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The long-term impact of urbanization on nitrogen patterns and dynamics in Shanghai, China

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ABSTRACT

Urbanization is an important process that alters the regional and global nitrogen biogeochemistry. In this study, we test how long-term urbanization (1952–2004) affects the nitrogen flows, emissions and drivers in the Greater Shanghai Area (GSA) based on the coupled human and natural systems (CHANS) approach. Results show that: (1) total nitrogen input to the GSA increased from 57.7 to 587.9 Gg N yr⁻¹ during the period 1952–2004, mainly attributing to fossil fuel combustion (43%), Haber–Bosch nitrogen fixation (31%), and food/feed import (26%); (2) per capita nitrogen input increased from 13.5 to 45.7 kg N yr⁻¹, while per gross domestic product (GDP) nitrogen input reduced from 22.2 to 0.9 g N per Chinese Yuan, decoupling of nitrogen with GDP; (3) emissions of reactive nitrogen to the environment transformed from agriculture dominated to industry and human living dominated, especially for air pollution. This study provides decision-makers a novel view of nitrogen management.

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1. Introduction

Human activities have more than doubled the global nitrogen inputs to terrestrial ecosystems and accelerated the nitrogen cycle to satisfy human's food, energy, fiber and other products and welfare needs (Erisman et al., 2008; Canfield et al., 2010). However, these perturbations to nitrogen cycles have also resulted in significant environment issues globally (Compton et al., 2011; Davidson et al., 2012). For example, more than half of the global top ten environmental issues (global warming, ozone depletion, biodiversity loss, acid rain, loss of forests, desertification, air pollution, water pollution, marine pollution and solid waste pollution) were related to the changes to nitrogen cycle in the 20th century (Gruber and Galloway, 2008; Compton et al., 2011; Sutton et al., 2011), especially in urbanized regions. Currently, over half of the population live in urban area (Grimm et al., 2008a), and human have substantially altered the nitrogen cycle in urbanized region even globally through urbanization related activities (Kaye et al., 2006; Duh et al., 2008; Grimm et al., 2008b; Ramalho and Hobbs, 2012).

Within urbanized regions, nitrogen cycles are mediated by complex interactions between human and natural factors that result in variations on the sources, magnitude, spatio-temporal patterns and drivers of the Nr fluxes (Kaye et al., 2006; Grimm et al., 2008b; Alberti et al., 2011). However, ecologists have shunned the ecological researches in urban areas owing to little knowledge to treat human's role on the biogeochemical cycles (Kaye et al., 2006; Grimm et al., 2008a; Gu et al., 2011). Thus, comprehensively quantifying changes of nitrogen cycles in urbanized region, as well as understanding the effects of human factors, such as urbanization, economic development, on the variations of reactive nitrogen (Nr) fluxes, have been a crucial topic in global biogeochemical research.

Shanghai is one of the most developed and urbanized regions in China (Shao et al., 2006). The population tripled (from 5.7 to 17.7 million), urban built-up area expanded over 14 times (from 78.5 to 1179.3 km²), while the gross domestic product (GDP) increased 202 times (from 3.7 to 745.0 billion Chinese Yuan) in Shanghai during the period of 1952–2004 (NBSC, 2005; Zhao et al., 2006). Currently, the urban built-up area has accounted for ~20% of the total area in Shanghai, much higher than the average value worldwide (about 1–3%, Grimm et al., 2008a). The expanded urban area is mainly converted from cropland in the GSA (Zhao et al.,

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2006). It intensively alters the regional nitrogen cycle since both the urban area and cropland are hotspots of nitrogen fluxes but have different effects on nitrogen cycle (Gu et al., 2009; Svirejeva-Hopkins et al., 2011). This rapid urbanization process in the GSA has resulted in a series of consequences on regional even global environment and human health. For example, the recorded inorganic nitrogen deposition rate was 78 kg N ha^{-1} (Zhang, 2006), much higher than the average value worldwide (Reay et al., 2008), and rapid degradation of water quality related to Nr pollution was also observed (Ren et al., 2003). Therefore, taking Shanghai as a case is unique and typical to test how long-term rapid urbanization affects regional nitrogen cycle and further changes the environment. The outcomes of this study are not only valuable for China as well as developing countries in the world.

