

GEOCHEMICAL REACTIVE TRANSPORT MODELING IN CONTAMINATED AQUIFERS, BEIJING AREA, CHINA

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(Received 19 October, 2016; accepted 19 June, 2017)

Key words: Geochemical, PHT3D, Modeling, Nitrate, Transport

ABSTRACT

Water supplies, which are vital to economic development, are severely at risk through pollution. Problems relating to water are more serious for some countries, such as China, where water is relatively scarce. A three-dimensional multicomponent reactive transport model was developed to predict the future development of groundwater quality in aquifers in and around Beijing. PHT3D, which combines the three-dimensional transport simulator MT3DMS with the geochemical model PHREEQC-2, was used as the model code. The model results showed that although nitrate in the groundwater was partially reduced by denitrification, nitrate was still present in excessive levels. The coupled model was able to quantify the influence of various land-use functions on groundwater quality, and it could identify the geochemical processes taking place in the aquifers. Finally, a novel conceptual model for an urban area that can be used to evaluate future site-remediation scenarios was developed as part of this study.

INTRODUCTION

Computer modeling and simulation are frequently applied to predict water movement and contamination migration in surface-water and groundwater regimes as well as to analyze the interaction between these two water sources. Groundwater simulation is more problematic than surface-water simulation; this is because subsurface monitoring of water and tracking the movements and hidden sources of water and various contaminants is a more complicated process. Modeling has long been used for groundwater investigation because of the difficulties involved with direct assessment and monitoring of underground reservoirs. Modeling methods have been shown to be reliable in determining groundwater flow and the

transport of contaminants by means of mathematical equations based on certain simplifying assumptions (Kumar, 2007).

The general lack of knowledge about historical source terms, the high cost of field investigations, and the limited data density relative to the heterogeneity of the subsurface make it difficult to determine reliably the risks from subsurface contaminants. In the present study, the MODFLOW/MT3DMS-based multicomponent reactive transport model PHT3D (Prommer, *et al.*, 2003) was used to interpret the geochemical fingerprint produced by subsurface contamination and also to determine the history of such contamination. Analysis of the historical data provides an important insight into whether the

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contamination still represents a threat to potential receptors. In addition to the hydrogeochemical data (contaminant mixture, estimated source geometry, and history) and physicochemical processes (advective-dispersive transport, sorption, and degradation), all secondary geochemical data from both contaminated and uncontaminated portions of the aquifers and the relevant processes for simulating these were individually integrated into the study model.

In this paper, a three-dimensional reactive transport model was constructed to represent the subsurface of central Beijing and its surroundings. The main aim of this modeling exercise was to quantify the influence of various land-use functions and changes in such functions on groundwater quality in the area around central Beijing (Fig. 1). It also aimed to determine the geochemical processes at work in Beijing's aquifers.

SITE DESCRIPTION

The Beijing urban area was evaluated in this study, and the results revealed that the aquifers in this region had accumulated high levels of contaminants from nearby nitrate and hardness sources since 1970 (Mande, 2011). The main aquifers in central Beijing are composed of Quaternary alluvial gravel-sand sediments. In Fig. 1, the line BB', from Haidian to Fengtai, divides this region into two parts: an unconfined aquifer consisting of a single gravel stratum in the west (Aquifer 1), and a confined aquifer consisting of multiple gravel and sand strata

in the east (Aquifers 2 and 3) (Fig. 2). The aquifers lie between the fan-shaped zone at the foot of the mountains on the plain, and they gradually change in character from a single pebble bed to multiple beds of pebble-sand and clay. From west to east, the thickness of the aquifers increases from 50 m to over 200 m, and the three principal aquifers lie at depths of 45 m, 50–60 m, and 70–80 m. The uppermost aquifer is the unconfined aquifer (Aquifer 1). This aquifer has the longest history of extraction and is subject to heavy pollution owing to municipal wastewater, and its discharge is no longer very great.

SITE CONCEPTUAL MODEL

The conceptual model provided the initial basis for development of the numerical model, and it included the following: (1) the distribution and hydraulic properties of the main hydrostratigraphic units underlying the site; (2) a basis for establishing boundary conditions at the upper surface of the model (infiltration) as well as lateral boundaries; and (3) configuration of the surface waterways. The numerical flow model was initially developed following an assessment of these features; it later underwent adjustment, as required, through calibration. The conceptual model and model discretization were developed using Visual MODFLOW via Hydro GeoBuilder (HGB) (Waterloo Hydrogeologic Inc. 2002) (Fig. 3).

Vertically, the domain is discretized into three layers of varying thickness. The model domain is



Fig. 1 Plan of Beijing.

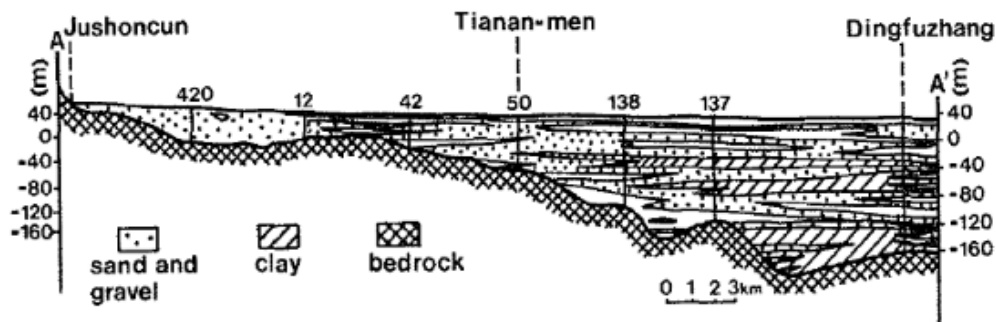


Fig. 2 Geologic cross section showing Quaternary aquifers in the Beijing area (A-A' geologic section: see Figure 1) (Mande et al. 2011).

