

Evaluation of nitrate pollution sources in surface water across the typical rural-urban interface: a case study of Wen-Rui Tang River, China

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Abstract

Nitrate (NO_3^-) pollution is of considerable concern because its threat to human health and ecosystems. Herein, we chose the Wen-Rui Tang River watershed, one of typical rural-urban watersheds in Southeast China, as a case study. According to the analyses based on hydro-chemical ions, land-use classification, dual nitrate isotopes ($\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$), and a Markov Chain Monte Carlo mixing model, the knowledge of contributions of potential NO_3^- pollution sources was obtained. Results showed that the study river was highly polluted by nitrogen, especially the increased riverine NO_3^- . Variations in $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ revealed that microbial nitrification was the main transformation process of nitrogen in surface water of the watershed, while bacterial denitrification was unlikely to be an important process at the specific sampling period. The $\delta^{15}\text{N-NO}_3^-$ vs. $\delta^{18}\text{O-NO}_3^-$ diagram incorporating chloride content qualitatively identified the main contribution of riverine NO_3^- was from municipal sewage discharges. On the basis of land-use characteristics, we applied hierarchical cluster method for subgrouping 44 sampling sites into four classes, namely, classes I (ecological), II (industrial), III (agricultural), and IV (urban). The Markov Chain Monte Carlo mixing model was employed to calculate proportional contributions of NO_3^- sources and articulated predominantly municipal sewage (23.5 – 42.2%) sourced nitrate in all classes. In addition, river sediments (13.8 – 20.8%) and atmospheric deposition (12.7 – 19.6%) were identified as important pollution sources. This study demonstrated that the comprehensive isotope tracing approach can effectively quantify the nitrate pollution source contributions for surface waters across the rural-urban interface.

1. Introduction

As rapid urbanization around the globe, urban areas gradually expand into rural land on city fringes. Consequently, rural-urban settings likely become more common in the future. The anthropogenic activity, hydrologic process, and migration and transformation of nitrate are very different between rural and urban zones. For example, the impervious surfaces in urban areas might cause increasing volumes and peak flows of runoff, which is attributed to the change of the hydrological mechanism (Barbosa et al., 2012). In an urbanized watershed, without through soil infiltration, the quick drain of nitrogen might hinder the nitrification process, resulting in higher NH_4^+ concentrations than that in waters of natural landscapes (Zhao et al., 2015). Evaluation of riverine NO_3^- pollution sources in such settings is an important global topic.

In the last few decades, many nutrient source apportionment models have been developed. Many of them are geographic information system (GIS)-based models, namely, Soil and Water Assessment Tool (SWAT), Hydrological Simulation Program-Fortran (HSPF), and Storm Water Management Model (SWMM), which can mathematically simulate hydrological processes and nutrient transport and transformation in terrestrial-riverine systems. Unfortunately, the shortcomings of geographic information system (GIS)-based models, such as requiring large and complex parameterization datasets, lack of appropriate calibration/validation data, possibly difficulty of use, especially the failure of to consider

inherent substantial distinction of nutrient sources and fate between urban and rural regions in their simulations, making them unsuitable for rural-urban settings (Arnold and Fohrer, 2005; Donigian et al., 1984; Rossman et al., 2015).

In recent years, the promising stable nitrate isotope (^{15}N and ^{18}O) approach has been recognized as a useful resolution to understand sources and fate of riverine NO_3^- based on the different nitrate sources exhibiting their unique stable isotopic signatures (Biddau et al., 2019). In general, stable nitrogen isotope value in nitrate ($\delta^{15}\text{N-NO}_3^-$) is more suitable for tracking NO_3^- derived from manure & sewage, soil nitrogen, and nitrogen fertilizer (Kendall and McDonnell, 1998), whereas oxygen isotope ($\delta^{18}\text{O-NO}_3^-$) value is more useful to distinguish NO_3^- derived from atmospheric deposition, nitrate-bearing fertilizer, and nitrification of reduced nitrogen forms (Kendall and McDonnell, 1998; Mayer et al., 2001). Presently, $\delta^{15}\text{N-NO}_3^-$ in combination with $\delta^{18}\text{O-NO}_3^-$ have been successfully applied in many scenarios including river, reservoir, lake, estuarine, and groundwater, which can provide insight resolution to trace the sources of nitrate (Ji et al., 2017; Soto et al., 2019; Jin et al., 2020; Shang et al., 2020; Wang et al., 2020).

However, most previous research focused on separate agricultural or urban water systems, and few research investigated riverine NO_3^- sources in highly heterogeneous rural-urban interface, although the potential environmental risks of nitrate have been recognized in these areas. Up to the present, due to the complex land-use categories along with a wide range of local pollution sources, it is still challenging to evaluate nitrate pollution sources in surface waters across the rural-urban interface. Especially, the spatial variations of individual nitrate pollution sources in surface water across the rural-urban areas have not been fully investigated by using nitrate isotopes. Therefore, this study was designed based on dual nitrate isotopes, land-use types and a MCMC mixing model to distinguish nitrate sources quantitatively for a typical river across the rural-urban interface of Southeast China. We expected that the results of this study could inform environmental and water resource agencies with quantitative data to further control nitrogen pollution in surface waters across the rural-urban interface for maintaining a healthy river system.

2. Materials And Methods

2.1 Study area

The Wen-Rui Tang (WRT) River watershed ($27^\circ 52' - 28^\circ 4' \text{ N}$ \times $120^\circ 28' - 120^\circ 46' \text{ E}$) in Southeast China was selected as the study site (**Fig. 1**). The WRT River is a typical coastal plain river network across the rural-urban interface in Wenzhou of Zhejiang province (China), covers an area of 740 km^2 and populated by ~ 9.25 million people. It originates from the south of Lishui Mountains, meanders through forests, rural areas with many farmlands, densely populated urban zones, and rural areas, from northwest to southeast, and ultimately drains into the East China Sea. This region belongs to a subtropical oceanic climate receiving 1500 to 1900 mm of annual rainfall, with 70% falling between April and September. Vegetated, agriculture, and residential are the dominated land use categories, accounting for 40%, 39.5%,

and 14.5% of the entire watershed, respectively. Due to the plain topography, the strongest noteworthy hydrologic characteristic of the WRT River is that the river waters nearly stagnant during most periods of the year, except the sluice gates to the much larger Ou River are open during heavy rainfall events (Wang et al., 2018b).

2.2 Water sampling and analytical methods

River water sampling was carried out in April 2019 (normal season) at the onset of the wet season for 44 sampling sites (22 of them were chosen for nitrate isotope analysis) across the WRT River watershed (Fig. 1).

At each of the sites, a portable multi-parameter water-quality sonde (YSI-EXO2, Xylem, USA) was used to determine the dissolved oxygen (DO) in the field. Water samples were collected using a hydrophore sampler from 30 cm below the water surface. The samples were placed in pre-washed 500 ml high-density polyethylene bottles and subsequently stored at an icebox for transporting to the laboratory.

