

Nitrogen budget of a typical subterranean river in peak cluster karst area

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Abstract Karst groundwater is one of the important water resources for people in the world. There is an estimate that by 2028 karst groundwater will supply more than 80% of people in the world. However, several areas in the world are characterized by high nitrate concentrations in karst aquifers. In China, karst groundwater is also threatened by extensive use of fertilizer and pesticides, industry waste, septic systems and poultry, hog or cattle manure. In order to understand the water quality of a subterranean river in south China, especially the dynamic variation of nitrate, nitrogen input and output were determined via auto-monitored apparatus, manual observation and samples from 2004 to 2008 in Guancun subterranean river drainage area. Land use and anthropogenic activities were also investigated frequently. The results showed the range of nitrate variation was 2.56–15.40 mg l⁻¹, with an average value of 6.60 mg l⁻¹. Spatial variation of nitrate concentrations showed nitrate rose where there were villages and agriculture distribution. Long series of nitrate and discharge monitoring revealed there was a nitrate peak in spring just before the beginning of rainy season. Three rainfall events were selected for analysis of relations among hydrological process, water chemistry, and nitrate of the spring. The flood processes of the spring were divided into three or four phases according to change of water level and water chemistry. They were dominated by initial condition of aquifer, piston flow in soil and vadose, piston flow in conduit, diffuse recharge, and bypass recharge. The original condition of aquifer and rainfall

pulse controlled recharge flow and changes of nitrate and hydro-chemical graphs of the spring. The quantity of nitrogen input in a year was 66.61 t, and the output was 21.24 t. Nitrogen leaching loss in base flow accounted for 76.11% in a year. Some measures should be taken to protect karst water in the very near future, so that health risks to the local people can be decreased.

Keywords Subterranean river · Nitrate · Nitrogen loss · Hydrology · Water chemistry

Introduction

Water quality in many karst groundwater undergoes very high amplitude, but relatively brief variations following anthropogenic activities. Nitrate is a common contaminant for groundwater in the world. Especially groundwater in intensive agricultural or industrial areas may suffer from that. In karst areas, there is likely to be significant penetration of various pollutants into the aquifers due to hydrogeological peculiarity of the environment. Many studies focus on these areas (Buzek et al. 1998; Felton 1996; Boyer and Pasquarell 1996; Walther 1991). Elevated nitrate concentrations were found due to the application of fertilizers to cropland (Katz et al. 1999), and disposal of animal wastes (Berryhill Jr 1989; Molerio and Gutierrez 1999; Boyer and Pasquarell 1995).

There are two types of nitrate sources in groundwater. One is direct sources, which include leaching by fertilizer and direct sewage input. The other is indirect sources, which includes transformations of organic nitrogen and ammonia. For karst area in south China, nitrogenous fertilizer use is the primary nitrate source. Nitrogenous fertilizer or organic fertilizer is absorbed in the soil in the

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form of NH_4^+ , after mineralization by microorganisms. Some of it is adsorbed by crops and some is lost via volatilization, while some nitrogen is transferred to deep soil layers in the form of NO_3^- and NO_2^- by the process of nitrification. NO_2^- is unstable, and is easily transformed to nitrate. Nitrogenous fertilizer was necessary to enhance the production of land, but redundant nitrogen polluted karst groundwater. Nitrogen pollution was less understood in karst aquifers which had unique recharge and discharge.

There are 2,836 subterranean rivers which have been found in south China, with a total discharge of $1,482 \text{ m}^3 \text{ s}^{-1}$. Yet along with intensive agriculture and industry and urban expansion, subterranean rivers suffer from various degrees of contaminations. Previous studies showed some major ions had greatly increased in the past two decades, especially nitrate and sulfate (Guo et al. 2002, 2007).

Nitrogen monitoring had been done in Guancun subterranean river from 2004, and part results had been published (Guo et al. 2007). However, some important problem remained un-resolved, for example, nitrogen release accompanying with flood, balance of nitrogen, and source of nitrogen. On the other hand longer series of monitoring also made the behavior of nitrogen more clear.

