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ORIGINAL ARTICLE

The influence of urbanization on karst rivers based on nutrient concentration and nitrate dual isotopes: an example from southwestern China

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Abstract China is experiencing rapid urbanization that has changed the water quality of rivers, especially nutrient loads. In this study, a typical urban river located in a karst area, Chengguan River, was chosen to explore the influence of urbanization on river ecosystems based on nutrient concentration and nitrate isotopes. The results show monthly variability of water chemistry and nutrient concentration. Nutrient concentration in two tributaries and the mainstem showed significant spatial variability, with heavy N and P pollution in one tributary near a suburban area, indicating a response to different levels of urbanization. Measurements of nitrate dual isotopes suggest that volatilization, assimilation, nitrification, and denitrification all occur in the polluted river. Water chemistry and nitrate isotopes show that major nitrogen sources included domestic waste and agricultural input, such as chemical fertilizer and manure. The results suggest that urbanization increases nutrient concentrations and accelerates the riverine nitrogen dynamic, and point to the need to manage point sources of sewage effluents to improve the water quality of urban rivers in southwestern China.

Keywords Urbanization · Urban river · Nitrate isotopes · Southwestern China · Chengguan River

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1 Introduction

Over the past forty years, China has experienced a rapid increase in urbanization, especially due to dramatic economic development beginning in the mid-1980s. Urbanization changes land-use and water consumption patterns, which can accelerate nutrient cycling and increase anthropogenic inputs to the watershed. A previous study (Astaraie-Imani et al. 2012) demonstrated that climate change combined with increasing urbanization is likely to lead to worsening river water quality in terms of both frequency and magnitude of threshold exceedance of dissolved oxygen and ammonium concentrations. Urban expansion is a major driving force that alters local and regional hydrology and increases non-point source pollution (Tang et al. 2005).

Understanding the dynamic changes and tracing the source of nitrogen is of great importance in protecting the aquatic environment and managing water sources (Yue et al. 2015). Nitrate dual isotopes can provide powerful information on pollution sources through isotopic composition and isotopic fractionation (Granger et al. 2004; Liu et al. 2006; Kendall et al. 2007; Li et al. 2010).

Urbanization rates in western China are increasing quickly as part of the great western development strategy. Guizhou Province lies at the center of the southeast Asian karst region, the largest karst area in the world. Karstic aquifers are vulnerable to anthropogenic pollution because of their highly-developed conduit system (Liu et al. 2006). It is important to understand changes in water quality and element transformations during urbanization in karst areas. This study presents nutrient concentration and nitrate isotopic composition data from the Chengguan River and three tributaries—each representing different levels of urbanization—to identify sources and transportation routes of nitrate.

2 Study area

The Chengguan River is located in Puding County, Anshun City, Guizhou Province, in southwestern China. With three tributaries, it flows through a suburban area (SU), a rural and agricultural area (RA), and an agricultural area (A), which has less rural area than RA (Fig. 1). Land use includes paddy, dryland, shrub, and grass. Regional population and infrastructure have changed dramatically in recent years with the rapid expansion of Chinese urbanization, especially in the middle and upper reaches of the mainstem (between M2 and M4). Dense fruit agriculture (grape, peach, lotus, etc.) characterizes the downstream area while a wetland is located between M5 and M6. The river flows into Yelang Lake, a major source of drinking water for Anshun City.

3 Sampling and analyses

Water samples were collected monthly from August to December 2015, including six sites in the mainstem (M1 to M6) and seven tributary sites. Temperature (T), electrical conductivity (EC), dissolved oxygen (DO), pH, and water discharge were measured in the field. Nutrient concentrations (NO_2^-–N, NH_4^+–N, NO_3^-–N, and PO_4^{3-}–P) were analyzed after filtering through 0.22 μm membrane filters using an automatic flow analyzer (SKALAR Sans Plus Systems). Anions (Cl^- and SO_4^{2-}) were determined by