In the laboratory, half of every sample was filtered through 0.45 μm membrane filters within 12 hour of sampling. Both the raw and filtered water samples were stored at -20°C . Ten parameters, namely, total nitrogen (TN), ammonia nitrogen (NH_4^+), nitrite nitrogen (NO_2^-), NO_3^- , total phosphorus (TP), phosphate (PO_4^{3-}), total organic carbon (TOC), $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ were analyzed within a week of sampling. Specifically, TN, NO_3^- , NH_4^+ , NO_2^- , TP, and PO_4^{3-} were analyzed through the continuous-flow analyzer (Autoanalyser-3, Seal, German) with limit of detection (LOD) of ~ 0.02 mg/L for TN/TP and ~ 0.003 mg/L for dissolved inorganic nitrogen/phosphorus (NO_3^- , NH_4^+ , NO_2^- , PO_4^{3-}), respectively; TOC was measured using TOC Analyzer (LOD ~ 0.1 mg C/L; TOC-L, Shimadzu, Japan).

Twenty two samples for stable nitrate isotope ($\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$) analysis were stored in 20 ml high-density polyethylene bottles and then delivered with ice to the Environmental Stable Isotope Lab at Chinese Academy of Agricultural Sciences (China) follow bacteria denitrifier method proposed by Sigman et al. (2001) and Casciotti et al. (2002). This method using a denitrifying bacteria lacking gaseous nitrous oxide (N_2O) reductive activity known as *Pseudomonas aureofaciens* to reduced nitrate to N_2O . Next, N_2O was purified *via* a trace gas detection system. Finally, $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of N_2O were measured by using a continuous-flow isotope ratio mass spectrometer (Isoprime100, Cheadle, UK). The $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ values are reported in parts per thousand (‰) relative to atmospheric N_2 and Vienna Standard Mean Ocean Water, respectively (Kendall et al., 2007). The measured isotope values were calibrated by three international nitrate standards (USGS-32, USGS-34, and USGS-35). Sample analysis precisions for $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ were $\pm 0.2\text{‰}$ and $\pm 0.5\text{‰}$, respectively.

2.3 Land-use classification

Different land-use categories may contribute different pollution sources to riverine nitrate. Original land-use categories were aggregated by merging similar land-use types into seven broader categories:

vegetated land (forest, grassland and urban green belts), agriculture, commercial (cultural entertainment, commercial, administrative, municipal utility lands), industrial and mining, transportation, residential, and water (Wang et al., 2019). To better assess the sources in the selected watershed, hierarchical cluster method was used to group the sampling sites into different classes according to land-use proportions for sampling sites. As the quiescence nature of the river water as this case, different land-use percentages for each monitoring site may be able to calculate at a 500 m straight-line buffer of the sites rather than at a sub-watershed scale.

2.4 Markov Chain Monte Carlo (MCMC) mixing model

The MCMC mixing model, presented by Parnell et al. (2010), was employed to calculate the potential NO_3^- -N source contributions in the WRT River watershed. The equations of the system model are showed as:

$$\left. \begin{aligned} X_{ij} &= \sum_{k=1}^k P_k(S_{jk} + C_{jk}) + \varepsilon_{ij} \\ S_{jk} &\sim N(\mu_{jk}, \omega_{jk}^2) \\ C_{jk} &\sim N(\lambda_{jk}, \tau_{jk}^2) \\ \varepsilon_{ij} &\sim N(0, \sigma_j^2) \end{aligned} \right\} \quad (1)$$

where X_{ij} is isotopic signature j ($\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$) of the river water sample i ($i = 1, 2, 3 \dots N$); S_{jk} denotes the potential NO_3^- source k (e.g., municipal sewage) of isotope j ; P_k represents the estimated proportional contribution of source k , which obeys a Dirichlet distribution; C_{jk} refers to the isotopic fractionation caused by multiple nitrogen-cycling processes for isotope j of source k , and ε_{ij} is the residual error, which represents the unquantified variation among individual mixtures.

The MCMC mixing model takes three delimited text files as inputs consist of $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ of river water, means and standard deviations of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of each pollution source (end-member), and means and standard deviations of fractionation factor of ^{15}N and ^{18}O . The nitrate isotopic compositions for the pollution end-members were obtained from literatures (Guo et al., 2015; Yuan et al., 2018; Zhang et al., 2018; Zhao et al., 2019). **Table 1** summarized specific $\delta^{15}\text{N}$, $\delta^{18}\text{O}$ and fractionation factor for each of the expected NO_3^- sources.

Table 1 Isotopic characteristics (mean \pm standard deviation) and fractionation factor (mean \pm standard deviation) of suspected end members used for the Markov Chain Monte Carlo model

Source	N	Isotopic characteristics		Fractionation factor
		$\delta^{15}\text{N}$ (‰)	$\delta^{18}\text{O}$ (‰)	$\delta^{15}\text{N}$ (‰)
Atmospheric deposition	8	2.70±4.90 ^a	44.8±18.1 ^a	0 ^b
Nitrogen fertilizer	6	0.04±1.87 ^b	4.14±1.89 ^c	-4.1±1.4 ^b
Soil nitrogen	20	4.52±2.67 ^b	4.14±1.89 ^c	3.93±2.3 ^b
Municipal sewage	10	12.73±3.40 ^b	4.14±1.89 ^c	-0.6±1.2 ^b
Industry wastewater	4	4.10±0.90 ^d	1.50±1.10 ^d	-0.6±1.2 ^b
River sediments	12	6.40±2.50 ^e	4.14±1.89 ^c	3.93±2.3 ^b

^a Data obtained from Zhao et al. (2019);

^b Data obtained from Zhang et al. (2018);

^c The value of $\delta^{18}\text{O}$ in nitrogen fertilizer is calculated based on the measured $\delta^{18}\text{O}$ values of atmospheric O_2 and ambient water in Fuzhou station;

^d Data obtained from Yuan et al. (2018);

^e Data obtained from Guo et al. (2015).

In this study, the MCMC mixing model was created by Stable Isotope Analysis in R (SIAR V4) software package running on the statistical software R platform (version 3.5.3, R Core Team, 2019). The model operational parameters i.e., run iterations, burn-in, sample interval, and iteration maintainer were set as 500,000, 50,000, 15, and 30,000, respectively.