Hydrogeological setting and anthropogenic activity

Guancun subterranean river was located in the north of Guangxi Province, China. It covers an area of 30.5 km^2 characterized by peak cluster and poljes (Fig. 1). The aquifer lied in limestone of upper Devonian with an average thickness of 70 m. Soil on peaks was thin, but more than 2 m in depressions. The general karst conduit was 8.3-km radial long. There were swallow holes, sinkholes, karst windows along with the conduit. Seasonal rivers appeared when flooding in poljes. The depth of water level in depression and poljes were less than 10 m in dry season, but overflowed in down stream after heavy rainfall. A tributary conduit with radial length of 4 km joined with the general conduit near the spring. Tracer test in the general conduit indicated that the average flow velocity was 726 m per day (unpublished).

The annual average temperature at Guancun was 20°C , and the annual average rainfall was 1,750 mm. In the dry season (from September to February), rainfall accounted for only 11% of the annual total, and the rest occurred from March to August, with a maximum in May and June.

Rainfall was the important recharge for aquifer, while there was a creek in the source of Guancun subterranean river which entered into ground by swallow hole when there was no rain. Rainfall entered epikarst in bare bedrock area, infiltrated through covering soil, and rejected sinkhole and surface rivers bypassing soil when soil was saturated.

Land use in the catchment was agriculture in poljes or depressions and shrub or grass in peak or smaller depressions. Thousands of goats were fed in field in order to enhance domestic earning. Agriculture activities have a close relationship with the climate; in the catchment, farmers often fertilize dry land in February in order to plant sugar cane. The amount of compound fertilizer (K_2SO_4 included) used for the paddy field is $373\text{--}597 \text{ kg ha}^{-1}$ before cultivating in early May. After 1 week, farmers add 5–10 kg carbamide, and after 2 weeks 5 kg more of carbamide and 7.5 kg of potassium fertilizer (KCl). Fertilizer is rarely used from then on and how much is determined by the growth of the crop. After harvest in August, most of the cropland is left undisturbed, while some is planted with corn, vegetables and sugar cane (Guo et al. 2007).