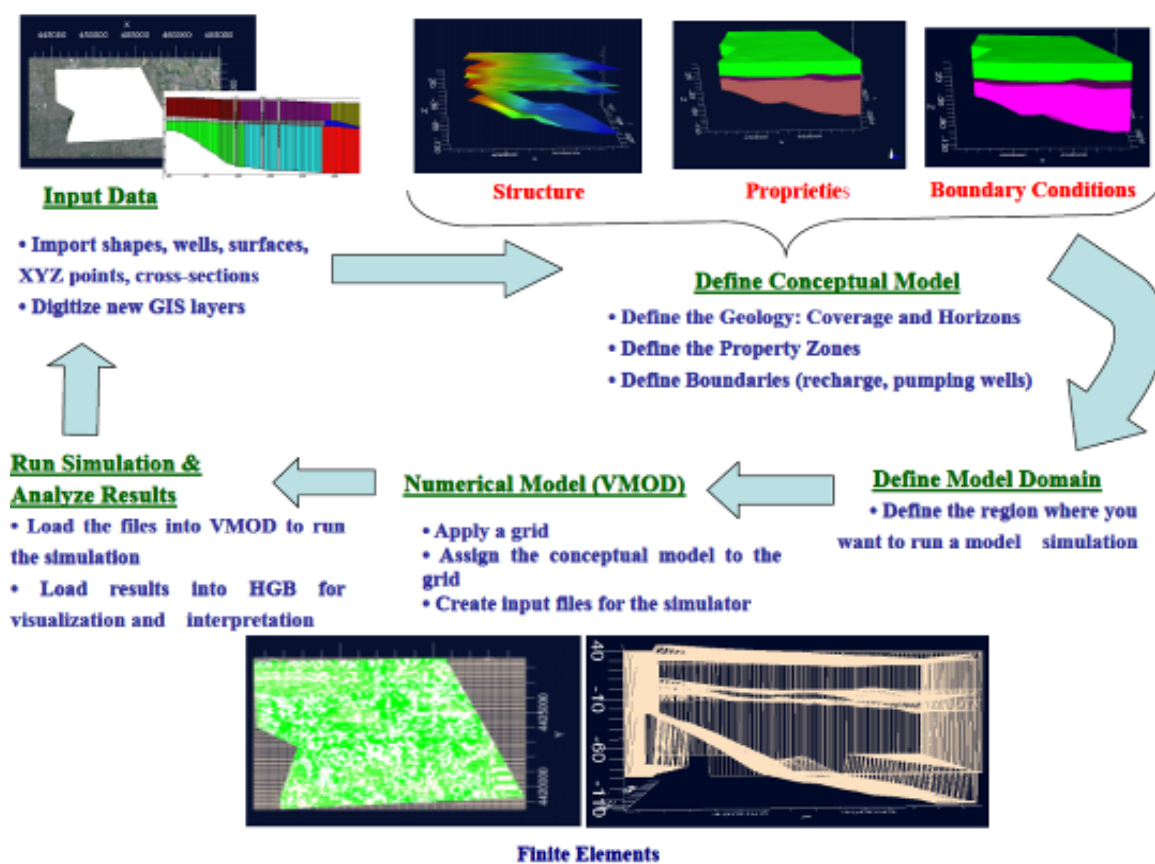


Fig. 3 Conceptual model workflow using Hydro GeoBuilder software, central Beijing.

approximately 140 m thick and of variable elevation. illustrates an example mode domain cross section and the variable thicknesses of the model layers. Model hydraulic conductivities derived during the calibration process are presented and compared with the average values calculated from the site data in Table 1.

GROUNDWATER FLOW AND CONTAMINANT TRANSPORT MODELING

Groundwater flow model code

Visual MODFLOW, version 4.2 (Waterloo

Hydrogeologic Inc., 2002) was selected to simulate groundwater flow and contaminant transport in the model. Visual MODFLOW is an internationally recognized software that integrates the United States Geological Survey groundwater flow model MODFLOW with the contaminant transport model MT3D99 as well as associated add-on packages (e.g., PHT3D, MODPATH, ZONE BUDGET, and FMBUDGET). It met the requirements of the site conceptual model for simulation of a complex three-dimensional flow system at the study site. Groundwater flow was evaluated under steady-

state conditions. Within Visual MODFLOW, the Bi-Conjugate Gradient Stabilized (Bi-CGSTAB) acceleration routine was used to solve partial differential equations for the groundwater flow. Convergence of the matrix solver for the calibrated model was determined with head changes set to 0.01 m and residual criteria set to 0.001 m. The model grid comprised 183,024 grid cells formed by 492 columns and 372 rows. Cell size at and near the boundaries was 1 km² (100 × 100 m), and it gradually decreased toward the central part of the grid to 625 m² (25 × 25 m) (Fig. 4). Groundwater flow was simulated for a period of 49 years, starting on January 1, 1960 and ending on December 31, 2008. The total flow simulation period was divided into 49 stress periods with 597 time steps ($\Delta t=30$ d). (See appendix).

REACTIVE MULTICOMPONENT TRANSPORT MODEL

Model description

It was decided that the hydrologic model

MODFLOW 2000 would be used for this modeling (Harbaugh et al. 2000); MODFLOW 2000 is able to analyze three-dimensional groundwater flow in a porous medium (Fig. 4). Recently, (Prommer, *et al.*, 2001) developed a MODFLOW/MT3DMS-based reactive multicomponent transport model. By means of a sequential approach, that model combines the three-dimensional transport simulator MT3DMS (Zheng and Wang, 1999) with the geochemical model PHREEQC-2 (Parkhurst and Appelo, 1999), and it is capable of solving simultaneously both equilibrium and kinetically controlled reactions; the coupled model can address a wide range of mixed equilibrium and kinetic reactive transport problems. This model uses total aqueous component concentration (Engesgaard and Kpp, 1992; Yeh and Tripathi, 1989) as the primary dependent variable. The reactive transport equation solved by the coupled model for the (mobile) aqueous species and components is then given as follows (Prommer, *et al.*, 2001).

Table 1. Hydrostratigraphic unit hydraulic conductivity boundary conditions

Hydrostratigraphic Unit	Estimate of Mean K (m/s)	Model K (m/s)
Shallow Aquifer	2.08×10^{-3}	$1.04 \times 10^{-3} - 1.73 \times 10^{-3}$
Intermediate Aquifer	6.94×10^{-4}	$6.94 \times 10^{-4} - 9.25 \times 10^{-4}$
Deep Aquifer	9.25×10^{-4}	$1.73 \times 10^{-3} - 2.89 \times 10^{-3}$

Note: Shallow, intermediate and deep bedrock was subdivided in the model into three zones with variable hydraulic conductivities.

