivers and the wells A and B are represented by wells 12 and 16, respectively (Fig. 3). Table 2 summarizes the relationship between groundwater levels and river stages in each phase of Fig. 7. A significant implication of Fig. 7 is that, at a minimum, the groundwater flow dynamics can be identified and classified by using two data sets of groundwater levels and river stages near the groundwater/surface-water interface. The duration in each phase is, however, site specific.

Figure 8 shows flow nets in four phases of groundwater flow dynamics as identified in Fig. 6. The repetition of phases I and II in November–December has similar groundwater flow patterns to those in January–May. Seasonally varying river stages (Fig. 6) is a predominant factor that controls the groundwater flow directions of the confined alluvial aquifer. The potentiometric surface is not a subdued replica of the land surface at all times. River flow dynamics alters groundwater flow directions continuously, particularly in areas near the rivers.

 DOI 10.1007/s10040-006-0110-8

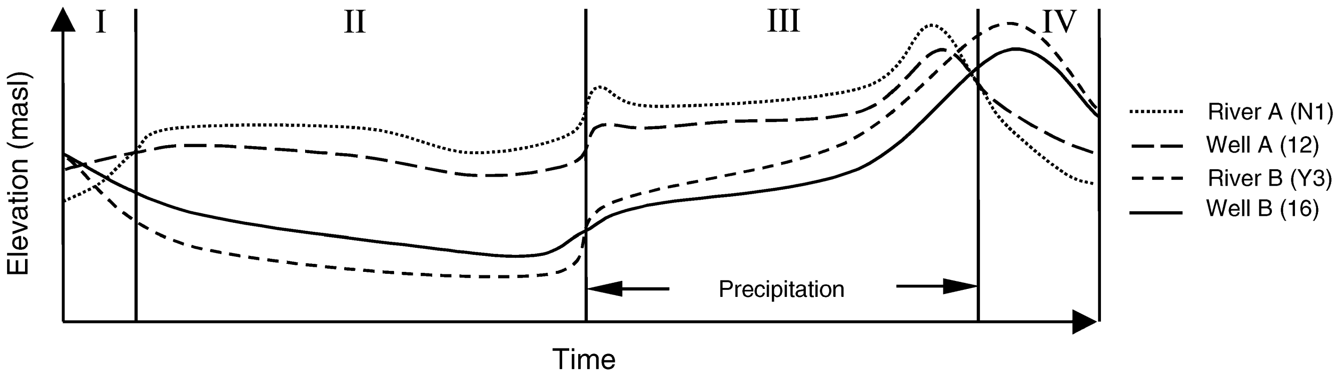


Fig. 7 Generalized hydraulic heads near the groundwater/surface-water interface of a confined alluvial aquifer between two rivers under dynamic conditions. This is a simplified model of Fig. 5 and a corresponding phenomenon in Fig. 2. Phase *I*/*II* and *III*/*IV* boundaries are indicated by abrupt changes at *river A*. Similarly, phase *II*/*III* and *I*/*IV* boundaries are marked by abrupt changes at *river B*. Well A is located next to the *river A* and *well B* next to *river B*, respectively

Based on Figs. 6 and 8, details of groundwater flow directions and flow paths are as follows. From 1–21 January, mounding groundwater in the transition areas discharges into both Nan (83°SE) and Yom rivers (16°SE) with flow paths of 5.8 and 5.6 m, respectively (Fig. 8a). From 22 January to 2 June, groundwater has flown continuously from the Nan River toward the Yom River along 18°SW with a flow path of 18.9 m (Fig. 8b). From 3 June to 26 September, the Yom River has begun to recharge into the aquifer along 88°NE with a flow path of 35.6 m, while the Nan River is still recharging the aquifer system along 5°SE with a flow path of 48.0 m (Fig. 8c). From 27 September to 31 October, groundwater flows continuously from the Yom River toward the Nan River along 85°SE–85°NE with a flow path of 11.2 m while the Nan River becomes a discharge area (Fig. 8d). Phase I repeats during 1–21 November when the aquifer discharges groundwater into the Nan and Yom rivers with flow paths of 5.8 and 5.6 m, respectively. Finally, phase II occurs at the end of the year, between 22 November and 31 December, with a flow path of 5.7 m from the Nan River to the Yom River.

These results are opposite to those found by Brunke and Gonser (1997) and Massmann et al. (2004), who consider water exchange processes at a single river. Clearly in the current study, at a particular moment in time, one river may be effluent while another influent. The baseflow from the aquifer into the stream does not always occur in the dry season, but it occurs at both rivers for 3 weeks in the study. To estimate the infiltration into the banks, hydraulic heads in nearby rivers must be carefully considered. Classification of the effluent or influent condition requires a thorough understanding of the groundwater flow system in three dimensions.

Table 2 Classification of groundwater flow dynamics by using the relationship between groundwater levels and river stages

Phase	Relationship at river A	Relationship at river B
I. Aquifer discharge	River A<well A	River B<well B
II. Direct river-to-river flow	River A>well A	River B<well B
III. Aquifer recharge	River A>well A	River B>well B
IV. Reverse river-to-river flow	River A<well A	River B>well B

