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RESEARCH ARTICLE

Quantitative evaluation of reactive nitrogen emissions with urbanization: a case study in Beijing megacity, China

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Abstract The rapid increase in anthropogenic nitrogen (N) load in urbanized environment threatens urban sustainability. In this study, we estimated the amount of reactive N (Nr) as an index of N pollution potential caused by human activities, using the megacity of Beijing as a case study. We investigated the temporal changes in Nr emissions in the environment from 2000 to 2012 using a multidisciplinary approach with quantitative evaluation. The Nr emissions presented slightly increasing during study period, and the annual emission was 0.19 Tg N, mainly resulting from fuel combustion. Nevertheless, the Nr output intensity resulting from inhabitants' livelihoods and material production had weakened over the study period. The evaluation results showed that the environmental measures to remove Nr in Beijing were efficient in most years, suggesting that progress in mitigating the growth of the Nr load in this urban environment was significant. Further measures based on N offset are suggested that could help alleviate the environmental pressure resulting from anthropogenic Nr emissions. These could provide theoretical support for the sustainable development of megacities.

Keywords Urbanization · Reactive N · Waste treatment · Data envelopment analysis · N offset · Beijing

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Urbanization is the global multidimensional process of human development and material consumption concentrated in urban areas; the urban ecosystem is an anthropogenic heterotrophic ecosystem that strongly relies on external material consumption, especially nutrients. As an essential element for life, nitrogen (N) is consumed to support the acceleration of city development, suggesting that urbanization has a major impact on the natural N cycle (Lin et al. 2014; Liu et al. 2015). Thus, it is important to understand the adverse effects of N cycle disturbance on the environment during urbanization. The improvement in inhabitants' livelihoods and industrialization are the main factors driving the increased demand for N consumption, resulting in increased N emissions to the environment (Liu et al. 2015). Especially in the megacity ecosystem, where the urban core strongly affects its periphery areas including suburban and rural regions (Gu et al. 2009), the magnitude of this increase is larger than that driven by natural processing (Duh et al. 2008). For instances, in terms of domestic food consumption, the N embedded in proteins from food for human consumption accounts for approximately 20 % of the total N input for food production (Galloway and Cowling 2002). This means that the majority of N is released to the environment before the food is consumed. This increase in the emission of superfluous N resulting from anthropogenic activities in urban environments might be partly responsible for regional eutrophication, acid rain, air pollution, global warming, and photochemical smog, as well as a general degradation of biodiversity (Galloway et al. 2008). Therefore, urban N consumption is thought to be the one of the main sources of territorial N pollution.

There is an attempt in urban areas to recover ecosystem services, such as waste treatment, by using discharged waste in the waste treatment system (Lin et al. 2014). However, the discharge paths of N fluxes from waste treatment facilities in urban ecosystems differ from those in natural ecosystems.

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Compared with direct urban N emissions, such as vehicle emissions, indirect N emissions from waste treatment, including the treatment of gaseous pollutants, sewage, and municipal garbage, are often unknown to the general public, who are unaware of this source of N pollution. In China, the number of urban areas designated as cities increased from 132 in early 1949 to 657 in 2012 with urban populations growing from 10.60 to 52.57 %, highlighting the increasing role of cites as sources of N, even after waste treatment (Gu et al. 2013a). Liu et al. (2015) found that the amount of N from industry and wastewater treatment discharged into water bodies in Shanghai city increased significantly from 60.1×10^3 t N in 1980 to 116.2×10^3 t N in 2000, despite the spread of sewage treatment systems and improvements in treatment technology. Although their study focused on the effects of N load on the water environment, they suggested that the analysis of N load discharged to the whole of the urban environment, including air, soil, and water, should be studied to provide more understanding of N fluxes in urban socio-ecological systems undergoing rapid growth. Therefore, in this study, we focused on N emissions to the air, soil, and water in an urban environment (Lin et al. 2014).

As a "super city," that is, one where the population is over ten million more than before the start of the twenty-first century, Beijing is now facing many environmental problems because of rapid urbanization within its boundaries. To feed the increasing urban population, megacities need to consume more nutrients including N. However, the interactions of social, economic, and ecological drivers of urban ecosystem structure and function are particular challenges in the N metabolism analysis of Beijing during urbanization. In view of the dynamic variation of N flows arising from human activities in urban regions, it is important to evaluate the temporal changes in anthropogenic N emissions in densely populated cities, such as Beijing (Han et al. 2011). The specific objectives of this study were to (i) provide preliminary quantitative estimates of annual anthropogenic N emissions of Beijing and analyze their temporal variations from 2000 to 2012, (ii) evaluate the efficiency of urban pollutant removal during the study period using an economic input-output model, and (iii) construct a conceptual framework based on N offset to provide theoretical supports for the government to mitigate N pollutions resulting from urbanization.

Study area

Beijing, the capital city of China, is at the northern tip of the North China Plain (Fig. 1). By 2012, the Beijing metropolitan region was 16.411×10^3 km^2, with a residential population of around 21 million. As one of the megacities with the highest population density worldwide, the rapid urbanization of Beijing has resulted in environmental problems related to the enrichment of N load such as air pollution, eutrophication, and white pollution (Sun et al. 2008). Although Beijing city has more advanced wastewater and municipal garbage treatment facilities compared with many of the cities in China and, thus, higher disposal rates of 83 and 99.1 %, respectively (Beijing Statistics Bureau 2013), the magnitude of N loss after waste treatments remains high.

Estimating Nr emissions

Methodology

To integrate the anthropogenic N flows in Beijing, we took the Beijing metropolitan regions, including urban and suburban areas, as the system boundary for calculations, enabling us to focus on anthropogenic N emissions within this region. The forms of consumed N resulting in Nr (Galloway et al. 2008) included all activated N atoms contained in organic N, ammonium, NO_x, N_2O, and nitrate. The amount of Nr emissions was estimated by accounting for anthropogenic Nr outputs in four units based on the sources of terminal emissions: fuel combustion, wastewater treatment, municipal garbage disposal, agricultural livestock farming, and fertilizer application (Fig. 2). The emission inventories mainly included fuel combustion caused by residents and commodity production in city sectors (agriculture, industry, and commerce) and indirect release through agricultural ammonia volatilization, as well as the N losing by waste treatment including emissions from incineration, denitrifying volatilization from treatment processes, discharging of treated and untreated sewage, leaching from landfill, and discarding of untreated garbage and sludge. Waste recycling and water reuse were not considered as Nr outputs from the region because they reflect a redistribution of Nr within the urban ecosystem, rather than being discharged to the environment. Besides, it is still hard to clearly quantify the highly uncertain emissions such as ammonia emissions from combustion sources especially in China (Reis et al. 2009), and these ammonia emissions would not be included in estimation in this study.