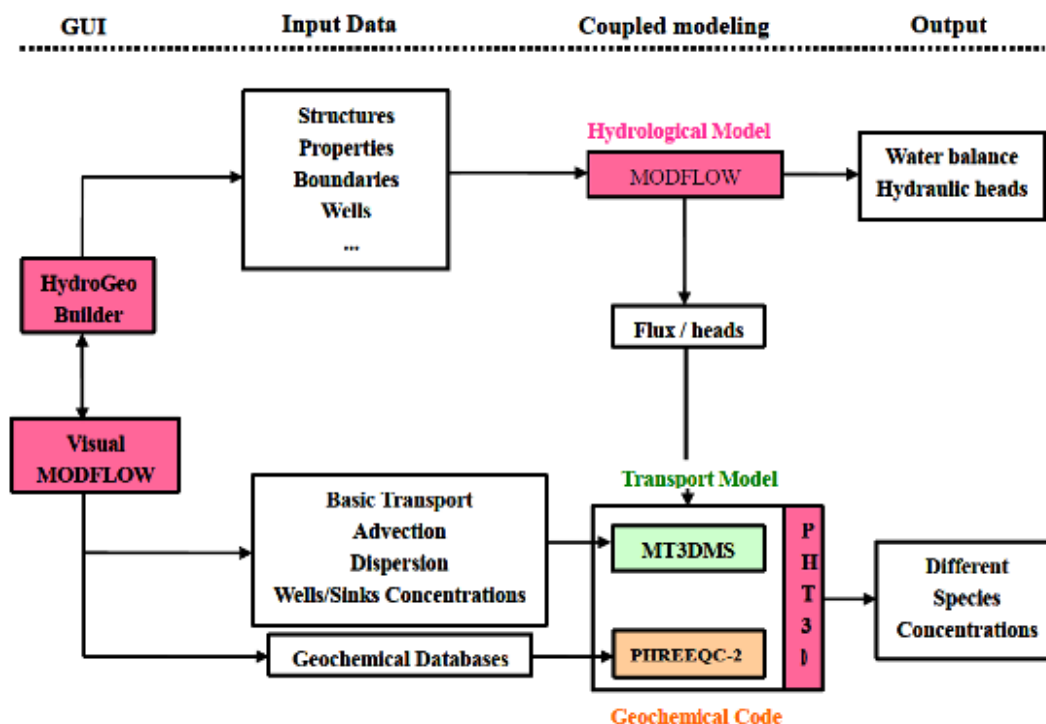


Fig. 4 Architecture of the coupled model MODFLOW/PHT3D.

For mobile components:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i} \left(D_{ij} \frac{\partial C}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (v_i C) + r_{\text{reac}} \quad (1)$$

And for immobile components:

$$\frac{\partial C}{\partial t} = r_{\text{reac}} \quad (2)$$

where v_i is the pore water velocity in direction x_i , D_{ij} is the hydrodynamic dispersion coefficient tensor, r_{reac} is a source/sink rate due to the chemical reaction, and C is the total aqueous component concentration, defined as: $C = c + \sum_{i=1, n_s} \gamma_i^s S_i$, where c is the molar concentration of the (uncomplexed) aqueous component, n_s is the number of species in dissolved form that have complexed with the aqueous component, γ_i^s is the stoichiometric coefficient of the aqueous component in the i^{th} complexed species, and S_i is the molar concentration of the i^{th} complexed species. The PHT3D model was selected because it allows the inclusion of new reactions to those already programmed into the database and whose levels can be defined by other species. Visual MODFLOW allows the easy formatting of the input data to both the MODFLOW model (geometry and permeability) and to the PHT3D model (advection, dispersion, and concentration), and it is able to visualize the outputs of the model (head changes and concentrations).

Generation of PHT3D input data

The default PHREEQC-2 database was used in this study. This modeling exercise attempted to investigate reactive transport in the local hydrogeologic setting of the Beijing urban region for eight components: calcium (Ca), magnesium

(Mg), sodium (Na), potassium (K), chloride (Cl), bicarbonate (HCO_3), sulfate (SO_4), and nitrate (NO_3) (Table 1). In this model—as with a one-dimensional reactive transport model—the minerals calcite, dolomite, and gypsum formed the reactive components. Mineral dissolution, precipitation, and oxidation were modeled in this study by equilibrium phases. PHT3D requires that the exchange species and the initial occupation of these spaces by various available ions, e.g., NaX , CaX_2 , and MgX_2 , be defined in the modeling exercise (Table 2).

In this modeling exercise, the point source concentrations were assigned to constant head and pumping wells. The drain package, river package, and General Head Boundary (GHB) package (MODFLOW) were not specified in this study. A central issue in this study was the quantification of the influence of various land-use functions and the changes in these functions on groundwater quality in the area in and around central Beijing. It was therefore important that the recharge concentrations be well defined for the different land-use functions. Furthermore, it was necessary to clearly determine the load at surface level resulting from the different functions as a result of atmospheric deposition, the application of fertilizers and manure in agricultural areas, and the use of such substances in urban areas as fuels, cleansing agents, and salt on icy roads.

GROUNDWATER FLOW-MODEL CALIBRATION

The groundwater flow-model calibration procedure involved adjusting the model parameters so that the simulated results could provide an acceptable match to observed conditions while maintaining

Table 2. Initial concentration (mmol/l) of aqueous components, minerals, and exchange species as defined in the study model

Components	Aquifer 1				Aquifer 2	Aquifer 3
	West area	North area	Central area	East area	All	All
Ca	0.00099	0.00105	0.00104	0.0012	0.00095	0.00112
Mg	0.00101	0.00123	0.00118	0.0013	0.0013	0.0012
Na	0.00082	0.00093	0.00055	0.00036	0.00054	0.00037
K	0.0003	0.0001	0.00007	0.00005	0.00006	0.00004
Cl	0.00082	0.00059	0.00039	0.00088	0.00034	0.0003
HCO_3	0.00372	0.00397	0.00379	0.00399	0.00395	0.00403
SO_4	0.00045	0.00041	0.00037	0.00049	0.00039	0.00039
NO_3	0.00013	0.00021	0.00014	0.00015	0.0001	0.0001
Calcite	0.1204	0.2123	0.32095	0.2350	0.2655	0.1652
Dolomite	0.023	0.0301	0.0450	0.0256	0.052	0.042
Gypsum	0.001	0.0015	0.0021	0.0018	0.0025	0.001
NaX	0.0013	0.0016	0.0019	0.0017	0.00168	0.0012
CaX_2	0.0208	0.0288	0.0299	0.0250	0.0350	0.0200
MgX_2	0.0015	0.0019	0.00195	0.00185	0.0020	0.001

reasonable parameter values. The calibration of the steady-state, three-dimensional finite difference flow model of Central Beijing was confirmed using the root mean squared error (RMS), mean absolute error (MA), normalized RMS and mass balance percent discrepancy. A normalized RMS error of 4.205% was obtained for the calibrated model, indicating an acceptable calibration (ASTM, 1995; Anderson and Woessner, 1992).