Materials and methods

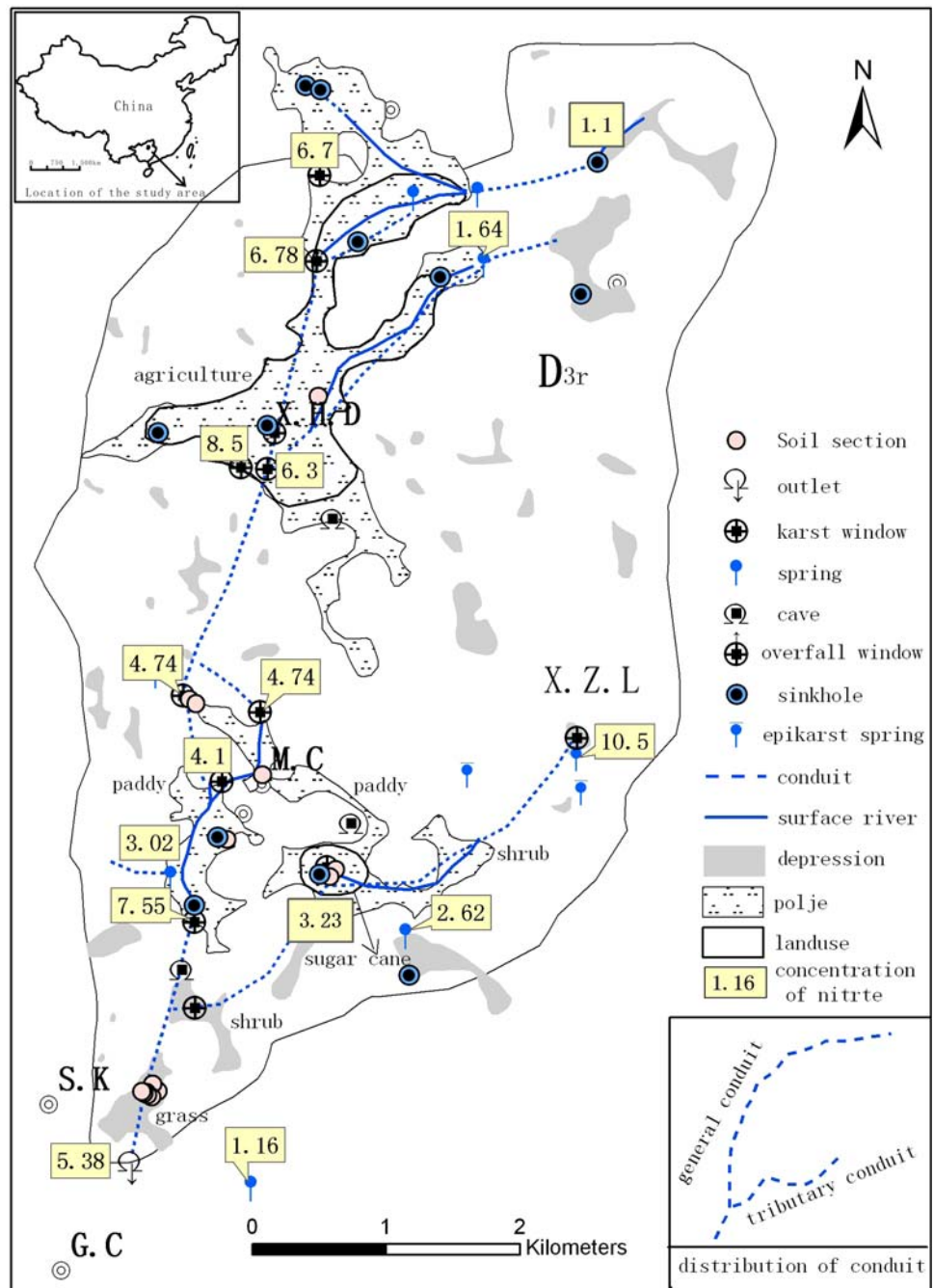
Guancun subterranean river was selected for the study. A Greenspan CTDP300 multichannel data logger was used to auto-monitor water level, water temperature, pH, specific electrical conductivity (SEC) and precipitation at the outlet of the subterranean river (once per 30 min) during the sample collection period. The precision of them was 0.01 m, 0.01°C , 0.01 pH, $0.01 \mu\text{s cm}^{-1}$ and 0.5 mm, respectively. From June 2004, pH, SEC and water temperature were determined monthly at the site with the help of pH/Cond 340i WTW Meter. The discharge was measured at a gauging station using a rectangular weir about 20 m away from the outlet. Water samples were collected monthly from June 2004 for determining the concentration of K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , NO_3^- , NO_2^- and NH_4^+ in the laboratory of Institute of Karst Geology, China. K^+ and Na^+ were determined by atomic absorption. Ca^{2+} , Mg^{2+} and SO_4^{2-} were determined titrimetrically using standard EDTA. Chloride (Cl^-) was determined by standard AgNO_3 titration. Nitrate (NO_3^-), NO_2^- and NH_4^+ were tested by colorimetry with an UV-visible spectrophotometer.

Water samples were collected daily for determining nitrate from April 2007 to April 2008. Several floods were selected to observe in which 1–3 samples were collected. Land use and human activity in the catchment area were surveyed seasonally.

Results and discussion

Figure 1 showed spatial variation of nitrate concentration in May 2008. Water samples were taken in creek, springs and karst windows. Nitrate concentrations were lowest in the source of general conduit. It rose in X.H.D. polje where there were villages and agriculture. Then it decreased after

Fig. 1 Hydrogeological map of the study area



flowing under peak cluster. However, it rose again at the sinkhole of M.C polje where there were villages and paddy field. It became lower in the outlet after going through peak cluster which land use was shrub and grass. The tributary conduit had lower nitrate concentration than the general one, for there was only a small block of sugar cane field among shrub field. Nitrate in X.Z.L epikarst spring was the highest because of a sheep pen there; hence, agriculture and villages polluted the karst groundwater with nitrate.

Nitrate changes of time series in the outlet was analyzed below.