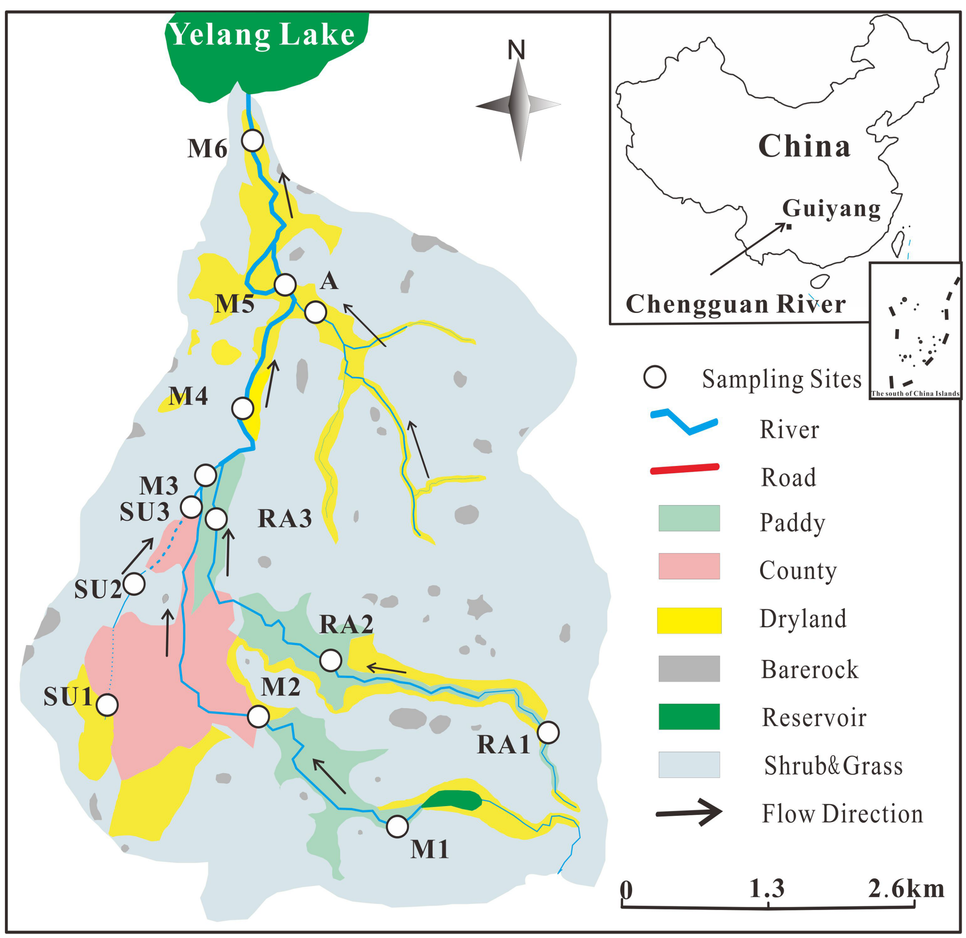

Fig. 1 Land use and sample sites in Chengguan River. M (1–6), SU (1–3), RA (1–3) and A represent the mainstream sites, the suburban tributary sites, the rural and agricultural tributary sites and the agricultural tributary site, respectively

ionic chromatography using a Dionex ICS-90 (USA). Nitrate isotopes were measured by the denitrifier method (McIlvin and Casciotti 2011) in the State Key Laboratory of Environment Geochemistry, Chinese Academy of Science, Guiyang, China. With this method, NO_3^- and NO_2^- are converted by denitrifying bacteria to N_2O gas, which is concentrated by a trace gas pre-concentrator unit (Isoprime Ltd., Cheadle Hulme, UK) before being analyzed by an isotope ratio mass spectrometer (Isoprime, GV, UK). The analytical precision for the samples analyzed in duplicate was 0.3‰ for $\delta^{15}N$ and 0.5‰ for $\delta^{18}O$ of nitrate.

Isotope ratios are expressed in delta (δ):

$$\delta X(\text{‰}) = \left(R_{sample}/R_{standard} - 1\right) * 1000$$

where R_{sample} and $R_{standard}$ are the $^{15}N/^{14}N$ and $^{18}O/^{16}O$ ratios of the sample over the sample standard for $\delta^{15}N$ and $\delta^{18}O$, respectively. The ratio of $^{15}N/^{14}N$ uses N_2 in air as the reference and $^{18}O/^{16}O$ uses Vienna Standard Mean Ocean Water as the reference.

4 Results and discussion

4.1 Monthly variation of aqueous chemistry and chemical composition

Temperature is a key parameter for nutrient dynamics because it can affect microbial activities. Variability was significant between some of the samples. Samples collected in August and September had higher average T than November and December. The nutrient variability was large among samples collected at different sites but in the same month, indicating a significant difference in riverine nutrients. The [PO_4^{3-}–P] content showed monthly variability with high concentrations in November and December, but low [PO_4^{3-}–P] in the other three months, which also had high water discharge (show Fig. 2a). One possibility is that [PO_4^{3-}–P] was diluted by heavy rainfall in these three months. Low dissolved inorganic nitrogen (DIN) and water discharge were measured in December. High EC was measured in November and December, indicating a decrease in the dilution effect.