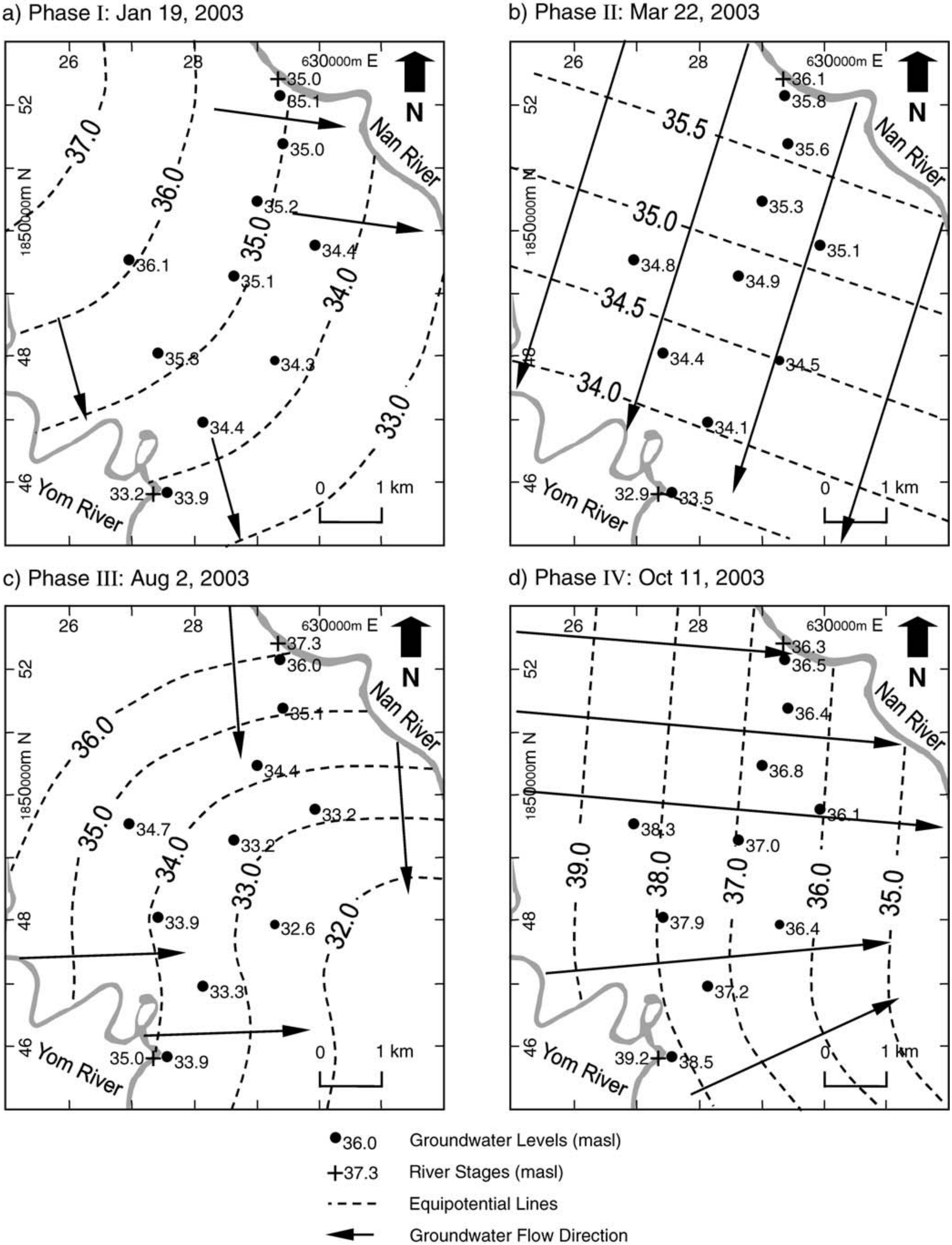
Flow paths of oxic lateral recharge have, therefore, a zigzag pattern near recharge-discharge areas at the banks rather than a continuous curvilinear one across the entire flow system. The Phitsanulok study site does not conform to the conceptual model of a continuous flow regime across the entire system (i.e., Tóth 1963; Meyboom 1966, 1967; Winter 1976, 1999). Figure 9 shows that lateral recharge from oxic rivers does not penetrate into transition areas of the aquifer. Groundwater flow paths in each time period are very short, 5.6–48 m, in comparison with the distance of 6–7 km between the two rivers.

In general, the groundwater flow direction in transition areas has a similar zigzag pattern while flowing toward 47°SE. In contrast to the steady-state concept in Fig. 1, the regional groundwater flow direction in transition areas is nearly parallel to the river flow (Fig. 9). This observation is consistent with what Larkin and Sharp (1992) refers to as the "underflow-component dominated stream-aquifer system," in which the groundwater moves parallel to the river channel and in the same direction as the streamflow. The underflow component is predominant in fluvial systems of mixed-loaded to bed-loaded character and in systems with large channel gradients, small sinuosities, large width-to-depth ratios, and low river channel penetrations.

Flow paths between groundwater and surface water are often treated approximately as two-dimensional and steady state (e.g., Meyboom et al. 1966; Meyboom 1966, 1967; Winter 1976; Winter et al. 1999; Tóth 1962, 1963, 1999). However, this study shows that the interactions between groundwater and surface water are three-dimensional and highly dynamic. A thorough understanding of the groundwater/surface-water interactions

Fig. 8 Illustration of groundwater flow dynamics in flow nets: **a** ▶ discharge from groundwater mounds to rivers; **b** flow from the *Nan River* toward the *Yom River*; **c** recharge from both rivers into the aquifer; and **d** flow from the *Yom River* toward the *Nan River*