We obtained environmental and economic data mainly from yearbooks published by Beijing Municipal Bureau of Statistics and National Bureau of Statistics of China (2000–2013a, b, c), which, in recent years, have supplied the best available data for the calculation of anthropogenic N fluxes in China (Gu et al. 2009). In this study, the official statistical data from 2000 to 2012 were used, a time period in which an improved system of up-to-date data collection was in place. Uncertainties of estimation were based on data from the yearbooks, but because they used the same system for the statistic, the uncertainties were assumed to fall in the range of ±5 % (Gu et al. 2012a). The coefficients used for the calculations of N fluxes were derived from field surveys and peer studies.
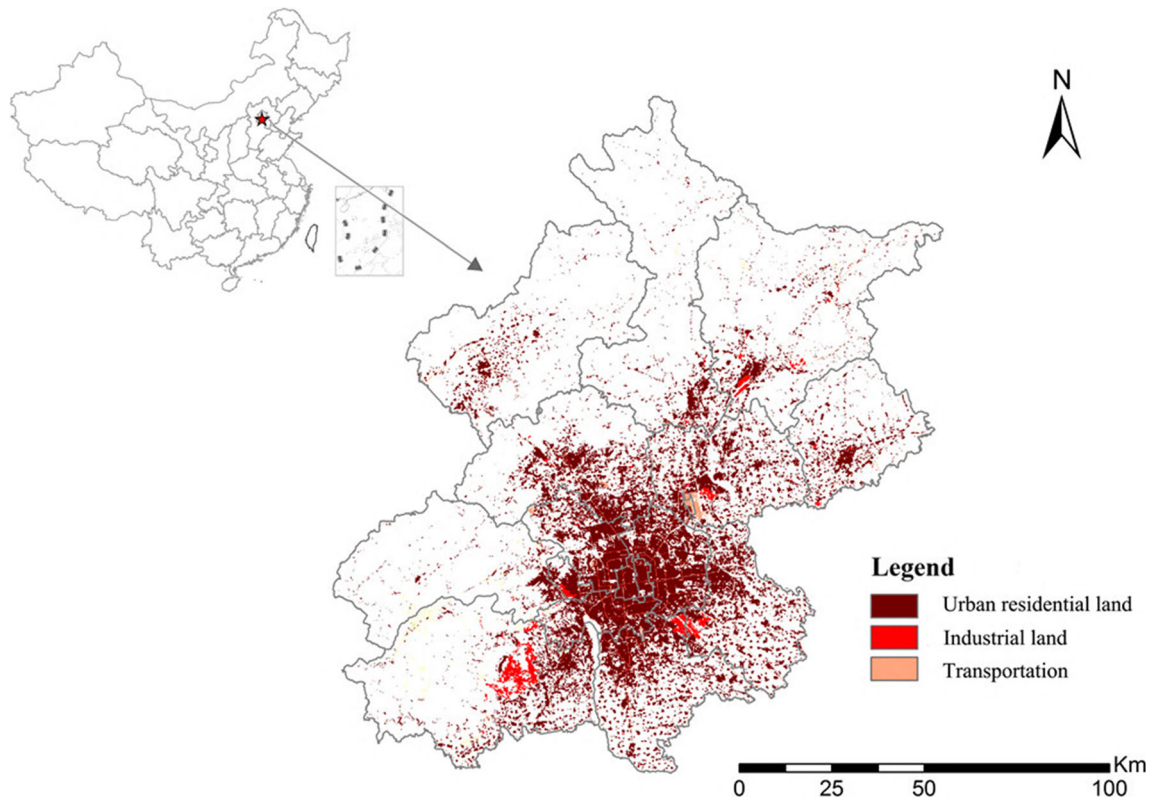
Fig. 1 Map of Beijing, China showing areas of urban residential land, industrial land, and transportation
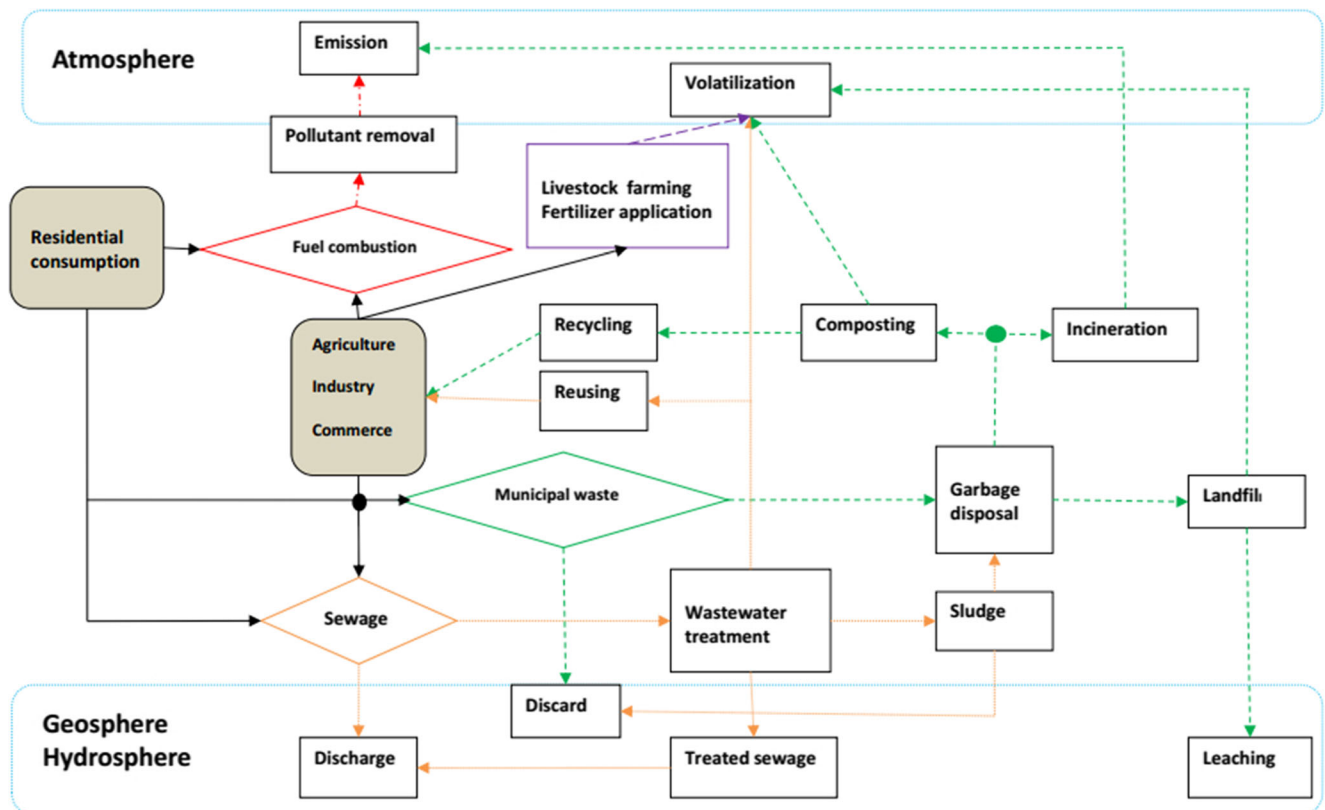