The highest EC and Cl^- concentrations at SU (584 ± 120 μs/cm, 15.1 ± 7.1 mg/L) and M (658 ± 142 μs/cm, 8.6 ± 4.3 mg/L) might have come from wastewater input. [DO] ranged from 0.2 to 9.3 mg/L with a mean value of 4.8 ± 2.6 mg/L, suggesting that a fraction of the water was under anaerobic conditions. [NO_3^-–N] ranged from below the detection limit (BDL) to 11.4 mg/L, with a mean value of 3.0 ± 2.2 mg/L. [NH_4^+–N] ranged from BDL to 3.4 mg/L with a mean value of 0.6 ± 1.1 mg/L. High [NH_4^+–N] were detected in samples from SU tributary and two mainstem sites (M3 and M4). [NO_2^-–N] was lower than the other two inorganic nitrogen nutrients, with a narrow range between BDL and 0.3 mg/L. Nitrate and ammonium were major inorganic components, and the composition of nitrogen species in different months showed large variability, indicating that riverine nitrogen was influenced by anthropologic activities. This may also relate to nitrogen transformations during the sampling period.

4.2 Variability of the nutrient load among sites of different land use

Figure 3a shows that water samples from sites of different land use showed significant variability in [DIN] with a high concentration in the SU tributary and a low concentration in the RA tributary. This variability mirrors different levels of urbanization, with low urbanization in the rural area (RA tributary) and high urbanization in the urban area (mainstem). Note that the SU tributary had the highest nitrogen concentration and $\delta^{15}N$–NO_3^- values (Fig. 3b) and that this area also had the highest rate of urbanization in recent

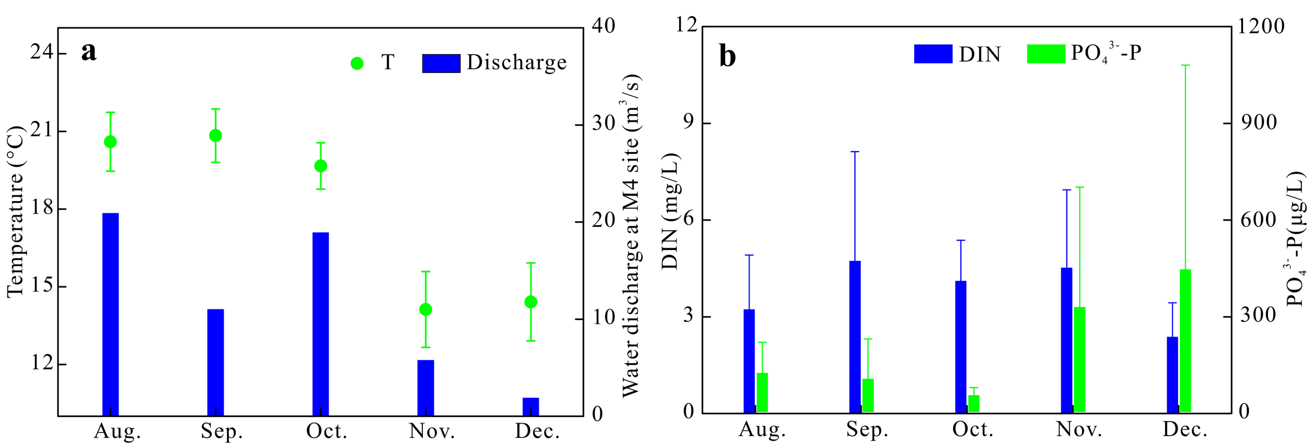

Fig. 2 **a** Average water temperature and water discharge at M4 site **b** average [DIN] and [PO_4^{3-}–P]