ANALYTICAL METHODS

Groundwater samples (500 mL per well collected via peristaltic pump over ~10 min) were obtained from the monitoring wells. Nitrate concentrations were quantified by ion chromatography (DX-600, DIONEX Co., Sunnyvale, USA). The detection limit for each analyte was 0.1 mg/L; the standard deviation for replicate samples was $\pm 10\%$. Major metals and cations were analyzed by Inductively Coupled Plasma Atomic Emission Spectrometry (IRIS Intrepid, Thermo Elemental, Maryland USA). Anion samples were determined by ion chromatography (DX-600, Dionex, USA).

SIMULATION RESULTS

Calcium and magnesium

As depicted in (Fig. 5), the simulated calcium and magnesium concentrations averaged for all wells started to increase gradually in the early 1960s. The simulated calcium and magnesium concentrations were, respectively, about 1.2 mmol/l and 1.5 mmol/l in 1960, and they continued rising to about 2.5 mmol/l and 3 mmol/l in the late 1990s. Subsequently, the concentrations for both remained constant until the end of the simulation period (2008).

The simulated and observed calcium and magnesium concentrations for the wells in Group 1 (central: 107, 108, 109, 125, 133) and Group 2 (northern: 112, 122, 127, 128) are presented in (Fig. 5). However, there is a difference in the simulated calcium and magnesium concentrations in the groundwater between Groups 1 and 2. It is evident that calcium and magnesium concentrations for the wells in Group 1 gradually increased; the exception was with well 107, where calcium and magnesium concentrations attained a maximum value in the early 1960s and remained constant until the end of the simulation period. For the wells in Group 2, the calcium and magnesium concentrations showed a slight increase; however, the magnesium concentration in well 127 remained constant. Although the differences in calcium and magnesium concentrations between the wells in Groups 1 and 2 are clear, it is evident that calcium

and magnesium values in the groundwater beneath the central area increased more than those concentrations in the northern area. This result can be explained by the fact that with calcium and magnesium, differences in land use were obscured by the process of calcite and dolomite dissolution, which released calcium and magnesium into the groundwater (Mande, *et al.*, 2011a).

As with nitrate and chloride, well 107 showed a maximum in calcium and magnesium concentrations in the early 1960s. This well clearly underwent changes in the surface-level load to a greater extent than the other wells in Group 1. This can be explained by the fact that well 107 extracts groundwater from Aquifer 1 and Aquifer 2; Aquifer 1 has the longest history of extraction and heavy pollution, and its discharge is no longer very great (Mande, *et al.*, 2011a). Moreover, the wells in Group 1 show higher calcium and magnesium concentrations than those in Group 2 (Fig. 5). Thus, with respect to calcium and magnesium, the differences in the land-use functions in the central and northern areas are clearly apparent. Finally, in Groups 1 and 2, the simulated values are somewhat lower than the observed values; this is due to an underestimation of the load at surface level. For most wells, the simulated and observed calcium and magnesium concentrations show relatively good agreement.

In all Group 1 and 2 wells, the simulated calcium and magnesium concentrations in the groundwater showed an increase from 1960 to 1985. From 1985, the concentrations were constant until approximately 2008. Over the final 23 years of the simulation, the calcium and magnesium concentrations evidenced a slight increase in most wells. However, the concentrations in wells 107 and 108 were different. In well 107, the calcium and magnesium concentrations increased from 1965 to 1980. From 1980 until the end of the simulation, the concentrations remained constant. The calcium concentration in well 108 increased relatively rapidly from the late 1960s until approximately 2008. Though the calcium concentration in most wells varied between approximately 1 and 2.5 mmol/l, it attained a value of about 3.3 mmol/l in well 108 in the simulation model. Finally, in Group 1, the simulated calcium and magnesium concentrations were lower than the observed concentrations. In Group 2, the simulated calcium and magnesium concentrations showed better agreement with observed values, although they were still relatively low.