Fig. 2 Flow diagram showing emissions of forms of consumed N

Nr from fuel combustion

The development of megacities, such as Beijing, with resource scarcity strongly relies on the "exotic" fossil fuels mainly raw coal, coke, crude oil, kerosene, diesel, and natural gas. Through the combustion of these resources, the reactive N fixed in the fuel is emitted directly into the atmosphere in the form of oxynitride (mainly NO_2) since the fuel combustion sector was a less critical source of N_2O emissions in China (Reis et al. 2009), contributing to air pollution and the greenhouse effect. Generally, both historical and future emissions are derived from fuel consumption, emission factors, and assumptions on the removal efficiency by the penetration of control technologies (Zhao et al. 2013). Based on the resource consumption structure of Beijing, the sectors related to fuel combustion generally include petrochemical refining, electricity production, transportation, commercial activity, residential consumption, agricultural, and industrial and constructional activities. The emission factors for each fuel in the sectors were obtained from Gu et al. (2012b) and Zhou et al. (2014a) (Table 1), which are the most widely applied Nr emission factor datasets in China (Gu et al. 2012a, 2013b, 2015). Given that the integrated statistics of Nr removal rates (i.e., the percentages of Nr emissions reduced by pollution control measures) in the sectors mentioned above are unavailable in Beijing, we set the annual Nr removal rates based on the NO_x removal efficiency of sectors in China concluded by Hao et al. (2002) and Shi et al. (2014). Here, we calculated the Nr emissions by the bottom-up emission inventory approach using Eq. 1:

$$Q_{ij}^N = \sum_{i=1}^{n} \sum_{j=1}^{n} C_{ij} \cdot E_{ij} \cdot (1 - P_D), \tag{1}$$

where Q^N was the amount of Nr emitted by the fuel combustion with i and j representing the fossil fuels and sociometric sectors in Beijing, respectively. C_{ij} was the total amount of i fuel consumed in the j sector, and E_{ij} was the emission factor of i fuel in the j sector. P_D denoted time series of Nr removal

rates and assumed to be 3 % in 2000–2005, 4.5 % in 2005–2010, and 9 % in 2010–2012, based on NO_x removal efficiency (presuming NO_2 removal rates due to instability of NO) as 10 % in 2000–2005, 15 % in 2005–2010, and 30 % in 2010–2012.

Nr from wastewater treatment

Beijing relies on water sources from other regions because it has limited water supply of its own. For example, the national "South-to-North Water Diversion" project, which took nearly 13 years to complete, pipes water from Southern China to mitigate the water shortages in Beijing and Northern China. Widespread wastewater treatment facilities have a key role in alleviating the increase in Nr discharge into surface water. Although the number of such treatment plants in Beijing is increasing, from 4 in 2000 to 24 in 2012, with average sewage treatment rates as high as 80 %, the increased facilities are unable to treat all the wastewater from the city, which results in the discharge of raw and even treated sewage directly into the rivers. The direct and indirect discharge of sewage are assumed to be the main sources of dissolved Nr release and significantly contribute to the N pollution of urban rivers in Beijing (Gu et al. 2009; Ren et al. 2014).

As an emerging N source, wastewater treatment in urban ecosystems not only emits dissolved Nr to the environment but also results in the emission of gaseous nitrogen oxides (mainly nitrous oxide (N_2O)) and sludge, in which Nr are embedded. The former contributes to the greenhouse effect and the latter to secondary pollution if the sludge is not properly treated. The Nr emission from wastewater treatment in Beijing was estimated using Eq. 2:

$$L_S = L_g + L_{sl}(1 - P_{DSL}) + L_w + M \cdot C_{TNp}(1 - P_D), \tag{2}$$

where L_S was total amount of Nr output from wastewater treatment and M was the annual amount of sewage produced by Beijing; L_g, L_{sl}, and L_w presented the Nr outputs embedded in N_2O, sludge, and treated wastewater, respectively. P_D was

Table 1 Nr emission factors of fossil fuel combustion in different sociometric sectors (g N kg^{-1})

Sectors	Coal	Coke	Crude oil	Gasoline	Kerosene	Diesel	Natural gas[a]
Commerce	1.1	1.4	0.9	5.1	1.4	0.8	0.4
Refining	0.3	–	0.1	–	–	–	–
Construction	2.3	2.7	–	5.1	2.3	2.9	0.6
Electricity	3.0	–	2.2	5.1	6.5	8.3	1.2
Agriculture	3.0	–	–	6.7	–	9.4	–
Industry	2.3	2.7	1.5	5.1	2.3	2.9	0.6
Residents	0.6	0.7	0.5	5.1	0.8	1.0	0.4
Transportation	2.3	2.7	1.5	7.4	8.3	16.5	0.6

[a] Unit of emission: g N m^{-3}

the sewage treatment rate, whereas P_{DSL} was the sludge disposal rate. C_{TNp} was N concentrations of sewage.