The primary purposes of this study are to investigate how and why the Nr fluxes vary on spatio-temporal scale over the past half century and how the long-term urbanization affects the nitrogen patterns and dynamics in Shanghai. To achieve these goals, we conduct a full cycle analysis based on the coupled human and natural systems (CHANS) approach to cover and integrate all specific Nr fluxes and their interactions that can identify the detail sources of Nr emission to the environment. The CHANS approach is an explicit acknowledgment that human and natural systems are coupled via reciprocal interactions, such as material flows (Liu et al., 2007; Alberti et al., 2011). It is a comprehensive way to fully analyze the patterns and processes of nitrogen cycle and further assess how human and natural factors affect these patterns and processes. Thus, in this study, we quantify the variations in Nr fluxes both on temporal (from 1952 to 2004) and spatial (land use) scales and the causes of variations of Nr fluxes by considering natural and human factors via the CHANS approach. Finally, we analyze how to mitigate the negative effects of disturbed nitrogen patterns and dynamics during the urbanization.

2. Methodology and data

2.1. Study area and system boundary definition

To integrate the anthropogenic originated and natural originated nitrogen fluxes into the CHANS, we take the Greater Shanghai Area (GSA) as study area, including Shanghai city and its periphery cropland and wild-land, which all belong to the Shanghai district. Nitrogen cycle in the whole Shanghai district is affected by urbanization and policy regulations (e.g., Reform and Opening up). Therefore, taking the GSA as study area is beneficial to analyze how socioeconomic development

impacts regional nitrogen dynamics. The GSA locates at eastern coast of China with latitude from $30^{\circ}40'N$ to $31^{\circ}53'N$ and longitude from $120^{\circ}51'E$ to $121^{\circ}12'E$ (Fig. 1). The total area of the GSA is 6340.5 km^2 , of which cropland, urban built-up area, and natural land (mainly including water bodies, forest, urban green land) accounting for $\sim 40\%$, 20% and 40% , respectively (Zhao et al., 2006). The GSA belongs to humid subtropical climate with an annual precipitation of 1200 mm and a mean annual temperature of 18.1°C .

The horizontal boundary of the GSA follows the district plan (Fig. 1). The vertical boundary definition follows Gu et al. (2009); the upper boundary is defined as 1000 m above the ground surface taking into account nitrogen deposition; the lower boundaries consider the thin soils in mountainous regions, deep groundwater in lowlands, and other ground media above the bedrock.

2.2. System dynamics

The hierarchical structure of the CHANS approach is established based on the mutual services among different groups in this study (More details can be seen in Supplementary material Table S1). The GSA is divided into four functional groups: processor, consumer, remover, and life-supporter, and further to 13 subsystems (the forest and grassland was integrated into one subsystem in this study owing to the relatively small area of grassland in the GSA). The CHANS approach seeks understanding of the complexity through the integration of knowledge of constituent subsystems and their interactions (Liu et al., 2007). This involves linking sub-models to create coupled models capable of representing human (e.g., economic, social) and natural (e.g., hydrologic, atmospheric, biological) subsystems and, most importantly, the interactions among them (Gu et al., 2011; Alberti et al., 2011). The diagram of CHANS is useful in identifying the crucial system components and flows, and the consequences of linkages between subsystems, as well as analyzing the role of humans in the CHANS (Fig. 2).

The forms of nitrogen inputs and cycling refer to Nr (Galloway et al., 2008), including organic nitrogen, ammonium ($\text{NH}_4\text{-N}$ in water and NH_3 in air), NO_x , N_2O , and nitrate. Inputs from outside the GSA include Haber–Bosch nitrogen fixation (including synthetic fertilizer and industrial Nr use), fossil fuel combustion, biological nitrogen fixation, feed and food import, upstream riverine Nr inputs, etc. Outputs primarily include riverine Nr export to the sea, atmospheric export via gaseous Nr, nitrogen product export, denitrification, etc. Most Nr in the GSA is transferred among subsystems, for example, human excreta can be deliberately recycled into cropland as manure that is then absorbed by crops or volatilizes to the near-surface atmosphere subsystem.