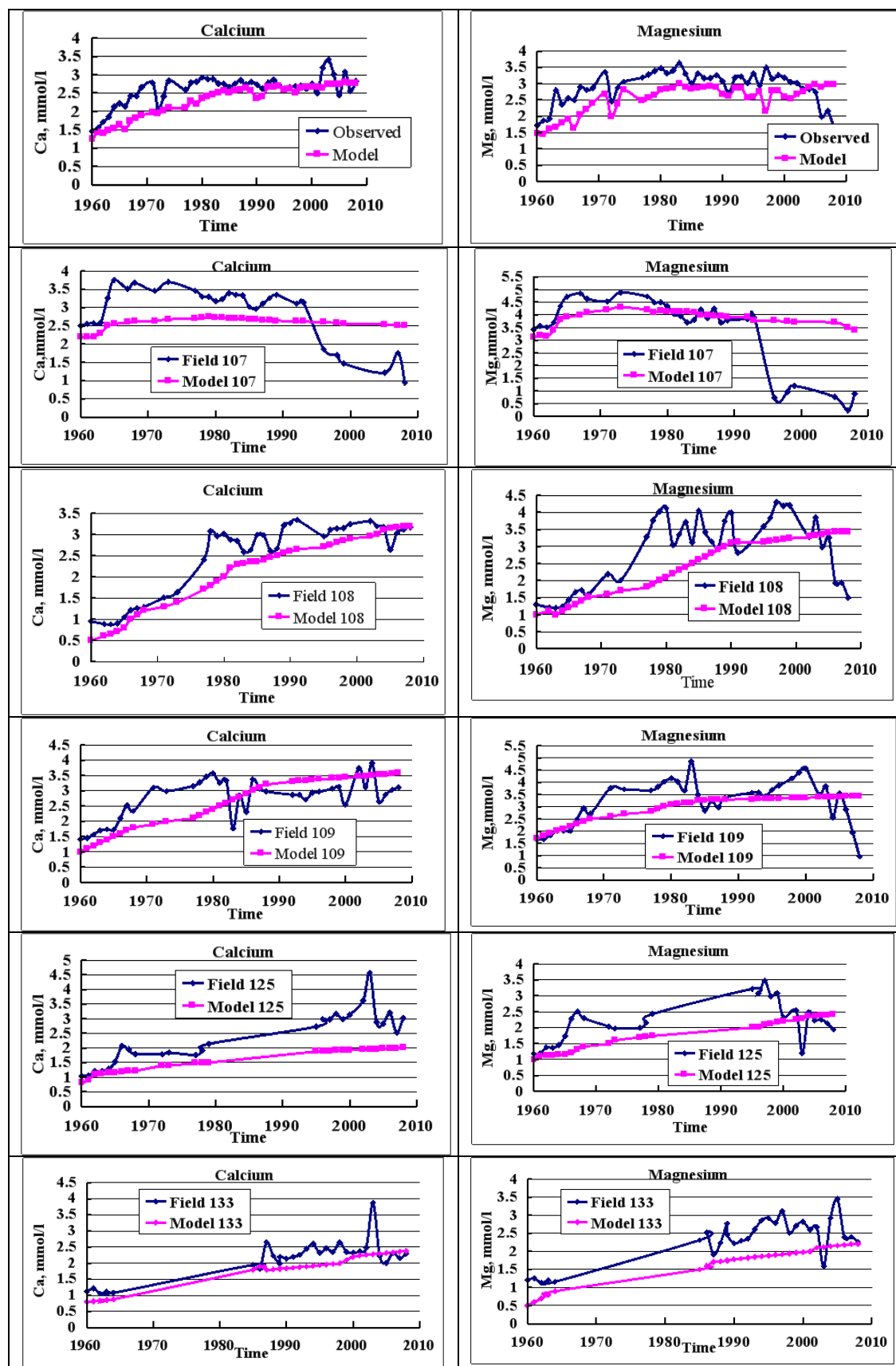
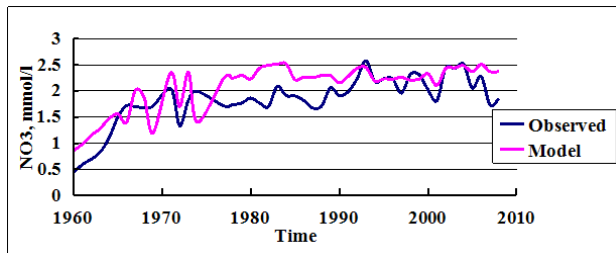


Fig. 5 Simulated and observed calcium and magnesium concentrations for the wells in Group 1 (107, 108, 109, 125, 133), Group 2 (122, 127, 128), and all wells.

Nitrate

With all wells, there was apparently a rise in nitrate concentrations prior to 1960, although it is difficult to determine accurately when the concentrations began to increase since no data are available for pre-1960. It can be seen in (Fig. 6) that the observed nitrate concentrations show good agreement with

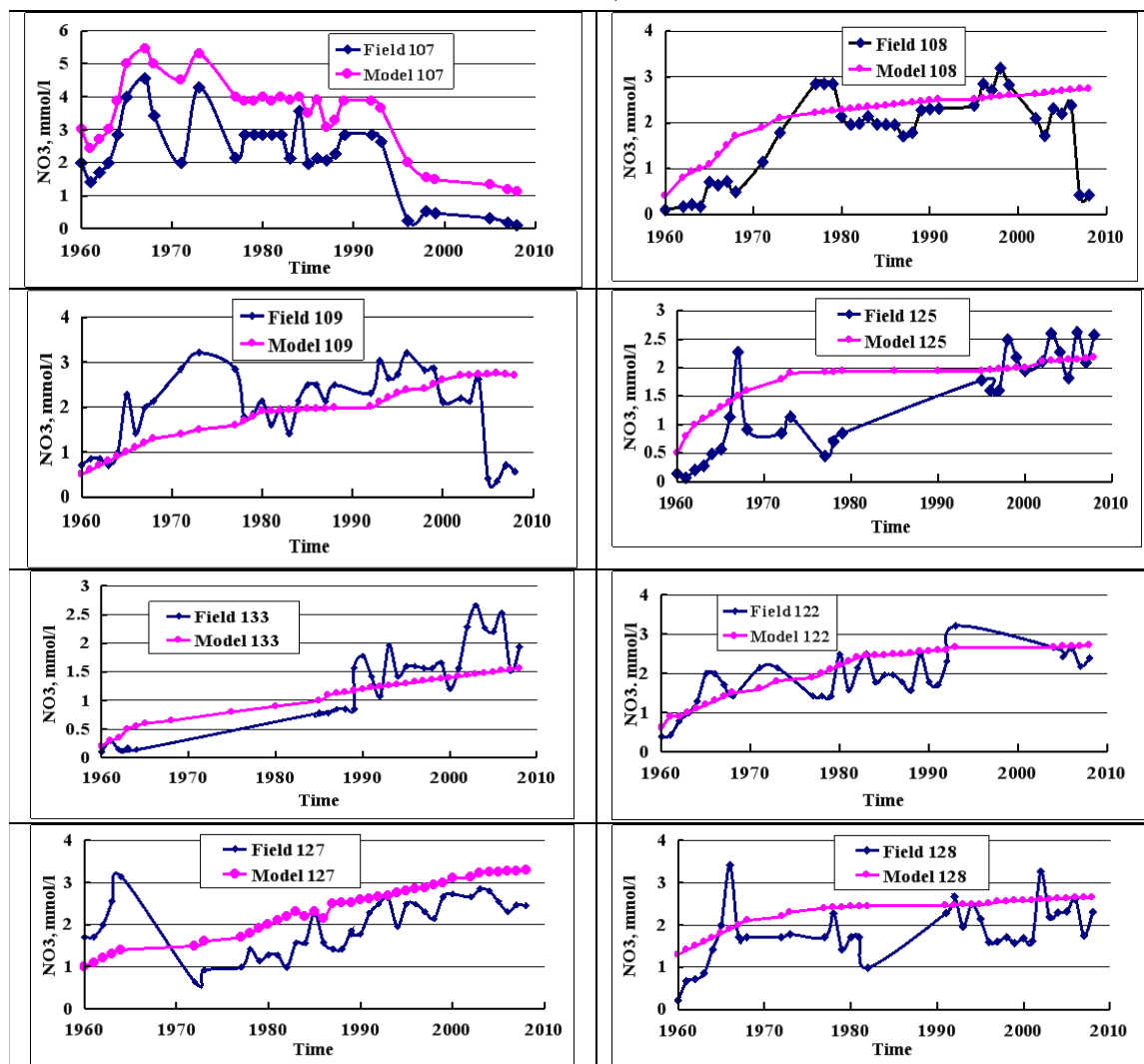
Fig. 6 Simulated and observed nitrate concentrations averaged for all wells.