The annual production of N₂O can be calculated on the basis of the total N removed during treatment (Yan et al. 2014) (Eq. 3), and the production of sludge can be estimated based on the production of mixed liquor volatile suspended solids (MLVSS), with the average percentage of it in sludge being approximately 60 % in Beijing (Yu and Wang 2003) (Eq. 4). Based on a survey conducted in 2008, the treatment rate of sludge in Beijing was 46.4 %, and the average N content of sludge was approximately 4.61 % (Tan et al. 2011a, b). The treated sludge is proposed not to have a negative impact on the environment because its recycling has no adverse environmental effect; therefore, the Nr included in this sludge was not included in our calculations. According, the L_w was estimated by Eq. 5.

$$Lg = M \cdot PD(CTNp - CTNf) \cdot Cg \cdot CgN, \quad (3)$$

where C_{TNp} and C_{TNf} were the annual total N concentrations of sewage before and after treatment, respectively, the values of which referred to the average daily values of 365 days in 2009 provided by Qinghe sewage treatment plant, one of the biggest sewage treatment plants in Beijing. C_g was the yield coefficient of N₂O, and C_{gN} was the N content of that yield.

$$Lsl = M \cdot PD (CBODp - CBODf) \cdot CVSS \cdot Csl \cdot CslN, \quad (4)$$

As above, C_{BODp} and C_{BODf} were the annual 5-day biochemical oxygen demand (BOD₅) concentrations of sewage before and after treatment, respectively, from the same source as for Eq. 3. C_{VSS} was the yield coefficient of MLVSS (generally half the amount of BOD₅ removed during the processes of sewage treatment in Beijing) (Yu and Wang 2003), and C_{sl} was the yield coefficient of sludge with its N content being C_{slN}.

$$Lw = M \cdot PD (1 - Pr) \cdot CTNf, \quad (5)$$

where P_r was the percentage of treated sewage reuse, which increased from 23 to 61 % during 2000–2012. The values related to the ratio of the amount of reclaimed water: The total wastewater sent for treatment, retrieved from the China statistical yearbook on the environment.

Nr from municipal garbage disposal

Municipal solid waste runs through the processes of production, consumption, and recycling, eventually being partly discharged into the environment as waste excretion (Kennedy et al. 2007). This has a close relationship with urban environment pollution, such as white pollution, eutrophication, and insanitation. The Nr embedded in municipal garbage in Chinese cities can easily contaminate the environment as a result of garbage discarding (Zhou et al. 2014b). In addition, some Nr will be gradually emitted to the environment during or after the disposal processes, including via emissions, volatilization, and leaching, resulting in the growth of potential urban Nr sources. Similar to wastewater treatment, Beijing has many advanced waste disposal facilities with municipal garbage disposal rates reaching 99.1 % in 2012, which is higher than most cities in China (Beijing Statistics Bureau 2013). However, the Nr emissions after garbage disposal generally are ignored by inhabitants in most cases compared with those resulting from untreated garbage.

Based on the survey statistics in 2000 (Gao et al. 2000), the composition of municipal garbage in Beijing included organic waste, such as food waste, paper, fabric, and plastic, and inorganic waste, such as metal, glass, and ash. Given the lack of annual data relating to the composition of garbage following 2000, we assumed that the garbage composition remained the same until 2012; the Nr embedded in the garbage was calculated using the N content of the different waste materials, as detailed in Table 2 (Nie 2000; Wu et al. 2006; Gu et al. 2013b) (Eq. 6). Given that the N content of metal and glass are low and cannot be degraded naturally, the Nr from these was not included in our calculation.

$$MN = (1 - PD) \cdot \sum_{i=1}^{n} (Pi \cdot M \cdot PN), \quad (6)$$

where M_N represented the N content of untreated garbage, P_D represented the garbage disposal rates, and M was the total amount of garbage. P_i represented the mass fraction of waste i with P_N as the N content coefficient.

The disposal of municipal garbage in Beijing relied on sanitary landfill (94 %) with composting (4 %) and incineration (2 %) (Xiao et al. 2007). Therefore, the Nr from garbage treatment can be summarized using the N embedded in the nitrous oxide emissions caused by incineration and the gas volatilization from composting and landfilling, as well as by N loss from uncollected leaching from landfilling (Liu et al. 2001; Intergovernmental Panel on Climate Change 2006)

Table 2 The percentages and N content factors of municipal garbage

Garbage	Percentage (%)	N content (%)
Food waste	39	2.6
Paper	18.18	0.3
Metal	2.96	<0.1
Glass	13.02	<0.1
Fabric	3.56	10
Plastic	10.35	0.5
Coal ash	10.93	0.98
Others	2	–

(Eq. 7). The Nr flows with recycling were regarded as being redistributed within the city and so were excluded from the output calculation. In addition, the annual data relating to the treatment rates of leaching in Beijing were lacked, and so, we assumed that all the leaching infiltrated the groundwater in the same year as the preliminary treatment of landfilling. Thus, the total Nr emissions from treated and untreated garbage were evaluated using Eq. 7:

$$LN = \sum_{j=1}^{n} (Pj \cdot M \cdot PD \cdot Cg \cdot CgN) + MlN \cdot Ll + MN, \quad (7)$$

where L_N denoted the total Nr emissions from treated and untreated garbage, P_j was the percentage of disposal approach j, C_g was the emission factor of nitrous oxide with 67 g kg^{-1} for incineration and 0.6 g kg^{-1} for volatilization, and C_{gN} was the N content of the former. M_{IN} was the N embedded in the garbage for landfilling, with L_l representing the N loss factor by leaching (16 %).

Nr from agricultural ammonia volatilization

Ammonia nitrogen, as an important species of reactive nitrogen, is very crucial on secondary aerosol formation. The agricultural ammonia emissions from suburban contribute to China urban air pollutions especially the higher PM$_{2.5}$ level in Beijing (Gu et al. 2014). Reis et al. (2009) found that livestock farming and synthetic fertilizer application in China were the major contributions (52 %) and (41 %) to total ammonia emissions by the end of last century (Reis et al. 2009). Given that suburban regions occupy most territories of Beijing megacity where agricultural activities occurs frequently, we estimated Nr emissions from agricultural ammonia volatilization from 2000 in this study by using Eq. 8:

$$LA = Vl + Vf, \quad (8)$$

where L_A represented the total Nr losing through agricultural ammonia volatilization. V_l and V_f indicated the annual Nr volatilization from livestock farming and synthetic fertilizer application in Beijing, respectively.