Figure 2 showed daily nitrate concentrations and discharge of the subterranean river from April 2006 to May 2007. The series was much longer than that in the former article (Guo et al. 2007). Figure 3 was monthly nitrate concentrations and rainfall from 2004 to 2007. The main form of inorganic N for groundwater in Guancun subterranean river was NO_3^- -N, while the concentration of

Fig. 2 Nitrate and discharge curves in the spring from April 2006 to May 2007

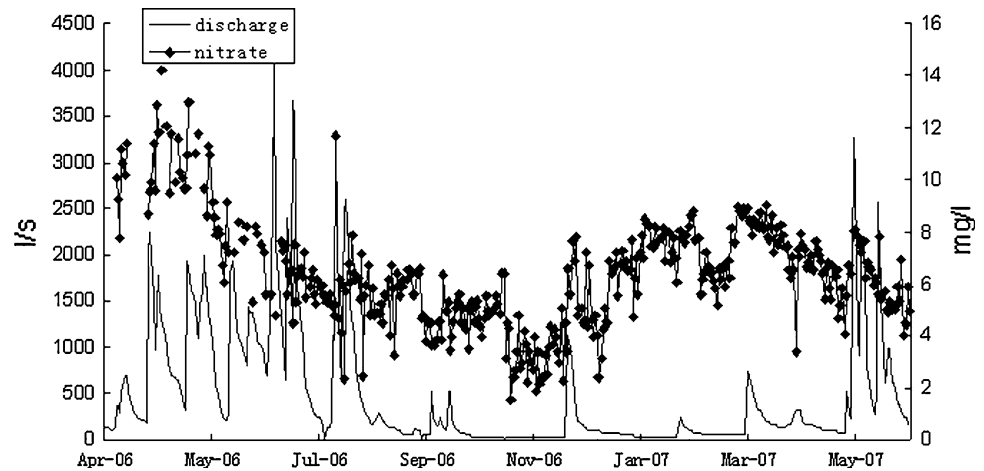
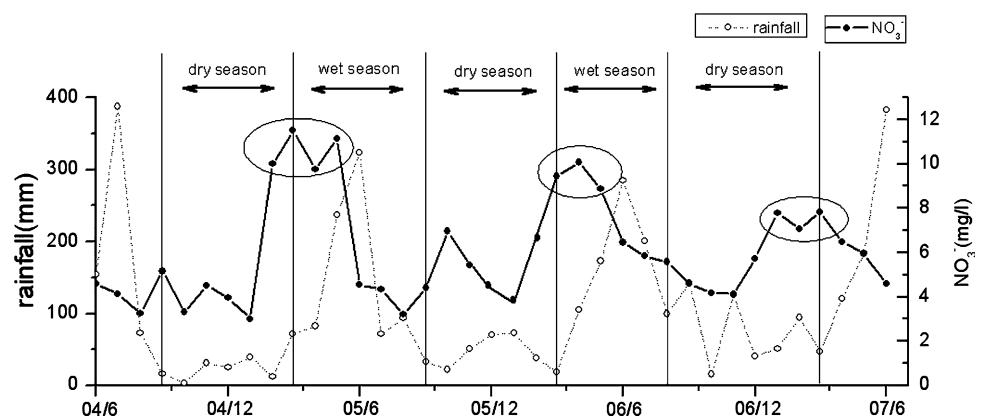


Fig. 3 Seasonal variation of nitrate in the spring



$\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ was very low, with an average value of 0.02 mg l^{-1} and less than 0.002 mg l^{-1} , respectively. The variation range of NO_3^- was $2.56\text{--}15.40 \text{ mg l}^{-1}$, with an average value of 6.60 mg l^{-1} . The behavior of nitrate variations indicated that there was a nitrate peak in spring as well as just before the beginning of rainy season. What happened in this period? The reason might be that fertilization, dejecta of animal and waste in villages accumulated in soil surface which resulted in nitrogen enrichment in dry season. Fertilization in autumn and winter was not as popular as spring. It was mainly used in domestic vegetable field. Animals like goat, chicken, duck, pig, dog and cow were common in villages. They were depastured in field and poorly managed. Waste of villages was often placed in river's dry bed or dumped near sinkholes. Villagers wanted them to be washed away by flow of next rain. Rainfall made nitrogen in fertilizer, dejecta and waste leach to aquifer, which led to increase of nitrate concentration in the spring. Slowly enhanced rainfall diluted groundwater repeatedly; and finally, it stabilized after sequential dilution by storm. Popular fertilization in May for paddy field also plays an important role in the formation of nitrate peak.