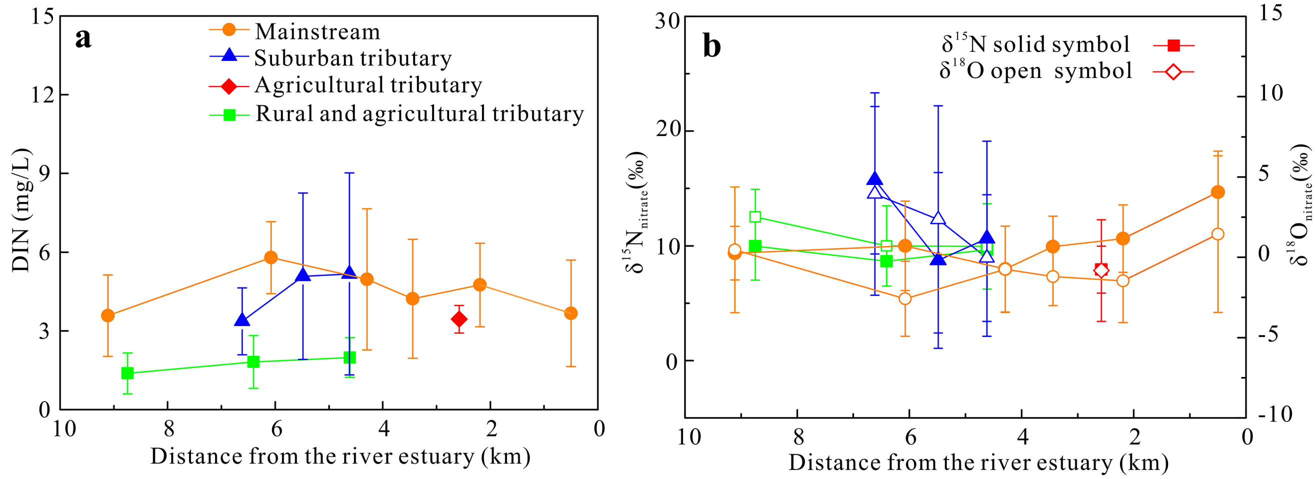

Fig. 3 Variability in average [DIN] (**a**) and dual nitrate isotopes (**b**) between the mainstream and tributaries. *Solid squares*, *circles*, and *triangles* indicate $\delta^{15}N$ of the rural and agricultural tributary, mainstream and suburban tributary, respectively. *Open squares*, *circles* and *triangles* indicate $\delta^{18}O$ of the rural and agricultural tributary, mainstream and suburban tributary, respectively

years. Urbanization has led to a population concentrated in the central county and stimulated the development of the suburban area, where water treatment infrastructure is insufficient. Point pollution directly discharging into the river was occasionally observed during sampling.

4.3 Major transformations in the urban river system

The potential processes that control nitrogen dynamics in this river system include volatilization, assimilation, nitrification, and denitrification. All of these processes can increase $\delta^{15}N$ of substrates and decrease $\delta^{15}N$ of products (Kendall et al. 2007). The high $\delta^{15}N$ detected in SU tributary samples indicates that these processes may affect nitrogen isotopic composition. The range of pH values was between 7.4 and 8.4, which might favor the loss of ammonia gas by volatilization in the aquatic environment. $\delta^{18}O$ ranged from −5.8‰ to −9.5‰ with an average value of −7.9‰ ± 0.6‰ (n = 119) in the adjoining Houzhai catchment (Yue et al. 2015). The $\delta^{18}O$ of nitrate has been largely interpreted as a mixture of surrounding H_2O and O_2 with a ratio of 2:1. If the new nitrified $\delta^{18}O$ of nitrate is calculated using this ratio, the $\delta^{18}O$ of nitrate ranges between 2.2‰ and 4.7‰, which is within the range of this study (−4.7‰–10.5‰). However, there were samples with lower $\delta^{18}O$–NO_3^- values than those calculated, and there were ten measured values of DO below 1 mg/L. This suggests that the oxygen exchange between water and nitrite may have occurred during nitrification (Kool et al. 2011) or that different ratios of aqueous oxygen to atmospheric oxygen may apply during nitrification (Kendall et al. 2007, Yue et al. 2015). The variability of [NH_4^+–N] among sites in the urban area also suggests that nitrification has occurred in the study area. Consistently high [NH_4^+–N] concentrations in the SU tributary indicate that suppression of nitrification is due to biochemical oxygen demand as indicated by low DO concentrations in river water. These results suggest that NH_4^+ was gradually transformed to NO_2^- or NO_3^- between SU and the mainstem.