The Nr emissions in terms of ammonia volatilization from livestock farming were estimated by multiplying the rearing amounts by emission factors for different types of livestock (Eq. 9). The livestock species in Beijing mainly included beef cattle, pig, sheep, rabbit, duck, chicken, and hen, and the Nr emission rates of these livestock were referred to the volatile coefficients concluded by Gu et al. (2015), which included Nr embedded in ammonia emissions from the storage, manure, and grazing during livestock rearing.

$$Vl = \sum_{l=1}^{n} (Ql \cdot El), \quad (9)$$

where Q_l denoted the rearing capita of livestock species l by the end of year and E_l represented the annual ammonia emissions factors for beef cattle (18.6 kg N capita^{-1}), pig (2.33 kg N capita^{-1}), sheep (4.18 kg N capita^{-1}), duck (0.25 kg N capita^{-1}), rabbit (0.20 kg N capita^{-1}), chicken, and hen (0.04 kg N capita^{-1}).

Current agricultural productions in China are still dependent on intensive fertilizer use, and synthetic fertilizer application is one of the important sources of gaseous Nr emissions through ammonia volatilization. We estimated these Nr emissions in Beijing by multiplying the used fertilizers (nitrogenous fertilizer and compound fertilizer) by the emission factors using Eq. 10:

$$Vf = (FN + QC \cdot PN) \cdot Ef, \quad (10)$$

where F_N represented the annual net N amount embedded in nitrogenous fertilizer applied in agriculture and Q_C denoted the annual amount of compound fertilizer, they could be retrieved from the statistics by Ministry of Agriculture of China (2000–2013). P_N was average nitrogen content (15 %) of compound fertilizer based on survey in Beijing (Irie et al. 2014), and E_f was the loss rate (16 %) of N applied as inorganic N in Beijing's farmland through ammonia volatilization (Gu et al. 2015)

Nr from different sources

Exploring the characteristics of Nr emissions from different sources can demonstrate the main sources driving Nr outputs in Beijing. Recently, as Liu et al. (2015) suggested, the impact of urbanization on N flow was reflected in the changes in urban lifestyles and urban production styles. Thus, we categorized the total Nr outputs into two groups based on the emission source. The first was residential emissions (Nr_r), which included emissions from fossil fuel combustion by inhabitants, sanitary sewage treatment, and municipal garbage disposal. The second was industrial emissions (Nr_p) caused by primary, secondary, and tertiary industries, including direct emissions from fossil fuel combustion by commodities and services production, as well as indirect emissions from agricultural activities and industrial sewage treatment. Given that the rainy season in Beijing is short with little rainfall and that the limited agricultural wastewater is not collected for treatment in Beijing, the wastewater mentioned above mainly comprised sanitary and industrial sewages, and their percentages were based on the statistics from China statistics yearbooks and China environmental statistics yearbooks. Given the lack of data relating to industrial waste residue and the fact that they generally were treated in a different way to municipal garbage, the emissions from the disposal of these wastes were not included here, unavoidably causing us to underestimate the total industrial emissions. We evaluated the Nr

emissions from these two sources using Eqs. 11 and 12, respectively:

$$E_r = \frac{Nr_r}{P}, \tag{11}$$

$$E_p = \frac{Nr_p}{G}, \tag{12}$$

where E_r and E_p denoted the residential and industrial Nr output intensity, respectively, which could reflect the ratio between Nr output and economic or human welfare output (Cui et al. 2013). The lower these indicators are, the lower the environmental costs for urbanization. P was the annual residential population, and G was the gross domestic product (GDP) of Beijing in the same year. Generally, E_r represented the amount of Nr emitted to the environment resulting from the feeding of one inhabitant in Beijing; similarly, E_p represented the amount of Nr discharged to the environment to produce the commodities and services with the value of 100 million RMB.

Evaluating Nr removal efficiency

Given that the development of an urban ecosystem consumes N and results in Nr emissions to the environment, it is useful to evaluate the Nr removal efficiency of that urban ecosystem from the perspective of urban metabolism, especially in megacities with rapid urbanization. In this study, data envelopment analysis (DEA), which was widely applied in economic analysis, was used to measure the Nr removal efficiency of Beijing. This model is a linear programming-based technique for evaluating the relative efficiency of a decision-making unit (DMU) with other DMUs with the same resource consumption (material input) to produce the same output. It recently was applied as a method for the eco-efficiency assessment of urban material metabolism in China, with N discharge being one of the undesirable outputs (Zhang et al. 2008; Liu et al. 2010). To focus on the removal efficiency of Beijing from 2000 to 2012, the application of DEA developed by Coelli (1996) was conducted as suggested by Liu et al. (2010), and the evaluation accounting for variable returns to scale (VRS) situations was carried out using DEAP version 2.1 program. By considering DMUs with time series data (years) and assuming that the environmental technology for pollutant removal did not vary across years to enable a comparison among DMUs based on the extent to which inputs are used efficiently in the output production, the DEA model can be used with time series data. For each DMU for a specific year, its inputs and outputs are considered in the model. For the purpose of this study, Nr discharge was recognized as the only output item; the input items included the governmental investment for pollution control, total amount of water consumption, and the land exploration for urbanization (Table 3).

Energy consumption was not considered to avoid repetition because of the Nr output calculation based on the amount of energy consumption. During the evaluation, the undesirable Nr outputs were treated as normal outputs after taking their reciprocals to match the model application (Lovell et al. 1995). The output slack will occur only if it is possible to increase the amount of output when keeping the same input (Coelli 1996). Therefore, the DMU could be assumed to be efficient (value = 1) if the output could not be increased anymore on the premise of maximum input; otherwise, the DMU remains inefficient (value <1) with output slack. In the current study, this means that, in an efficient year, the Nr output could not be reduced further based on the realistic input of money, water, and land. All the input item from 2000 to 2012 for the model were mainly collected from China City Statistical Yearbooks, China Statistical Yearbooks, Beijing Statistical Yearbooks, and China Environmental Statistical Yearbooks.