DOI 10.1007/s10040-006-0110-8



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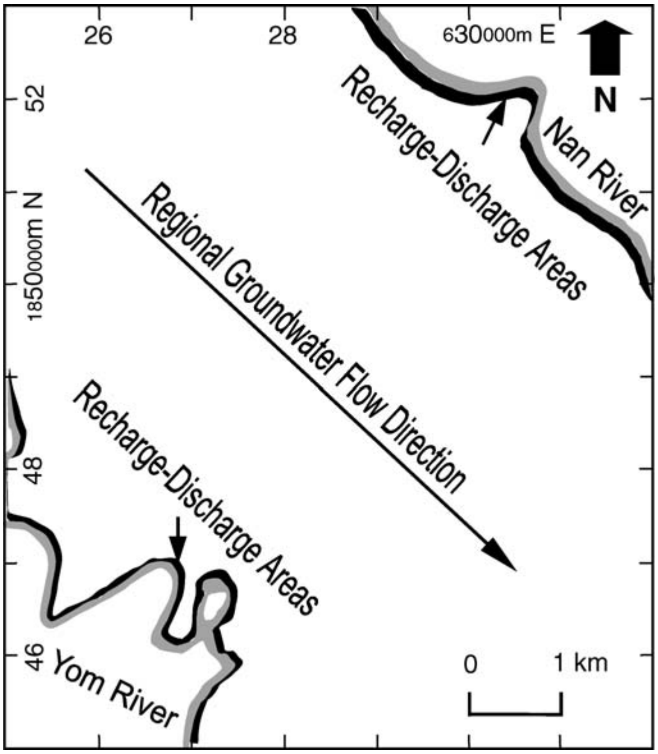

Fig. 9 The regional groundwater flow direction and local recharge-discharge areas. The generalized regional groundwater flow direction is toward 47°SE, which is nearly parallel to the river flow direction. Recharge-discharge areas are located within 48 m of the groundwater/surface-water interface because of the zigzag groundwater flow pattern

requires a three-dimensional transient analysis of the groundwater flow dynamics in the vicinity of the surface-water bodies (Sophocleous et al. 1988; Sophocleous 1991, 2002; Harvey and Bencala 1993; Wondzell and Swanson 1996; Woessner 2000).

Evaluation of chemical analysis

Tables 3 and 4 show results of groundwater analysis in the dry and rainy seasons, respectively. Table 5 presents the river-water quality. Average values of charge balance are 1.99 and 1.94% for the samples from the dry and rainy seasons, respectively. Quality-assurance samples also meet the standard duplicated sampling criteria. Therefore, the chemical analysis is reliable.

According to Berner (1981), the presence of redox species found in the aquifer indicates that the groundwater is under anoxic (post-oxic) conditions (Tables 3 and 4), whereas the river water is oxic (Table 5). The post-oxic conditions in groundwater are indicated by very high Fe^{2+} concentrations, low SO_4^{2-}, and negligible DO and NO_3^-. A couple of unstable species, S^{2-} and NO_2^-, are undetectable. The Mn_{total} is also high but does not show the high anomaly in the transition areas. Eh values in the rainy season increase slightly with respect to those in the dry season, whereas the DO remains undetectable.

High iron anomaly

High iron anomaly appears in transition areas of a confined alluvial aquifer between two rivers (Fig. 10). This anomaly is apparently a result of strong anoxic condition in the transition areas, which are isolated from oxic river water by a zigzag groundwater movement (Fig. 2). Fe^{2+} is oxidized immediately upon exposure to the DO at the banks. Anoxic conditions prevail in the transition areas where the DO is consumed completely. In this environment, the Fe^{2+} concentrations are elevated. The rationale for appearance of moderate concentrations of Fe^{2+} at the banks and the fast oxidation is not fully understood.

Figure 10 also illustrates that the high iron anomaly is nearly constant in space and time. In other words, the high iron anomaly has developed for many years. Also, seasonal changes of the groundwater flow regime do not significantly affect the Fe^{2+} distribution in transition areas. The trend of the high iron anomaly is thus nearly parallel to the shape of the two rivers.

Elevated Fe^{2+} concentrations in the groundwater are a result of the dissolution and redox processes of iron-bearing minerals in the aquifer. These minerals, including hematite, pyrite, siderite, biotite, amphibole, and pyroxene, were observed by visual inspection. The aquifer material is composed of at least 95% quartz, which does not contribute to the appearance of Fe^{2+}. According to Appelo and Postma (1993), important sources of Fe^{2+} in groundwater include: (1) oxidative dissolution of pyrite, (2) dissolution of siderite, (3) dissolution of amphibole and pyroxene, and (4) reductive dissolution of hematite and goethite coating on the surface of quartz grains. As indicated by high bicarbonate concentrations, siderite is an important solubility control. In addition, microorganisms are expected to play an important role in the release of Fe^{2+} in groundwater (Chapelle and Lovley 1992).

The dissolved Fe^{2+} is the stable phase in anoxic groundwater, whereas $Fe(OH)_3$ is the dominant species in river water. $Fe(OH)_3$ is a typical iron species in natural waters having measurable DO (Kehew 2001). Figure 11 shows a pH-Eh diagram of the Fe–O–H_2O system with values found in this study. Although the aquifer is shallow, the anoxic conditions strongly control the appearance of high Fe^{2+}. Vertical recharge from rainfall in the rainy season slightly influences the redox conditions of the groundwater as indicated by an upward shift in Eh values in Fig. 11. In contrast, the redox condition of the river is homogeneous with a slight decrease of DO in the Yom River in the rainy season (Table 5). Although the Eh was measured quantitatively onsite, Fig. 11 should be evaluated as qualitatively as possible (Appelo and Postma 1993).