3. Results And Discussion

3.1 Descriptive statistics of water quality

Of the 44 surface water samples measured, DO concentrations ranged from 0.30 to 8.60 mg/L, with ~70% sites having > 2 mg/L (threshold for hypoxic condition to facilitate microbial denitrification) (**Fig. 2**). TN concentrations varied greatly from 0.55 to 8.62 mg/L, with 93% and 77% of the samples worse than national water quality standard Type III (1 mg/L, threshold for drinking water) and Type V (2 mg/L, minimum quality for supporting aquatic ecosystem health), respectively. Mean concentration of NH_4^+ was 1.81 mg/L; more than 35% of the samples did not meet water quality standard Type V of 2 mg/L. NO_2^- concentrations ranged within 0.01 to 0.36 mg/L. With respect to NO_3^- , concentrations of samples within a wide range from 0.34 to 3.56 mg/L, with a mean value of 1.57 mg/L. Concentrations of TP and PO_4^{3-} were 0.05 – 0.79 mg/L and < 0.01 – 0.24 mg/L, respectively; median value of TP was 0.17 mg/L

demonstrating that most sites were meet type III water quality standard (0.2 mg/L). For TOC, concentrations with 0.81 – 10.41 mg/L (mean = 3.56).

3.2 Classification of sampling sites

The hierarchical cluster algorithm to classify sampling sites yielded four classes (**Fig. 3**). Class I (ecological) consisted of eleven sites possessing 38.7% non-agricultural vegetated land mixed with 37.5% urban land and 18.4% agricultural land. Class II (industrial) was composed of four sites having the highest industrial lands (39.8%), 41.9% urban land and 16.2% agricultural land. Class III (agricultural) corresponded to the rural and suburban areas that were dominated by agriculture (62.0%) but also had mixed residential areas (30.2%). This class contained eleven sites that were mainly located in western and southern parts of the watershed. Class IV (urban) included 18 sites and characterized by a relatively developed region with 80.4% residential areas that were mainly located in the northern part of the watershed.

The surface water across the rural-urban interface of Southeast China, receiving nitrogen inputs from a variety of point sources e.g., industry wastewater, and municipal sewage and diffuse sources e.g., atmospheric deposition, nitrogen fertilizer, and soil nitrogen. Moreover, as an internal source, the river sediments should also be taken into account in the investigation of riverine nitrogen enrichment as they can continue to release nitrogen, especially NH_4^+ , into the water under special condition (Wang et al., 2018a). Here, different land-use classes receiving varied pollution source inputs as follows: For classes I and III, atmospheric deposition, nitrogen fertilizer, soil nitrogen, municipal sewage, and river sediments, were identified as the potential nitrate sources. Industry wastewater was not considered because only ~5% industry lands existed in these classes; For class II, all the sources may contribute to the riverine nitrate pollution due to the mixed industrial, agricultural and residential lands; Class IV was characterized by having highest residential land (> 80%), moderate industrial land (> 10%), as well as low agricultural (3.2%) and vegetable (5.6%) lands; as such, atmospheric deposition, industry wastewater, municipal sewage and river sediments were believed to be the potential pollution sources.

3.3 Transformations of nitrate

Mean values of $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ over all sampling sites were $8.63 \pm 3.77\text{‰}$ (range = 2.85 – 14.17‰) and $9.98 \pm 3.24\text{‰}$ (range = 5.18 – 16.56‰), respectively (**Fig. 4**). Concretely speaking, $\delta^{15}\text{N-NO}_3^-$ ranges for classes I, II, III, and IV were 4.35 – 12.12‰, 4.14 – 8.70‰, 4.52 – 13.30‰, 2.85 – 14.17‰, respectively; and $\delta^{18}\text{O-NO}_3^-$ compositions for classes I, II, III, and IV were 9.73 – 16.20‰, 11.28 – 11.43‰, 6.23 – 11.18‰, 5.18 – 16.56‰, respectively. Herein, we used the dual nitrate isotopes to provide powerful insights into crucial nitrogen-cycle processes (i.e., nitrification and denitrification) regulating NO_3^- content within watersheds (Li et al., 2019; Yang and Toor, 2016).

Depending on the $\delta^{18}\text{O}$ of 23.50‰ and (-14.16) – (-0.92)‰ in atmospheric O_2 and ambient water (collected from a nearby Fuzhou, China, station of International Atomic Energy Association, ~240 km),

respectively, we estimated microbially-produced $\delta^{18}\text{O-NO}_3^-$ were in a range of -1.61‰ to 7.22‰. However, it has been proved that $\delta^{18}\text{O-NO}_3^-$ derived from nitrification may exceed up to 5‰ higher than the theoretical maximum value (Kendall and McDonnell, 1998; Xue et al., 2009). Given this, we determined the expected range of $\delta^{18}\text{O-NO}_3^-$ values in the study River system from nitrification within -1.61‰ to 12.22‰. As shown in **Fig. 4 a**, the $\delta^{18}\text{O-NO}_3^-$ values ranged from 5.18‰ to 16.56‰ with that of most sites had good agreement with the theoretical values for nitrification, demonstrating that the nitrate produced by microbial nitrification appeared to be the primary source of NO_3^- .

During denitrification of NO_3^- , anaerobic microbes preferentially consume the light isotopes of NO_3^- (i.e., ^{14}N and ^{16}O), resulting in simultaneously enriching ^{15}N and ^{18}O of the residual NO_3^- with decrease of the NO_3^- content (Nestler et al., 2011). Typically, the ratios of $\delta^{15}\text{N-NO}_3^- : \delta^{18}\text{O-NO}_3^-$ ranged from 1.3 : 1 to 2.1 : 1 (Liu et al., 2006). These ratios along with obvious negative relationship between $\delta^{15}\text{N-NO}_3^-$ and NO_3^- contents often serve as a diagnosing of denitrification. In this study, no significant positive correlation between $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ as well as no negative relationship between $\delta^{15}\text{N-NO}_3^-$ and NO_3^- were found at this sampling time in all classes (**Fig. 4**). Thus, we posited surface water of the study River having insufficient hypoxic condition to allow for appreciable aerobic denitrification carry out; however, some denitrification may occur in the soils/riverine sediments with oxygen-depleted and carbon-rich environment.

3.4 Identification of main riverine NO_3^- sources

Using the classical dual isotope cross-plot diagram to acquire qualitative information about the main riverine NO_3^- contribution, the plot of $\delta^{15}\text{N-NO}_3^-$ versus $\delta^{18}\text{O-NO}_3^-$ of samples showed the typical characteristics of NO_3^- pollution sources from atmospheric deposition, nitrogen fertilizer, soil nitrogen and sewage (**Fig. 5**). According to **Fig. 5**, our sampling scatters of $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ did not distribute to atmospheric deposition source category, revealing little or no riverine NO_3^- derived from atmospheric deposition. Whereas, almost all data points distributed to sewage dominion, seven of them lied within the soil nitrogen-sewage overlap zone, five of them belonged to nitrogen fertilizer-soil nitrogen-sewage overlap zone. As a result, municipal sewage was recognized as the main riverine NO_3^- pollution source; soil nitrogen and nitrogen fertilizer also contributed somewhat NO_3^- to the study River. In summary, municipal sewage was identified as the main/key factor contributing to NO_3^- concentrations in the study river system. Additionally, the positive correlation between NO_3^- and $\delta^{15}\text{N-NO}_3^-$ further partly supported riverine NO_3^- most likely originated from sources having a high value of $\delta^{15}\text{N-NO}_3^-$ (i.e., municipal sewage) (**Fig. 4 b**).