Results and discussions

Beijing Nr emissions with pollution control

Using the equations detailed above, we determined the temporal changes in Nr emissions from fuel combustion, wastewater treatment, municipal garbage disposal, and agricultural ammonia volatilization from 2000 to 2012 in Beijing. As to Nr emissions by fuel combustion, we found that the emission amounts resulting from coke and crude oil consumptions reduced over this time period. As the biggest contributor, emissions by coal combustion fluctuated over the period and dropped to 42.3×10^3 t N in 2012, peaking at 60.3×10^3 t N; the obvious reduction of these emissions may have resulted from the efforts to upgrade the energy and industrial structure especially during the 11th 5-year plan period (2005–2010) in China; by contrast, emissions from secondary and clean energy combustion, including gasoline, kerosene, diesel, and natural gas, grew gradually (Fig. 3a). The consumption of coal, gasoline, and diesel was assumed to be the main source for burning Nr output by Beijing, and the secondary energy source, such as gasoline and diesel, mainly was used in the transportation sector. Thus, our results indicated that a boom in transportation had a key role in increasing regional air pollution in Beijing, as predicted by a previous study (Li et al. 2003). Generally, the Nr emissions from fuel combustion increased gradually from 2000, peaking at 119.7×10^3 t N in 2007 and then decreased slightly to the bottom 108.9×10^3 t N in 2011, which still increased by 39 % compared with the level in 2000, with average Nr emissions of approximately 102.6×10^3 t N during the study period. Compared with the results of provincial NO_x (presuming NO_2) emissions conducted by Zhao et al. (2013), our Nr emission estimations (103.2×10^3 t N in 2005 and 112.6×10^3 t N in 2010) were

Table 3 Summary of input indicators

| Indicators	Units	Mean	Std. deviation	Min	Max
Governmental investment	10,000 RMB	53,795.92	30,364.65	10,512	99,046
Water consumption	10,000 t	357,000	15,247.95	343,000	389,000
Land exploration	100 ha	73.62	94.58	0	292

lower than his estimations around 108.9×10^3 t N in 2005 and 144×10^3 t N in 2010 in Beijing, approximately resulting from our applications of Nr removal rates covering all the sectors mentioned above while removal efficiency in his study focusing on the industrial sector and power plants.

Nr emissions from wastewater treatment declined from 2003 onwards and remained stable between 2008 and 2012, with the percentage of Nr embedded in untreated sewage dropping sharply (Fig. 3b). This indicated that Beijing effectively reduced Nr emissions originating from wastewater by increasing the sewage treatment rate. The average Nr emission from 2000 to 2012 was 35.1×10^3 t N and declined by 29.9×10^3 t N during the last 5 years of the study period, highlighting the positive impacts of wastewater treatment on the Beijing environment. However, because sludge could remove more Nr from sewage with the improvement in treatment technology, the growth of sludge production might, in turn, become a potential Nr source.

Nr emissions caused by the discard of untreated municipal garbage decreased rapidly, especially between 2000 and 2001, with a reduction of more than 50 % (Fig. 3c). The improvement of municipal garbage treatment rates supported by the construction of more treatment facilities and advanced technologies is likely to have prevented the direct channeling of Nr emissions to the environment. However, there was a rising trend in Nr emissions via gaseous and liquid carriers following disposal over the study period. The amount of Nr loss by landfill leaching rose dramatically, resulting in it becoming the fastest growing source of nitrate contamination in groundwater, secondary only to farmland leaching (Gu et al. 2013a). Similarly, the amount of gaseous Nr emissions increased gradually from 2000 to 2012. In particular, the exhaust gas emissions resulting from incineration significantly contributed to these Nr emissions, despite it having the lowest percentage (2 %) for garbage disposal in Beijing. In summation, the amount of Nr emissions from municipal garbage disposal dropped from 2000 and returned to a high level in 2006 and was maintained until 2012, with the overall average of 22.2×10^3 t N and an average of 24.8×10^3 t N between 2006 and 2012. These results indicate that the process of garbage disposal is fast becoming a potential source of N pollution in Beijing.

Gaseous Nr emissions resulting from livestock farming and fertilizer application exhibited rapid downtrend between 2003
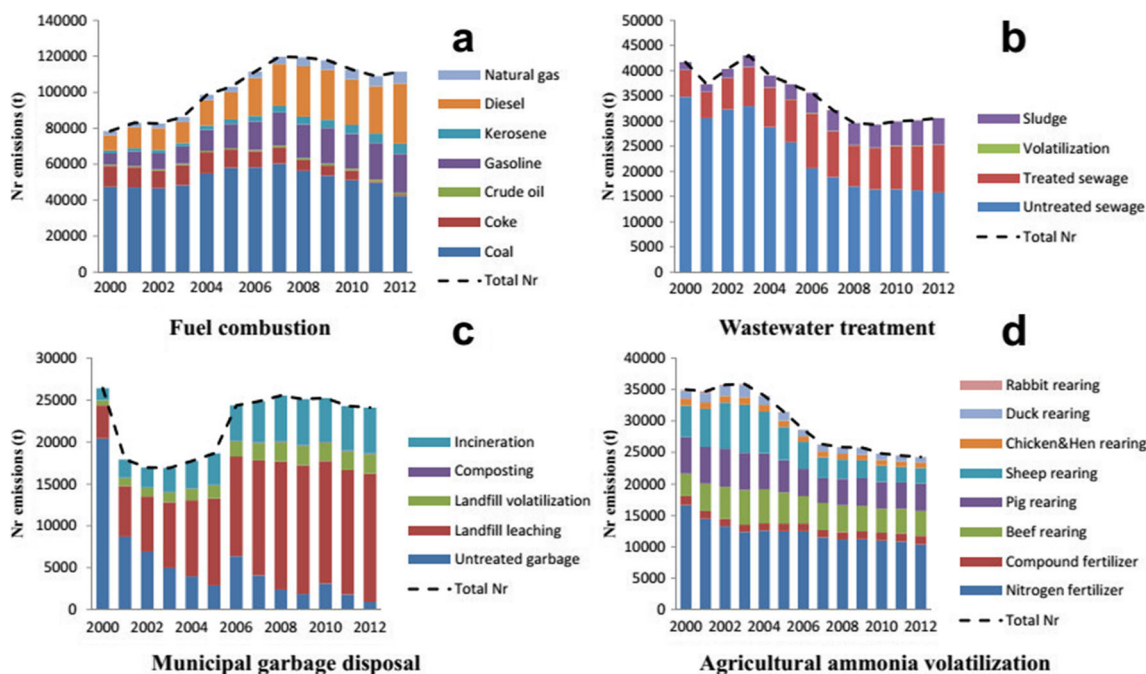
Fig. 3 Graph showing the relationship between Nr emissions and fuel combustion (**a**), wastewater treatment (**b**), municipal garbage disposal (**c**), and agricultural ammonia volatilization (**d**)