Figure 12 shows that the dissolved Fe^{2+} is directly proportional to the total mobile Fe. This linear relationship is a result of filtration. The dissolved Fe^{2+} is about 89.3% of the total mobile Fe (Table 3). According to Puls and Barcelona (1989), the filtration of groundwater samples by using 0.45-μm filters for iron analyses will not provide accurate information concerning the mobility of iron. If

 DOI 10.1007/s10040-006-0110-8

Table 3 Groundwater quality in dry season of a confined alluvial aquifer, Phitsanulok, Thailand[a]

Well No.	Date (M/D/Y)	pH	Eh	SC	T	DO	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	Mn_{total}	Fe_{total}	Fe^{2+}	Fe^{3+}	CB
1	02/17/06	6.32	−77.91	275	28.01	<0.2	165	21.1	1.78	23.4	5.9	2	134.17	0.01	7.5	<0.01	<0.01	<0.01	0.80	24	0.44	8.21	7.20	1.01	4.1
2	02/21/06	6.68	−79.46	242	28.62	<0.2	140	8.5	1.04	27.5	7.0	7	118.28	0.03	<0.1	<0.01	<0.01	<0.01	0.94	25	0.40	9.51	8.36	1.15	4.6
3	02/17/06	6.51	−59.31	290	28.45	<0.2	165	24.4	1.79	22.4	5.1	2	148.79	0.02	4.5	<0.01	<0.01	<0.01	0.72	26	0.35	10.75	9.05	1.70	1.1
4	02/17/06	6.47	−44.74	293	28.60	<0.2	175	26.6	1.68	22.0	5.0	2	146.36	0.02	5.8	<0.01	<0.01	<0.01	1.04	25	0.36	10.35	9.02	1.33	2.5
5	02/17/06	6.52	−51.76	311	28.73	<0.2	180	15.9	1.72	26.8	5.7	12	115.86	0.02	12.5	<0.01	<0.01	<0.01	0.32	21	0.78	8.82	7.61	1.21	0.9
6	02/19/06	6.49	−43.18	270	28.42	<0.2	160	7.0	1.19	29.5	8.2	8	114.64	0.02	7.0	<0.01	<0.01	<0.01	0.58	21	0.55	18.52	15.50	3.02	4.9
7	02/19/06	6.65	−74.46	320	26.40	<0.2	192	16.2	1.57	33.7	6.2	3	158.53	0.03	<0.1	<0.01	<0.01	<0.01	0.98	28	0.62	23.10	21.00	2.10	4.5
8	02/17/06	6.50	17.87	328	27.70	<0.2	198	20.8	1.54	30.0	7.2	2	150.01	0.02	14.0	<0.01	0.03	<0.01	0.87	22	0.48	15.32	13.17	2.15	3.9
9	02/20/06	6.63	−81.20	135	28.33	<0.2	78	4.6	0.99	11.1	5.1	4	67.07	0.01	<0.1	<0.01	<0.01	<0.01	1.46	22	0.29	4.80	4.53	0.27	−0.6
10	02/22/06	6.45	−91.38	312	28.20	<0.2	186	24.4	1.91	24.2	5.5	2	152.46	0.02	1.0	<0.01	<0.01	<0.01	1.20	28	0.09	12.65	10.85	1.80	3.6
11	02/22/06	6.69	−99.33	265	28.70	<0.2	157	14.4	0.91	28.9	7.6	3	145.11	0.04	<0.1	<0.01	<0.01	<0.01	0.62	31	0.05	11.38	10.05	1.33	4.9
12	02/21/06	6.83	−128.62	421	28.91	<0.2	246	9.1	1.79	40.3	11.7	20	164.59	0.05	13.0	<0.01	<0.01	<0.01	4.30	20	0.11	8.72	7.52	1.20	−1.7
13	02/21/06	6.63	−107.89	380	28.43	<0.2	225	22.0	1.32	33.3	9.1	4	190.24	0.04	<0.1	<0.01	<0.01	<0.01	1.58	21	0.10	19.03	18.20	0.83	2.6
14	02/21/06	6.71	−93.82	295	28.13	<0.2	170	23.9	1.28	28.9	5.2	3	158.52	0.04	2.0	<0.01	<0.01	<0.01	0.80	24	0.05	17.14	15.30	1.84	3.8
15	02/18/06	6.90	−96.45	320	28.05	<0.2	191	19.1	1.42	39.0	2.7	5	170.66	0.07	<0.1	<0.01	<0.01	<0.01	0.46	21	0.01	1.32	1.15	0.17	1.6
16	02/18/06	6.79	−84.49	250	28.65	<0.2	143	13.3	1.76	21.6	4.6	3	128.02	0.04	4.0	<0.01	<0.01	<0.01	0.52	20	0.18	9.55	8.37	1.18	−4.3
17	02/18/06	6.45	−138.65	300	27.72	<0.2	175	14.7	1.31	25.6	8.0	3	153.68	0.02	2.5	<0.01	<0.01	<0.01	0.84	22	0.47	10.37	9.25	1.12	−0.9
18	02/18/06	6.62	−97.97	322	27.19	<0.2	191	19.7	1.00	24.6	7.6	1	158.53	0.03	5.5	<0.01	<0.01	<0.01	1.10	22	0.66	11.64	10.06	1.58	−0.1
19	02/22/06	6.65	−96.66	318	26.96	<0.2	188	18.6	1.15	24.3	8.0	5	164.63	0.04	<0.1	<0.01	<0.01	<0.01	0.70	24	0.11	8.65	7.79	0.86	−2.4
20	02/20/06	6.74	−123.83	360	24.48	<0.2	223	32.3	0.26	27.4	5.7	4	189.00	0.05	<0.1	<0.01	<0.01	<0.01	2.36	24	0.47	14.95	12.59	2.36	0.6
21	02/19/06	6.63	−108.01	243	28.23	<0.2	144	16.0	0.30	17.6	5.9	3	117.07	0.02	1.5	<0.01	<0.01	<0.01	0.62	20	0.68	19.35	17.21	2.14	0.8
22	02/19/06	6.65	−108.36	372	27.62	<0.2	225	26.9	0.29	38.6	8.1	3	203.65	0.04	0.5	<0.01	<0.01	<0.01	0.70	18	0.55	14.78	13.02	1.76	4.7
23	02/19/06	6.64	−115.37	331	27.63	<0.2	196	21.7	0.27	22.9	7.1	2	154.87	0.03	<0.1	<0.01	<0.01	<0.01	0.76	19	0.38	17.89	15.41	2.48	1.6
24	02/21/06	6.73	−110.07	301	27.30	<0.2	178	20.0	0.31	17.7	6.7	3	121.93	0.03	1.5	<0.01	<0.01	<0.01	0.89	20	0.24	15.75	13.38	2.37	4.5
25	02/22/06	6.70	−120.20	384	27.55	<0.2	232	32.7	2.17	20.4	6.8	4	152.42	0.04	7.5	<0.01	<0.01	<0.01	0.87	20	0.47	21.98	20.05	1.93	4.9