Denitrification through a series of intermediate gaseous nitrogen oxide products is an important nitrate sink in the aquatic system (Kendall et al. 2007; Li et al. 2010). One such intermediate, N_2O, can accumulate at high concentrations. Liu et al. (2015) found urban rivers with high nitrogen loading emitted more N_2O than rural rivers with high nitrogen loading. Denitrification can result in an increase in heavier nitrogen and oxygen isotopes in the remaining sources with a ratio of 2:1. We found a negative relationship of $\delta^{15}N$ versus ln [NO_3^-–N] (Fig. 4) and a

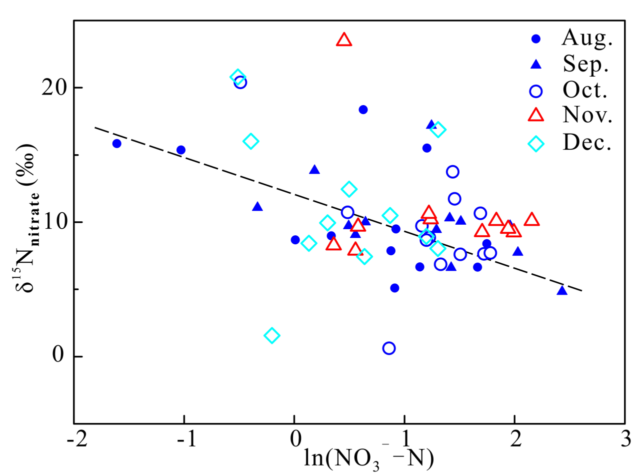

Fig. 4 The relationship between $\delta^{15}N$–NO_3^- and ln(NO_3^-–N)

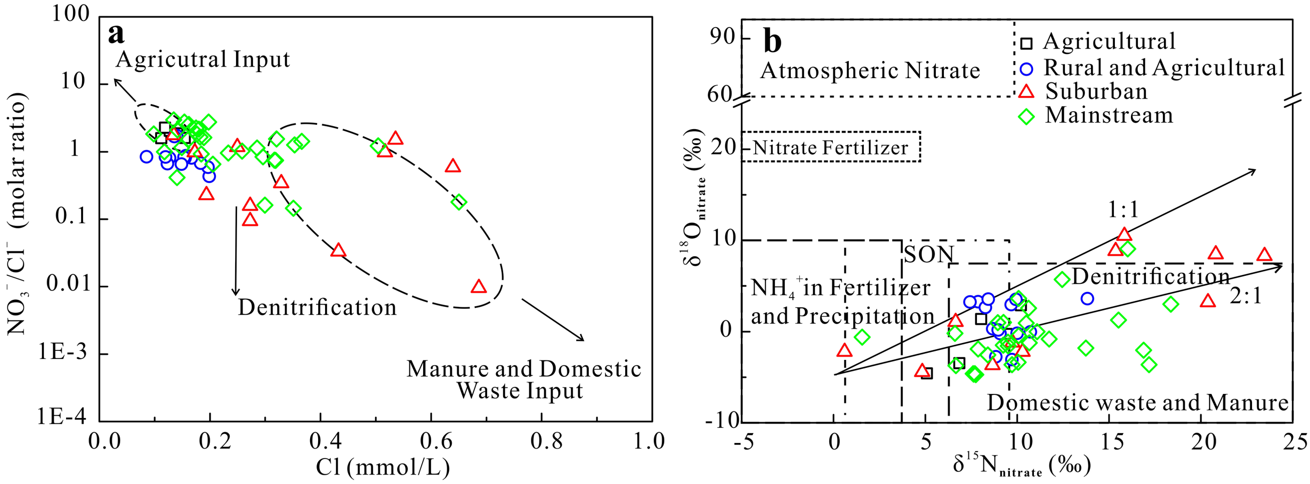

Fig. 5 **a** Relationship between NO_3^-/Cl^- and Cl^-. **b** Relationship between $\delta^{15}N$ and $\delta^{18}O$. The isotopic range of the sources in the diagram was modified from Kendall et al. 2007

positive relationship of $\delta^{15}N$ versus $\delta^{18}O$ ($\delta^{18}O = 0.51 \times \delta^{15}N–4.9‰$, $R^2 = 0.32$, $P < 0.001$, $n = 59$), suggesting that denitrification did occur during transport.

Assimilation refers to the transformation of inorganic nitrogen into an organic form wherein the oxygen fractionation changes to 1:1 in the $\delta^{15}N$ and $\delta^{18}O$ of nitrate (Granger et al. 2004). The decrease in nitrogen concentration and the increase in isotope value downstream (M5 and M6) might be caused by assimilation and denitrification at the wetland as shown in Fig. 3.