the modeled concentrations. In wells 107, 108, and 109, the observed nitrate concentrations began to decrease in 1995 owing to denitrification though the concentrations in other wells continued increasing. There was thus a rapid response of the nitrate concentration in the groundwater to the increasing load at surface level. Until approximately 2008, the concentrations in the groundwater continued rising toward a value of 2.5 mmol/l (160 mg/L).

The PHT3D model results for the wells in Group 1 (central areas) showed a more gradual increase in nitrate concentrations (Fig. 7). Moreover, the maximum concentrations in Group 1 were at around 3 mmol/l, i.e., higher than the averaged maximum concentration for all the wells (Fig. 6); the exception was well 107, where the maximum concentration was around 5 mmol/l in 1968. The simulated nitrate

Fig. 7 Simulated and observed nitrate concentrations for the wells in Group 1 (107, 108, 109, 125, 133) and Group 2 (122, 127, 128).



concentrations in Group 1 agreed relatively well with the observed concentrations for that group; the exception was the period from 1995 to 2008, when the model concentrations were higher than the observed values. This point will be explained below, when the simulated concentrations in wells 107, 108, and 109 are discussed (Fig. 7).

For the wells in Group 2 (northern areas), the PHT3D simulations showed better agreement with the observed concentrations. Nitrate concentrations for the wells in Group 2 evidenced a smoother increase than those for the wells in Group 1 (Fig. 7). From 1995 to 2008, wells 107, 108, and 109 showed a gradual decrease in the field concentrations of nitrate. For this period, the model concentrations were higher than the observed values and thus did not show good agreement. This was due to the probable presence of pyrite in those areas: pyrite was not taken into consideration in the model. Except for wells 107, 108, and 109, there was relatively good agreement between simulated and observed concentrations for all the wells. In the period 1960–95, the PHT3D results for wells 107, 108, and 109 displayed better agreement with field measurements. However, after 1995, there was a difference between the PHT3D simulation results and field values. This can probably be explained by the fact that the model did not incorporate pyrite and also that the nitrate was susceptible to denitrification (with high organic C content) in the areas in question.

Chloride

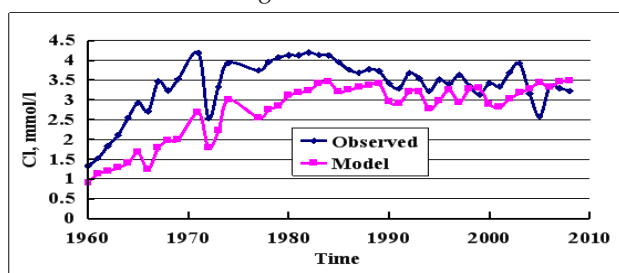
As depicted in (Fig. 8), the simulated chloride concentrations averaged for all wells began to increase gradually in the early 1960s. The simulated chloride concentration was about 1 mmol/l in 1960, and it continued to rise, reaching about 3.5 mmol/l in the late 1980s. Subsequently, the concentration remained constant until the end of the simulation period (2008). It may be supposed that the constant chloride concentration in around 1995 represents the maximum load at surface level. The observed chloride concentrations averaged for all wells also

increased after 1960, attaining a maximum of 4 mmol/l in the late 1980s. Thereafter, the observed chloride concentrations exhibited a slight decrease. However, since no data are available for 1940–60, it cannot be determined when exactly the chloride concentrations began increasing. Nevertheless, the observed chloride concentrations rose faster than simulated ones, and after around 1971 the observed concentrations were slightly greater than the simulated values.

Except for wells 125 and 133, the overall simulated chloride concentrations were lower than observed values in the Group 1 wells, and the overall simulated chloride concentrations were higher than observed values in the Group 2 wells—except for well 122. However, the general pattern of the gradual increase in concentrations from 1960 until the late 1980s showed good approximate agreement with averaged observed values for these two groups (Fig. 8 and 9). Moreover, all wells, except wells 107 and 127, showed a constant concentration from the late 1980s until 2008. The concentrations in well 107 continued to decrease until the end of the simulation period. However, the concentrations in well 127 remained constant from the 1960s until the end of the simulation period.

As with calcium, magnesium, and nitrate concentrations, well 107, which extracts groundwater from a shallower depth than the other wells, showed higher chloride concentrations in the early 1960s. This result was to be expected since differences in land use are conspicuously reflected in nitrate, calcium, magnesium, and chloride concentrations in the groundwater. This finding is in accordance with the differences in the load at surface level between the land-use types. The observed chloride concentrations agree relatively well with the simulated concentrations for the wells in Group 1: wells 108 and 109 showed the best agreement for 1960–2008; wells 125 and 133 showed the closest agreement for 1960–90; and well 107 showed the best agreement for 1980–92 (Fig. 9). The observed and simulated chloride concentrations in the Group 2 wells corresponded moderately well: for 1960–2008, the simulations were relatively low compared with the observed values, whereas for 1990–2008 the agreement was relatively poor for well 122 (Fig. 9). The simulated chloride concentrations in the deep wells appeared to be almost constant throughout this period. This can be explained by the fact that a clay layer (Aquifer 2) separates Aquifer 1 from Aquifer 3; the interactions of physical and chemical processes of clay formation in the research area may therefore

Fig. 8 Simulated and observed chloride concentrations averaged for all wells.



have prevented the movement of chloride ions while permitting groundwater to flow freely (Mande, *et al.*, 2011b).