[a] All parameters in mg/L except pH, Eh (mV), SC (μS/cm), T (°C), and CB (%); *CB* charge balance

DOI 10.1007/s10040-006-0110-8

Table 4 Groundwater quality in rainy season of a confined alluvial aquifer, Phitsanulok, Thailand[a]

Well No.	Date (M/D/Y)	pH	Eh	SC	T	DO	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	Mn_{total}	Fe_{total}	Fe^{2+}	Fe^{3+}	CB
2	09/13/03	6.68	−6.57	235	27.52	<0.2	138	9.1	1.01	26.9	7.20	5	120.73	0.03	1.3	<0.01	<0.01	<0.01	0.85	21	0.38	9.12	8.05	1.07	4.6
8	09/13/03	6.50	−10.37	320	27.63	<0.2	191	20.5	1.43	29.7	7.00	3	151.23	0.02	13.0	<0.01	<0.01	<0.01	0.83	23	0.45	14.71	12.99	1.72	2.6
12	09/14/03	6.97	1.64	423	28.18	<0.2	250	9.0	1.65	39.5	11.30	15	163.33	0.08	14.0	<0.01	<0.01	<0.01	3.10	20	0.10	8.10	7.15	0.95	−0.9
13	09/14/03	6.62	62.32	379	27.76	<0.2	234	20.5	1.25	32.3	9.20	3	187.80	0.04	<0.1	<0.01	<0.01	<0.01	1.20	19	0.15	19.32	17.06	2.26	2.0
14	09/14/03	6.83	1.05	290	27.61	<0.2	179	23.7	1.23	29.0	5.10	2	158.49	0.05	1.0	<0.01	<0.01	<0.01	1.20	23	0.10	16.50	14.57	1.93	4.5
15	09/14/03	6.95	−39.12	315	27.69	<0.2	197	18.5	1.41	37.3	2.90	5	171.87	0.08	1.0	<0.01	<0.01	<0.01	0.61	20	0.05	1.20	1.06	0.14	−0.7
16	09/14/03	6.74	10.88	244	26.69	<0.2	152	13.8	1.73	21.5	4.20	2	121.93	0.03	3.0	<0.01	<0.01	<0.01	0.50	21	0.13	8.04	7.10	0.94	−1.3
21	09/13/03	6.63	−80.37	248	27.30	<0.2	150	15.7	0.50	17.7	5.50	3	109.77	0.02	3.0	<0.01	<0.01	<0.01	0.32	22	0.70	19.64	17.34	2.30	2.1
22	09/13/03	6.65	−58.68	361	27.64	<0.2	220	26.9	0.32	38.0	7.80	6	207.32	0.04	1.0	<0.01	<0.01	<0.01	0.63	19	0.50	14.63	12.92	1.71	1.7
25	09/13/03	6.70	−120.55	380	27.50	<0.2	228	32.5	2.15	21.0	6.90	5	152.42	0.04	8.0	<0.01	<0.01	<0.01	0.85	19	0.52	21.01	18.55	2.46	4.7

[a] All parameters in mg/L except pH, Eh (mV), SC (μS/cm), T (°C), and CB (%); *CB* charge balance

the purpose of the investigation is to evaluate the total mobile Fe species, which includes dissolved Fe^{2+} and suspended Fe colloids (<10 μm in diameter) in groundwater, which is the objective of this work, significant underestimation of the mobility may result because the Fe colloids are excluded. In contrast, if the objective is to investigate the truly dissolved Fe^{2+}, the use of 0.45-μm filters still results in the overestimation of dissolved Fe^{2+} because the Fe colloids smaller than 0.45 μm in size can pass through the filters.

Values for Fe^{3+} in Tables 3 and 4 represent the amount of all suspended Fe^{3+} species such as Fe oxyhydroxides, Fe organic complexes, among others, calculated by subtracting the dissolved Fe^{2+} from the total mobile Fe. This method shows that the calculated Fe^{3+} is about 11.7% of the total Fe. However, the calculated Fe^{3+} concentrations are much higher than theoretical values as described by Freeze and Cherry (1979); that is, Log $[Fe^{3+}]$=0.32–3 pH. Table 6 shows the comparison of both methods. The latter method yields Fe^{3+} concentrations so small that the total mobile Fe is almost entirely the dissolved Fe^{2+}, which is a common assumption in hydrogeology. The discrepancy between calculated and theoretical values of Fe^{3+} may be caused by the accumulation of suspended Fe^{3+} colloidal species on the filters as time proceeds.