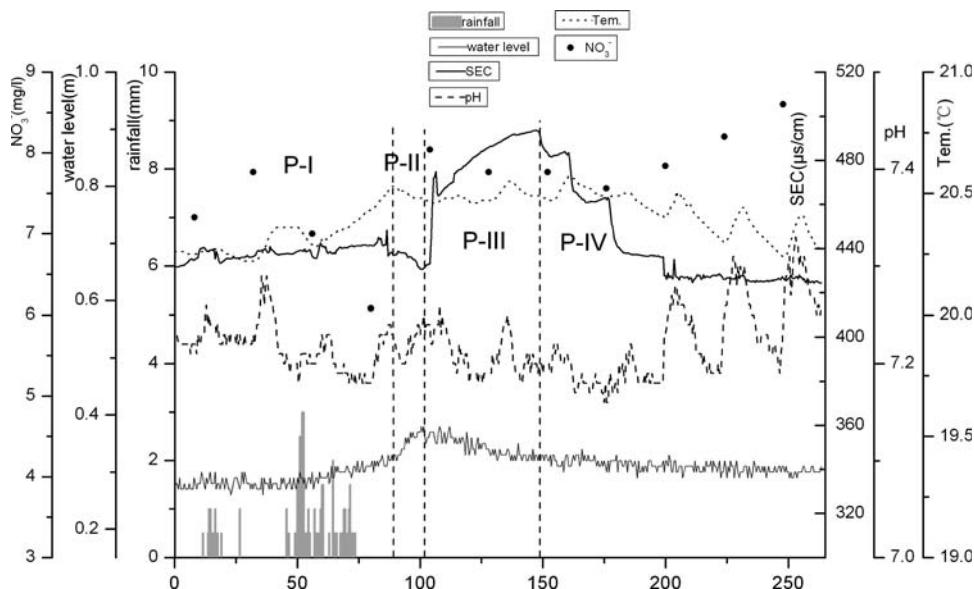
Many studies revealed that rainfall was the predominant reason for change of nitrate values (Wei et al. 2007).

Different rainfall and initial conditions of aquifer made inconsistent hydrological and water chemistry processes, and also influenced changes of nitrate. Recharge and flow of the aquifer were necessary to explain the chemical graphs of the spring.

Rainfall events of May 2005, January 2007 and March 2008 were selected for analysis of relations among hydrological process, water chemistry, and nitrate of the spring. Three storms of the spring could not reveal the entire role which controlled nitrate and chemical change, but key effects in the aquifer could be explained.

The total rainfall in 10 days from 0:00 18 January 2007 to 0:00 28 January was 44.5 mm (Fig. 4). It happened in the dry season; only little rain occurred before that. The pH had no obviously change, and rhythmic fluctuation reflected alternation of day and night because sensor was in a pool with an area of about 100 m^2 . Water temperature had little increase after the rain and obvious fluctuation just like pH. Specific electrical conductivity had sharp increase after the main rainfall, and decrease in recessional flow phase. Time interval for initial change between water level and SEC reflected piston effect for conduit water (Nur Ozyurt and Serdar Bayari 2007; this time interval was 12 h. Pressure transported much faster

Fig. 4 Variation of nitrate, hydrology and water chemistry in rainfall event of January 2007