Sulfate

The observed sulfate concentrations in most wells agreed relatively well with the modeled sulfate values; an exception was well 107, where the modeled sulfate concentration was lower than observed level (Fig. 10). As already mentioned in relation to the nitrate reduction in Aquifers 1 and 2, the modeled sulfate concentrations of wells in Aquifer 1 (wells 109 and 127) and Aquifer 2 (well 108) began increasing in around 1960 (Fig. 10). The concentrations in wells 109, 108, 125, and 133 continued rising until the end of the simulation period, whereas the concentrations in wells 122 and 128 remained constant from the

late 1980s until 2008. There was good agreement between the simulated and observed concentrations with respect to when they started to rise. However, the simulations showed lower concentrations than the observed values except for well 125, where the simulated concentration was higher than the observed. The oxidation of pyrite was not taken into account to this model, this maybe account for the higher field values.

DISCUSSION

This three-dimensional model study has shown that the surface-level load and reactive components in aquifers determined the groundwater quality in the area in and around Beijing. The changing concentration of less reactive species, such as chloride, was largely determined by the load at surface level.

Fig. 9 Simulated and observed chloride concentrations for the wells in Group 1 (107, 108, 109, 125 and 133) and in Group 2 (122, 127, 128).

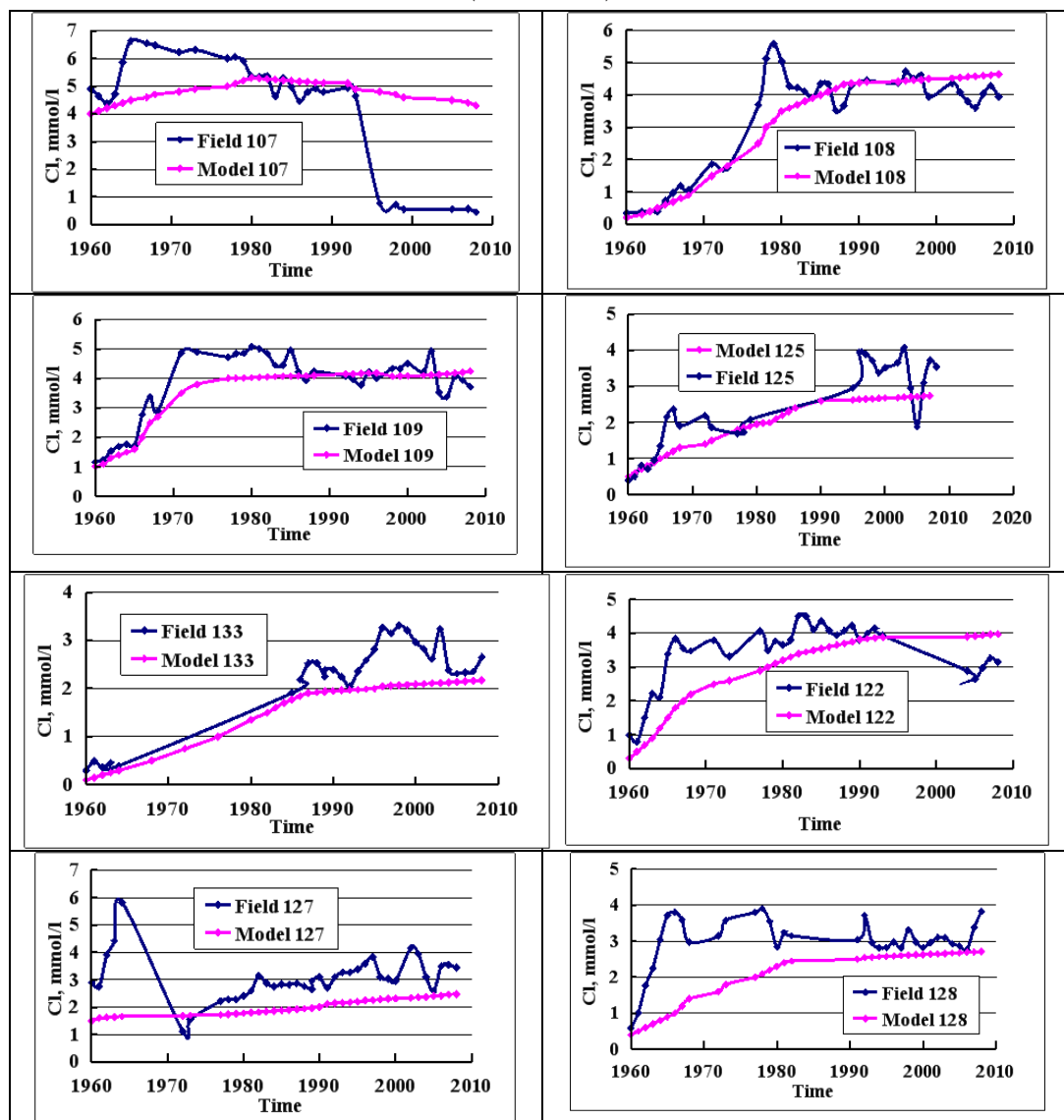
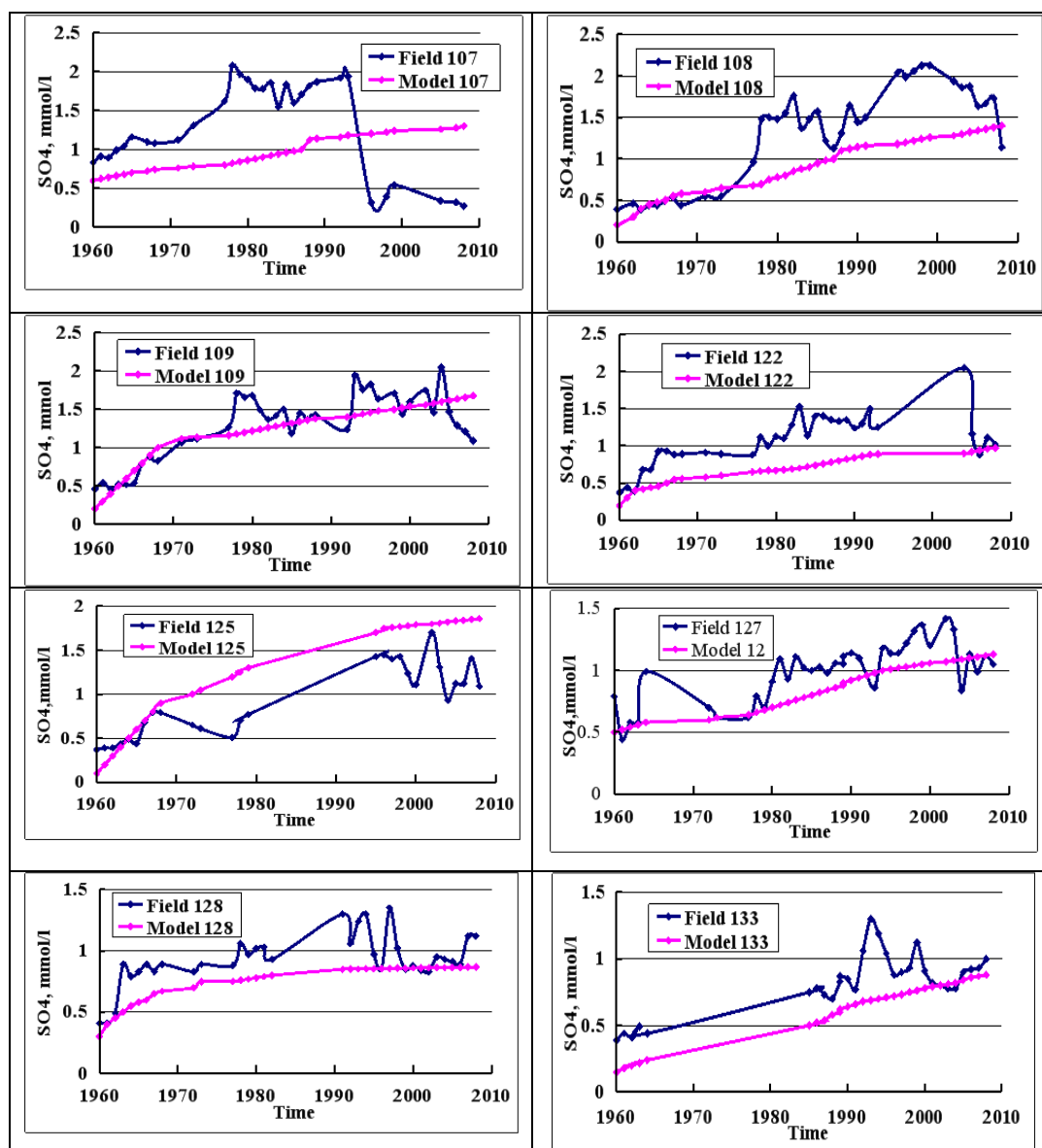