4.4 Nitrogen sources based on nitrate isotopes

In this study area, potential nitrate sources include soil organic nitrogen (SON), domestic waste, chemical fertilizer, and precipitation. Nitrate derived from manure and sewage had isotope values exceeding 6.0‰ and ranged from 2.0‰ to 8.0‰ for SON (Kendall et al. 2007). The dual isotopic values of nitrate are plotted in Fig. 5b together with the typical isotope range of different nitrate sources. As shown in Figs. 3 and 5, spatial variability in $\delta^{15}N\text{-}NO_3^-$ values and water chemistry identifies the major nitrogen sources to be domestic waste and agricultural input—a mixture of chemical fertilizers and manure.

5 Conclusion

Urbanization is the major driving force for deterioration in urban river environments. It can induce nutrient fluxes and their biogeochemical processes. We took Chengguan River as an example to understand the impact of urbanization on river water quality. The chemical compounds displayed spatial and temporal variability. A high DIN concentration was detected in the study area. Nitrate and ammonium were two major inorganic nitrogen species. Water chemistry and dual nitrate isotopes suggest multiple nitrogen transformations, including nitrification, volatilization, denitrification, and assimilation. Nitrate produced from nitrification had relatively low $\delta^{18}O–NO_3^-$ values because water contributed more oxygen under anaerobic environments in the urban river. The major nitrogen sources in the urban river were domestic waste, chemical fertilizer, and manure. Urbanization can lead to increased riverine nitrogen and phosphorous, affecting the water environment. The input of nitrogen and phosphorus into the reservoir may deteriorate water quality and threaten the safety of drinking water. This issue deserves special attention in the karst area of southwestern China, where reservoirs are widely distributed. The results also suggest that artificial wetlands were useful for nitrogen removal and that micro-water treatment equipment should be installed for urban rivers in this karst area.

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References

Astaraie-Imani M, Kapelan Z, Fu GT, Butler D (2012) Assessing the combined effects of urbanisation and climate change on the river water quality in an integrated urban wastewater system in the UK. J Environ Manag 112:1–9. doi:10.1016/j.jenvman.2010.06.039

Granger J, Sigman DM, Needoba JA, Harrison PJ (2004) Coupled nitrogen and oxygen isotope fractionation of nitrate during assimilation by cultures of marine phytoplankton. Limnol Oceanogr 49(5):1763–1773. doi:10.4319/lo.2004.49.5.1763

Kendall C, Elliott EM, Wankel SD (2007) Tracing anthropogenic inputs of nitrogen to ecosystems. Stable Isot Ecol Environ Sci 2:375–449

Kool DM, Wrage N, Oenema O, Van Kessel C, Van Groenigen JW (2011) Oxygen exchange with water alters the oxygen isotopic signature of nitrate in soil ecosystems. Soil Biol Biochem 43(6):1180–1185. doi:10.1016/j.soilbio.2011.01.006

Li SL, Liu CQ, Li J, Liu XL, Chetelat B, Wang BL, Wang FS (2010) Assessment of the sources of nitrate in the Changjiang River, China using a nitrogen and oxygen isotopic approach. Environ Sci Technol 44(5):1573–1578. doi:10.1021/es902670n

Liu CQ, Li SL, Lang YC, Xiao HY (2006) Using δ15 N-and δ18O-values to identify nitrate sources in karst ground water, Guiyang, Southwest China. Environ Sci Technol 40(22):6928–6933. doi:10.1021/es0610129

Liu XL, Bai L, Wang ZL, Li J, Yue FJ, Li SL (2015) Nitrous oxide emissions from river network with variable nitrogen loading in Tianjin, China. J Geochem Explor 157:153–161. doi:10.1016/j.gexplo.2015.06.009

McIlvin MR, Casciotti KL (2011) Technical updates to the bacterial method for nitrate isotopic analyses. Anal Chem 83(5): 1850–1856. doi:10.1021/ac1028984

Tang Z, Engel BA, Pijanowski BC, Lim KJ (2005) Forecasting land use change and its environmental impact at a watershed scale. J Environ Manag 76(1):35–45. doi:10.1016/j.jenvman.2005.01.006

Yue FJ, Li SL, Liu CQ, Lang YC, Ding H (2015) Sources and transport of nitrate constrained by the isotopic technique in a karst catchment: an example from Southwest China. Hydrol Processes 29(8):1883–1893. doi:10.1002/hyp.10302