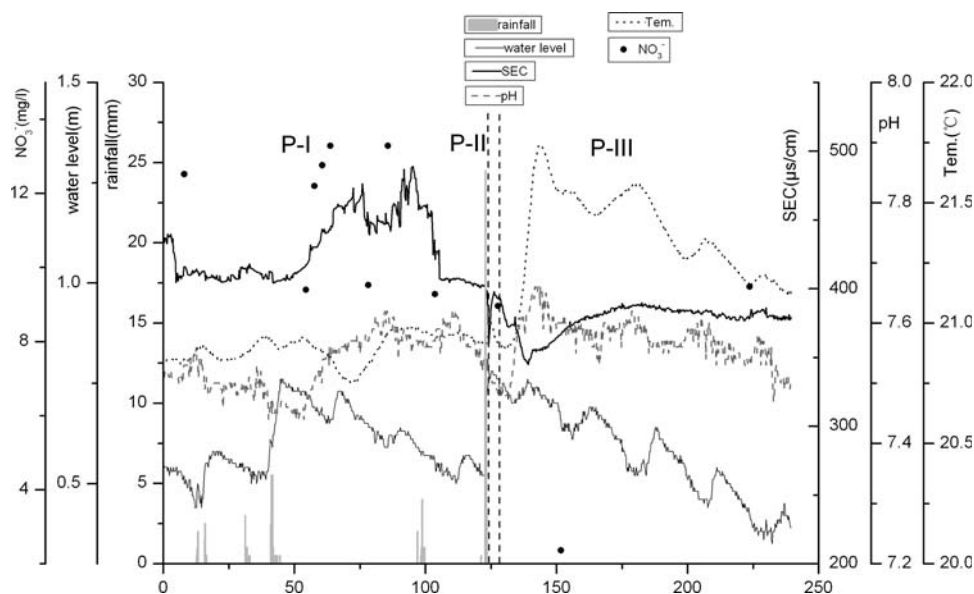


than SEC which indicated the arrival of event flow in the conduit. The spring discharged old groundwater stored in the conduit during the interval period. The flood process of the spring could be divided into four phases according to change of water level and water chemistry. Phase I was the initial phases for post-rainfall. It was in base flow, while soil and vadose zone had no flow because of long rainless days. Phase II was piston effect phases in conduit. Its lasting time was equal to traveling time of event recharge in conduit. And Phase III indicated that piston flow in soil and vadose had reached the outlet, IV meant that event recharge arrived. Old soil water and vadose water had higher SEC because of longer storage time. It arrived in conduit before event recharge because of piston

effect. Event recharge was characterized by higher nitrate concentration because of dissolution of fertilizer, dejecta, and waster. As a result piston flow coming from soil and vadose with higher SEC enhanced the SEC of the spring. Nitrate increased in Phases III and IV showed piston flow from soil and vadose and event recharge had higher nitrate concentration. This rainfall event eluviated nitrogen which accumulated in surface to underground, showing nitrate concentration increasing.

The total rainfall in 9 days from 22 May 2005 to 31 May 2005 was 99 mm (Fig. 5). After a heavy rainfall with intensity of 25 mm for 30 min, SEC curve had a sharp negative peak, while temperature curve had a positive peak. It was because the heavy rainfall made a transitory

Fig. 5 Variation of nitrate, hydrology and water chemistry in rainfall event of May 2005



change in the pond water in the outlet. Water level curve rose rapidly following rainfall, while SEC, pH, and temperature had isochronous changes lagging water level for about 6 h; the lag reflected piston effect in conduit. Decrease of SEC indicated that bypass flow diluted old groundwater. Bypass flow occurred only when soil was saturated. The flood of spring could be divided into three stages. The first one (Phase I) was still initial condition, but frequent rainfall made soil saturated which was different with that in Fig. 4. The second one was piston flow in conduit too, but its lasting time became shorter for discharge was larger. Piston flow in soil and vadose did not occur after Phase II for bypass flow was too strong to cover it. So bypass flow became Phase III after piston flow in conduit. Nitrate concentration stayed high before bypass flow reached the outlet. Following heavy rain, nitrate dropped due to dilution. It resumed to initial values after the flood. The range of nitrate concentrations was 2.56–12 mg l⁻¹. It was higher and had a wide range of variation than that in January. The reason was that fertilization was largely used in May.

Total rainfall in 13 days from 15 March 2008 to 27 March 2008 was 75.5 mm (Fig. 6). This was the first rainfall after the dry season in 2008, so it had a very important effect on nitrate movement among different media. The flood could be separated into four stages. Phase I was the initial stage which was characterized by small rain for several days following long rainless days. Phase II was piston flow in soil and vadose when SEC and temperature increased together. Phase III was still piston flow in conduit. And Phase IV was characterized by two dilutions of new recharge because SEC decreased twice following rainfall, while pH increased and temperature