2.3. Data collection and calculation strategy

Data sources of this study mainly derive from governmental statistical yearbooks and bulletins (NBSC, 2005; SMSB, 2005), which supplied the best available data for the quantification of anthropogenic nitrogen in China. Meanwhile, data from published papers is also retrieved for meta-analysis and comparison (e.g., Gu et al., 2009). All the data can be divided into two categories: one is basic information of the GSA, such as population, GDP, land use, fertilizer usage, and crop/livestock/aquaculture production, which is mainly taken from the statistics of yearbook (NBSC, 2005); the other is coefficients that used for the calculations of nitrogen

Fig. 1. Land use and surface water network in the Greater Shanghai Area (GSA) and its geographical location. (a) Aerial view of the downtown area. (b) Map showing the location, land cover and land use of Shanghai. Red regions indicate urban land in 2004, highlighting red regions indicate urban land in 1952, and blue regions indicate water bodies while others indicate cropland and rural land. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 2. Nitrogen cycle in the GSA based on the coupled human and natural systems (CHANS) framework. Arrows represent nitrogen fluxes; internal transfers of nitrogen fluxes are shown as dashed arrows, system nitrogen inputs and outputs are shown as solid arrows, and nitrogen branch fluxes are generated when two crossing lines possess a node; solid rectangles represent subsystems or main nitrogen input/output terms. All values are given in Gg N yr^{-1} ($1 \text{ Gg} = 10^3 \text{ kg}$). For simplification, human subsystem and pet subsystem are integrated into one subsystem, and forest and grassland are integrated into one subsystem.

fluxes, such as biological nitrogen fixation rate, denitrification rate, excretion generated rate of livestock, which are mainly from research works or reports.

A detailed nitrogen budget is conducted via mass balance approach (Kaye et al., 2006; Gu et al., 2009; Hong et al., 2011). The nitrogen balance calculations of the whole system, functional group and subsystem follow the basic principle:

$$\sum_{h=1}^m \text{IN}_h = \sum_{g=1}^n \text{OUT}_g + \sum_{k=1}^p \text{Acc}_k \quad (1)$$

where IN_h and OUT_g represent the different nitrogen inputs and outputs, respectively, and Acc_k represents the different nitrogen accumulations. $h = 1 - m$ represents the nitrogen input terms, e.g., fertilizer, deposition, biological nitrogen fixation; $g = 1 - n$ represents nitrogen output terms, e.g., denitrification, runoff to surface water, NH_3 emission; $k = 1 - p$ represents nitrogen accumulation terms, e.g., organic nitrogen accumulated in cropland soil, nitrate accumulated in groundwater, industrial products accumulated in human settlement. We used the Nitrogen Cycling Network Analyzer (NCNA) model to compile the data set, and calculate all the nitrogen fluxes (Min et al., 2011). This model can standardize the parameter collections for the nitrogen flux calculations, and automatically calculate the nitrogen fluxes and their interactions based on the mass balance approach. More details of data sources and calculation can be seen in [Supplementary material](#).