3.5 Estimation of proportional contribution of potential nitrate sources based on land-use classes

Figure 6 showed the results of the MCMC mixing model for the evaluation of the proportional contribution of potential sources to riverine nitrate concentrations in the WRT River. The nitrate source contributions of classes I (ecological), II (industrial), III (agricultural), and IV (urban) were in the order: municipal sewage > atmospheric deposition > nitrogen fertilizer > river sediments > soil nitrogen, municipal sewage > atmospheric deposition > nitrogen fertilizer > industry wastewater \approx river sediments > soil nitrogen, municipal sewage > nitrogen fertilizer > river sediments > soil nitrogen > atmospheric deposition, municipal sewage > industry wastewater > river sediments > atmospheric deposition, respectively. Specifically, the MCMC mixing model outputs identified municipal sewage was the dominant pollution source causing NO_3^- pollution as it contributed most riverine NO_3^- for all classes, which fell within 23.5 – 42.2%. River sediments showed a moderate secondary NO_3^- contribution with a range from 13.8 to 20.8%. Atmospheric deposition contributed 12.7 – 19.6% riverine NO_3^- , suggesting atmospheric deposition was an unneglected source of NO_3^- in the WRT River. The contributions of soil nitrogen were 12.2% in class I, 13.3% in class II, and 13.9% in class III, respectively. 15.9%, 15.6%, and 16.3% riverine NO_3^- were found to derive from nitrogen fertilizer source in classes I, II, and III, respectively. In addition to other pollution sources, industry wastewater was considered to be another important contributor in classes II and IV because of it accounting for 14.6% and 20.9% riverine NO_3^- for these two classes. Comparing the bi-plots, Cl^- and MCMC mixing model results illustrated that both methods were consistent in identifying municipal sewage as a primary pollution source. However, MCMC mixing model appeared to make a more precise identification of not only the dominating sources, but also the other probable sources, which could not be inferred from bi-plots methods (**Fig. 5**).

In a whole, the comprehensive isotope tracing approach showed dramatical potential to evaluate nitrate pollution sources in surface waters across the typical rural-urban interface. The riverine NO_3^- source apportionment results in this study were practical and defensible, the reasons are listed below.

Annual domestic sewage discharge within the watershed is \sim 20 million tons in 2000 (Luo et al., 2019). Given the population increased from 7.4 to \sim 9.2 million during 2000 to 2019, we believe that the current annual sewage discharge is more than 20 million tons. Today, despite most of domestic sewage (> 95%) were collected and then transported to waste water treatment plants published by Wenzhou Municipal People's Government (2018), some sewage are entering to river segments from sanitary and combined sewer overflows caused by storm flow, or ageing, leaking sewer infrastructure of the study region. Locations of several waste water treatment plants are away from Ou River, Fei-Yun River or East China Sea; as such, a considerable proportion of treated waste water, which still contains high level of nitrogen concentrations ($\text{TN} > 15 \text{ mg/L}$, GB18918-2002) (State Environment Protection Bureau of China, 2002), ultimately discharges into the nearby river. Consequently, it is reasonable that the MCMC mixing model revealed municipal sewage contributed most riverine NO_3^- .

Moreover, large volumes of domestic/industrial wastewater currently and historically discharged directly into the river system. Some of nitrogenous pollutants in waters would ultimately stay in the sediment

environment as a legacy and internal nitrogen pollution source. Nitrogen-rich sediments would trigger river water re-contamination by releasing nitrogen into the water column based on concentration gradient between sediment and its overlying water. Guo et al. (2010) reported that it is disadvantageous for nitrogen release when the overlying water is seriously polluted, while it benefits for nitrogen release under condition of the overlying water quality is improved. Considering the improvement of surface water quality along with high turbulence caused by frequent boating activities, the overlying water of the WRT River exhibited conditions likely to release nitrogen from river sediments. Thereby the sediment was recognized as a moderate secondary NO_3^- contributor.

Furthermore, Wenzhou was well known for the birthplace regarding entrepreneur activities in China. There were many small and medium sized commercial enterprises, such as leather products, printing and dyeing, electroplating, chemical products, and machinery and hardware manufacturing (Xia et al., 2019). These small, old factories lacking proper disposal or treatment systems often discharge wastewater to the river or drainage without formal approvals and thus contributed appreciable nitrogen to the receiving segments of the WRT River in classes II and IV.

Another major reason is the high rate of fertilization in the region. The Wen-Rui plain is a traditionally agricultural region in Zhejiang province. Typical agricultural crops in the watershed include fruits (melons, oranges, bayberry), vegetables, rice, sweet potato, flower gardening, soybeans and tea. The application rates of nitrogen fertilizer in this region are ~ 300 kg N/ha (Wenzhou Statistic Bureau, 2013) with only $\sim 35\%$ can be absorbed by crops (Yu and Shi, 2015). These un-utilized fertilizers coupled with soil nitrogen will subsequently lost into the river by rainfall-runoff. So, appreciable NO_3^- loads might have been ascribed to nitrogen fertilizer and soil nitrogen for classes I, II, and III.

Finally, in particular, atmospheric deposition was identified as an important source, comprising 12.7 – 19.6% of riverine NO_3^- . This result was partly supported by Liao (2015), which suggested that atmospheric nitrogen depositions in this study region were up to 33.12 – 48.24 kg N/ yr. These atmospheric deposition-derived nitrogen pollutants are directly input into river system *via* surface runoff/erosion because high percentage of the impervious surface of the WRT River watershed. Therefore, atmospheric deposition had a great impact on the riverine nitrate.

3.6 Management implications for nitrate pollution improvement in rural-urban areas

Based on the NO_3^- source contributions calculated above, effective strategies for mitigating riverine NO_3^- pollution in surface water across the rural-urban interface should consider: (1) developing sewage pipeline systems to achieve rain and sewage diversion and renewing leaking sewer pipes; (2) improving wastewater treatment processes of wastewater treatment plants to reduce nitrogen concentrations of treated sewage effluents; (3) reinforcing the supervision of factories wastewater disposal; (4) increasing the fertilizer utilization rate included adopting slow-released fertilizer using fertilizer according to the crop demands and soil nutrients, precision fertilization, and deep placement of fertilizer in the root zones of the crops; (5) diverting water from the nearby river/reservoir (e.g., Ou river in this study), where nitrogen

concentrations are much lower than those in surface water across rural-urban interface, is capable of mitigating nitrogen pollution effectively within a short period of time. In addition to input control actions of municipal/industrial/agricultural effluents, we should pay particular attention to internal and natural sources given their appreciable contributions of NO_3^- . Thus, there is an urgent need to periodic dredging for avoiding re-contamination of river sediments. Besides, best management practices (e.g., rain garden, constructed wetland, grass swale, riparian plantings, buffer strips) should be developed to reduce runoff from atmospheric deposition, soil nitrogen as well as municipal/industrial/agricultural effluents, and further relieve riverine NO_3^- sourced from natural sources.