Fig. 10 Simulated and observed sulfate concentrations.



However, the changing concentrations of nitrate, sulfate, calcium, and magnesium was determined by hydrogeochemical reactions in the aquifers in addition to the load at surface level. The observed nitrate concentration averaged for all pumping wells demonstrated an increasing trend, which indicates that the growing load at surface level was the main factor affecting groundwater quality. The coupled model showed that the nitrate in the groundwater was still present in excessive levels. With respect to sulfate, the model results in the aquifers revealed that increasing concentrations were due to the growing load at surface level. The model concentrations for sulfate were lower than observed values. This can be explained by the fact that the production of sulfate through pyrite oxidation was not taken into

account in the model. The calcium and magnesium concentrations were influenced by both calcite and dolomite dissolution.

It was noted earlier that underestimations of the surface-level load resulted in differences between the simulated and observed concentrations for nitrate and sulfate. It is necessary to investigate the recharge concentration data for nitrate, sulfate, pyrite, and others minerals capable of releasing sulfate ions into the groundwater. In a future study, the change of such factors over time in the Beijing area should be analyzed and entered into the PHT3D-model as recharge and mineral concentration data.

The PHT3D model results for other components indicate that the scenario presented here does not

as yet fully represent the hydrogeochemistry in the subsurface of Beijing. The initial concentrations in the aquifers appeared to reflect the load at surface level for NO_2^- , N_2 , NH_4^+ , HS^- , $\text{Fe}(2)$, $\text{Fe}(3)$, and O_2 . However, additional components also need to be incorporated into the model. Soil organic matter (SOM) was not taken into account since the behavior of organic matter was beyond the scope of this study. Likewise the exchange species KX and FeX_2 were not considered. It is therefore recommended that a future study should expand the model by incorporating SOM, KX , and FeX_2 as chemical components and including SOM oxidation as a geochemical process.

It was pointed out above that in addition to overestimating the initial concentrations and load at surface level, the high calcium and magnesium concentrations in the model were caused by excessive calcite and dolomite dissolution through underestimating the bicarbonate concentration in the recharge water. It is therefore recommended that future studies should improve the assessment of the bicarbonate concentration in the recharge water in addition to achieving a more accurate estimation of the initial bicarbonate concentration in the aquifers. It would also be desirable to apply isotope chemical analysis of the dissolved sulfate to characterize and quantify these redox processes to enhance the accuracy of the numerical modeling—particularly those processes associated with acid sulfate soils, and sulfide mineral exploration. Stable isotopes of sulfur and oxygen in sulfate can be used to characterize the geochemical processes and thereby improve reactive transport models in the study area. Furthermore, it would be advantageous to determine the groundwater age at several sites, such as through tritium measurements. If the groundwater age could be established, field observations and model results could be more accurately compared, which would facilitate calibration of the model. This would then allow more accurate adjustments of the model input. Finally, if the simulation period were increased by a few decades, a more realistic prediction of the future development of Beijing's groundwater quality could be effected.

CONCLUSION

The PHT3D model showed that although nitrate in the groundwater was partially reduced by denitrification, nitrate was still present in excessive levels. The coupled model was able to quantify the influence of various land-use functions on groundwater quality, and it could identify the geochemical processes taking place in the aquifers. Finally, a novel conceptual model for an urban area

that can be used to evaluate future site-remediation scenarios was developed as part of this study. Used alone or in combination, the models presented in this paper demonstrated their adaptability to various scales and issues related to water in both quantitative and qualitative terms.

ACKNOWLEDGMENTS

This work was supported by the 863 Program (2007AA06A410) of the Chinese Ministry of Science and Technology and Studies of Safety Evaluation and Pollution Prevention Technology and Demonstration for Groundwater Resources in Beijing (D07050601510000).

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