3. Results and discussion

3.1. Nitrogen input to the GSA and its drivers

Total nitrogen input to the GSA increased ~ 9 times from 57.7 Gg N ($1 \text{ Gg} = 10^3 \text{ kg}$) in 1952 to 587.9 Gg N in 2004, mainly attributed to fossil fuel combustion, nitrogen fertilizer, industrial Nr use (nylon, plastic, paint, dye, etc.), food/feed import and biological nitrogen fixation (Fig. 3a). During this period, the contributions of different inputs to the total input exhibited non-linear variations. Biological nitrogen fixation remained stable, ranging from 15 to 20 Gg N yr^{-1} ; however, its contribution decreased from 26.2 to 3.1% owing to the substantial increase of anthropogenic nitrogen input, which has enormously altered the patterns of nitrogen input to the GSA. Haber–Bosch nitrogen fixation (including nitrogen fertilizer and industrial Nr use) fluctuated enormously (Fig. 3a): slowly increased before 1962, then rapidly increased till 1980 (accounting for 66% of the total nitrogen input in 1980), remained stable after

Fig. 3. Nitrogen (N) balance of the GSA from 1952 to 2004. (a) Total nitrogen input. (b) Total nitrogen output and the nitrogen use efficiency (NUE) of the agricultural subsystems. “Cultural Revolution” is a social-political movement that took place in China from 1966 to 1976. “Reform and Opening up” refers to the program of economic reforms called “Socialism with Chinese characteristics” in China that were started in 1978 and are ongoing in the early 21st century. FFC = fossil fuel combustion, BNF = biological nitrogen fixation.

1980, and started to decrease since 2000. Fossil fuel combustion and food/feed import exhibited a steady increase during 1952–2004, accounting for two third of total nitrogen input to the GSA in 2004 (Fig. 3a). These findings revealed that human activities have dominated about 97% of the total nitrogen input to the GSA, compared to the value of 73% that in 1952.

Population growth, policy regulation, economic development and urban expansion intensively affect the regional nitrogen patterns and dynamics (Grimm et al., 2008b; Gu et al., 2011; Svirejeva-Hopkins et al., 2011). Population linearly correlates to the total nitrogen input with per capita nitrogen input increasing from 13.5 to 45.7 kg N yr⁻¹ in the GSA (Figs. 4 and 5a). Population driven nitrogen fluxes vary with policy regulations and economic development (Aneja et al., 2009; Svirejeva-Hopkins et al., 2011). For example, the “Great Cultural Revolution” event (from 1966 to 1976) is an important policy regulation that affects China’s society. During the Cultural Revolution, annual population growth rate decreased from 3 to -0.2%, annual GDP growth rate decreased from 13 to 8%, and food import reduced by 50% in the GSA (Fig. 4b). These changes led to the annual nitrogen input increase rate decreased from 17 to 6%. However, owing to the population decrease, the per capita nitrogen input increased rapidly, from 13.7 to 32.3 kg N yr⁻¹ during the Cultural Revolution (Fig. 4a), although the total nitrogen input increase slowed down (Fig. 3a).

After the Cultural Revolution, China implemented “Reform and Opening up” policy (Zhao et al., 2006), which largely increased the nitrogen input, promoted the increase in population and GDP, and expansion of urban area in the GSA (Fig. 4b). For example, the per capita food consumption had increased from 11 g N day⁻¹ in 1982 to 19 g N day⁻¹ in 2002 within the GSA (Zhou et al., 2006), close to Hong Kong and other developed cities (20 g N d⁻¹) (FAO, 2012). This substantially promoted the food related Nr input (e.g., food import and agricultural production) (Fig. 3a). The one-child policy, lower

Fig. 4. Nitrogen (N) input and socioeconomic development in the GSA from 1952 to 2004. (a) Per capita and per GDP nitrogen input changes. (b) Total nitrogen input, population, urban built-up area, and GDP changes. “Cultural Revolution” is a social-political movement that took place in China from 1966 to 1976. “Reform and Opening up” refers to the program of economic reforms called “Socialism with Chinese characteristics” in China that were started in 1978 and are ongoing in the early 21st century.

fertility rates as well as an increasing divorce rate all together contributed to a decrease in household size within the GSA from 4.6 persons per household in 1952 to 2.8 in 2004 (Liu and Diamond, 2005; NBSC, 2005), subsequently increasing the number of households by five million (approximately equal to the entire number of household in the Netherlands). These smaller households consume more resources leading to significant environmental consequences (Liu et al., 2003). Promoted living standard together with declined household size result in the per capita Nr discharged to surface water increasing from 1.4 kg N yr⁻¹ in 1952 to 3.4 kg N yr⁻¹ in 2004.