4. Conclusions

In this study, the spatial variations of water chemistry measurements as well as dual nitrate isotopes were investigated in the Wen-Rui Tang River across the rural-urban interface of the Southeast China. Our study found that stable nitrate isotopes combined with MCMC mixing model are very useful for quantitatively evaluating riverine NO_3^- source contributions, particularly in rural-urban circumstances where current available GIS-based models are unsuitable. Distributions of $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ indicated that riverine NO_3^- originated predominantly from the nitrification process. By contrast, evidence for microbial denitrification process was not found, which was accordant with the generally aerobic conditions (mean DO > 2.0 mg/L) associated with the surface waters. The cross-plot of $\delta^{15}\text{N-NO}_3^-$ versus $\delta^{18}\text{O-NO}_3^-$ and MCMC mixing model found municipal sewage was likely to be the dominant nitrate source. However, the MCMC mixing model provided more detailed information on the predominant NO_3^- sources, as well as the other potential sources. This model showed that riverine NO_3^- source contributions varied with four land-use categories produced by hierarchical cluster algorithm. The obtained results highlighted that river nitrogen pollution control necessitates particular attention to internal (river sediments) and natural (atmospheric deposition) sources management in addition to input control actions of municipal/industrial/agricultural effluents. Overall, the comprehensive isotope tracing approach articulated distinct advantages of being able to identify the nitrate pollution sources in surface waters across the rural-urban interface quantitatively and thereby will be an efficient tool for nitrate pollution control of rural-urban interface environment.

Declarations

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Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Availability of data and materials

All data generated or analyzed during this study are included in this published article.

Consent for publication

Not applicable.

Ethics approval and consent to participate

Not applicable.

Authors' contributions

Xiaoliang Ji: Conceptualization, Methodology, Formal analysis, Investigation, Writing-original draft, Writing-review&editing.

Xu Shang: Conceptualization, Methodology.

Leilin Shu: Investigation.

Kun Mei: Investigation.

Zheng Chen: Investigation.

Yue Yang: Investigation.

Zhengfeng Wang: Investigation.

Randy A. Dahlgren: Formal analysis, Writing-original draft, Writing-review&editing,

Minghua Zhang: Conceptualization, Writing-original draft, Writing-review&editing, Funding acquisition.

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Figures

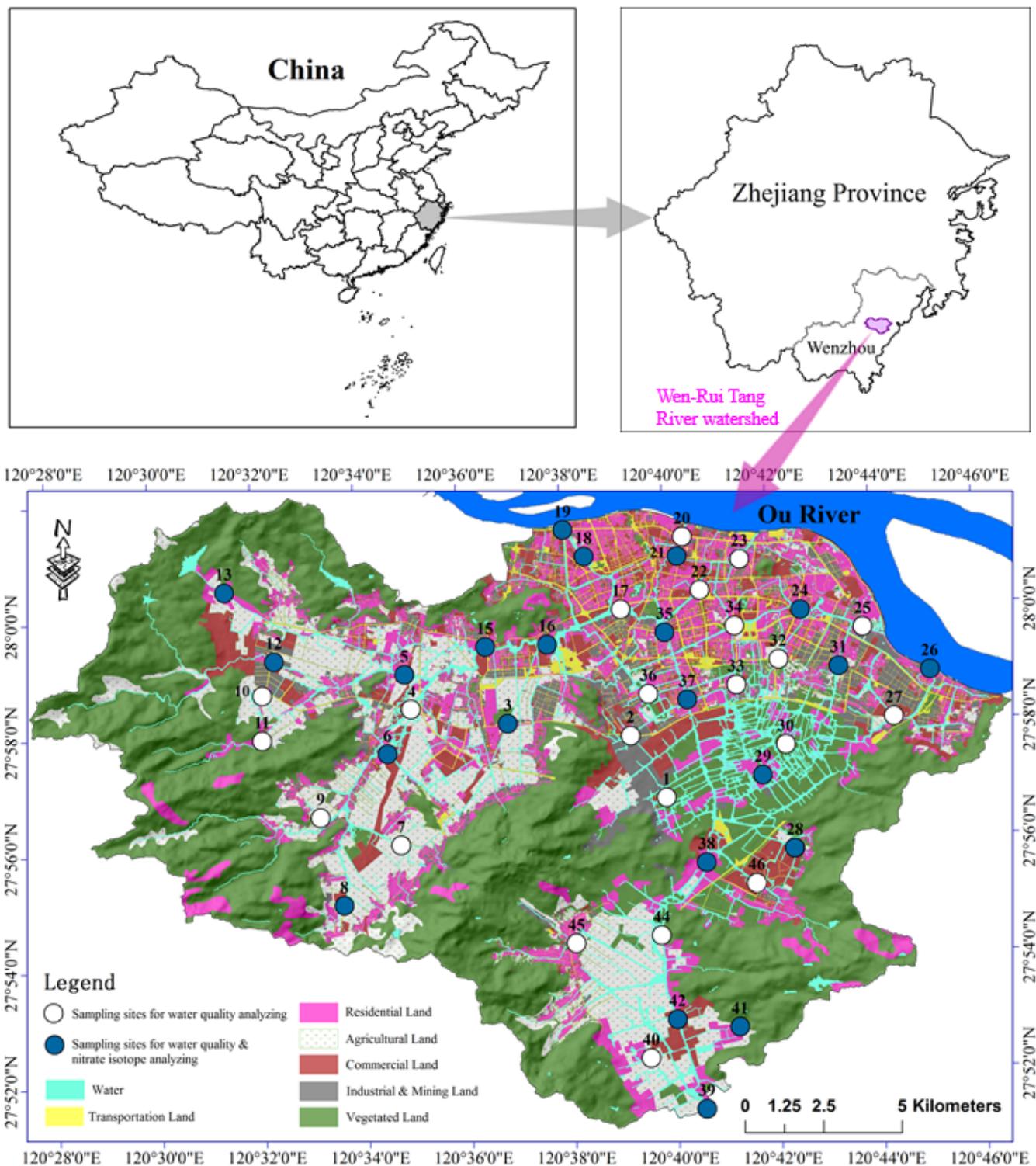


Figure 1

Location, sampling sites and land-use map of the Wen-Rui Tang River watershed. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