and 2007 and kept decreasing slightly until 2012 with overall annual Nr emissions of 29.8×10^3 t N (Fig. 3d). Nitrogenous fertilizer was the biggest contributor to the nitrogen load, and the Nr from chemical fertilizers declined gradually from 18.1×10^3 to 11.8×10^3 t N achieving around 35 % reduction in 12 years, which was consistent with the finding in other Chinese megacity Shanghai that the Nr release resulting from chemical fertilizer decreased with increasing urbanization in the same period (Liu et al. 2015). Meanwhile, the Nr emissions from livestock farming presented increasing until 2003 with two bigger contributors of pig and sheep farming, then decreased from 22.4×10^3 to 12.5×10^3 t N by 2012, which was mainly driven by significant scale-down of sheep farming with 51.6 % reduction in rearing capita. Although beef cattle per capita produces more Nr emissions than sheep and pig during rearing, the scale of sheep farming was the main factor driving the trend of livestock Nr emissions in Beijing during study time while the breeding number of beef cattle and pig remained stable since 2006. What should be noted that the amount of livestock Nr emissions exceeded those from chemical fertilizers since 2001, this indicated that livestock farming was the main source responsible for nonpoint Nr releasing in terms of agricultural ammonia volatilization. The overall decrease of these Nr emissions was due to urbanization resulting in reductions in farmland and local agricultural production in Beijing undergoing primary industrial transformation.

In conclusion, the total Nr emissions presented slightly increasing from 0.18 to 0.19 Tg N ($\times 10^6$ t N) during 2000–2012, peaking at around 0.20 Tg N in 2007 (Fig. 4). Since 2007, the Nr load of the Beijing turned to be reduced gradually toward relatively stable, because of the reduction in fuel combustion emissions, which annually represented the largest percentage (43–60 %) of total Nr output, with Nr emissions caused by wastewater treatment coming second. The average Nr emissions reached 0.19 Tg N during the study period, with an average Nr_r of 0.06 Tg N and Nr_p of 0.11 Tg N (Fig. 4), indicating that the domestic production was still the main source of N pollution in Beijing, in which the percentage of industrial land covering was lower. The treatment of residential waste (sewage and municipal garbage) resulted in more than 83 % Nr_r all the way, whereas fuel combustion caused approximately 72 % annual Nr_p along with the contribution of agricultural ammonia volatilization decreasing. Meanwhile, E_r showed a decreasing stepwise trend, with an average 3.87 kg per inhabitant; its value in 2012 had declined by 38 % compared with that in 2000. Similarly, E_p declined sharply from 33.90 to 5.59 t per commodities and services production, with a value of 100 million RMB in 2012, having reduced by 83 % over the 12-year study period, with an average E_p of 16.74 t (Fig. 5).

These results show that the Nr output intensity of both sources in Beijing had weakened over the study period, with more significant changes in industrial Nr output intensity. This suggests that N consumption in Beijing had become more efficient, with fewer negative impacts on the environment. Pearson correlations of the Nr output intensity and urbanization rates were −0.805 for E_r and −0.963 for E_p, which were both significant at the 0.01 level (two-tailed). From 2000 to 2012, the environmental costs of inhabitants in terms of their livelihood per inhabitant and domestic production per unit both were reduced, highlighting the fact that Beijing had made efforts to transfer from a "high N cost" role into the new "low N cost" model especially for hosting the Olympics Game in 2008, despite rapid urbanization having occurred since 2004.

Nr removal efficiency in Beijing

According to our results, the removal efficiency of Nr emissions of Beijing fluctuated over the study period (Table 4). There were eight efficient years and five inefficient years from 2000 to 2012. The average value of the removal efficiency was 0.993, reaching its lowest point (0.965) in 2003. There were 4 years (2007–2009, and 2012) that had output slack. This shows that Beijing could increase the amount of output and still keep the same input. For this study, this means that Beijing is capable of reducing its Nr emissions further based on its current natural and financial resource consumption in an inefficient year; the targeted Nr emissions simulated by the model to achieve Nr removal efficient for the years 2007, 2008, 2009, and 2012, respectively, were 199.72×10^3, 194.21×10^3, 191.61×10^3, and 188.75×10^3 t N, less than original ones (203.02×10^3, 200.36×10^3, 197.85×10^3, and 190.37×10^3 t N). Similarly, the environmental measures in Beijing had achieved the maximum Nr reduction in eight efficient years with no output slack. Thus, Nr removal efficiency could be an instrument for sustainability analysis that indicates how efficient Nr removal is with regard to environment protection. Given the higher percentage of efficient years, Beijing tried best to reduce its Nr emissions as much as it should have over study period.

Our study does have some limitations. Owing to the lack of annual statistic data in some sectors, several coefficients from these sectors for total Nr emissions calculation from 2000 to 2012 were based on the available data for 1 year during the study period, which leads to a degree of uncertainty in terms of our final results. Furthermore, some parameters used in this calculation were retrieved from the literature, which might also introduce potential uncertainties. For future research, more in-depth data-mining research is needed to improve the accuracy of these results. Moreover, we assumed that the environmental technology for Nr removal in Beijing did not vary significantly between 2000 and 2012 while applying the DEA model, which would lead to bias in evaluation