Generally, the nitrogen input significantly correlated to the GDP and urban built-up area (Fig. 5). But this correlation is a non-linear (logarithmic) relationship, which implies that there might be a decoupling of nitrogen input with GDP growth and urban expansion in the GSA, especially after 1995. The nitrogen input per GDP decreased sharply after the Reform and Opening up policy, from 14.2 to 0.9 t N per Yuan GDP in the GSA (Fig. 4a). This could be explained by the following reasons: (1) the proportion of nitrogen intensified secondary industry (e.g., fossil fuel related and industrial Nr use related) to total industry reduced from 77% (accounted as GDP) in 1978 to 48% in 2004, while the proportion of non-nitrogen intensified third industry (e.g., service and information industry) increased from 19% in 1978 to 51% in 2004 (NBSC, 2005; Zhang et al., 2008); (2) urban expansion sacrificed the agricultural land, which decreased by 21% from the Reform and Opening up to 2005 (Zhao et al., 2006), largely reducing the synthetic nitrogen fertilizer use; (3) the food import increased 13 times from 1978 to

Fig. 5. Relationships between total nitrogen inputs, reactive nitrogen (Nr) emitted to the environment and socioeconomic development. (a and b) Population. (c and d) Urban built-up area. (e and f) GDP.

2004 in the GSA (Fig. 3a), substantially reducing the pressure of agricultural production that decreases the nitrogen input intensity for agricultural production.

3.2. Human activities mediated nitrogen fluxes in main ecosystems

To evaluate how human activities affect nitrogen cycles among the main ecosystems of the GSA (urban, agricultural and forest), the appropriate subsystems (or portions of subsystems) are aggregated together (Gu et al., 2009). Although there is no direct anthropogenic nitrogen input like fertilizer to unmanaged forest ecosystem, which is still affected by human activity indirectly and receives elevated atmospheric deposition as high as $112 \text{ kg N ha}^{-1} \text{ yr}^{-1}$. This value was only about $30 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ in 1952 (Fig. 6), but still much higher than the average value found in Europe in 2000 ($12.1 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, de Vries et al., 2011a). The background nitrogen input is estimated at $15 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ that includes $5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ derived from natural deposition (Reay et al., 2008) and $\sim 10 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ from biological fixation (Gu et al., 2009). Generally, we can take the background nitrogen input as natural nitrogen input that is not disturbed by human activities (Gruber and Galloway, 2008). Therefore, human activities have enhanced nitrogen input to forest by about 8 times in the GSA compared with the natural nitrogen input.

Nitrogen input was promoted significantly in agricultural ecosystems, increased about 50, 89 and 20 times to cropland, aquaculture, and livestock in 2004, respectively, compared to the

background level (Fig. 6). For cropland, the total nitrogen input reached $773.2 \text{ kg N ha}^{-1}$ in 2004, increasing from $153.9 \text{ kg N ha}^{-1}$ in 1952, much higher than the average value found in Europe (less than $150 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, de Vries et al., 2011b). During the period of 1952–2004, the main nitrogen input terms changed from manure (39.8%) and biological nitrogen fixation (23.9%) to synthetic

Fig. 6. N input intensity within various ecosystems in the GSA for the year of 1952 and 2004.

fertilizer (50.4%) and manure (22.8%). The proportion of nitrogen input mediated directly by human activities has increased from 56 to 79% for cropland during this period. For aquaculture, feed and synthetic fertilizer was the main nitrogen inputs both for 1952 and 2004, accounting for approximately 80% of total nitrogen input. Owing to the relatively small farming area (SMSB, 2005), the per hectare nitrogen input of aquaculture is about 2–5 times that of cropland.