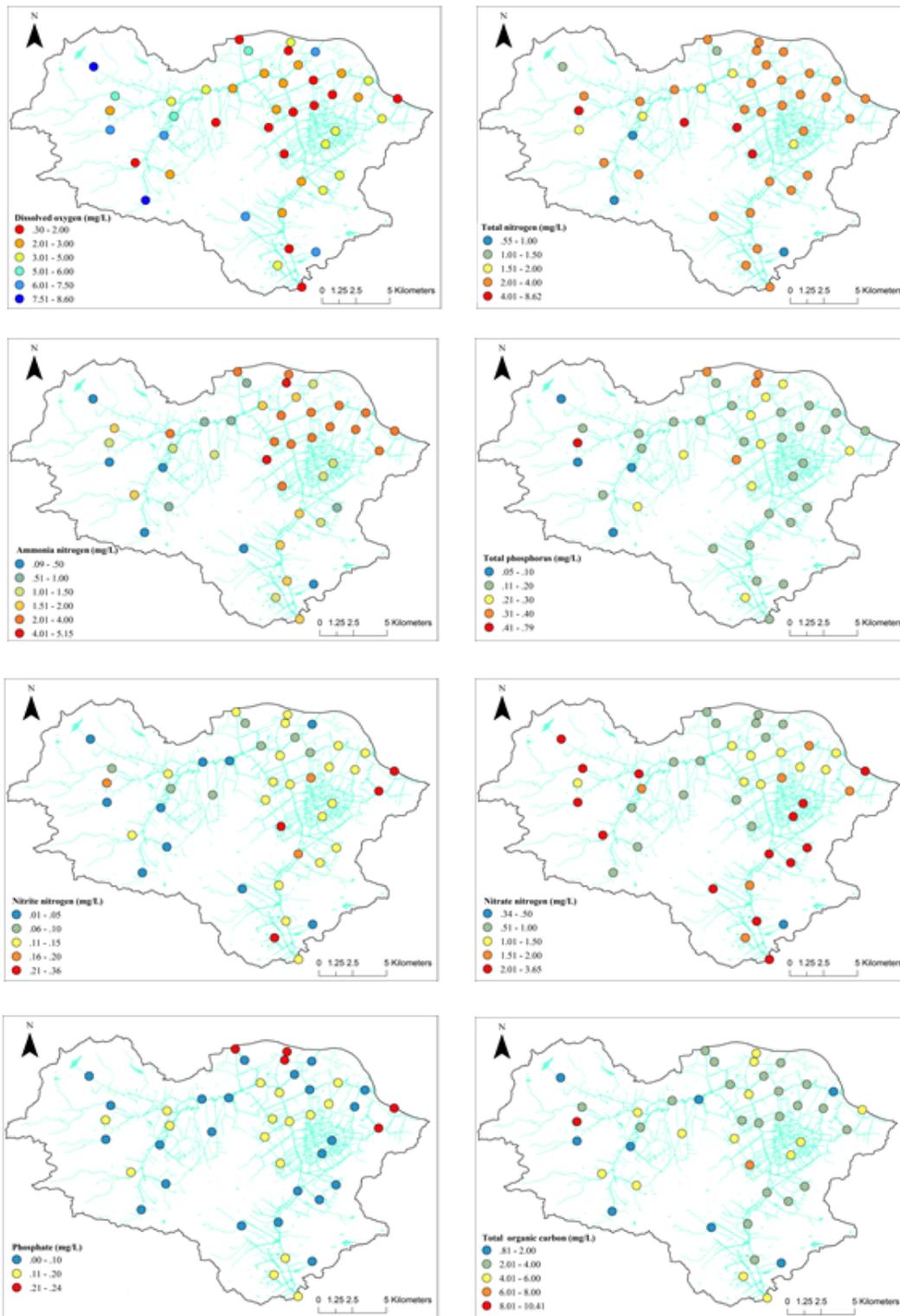


Figure 2

Spatial distribution of water quality parameters. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

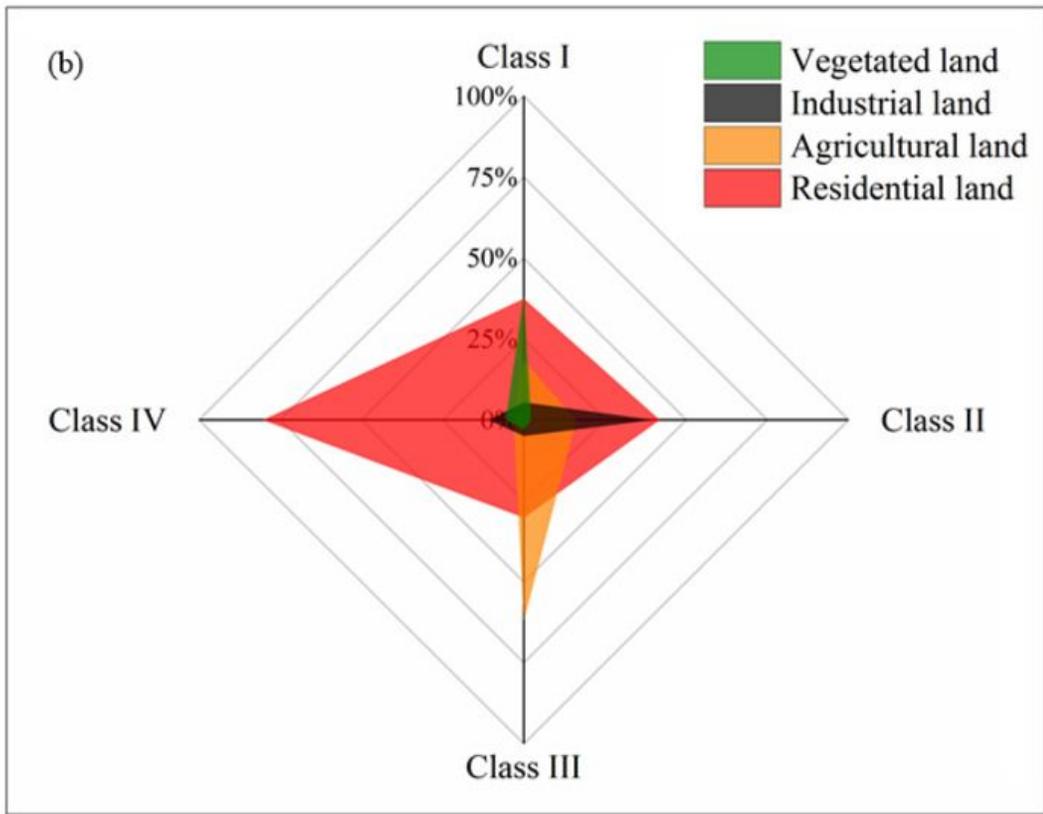
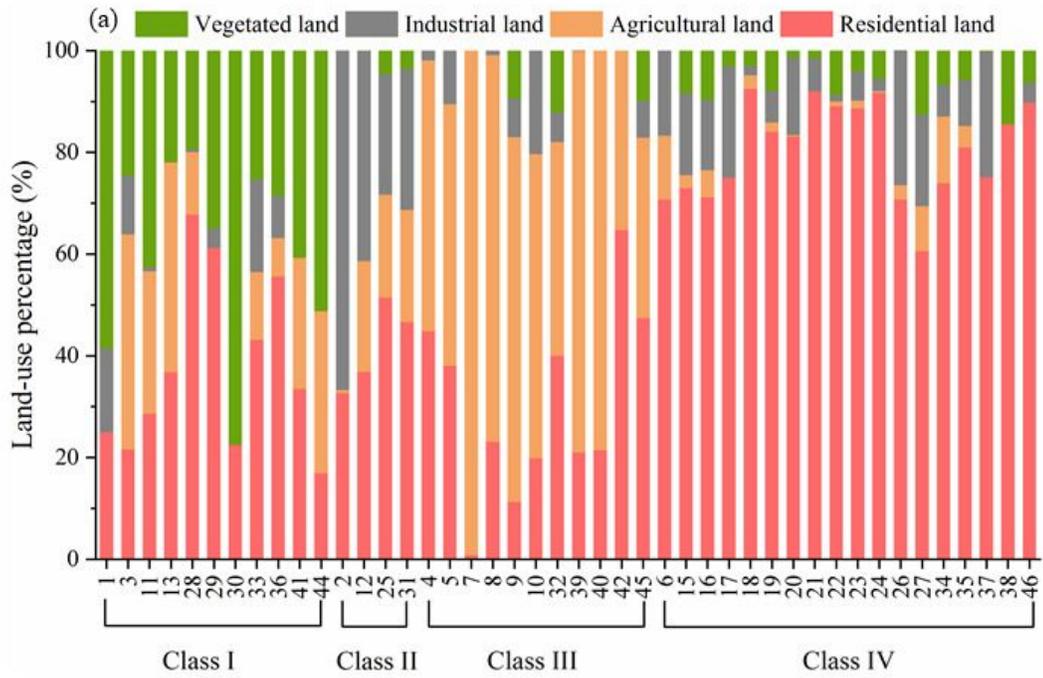