Effects of lateral recharge

Figure 10 shows that iron-rich groundwater exists in transition areas. This evidence has confirmed that the hypothesis stated here is plausible. The zigzag flow pattern limits the penetration of the river water into the transition areas. The transition areas are thus isolated and have strong anoxic conditions. The dissolved Fe^{2+} is highly stable in the anoxic environment. Consequently, the transition areas are characterized by high concentrations of dissolved Fe^{2+}. Figure 2 explains the conceptual models of the above processes.

The Fe^{2+} is a better mobility indicator of redox species in groundwater than the DO. The DO is not measurable because it is consumed by aerobic microorganism and used by other chemical reactions. Nevertheless, the Fe^{2+} concentrations in recharge-discharge areas at the banks are still moderate. Details of these hydrogeochemical processes should be further studied.

Redox processes at the Phitsanulok 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 two successive rivers may explain the contrast. At this study site, the Nan and Yom rivers are about 6–7 km apart causing the groundwater flow regime to be more dynamic. Fluctuation of the river stages in 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 subsequent patterns of hydrochemical facies.

DOI 10.1007/s10040-006-0110-8

Table 5 Water quality of Nan and Yom rivers, Phitsanulok, Thailand

Sample No.	Date (M/D/Y)	pH	Eh (mV)	SC (μS/cm)	T (°C)	DO (mg/L)	TDS (mg/L)	Fe^{2+} (mg/L)
Dry season								
N1	02/25/06	7.2	407.33	170	26.3	7.5	101	0.52
N2	02/25/06	7.1	416.05	168	26.5	7.2	99	0.51
N3	02/25/06	6.8	421.47	175	26.7	7.2	102	0.43
Y1	02/25/06	7.3	400.95	320	26.5	6.8	196	0.64
Y2	02/25/06	7.2	396.38	327	26.8	7.0	200	0.52
Y3	02/25/06	7.0	399.74	331	26.4	7.2	201	0.42
Rainy season								
N1	09/12/04	7.5	450.42	150	28.2	7.0	90	0.69
N2	09/12/04	7.2	423.82	144	29.2	7.2	85	0.54
N3	09/12/04	7.8	427.51	156	30.1	7.1	93	0.42
Y1	09/12/04	7.6	402.31	310	31.1	6.6	189	0.62
Y2	09/12/04	7.7	406.15	305	31.5	6.3	185	0.63
Y3	09/12/04	7.6	405.05	302	30.5	6.8	184	0.54

Effects of vertical recharge

The presence of vertical recharge is less important than the absence of lateral recharge, as evident by the high iron anomaly in transition areas (Fig. 10). At the study area, vertical recharge from rainfall is insignificant to redox conditions of the aquifer. This study is in contrast to results presented by Edmunds et al. (1987), Groffman and Crossey (1999), and Massmann et al. (2004). Results of this study are also contradictory to isotope analysis in nearby aquifers by Howard Humphreys (1986), who found that the groundwater at shallow depths of up to 50 m is likely to be less than 10-years old and that the groundwater recharge is almost entirely from rainfall. Vertical recharge is focused initially where the vadose