Total nitrogen input into the urban ecosystem includes industrial N_r use, fossil fuel combustion, food for human and pet (the three accounting for over 95% of the total input), etc., and reached 3751 kg N ha⁻¹ in 2004, about 250 times higher than background level in the GSA (Fig. 6). Surprisingly, the nitrogen input to the urban ecosystem in 1952 was as high as 4811 kg N ha⁻¹, larger than that in 2004, mainly owing to that the urban area in 1952 was only 7% of that in 2004. The urban expansion rate is faster than the nitrogen input increase rate, suggesting that the decoupling of nitrogen with urban expansion arises (Fig. 5c). Human activity mediated about 98% of the total nitrogen input in urban ecosystem, much higher than the forest and agricultural ecosystems, indicating that the nitrogen input intensity and human dominated proportion increase with the intensities of human perturbations to the nitrogen cycle.

The nitrogen use efficiency (NUE, nitrogen in the product leaving the system divided by the nitrogen input to the system) decreases with the increase of anthropogenic nitrogen input intensity (Erisman et al., 2011). For example, nitrogen input intensity to cropland increased from 153.9 to 773.2 kg N ha⁻¹, while the NUE decreased from 44% to 16%. Similarly, the NUE of aquaculture reduced from 14% in 1952 to 13% in 2004 with the nitrogen input increased from 732 to 1342.7 kg N ha⁻¹ yr⁻¹. Overall, the NUE for the whole agricultural ecosystem in the GSA experienced a significant decrease from 43% to 18% from 1952 to 2004 (Fig. 3b). We noticed that there was a sharp decrease of overall NUE from 1978 to 1982, which might mainly attribute to the rebound of synthetic nitrogen fertilizer use at the beginning of Reform and Opening up policy without fertilization technology improvement (NBSC, 2005). This resulted in a large amount of nitrogen surplus, which is a very important pressure for environmental problems related to nitrogen.

3.3. Emissions of reactive nitrogen to the atmosphere and hydrosphere

Emissions of N_r to the atmosphere and the hydrosphere are mainly caused by agricultural and industrial activities as well as fossil fuel combustion and human domestic wastewater alongside the urbanization in the GSA (Fig. 7). Detailed source appointments of total emissions of N_r to these media from different economic sectors are helpful for understanding the occurrence of hotspots and could be the first step in identifying appropriate and well-targeted mitigation measures (de Vries et al., 2011b). We show here the most important fluxes of N_r, i.e. total emissions of NH₃, NO_x and N₂O to the atmosphere, as well as total N_r emissions to the hydrosphere.

3.3.1. Emissions of reactive nitrogen to the atmosphere

Generally, the total emissions of N_r to the atmosphere (including NH₃, NO_x and N₂O) were 1–1.8 times that of the total emissions of N_r to the hydrosphere (including N_r to surface water and groundwater) during the period of 1952–2004 in the GSA (Fig. 3b). NH₃ was the largest source of N_r emission to the atmosphere before 1965, after which the emission of NO_x replaced NH₃ to be the largest contributor and accounted for about 80% of total N_r emission to the atmosphere in the GSA. This transformation

Fig. 7. Emission source appointments of reactive nitrogen to the environment. (a) To atmosphere. (b) To surface water. (c) To groundwater. "Cultural Revolution" is a social-political movement that took place in China from 1966 to 1976. "Reform and Opening up" refers to the program of economic reforms called "Socialism with Chinese characteristics" in China that were started in 1978 and are ongoing in the early 21st century.

indicates that the majority of N_r emission to the atmosphere shifts from agriculture dominated to industry and transportation dominated alongside the urbanization.

NH₃ emission quadrupled from 16.8 Gg N in 1952 to 68.6 Gg N in 2000, after which decreased to 56.0 Gg N in 2004 (Fig. 3b). The contribution of agriculture is rather stable across the half century in the GSA, with a highest contribution in 1980s–1990s (99%), and a lowest contribution in 2000s (97%). The turning point of NH₃ emission emerged is mainly owing to the stopping increase of application rates for nitrogen fertilizer (the largest nitrogen input). Similarly, the turning point was also found in Europe (de Vries et al., 2011a), United States (Reis et al., 2009) and other developed countries in the 1980s owing to the development of precision agriculture that improved the NUE and reduced the nitrogen fertilizer usage (Mosier et al., 2002; Aneja et al., 2009). For example, the NUE of maize production in United States has increased 36% from 1980s to 2000s (Cassman et al., 2002).