Figure 3

(a) Land-use characteristics of 44 sampling sites, and (b) different land-use percent of the four land-use classes (Class I ecological, Class II industrial, Class III agricultural, Class IV urban).

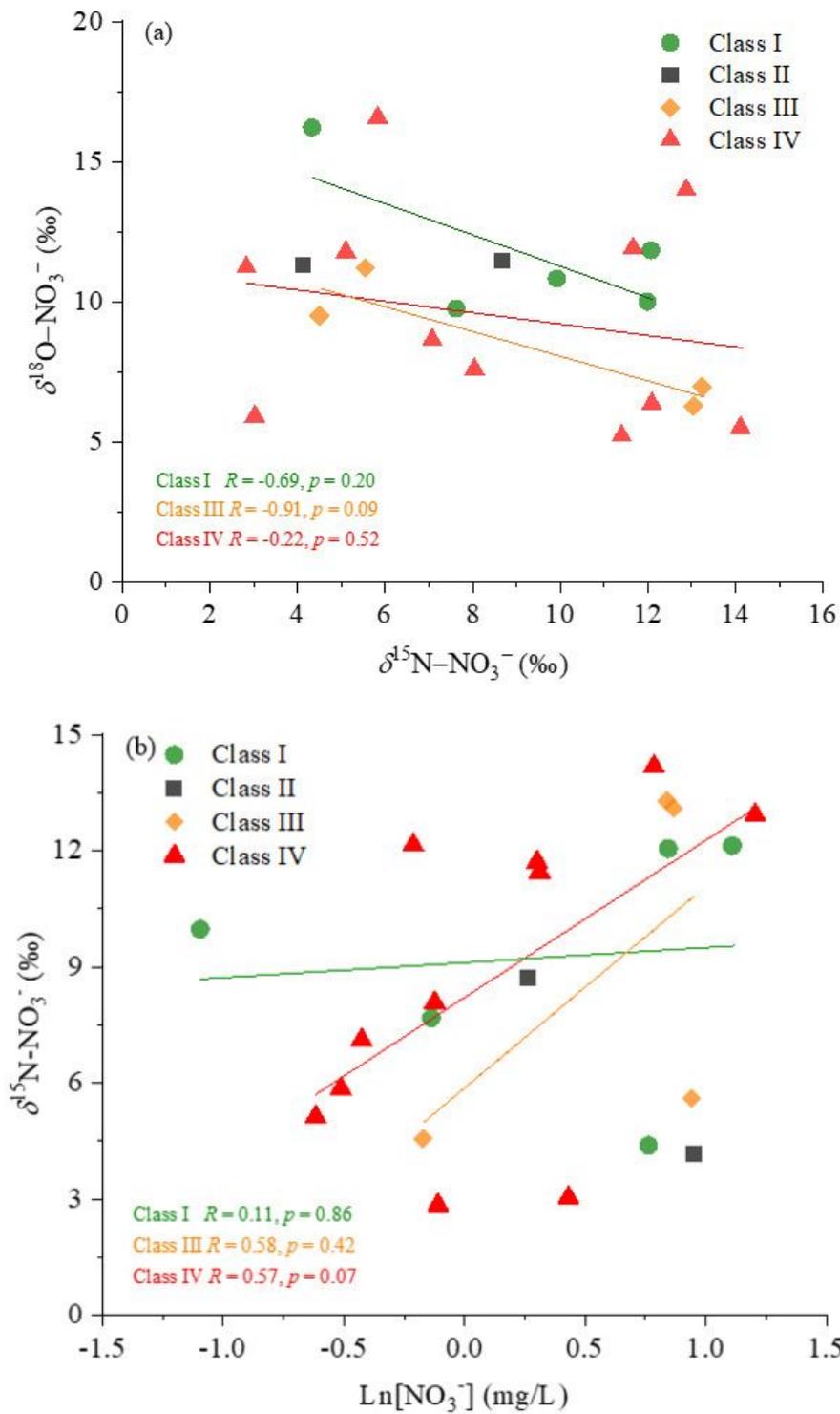


Figure 4

(a) Correlation diagram between $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ values, and (b) relationship between $\delta^{15}\text{N-NO}_3^-$ and NO_3^- -N concentrations (There was no correlation for class II due to only two sites in this class).