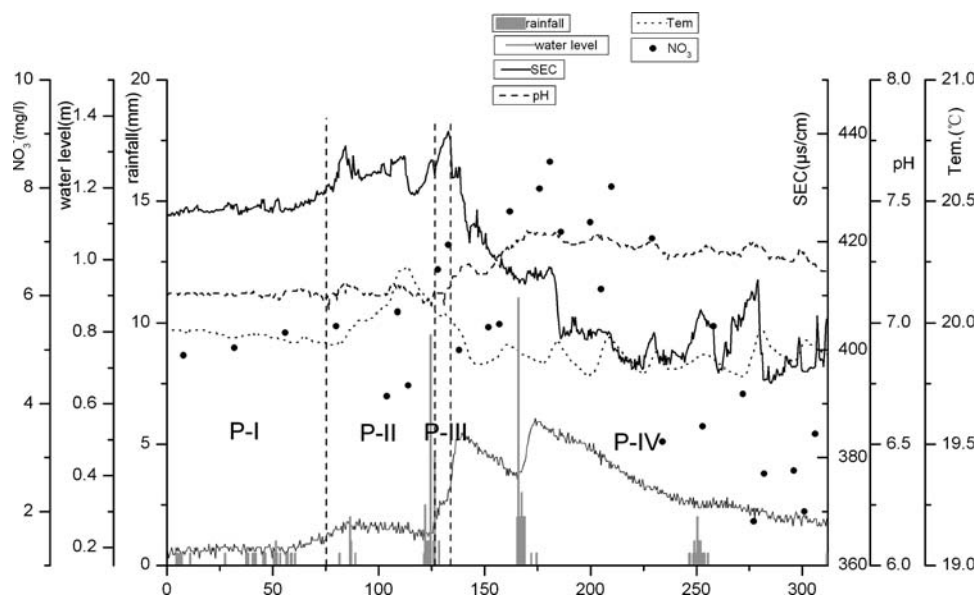
decreased simultaneously. The new recharge was not bypass flow because bypass flow lasted only for short time. It clearly showed that nitrate rose slightly in Phase II, and increased quickly in Phase IV due to eluviations. After that it was mostly effected by dilution, until the concentration resumed to the low value. In Phase IV nitrate concentration had a positive relation with water level, while it had a negative relation with SEC.

There were three or four phases in floods of the spring. They were characterized by initial condition of aquifer, piston flow in soil and vadose, piston flow in conduit, recharge by infiltration (diffuse recharge) and bypass recharge. The initial condition of aquifer and rainfall pulse controlled recharge flow and changes of nitrate and hydro-chemical graphs of the spring.

Quantity of nitrogen input

There were many forms of nitrogen in the natural environment. Generally concentration of nitrogen in groundwater would not increase if not for anthropogenic inputs. In addition to fertilizers, other potential sources of nitrogen include on-site waste disposal system (septic tanks), atmospheric deposition, livestock wastes, and storm water runoff. Nitrogen cycle style was important to understand nitrogen behavior in groundwater. For example, manure used for crop and effluent from septic tanks had similar nitrogen concentrations. But manure would be affected by many functions such as volatilization and nitrification, which would decrease the concentration before they enter groundwater. Leaching from septic tanks would enter groundwater directly without influenced by these processes. Potential artificial nitrogen sources could be confirmed by land use type. Land use

Fig. 6 Variation of nitrate, hydrology and water chemistry in rainfall event of March 2008



type was usually taken as a summary index for nitrogen sources. The quantity of fertilizer could be calculated by sales data.

The main nitrogen inputs in Guancun subterranean river drainage area were fertilizer, livestock manure, sewage, and rainfall. All of them would be calculated as follows.

1. *Fertilizer* According to investigation, fertilizer applied on Guancun area was 50 kg per unit, which contain 25 kg carbamide and 25 kg compound fertilizer. The grade of carbamide was GB2440-2001, which contains 46% of nitrogen. The grade of compound fertilizer was GB15063-2001, which contains 25% of nitrogen.

According to statistics, Guancun drainage area had a field area of 76.38 ha, in which paddy fields were 58.42 ha. Because the differences of nitrogen concentration in fertilizer were very little, the same values for both types were assumed in this paper, resulting in a total of 40,470 kg.

2. *Livestock manure* There were great differences in concentrations of nitrogen in different species of livestock (Table 1). There were 2,000 sheep, 100 buffalos, 60 pigs, and 400 poultry (chicken, duck and goose) in Guancun drainage area. The result was a total nitrogen input of 16,851.69 kg.
3. *Sewage* There were 400 residents in Guancun area. Calculation based on 40 l of effluent letting by one person per day, resulting in a total of nitrogen inputs of 5,559.68 kg.
4. *Rainfall input* Nitrogen input was 4,925.75 kg bases on an annual rainfall of 1,700 mm and a total area of 30.5 km².