NO_x emission exponentially increased 20 times from 12.0 Gg N in 1952 to 245.4 Gg N in 2004, of which fossil fuel combustion contributed 95–99% of total emission, and the rest mainly attributed to straw burning and forest wildfire. Although there is a decoupling of nitrogen input with GDP growth and urban expansion (Fig. 5), the emission of NO_x still exhibits a rapid

increase owing to the energy supply processes, such as the promoted living standard leading to the number of private vehicles tripled from 1996 to 2004 in the GSA (SMSB, 2005).

The main sources of N_2O are biogenic sources including agricultural soils, manure management, as well as forest soils and the waste sector, accounting together for 60–90% of all N_2O fluxes in the GSA from 1952 to 2004. The most important non-biogenic sources of N_2O are fossil fuel combustion and industrial processes, such as the production of nylon, nitric acid, adipic acid and glyoxal, accounting for about 40% of total N_2O emission in the GSA in 2004. The temporal trend of N_2O emissions is thus a combination of the one observed for NH_3 (mainly agriculture) and NO_x (mainly fossil fuel combustion). Therefore, we found the N_2O emission linearly increased from 1952 to 2000, and then started to decrease with the shrink of agriculture related nitrogen fluxes (Fig. 3b).

3.3.2. Emissions of reactive nitrogen to the hydrosphere

The inputs of Nr to the surface water increased 7 times during the period of 1952–1999, from 20.5 to 187.4 Gg N yr^{-1} , and then decreased to 153.2 Gg N yr^{-1} in 2004, contributed both by point sources through domestic and industrial wastewater and diffuse sources from agriculture (Fig. 7b). Although the contributions of point source and diffuse source are both close to 50% of total emissions of Nr to the surface water in the GSA, their compositions varied across different years. For example, the contribution of domestic wastewater reduced during the Cultural Revolution (1966–1976) owing to the population and food consumption decrease, and after the Cultural Revolution, the rapid population growth and the transition of industry from secondary to third industry facilitated the domestic waste to be single largest point source emission of Nr to surface water (Fig. 7b). Meanwhile, the technological improvement in industrial sectors also largely reduced the generation and discharge of industrial wastewater (SMSB, 2005). For diffuse sources of agriculture, cropland was the single largest contributor before 1980, after which aquaculture and livestock rapidly increased to be important sources, accounting for 31% of total Nr emission to the surface water in the GSA in 2004. This transition mainly reflects the human diet changes from vegetable protein (from 72 to 43%) to animal protein (from 28 to 57%) in the GSA.

Emission of Nr to the groundwater increased from 1.4 Gg N in 1952 to 15.9 Gg N in 2004, accounted for 6–18% of total emissions of Nr to the hydrosphere (Fig. 7c). Emission sources were dominated by cropland, forest, domestic and industrial wastewater leakage before 1965, after which the cropland (50–70%) to be the single largest source to groundwater Nr accumulation.

3.4. Nitrogen surplus and the insufficient removal capacity

Although the decoupling of Nr emission with urban expansion and GDP growth also arises (Fig. 5), the rapid expansion of urban area and GDP growth still results in a large amount of Nr emission to the environment (Fig. 7). The GSA has been challenged that Nr input lagging behind its removal capacity (Fig. 2), leading to a series of ecological and environmental consequences (Zhang, 2006; Zhang et al., 2008). There is no compelling evidence that elevated Nr input must lead to the imbalance situation (Galloway et al., 2008); however, insufficient Nr removal capacity should be one of the major limit factors of the imbalance between nitrogen input and output (Gu et al., 2011). In 2004, for instance, Nr input to the processor group in the GSA was 561.8 Gg N, while the N-containing in the output products was only 48.6 Gg N (Fig. 2), most of the Nr surplus was emitted to the environment except the 135.7 Gg N was denitrified back to N_2 (Fig. 3). Emissions of Nr to the atmosphere

and hydrosphere are very important pressures for environmental problems (de Vries et al., 2011b). The qualities of surface water and groundwater within the GSA have fallen below the worst standards (30 mg N L^{-1} for groundwater and 2 mg N L^{-1} for surface water) on the indicators of total Nr concentration (Ren et al., 2003; Xia et al., 2006).