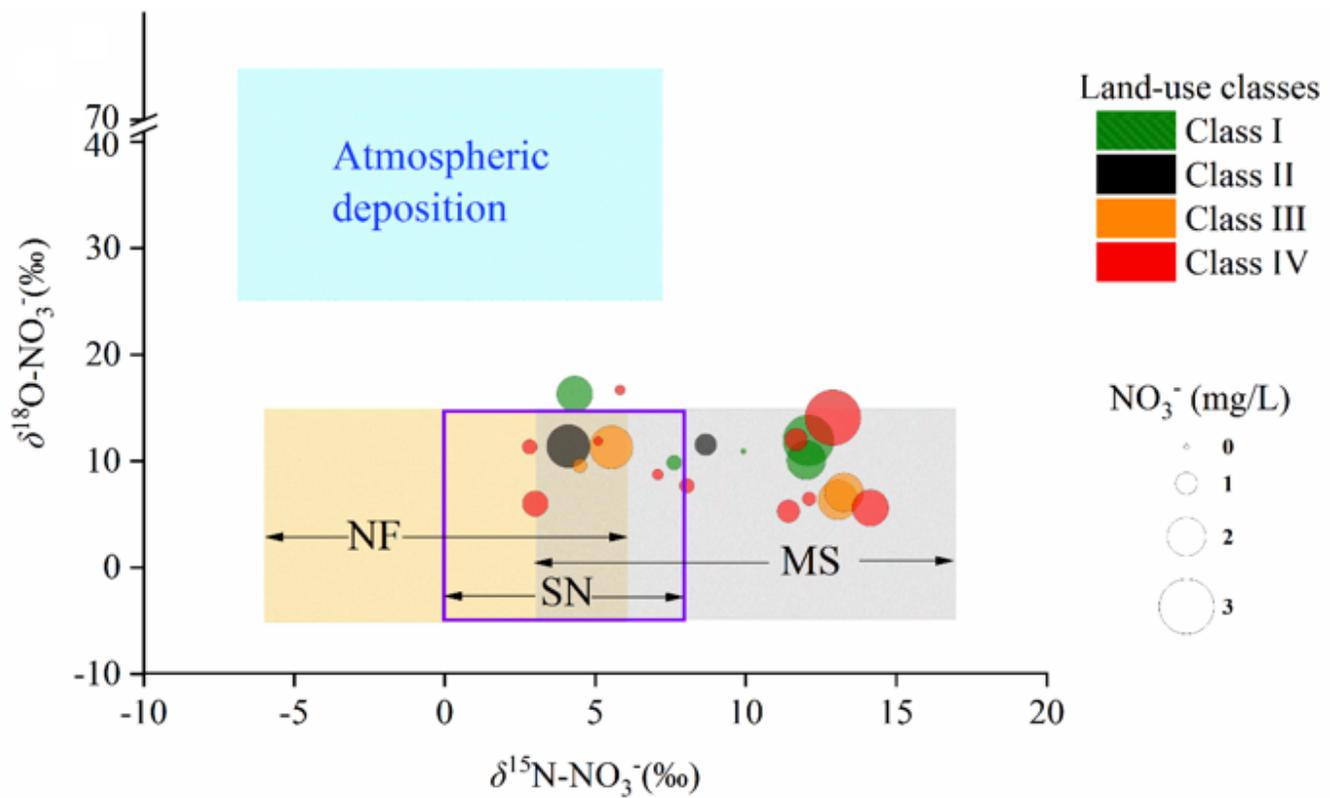


Figure 5

Isotopic compositions of $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ for surface water samples together with typical nitrate sources. NF, SN, MS denote nitrogen fertilizer, soil nitrogen, and municipal sewage. The isotopic composition ranges of the four potential sources were adapted from Nestler et al. (2011) with updated values from Xu et al. (2014).

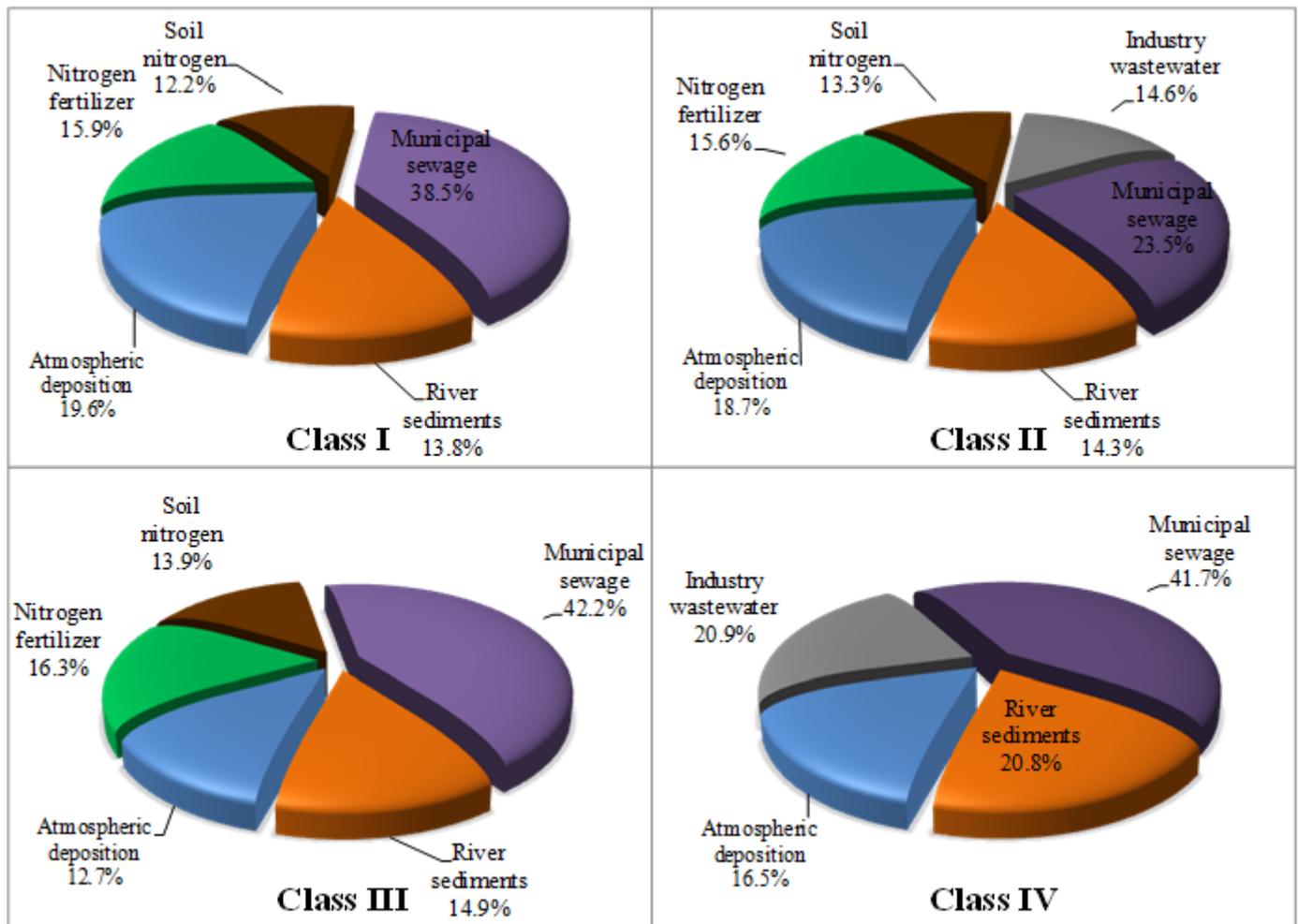


Figure 6

Mean proportional contribution of potential local nitrate pollution sources at different land-use classes (Class I ecological, Class II industrial, Class III agricultural, Class IV urban) according to the Markov Chain Monte Carlo mixing model.