The total of nitrogen input was 66,606.29 kg.

Table 1 The amounts and N content of animal excretion in China (Agriculture Technology Popularizing Services Center of China 1999)

Species	Excretion quantity (kg unit ⁻¹ a ⁻¹)	Nitrogen content (%)
Pig	3,419.0	0.238
Sheep	632.0	0.898
Milch cow	21,900.0	0.438
Scalper + buffalo	8,703.0	0.438
Meat cattle	15,500.0	0.438
Horse	5,237.0	0.520
Jennet	3,092.0	0.500
Ovi-chicken	60.0	1.032
Meat chicken	4.5	1.032
Duck	24.0	0.710
Goose	35.5	0.540

Nitrogen output from Guancun subterranean river

Nitrogen output quantity was calculated by multiplying discharge at the outlet and nitrate concentrations daily. Discharge calculational methods and nitrate sampling were expatiated in the above paragraphs. The discharge from April 2006 to June 2006 was 8,153,468 m³, accounting for 59% in a year. Discharge from July to September was 2,859,716 m³, accounting for 23%. Discharge from October to December was only 75,684 m³, accounting for 6% in a year. These data indicated that dynamic variation of the spring discharge was sharply affected by rainfall patterns.

Nitrogen daily output in the outlet had good relation with discharge, especially in rainy season. The total nitrogen output quantity in a year was 21,235.61 kg. The biggest daily flux was on 18 June 2006, with a total amount of 828.28 kg.

Nitrogen budget in Guancun subterranean river

Nitrogen budget was calculated by nitrogen output compared with input; the result was 32%. The reason for nitrogen imbalance was volatilization, absorption by soil, sediment or nitrogen existing in other forms. Perhaps denitrification was more important at some sites with low nitrate leaching. More work should be done on this in the future.

Monthly nitrogen leaching loss rate was taken as quantity of the loss divided by days. The result was nitrogen leaching loss rate in June was the biggest, with a rate of 213.25 kg per day. The second one happened in May with a rate of 113.14 kg per day. Nitrogen leaching loss rate in July was 89.78 kg per day (Table 2). Correlation coefficient was 0.676 between leaching amount with rainfall. It revealed that nitrogen leaching had a positive

Table 2 Quantity and rate of nitrogen loss monthly

Month	Quantity of nitrogen loss (kg)	Nitrogen loss rate (kg per day)
1	330.77	10.67
2	2,268.38	81.01
3	1,379.6	44.50
4	1,559.77	51.99
5	3,507.31	113.14
6	6,397.46	213.25
7	2,783.28	89.78
8	429.22	13.85
9	370.18	12.34
10	86.59	2.79
11	620	20.67
12	238.88	7.71

relation with rainfall in Guancun subterranean river drainage area.

Nitrogen leaching loss in the base flow was 16,162.15 kg, accounting for 76.11% in a year.

Conclusions

Nitrate is one of the prevalent and serious dangerous pollutants for karst groundwater. According to 3-year observation, the range of nitrate variation in Guancun subterranean river was 2.56–15.40 mg l⁻¹, with an average value of 6.60 mg l⁻¹.

Spatial and temporal variations of nitrate in the aquifer and spring were analyzed in order to find impact of rainfall and anthropogenic activities. Relations among hydrological process, water chemistry and nitrate of the spring were discussed through three rainfall events, indicating that the initial condition of aquifer and rainfall pulse controlled recharge flow, changes of nitrate and hydro-chemical graphs.

The quantity of nitrogen input and output from May 2006 to May 2007 in Guancun subterranean river was calculated. The amount of nitrogen input was 66.61 t, and the output was 21.24 t. The reason for the nitrogen imbalance was volatilization, absorption by soil or existing in other forms. The primary reason of nitrogen leaching loss was rainfall. Nitrogen output from April to June made up for 57% in a year. And water discharge of that made up for 59%. Nitrogen leaching loss in the base flow was 16,162.15 kg, accounting for 76.11% in a year. Nitrogen budget was compared with other drainage area in other background of the world, showing that nitrogen loss was decided by infield area, crop species, fertilizer quantity and it's manner of management mostly (Jansons et al. 2003; Panno and Kelly 2004).

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