Denitrification is an important way to remove the nitrogen surplus in the environment (Kulkarni et al., 2008). Although the denitrification intensity increased from 13.4 Gg N in 1952 to 135.7 Gg N in 2004 in the GSA, its ratio to total Nr input reduced from ~25 to ~20% (Fig. 3b). The elevated Nr flux and reduced natural Nr removal capacity implied an urgent challenge for the GSA to increase the capacity of artificial Nr removal. For example, with the acceleration of wastewater treatment in the GSA, Nr contained in wastewater being directly discharged into surface water has reduced about 9 Gg N from 2000 to 2004, although the denitrifying Nr back to N_2 representing a waste of the substantial amounts of energy put into human production of Nr (Erisman et al., 2011). Meanwhile, the Nr removal during the fossil fuel combustion is another important way to remove the nitrogen surplus. For example, the NO_x concentration within the urban area of the GSA has decreased by 30% as a result of the Clean Vehicle Program implemented recently (Zhao et al., 2006). Therefore, these regulations could also promote the decoupling of nitrogen with the urbanization related socioeconomic development, especially on the emission of Nr to the environment.

3.5. Analysis of uncertainties

Our estimates still contain several uncertainties caused by the methodological assumptions, limited field survey data as well as uncertainties for the difficulties in quantifying the complex biogeochemical processes. The major limitation is the assumption of ecological homogeneity throughout cropland and forest subsystems and the lack of detailed soil nitrogen dynamics. Although the percentage of nitrogen accumulated in soil in this study was calculated using the same scale adapted in other researches for cropland soil nitrogen (Xing and Zhu, 2002) and for forest soil nitrogen (Fang et al., 2008). Ongoing soil field studies would certainly help refine our estimates.

There are also uncertainties attributed to the data from governmental statistical yearbooks, but since they adopted the same system for the statistic, the uncertainties fall in the range about $\pm 5\%$ (SMSB, 2005; NBSC, 2005). Furthermore, some parameters used in this nitrogen budgets were retrieved from literatures, which might introduce potential uncertainties. More detailed research is needed in those areas in the future to improve the estimations of nitrogen budgets.

4. Conclusion

The rapid urbanization and the alongside policy regulations have reshaped the nitrogen patterns and dynamics in the GSA from 1952 to 2004. The nitrogen input has increased about 9 times during this period, and greatly promotes human's welfare via agricultural and industrial production as well as energy supply; however, the insufficient Nr removal capacity leading to the nitrogen surplus accumulated in the environment, especially for the emission of NO_x to the atmosphere (20 times) and Nr to the groundwater (10 times), resulting in a series of ecological and environmental consequences.

Human activities greatly enhance the nitrogen input intensities to the ecosystems along the gradient from forest to agricultural, further to urban ecosystems, mainly attributing to fossil fuel combustion and Haber–Bosch nitrogen fixation with the

urbanization during the period of 1952–2004. The main sources converted from agriculture to industry and transportation for air Nr pollutants, and from agriculture to industry and human for surface water Nr pollutants, while maintained as agriculture for ground-water Nr pollutants. Nitrogen flux exhibits a slow growth with urban expansion and economic development indicating a decoupling of nitrogen with socioeconomic development. Our results therefore suggest that although the urbanization process could elevate the nitrogen fluxes and alter the composition of nitrogen flows, the decoupling of nitrogen with socioeconomic development indicating a low nitrogen future.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.envpol.2012.07.015>.

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