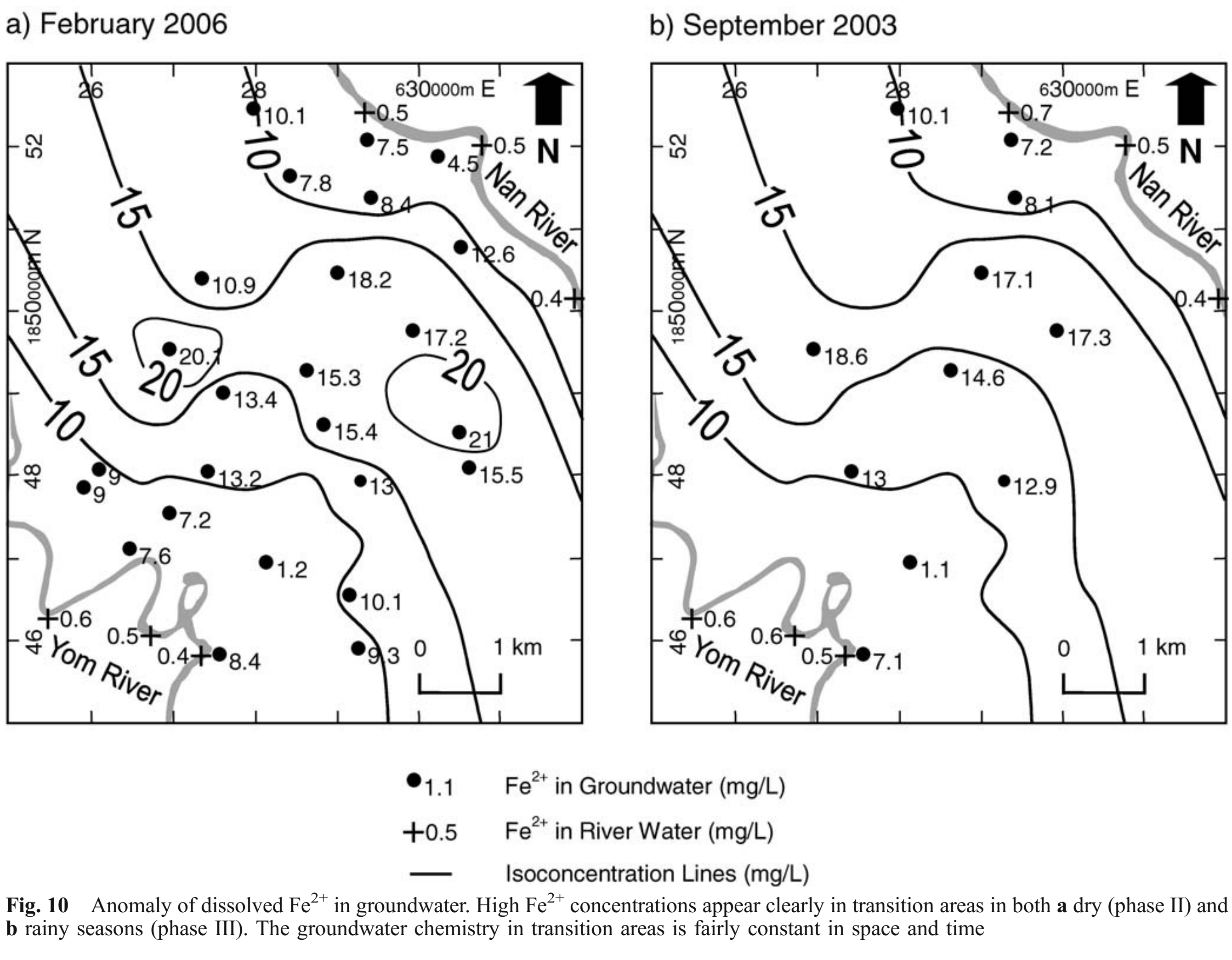

Fig. 10 Anomaly of dissolved Fe^{2+} in groundwater. High Fe^{2+} concentrations appear clearly in transition areas in both **a** dry (phase II) and **b** rainy seasons (phase III). The groundwater chemistry in transition areas is fairly constant in space and time

DOI 10.1007/s10040-006-0110-8

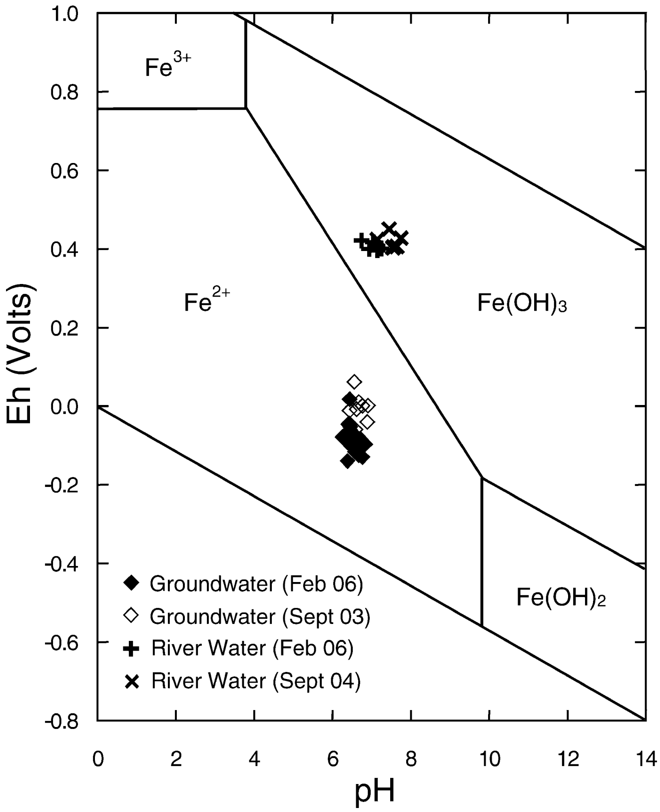

Fig. 11 pH–Eh diagram of Fe–O–H_2O system in natural waters (modified from Freeze and Cherry 1979; Kehew 2001). Stable phases of iron include Fe^{2+} in groundwater and $Fe(OH)_3$ in river water

Table 6 Calculated against theoretical values of Fe^{3+}

Well No.	Calculated Fe^{3+} (mg/L)[a]	Theoretical Fe^{3+} (mg/L)[b]
Dry season		
1	1.01	8.0×10^{-8}
2	1.15	2.7×10^{-8}
3	1.70	4.5×10^{-8}
4	1.33	5.1×10^{-8}
5	1.21	4.4×10^{-8}
6	3.02	4.8×10^{-8}
7	2.10	3.0×10^{-8}
8	2.15	4.7×10^{-8}
9	0.27	3.2×10^{-8}
10	1.80	5.4×10^{-8}
11	1.33	2.6×10^{-8}
12	1.20	1.7×10^{-8}
13	0.83	3.2×10^{-8}
14	1.84	2.5×10^{-8}
15	0.17	1.4×10^{-8}
16	1.18	2.0×10^{-8}
17	1.12	5.4×10^{-8}
18	1.58	3.3×10^{-8}
19	0.86	3.0×10^{-8}
20	2.36	2.3×10^{-8}
21	2.14	3.2×10^{-8}
22	1.76	3.0×10^{-8}
23	2.48	3.1×10^{-8}
24	2.37	2.3×10^{-8}
25	1.93	2.6×10^{-8}
Rainy season		
2	1.07	2.7×10^{-8}
8	1.72	4.7×10^{-8}
12	0.95	1.1×10^{-8}
13	2.26	3.3×10^{-8}
14	1.93	1.7×10^{-8}
15	0.14	1.2×10^{-8}
16	0.94	2.3×10^{-8}
21	2.30	3.2×10^{-8}
22	1.71	3.0×10^{-8}
25	2.46	2.6×10^{-8}

[a] $Fe^{3+}=Fe_{total}-Fe^{2+}$

[b] Log $[Fe^{3+}]=0.32-3$ pH (Freeze and Cherry 1979)

zone is thin with respect to adjacent areas. It then progresses laterally over time to areas with a thicker vadose zone (Winter 1983). The changing magnitude and distribution of vertical recharge affects the groundwater flow dynamics, particularly in transition areas. The oxic vertical recharge is also subject to DO consumption when entering the subsurface.

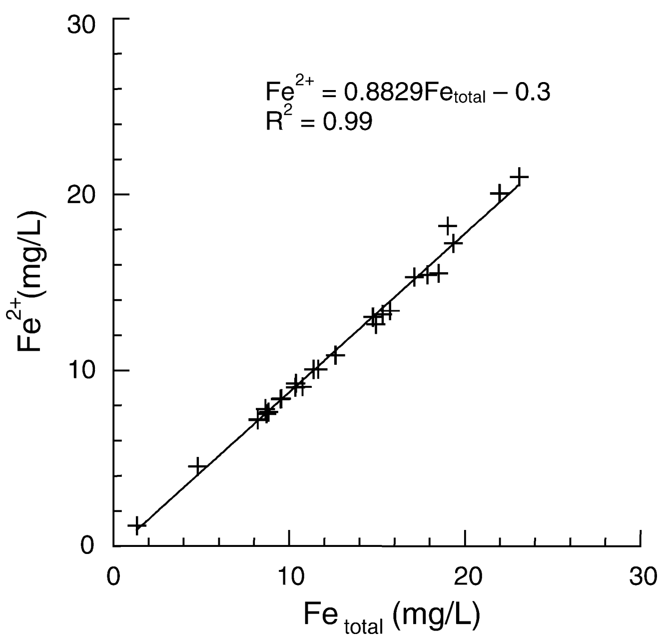

Fig. 12 Relationship between dissolved Fe^{2+} and total mobile Fe in groundwater. Fe^{2+} is directly, linearly proportional to the total mobile Fe. The 0.45-μm filters consistently filter suspended Fe colloids from the groundwater by about 11.7%

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

Evolutionary pattern

The evolutionary pattern of high iron concentrations along the regional groundwater flow direction does not exist (Figs. 9 and 10). Along the regional groundwater flow direction, the anomaly is constant in the transition areas at least for the two sampling periods. Although this feature

 DOI 10.1007/s10040-006-0110-8

supports the hypothesis of discrete hydrochemical zones (Back and Barnes 1965; Langmuir 1969, 1997; Chapelle and Lovley 1992), the high iron anomaly is not a result of chemical evolution along continuous flow paths. Additional understanding of the aquifer mineralogy, speciation modeling, and more frequent samplings will enhance the understanding about the anomaly present.

Conclusions

Nature is dynamic. Groundwater flow dynamics in the study area consists of four cyclic phases including aquifer discharge into the two neighboring rivers, direct flow from one river toward another, aquifer recharge from the two rivers, and the reversed river-to-river flow. The groundwater/surface-water interactions of a confined alluvial aquifer located between two rivers are governed by the positions of river-water bodies with respect to geologic characteristics of the aquifer, by infiltration into or exfiltration from the aquifer and, less importantly, by vertical recharge through the confining units. The degree of river incision into the aquifer, river sinuosity, and the seasonal fluctuation of river stages control the groundwater flow dynamics.

The groundwater/surface-water interactions affect redox conditions of the groundwater flow system. This paper presents an interesting situation where two rivers partially cut into a confined alluvial aquifer and the seasonal fluctuations of river stages lead to a highly dynamic groundwater flow system. The groundwater flow direction changes when water levels in both rivers alternate. This in turn results in seasonal reversal of groundwater flow paths in a zigzag pattern rather than a continuous curvilinear one. Transition areas are thus isolated from oxic lateral recharge. The above mechanism explains the occurrence of discrete zones of high redox constituents such as iron in the groundwater better than the theory of chemical evolution along groundwater flow paths. An evolutionary trend does not develop along short flow paths, particularly in a river-bounded groundwater flow system whose flow paths are truncated. Redox conditions and anomaly patterns of redox species are controlled by the groundwater flow dynamics.

Certain geologic settings should have typical characteristics regardless the spatial variability of hydrogeologic and hydrogeochemical properties (Voss 2005). A challenge is to recognize and to quantify these characteristics. The phenomenon identified in this study is believed to be characteristic of a confined alluvial aquifer between two rivers, particularly in tropical regions. Important characteristics and processes found in the study area can be transferred to aid in understanding of similar hydrogeologic settings in other parts of the world.

Streams and aquifers exchange water horizontally and vertically but most studies have relied on one- or two-dimensional models. A detailed three-dimensional study is needed for a better understanding of the groundwater/surface-water interactions. As Sophocleous (2002) notes, the present inability to characterize subsurface heterogeneity in sufficiently fine spatial and temporal details causes an upscaling problem and leads to uncertainties in data analysis and interpretation. The construction and use of simplified two-dimensional cross-sections under steady-state conditions to show groundwater flow directions and hydrochemical facies must consider the implications of three-dimensional and transient effects.

Acknowledgements Thailand Research Fund provided financial support (TRG4580065) for this study. We thank Roongwit Promma, Sanong Patanompee, Rath Wongnete, Prajonyuth Yimprae, and Siam Munmaung for field assistance. We are grateful to the Hydrology and Water Resources Management Center-Lower Northern Region, Royal Irrigation Department, for providing the river-stage data. We are also grateful to the editors and three anonymous reviewers whose detailed constructive comments have led to significant improvement of this paper.

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