Fig. 4 Total Nr emissions of Beijing comprising agricultural ammonia volatilization, wastewater treatment, total Nr, garbage disposal, and fuel combustion during the period 2000–2012
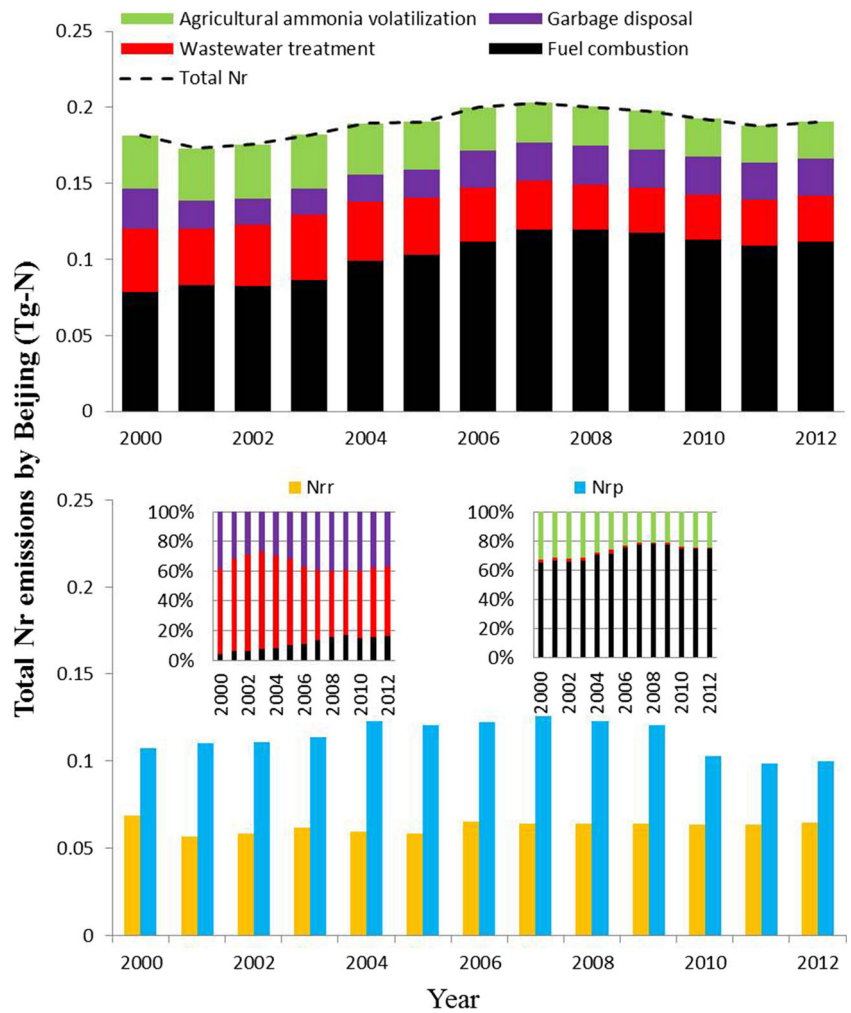
results of annual Nr removal efficiency. In reality, it is likely that technology improved gradually over the study period. The further refinements in the model extensions coupling with weight factors setting for DMUs might contribute to overcome this limitation.

Further environmental measures for Nr removal based on N offset

These results provide suggestions for further reducing local Nr emissions in Beijing. The countermeasures of N offset could

Fig. 5 Difference between industrial Nr output intensity from residential output intensity from year 2000 to 2012
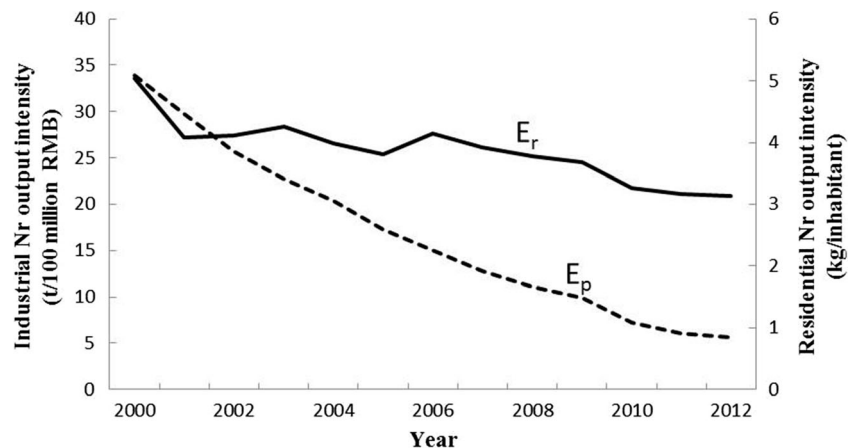
Table 4 Removal efficiency of Beijing from 2000 to 2012

Year	Efficiency from VRS	Output slack
2000	1	0
2001	1	0
2002	1	0
2003	0.965[a]	0
2004	1	0
2005	1	0
2006	1	0
2007	0.986	0.077
2008	0.982	0.159
2009	0.986	0.169
2010	1	0
2011	1	0
2012	0.987	0.048

[a] The Nr removal inefficiency in 2003 might have resulted from input slack, in that the amount of input used could be reduced with the same output production

be developed to heighten Nr removal efficiency to avoid inefficient Nr removal, resulting in the overall reduction of Nr emissions. The concept of N offset is similar to the "N neutrality" concept defined by Leip et al. (2014) in that the purchase of N offsets compensates for residual Nr releases after removal. In this case, N offset could be purchased by government to neutralize the excess Nr emissions in a previous inefficient year with output slack by supporting low N-producing projects, thus encompassing a reduction of Nr release elsewhere in Beijing during a specific period. For example, cleaner energy promotion and low-nitrogen technology in the production of heavy industrial sectors could be encouraged by governmental subsidies to avoid substantial Nr loss resulting from fuel combustion after 2012, balancing the remaining Nr emissions to achieve efficient Nr removal in what would otherwise be an inefficient year such as year

2012. Consequently, Beijing government had to spend extra investment in preventing future Nr emissions to offset the excess emissions (1.62×10^3 t N) after Nr removal in a previously inefficient year 2012 (Fig. 6). This measure would stimulate the government to achieve more efficient years since the costs of subsequent N offset were higher due to compensation project establishment. Thus, this N offset measure could help Beijing progress toward minimal Nr emissions despite increasing urbanization.

Based on the characteristics of Nr emissions in Beijing detailed in this study, we suggest the following new environmental measures to help reduce such emissions: (i) systematically estimate the amount of realistic Nr emissions in Beijing following pollution control, (ii) evaluate and record the annual Nr removal efficiency of the city, (iii) implement compensation projects toward N offset to reduce superfluous Nr emissions in years lacking efficient Nr removal, and (iv) build a "N-friendly society" in the city to move it from an "Nr source" stage to an "Nr neutrality" stage.

Conclusions

As the basis for mitigation strategy making, effective approaches for main emission source identification and emission estimation have been a necessity. This study estimated and quantified anthropogenic Nr emissions from the Beijing megacity and presented a first attempt to evaluate the Nr removal efficiency of a city based on actual emissions and pollutant control. Our results could help not only policymakers but also other stakeholders, including producers and residents, to optimize strategies to minimize urban Nr emissions and enable an N-friendly way forward for urbanization.

Our results can be summarized as follows: (i) The total amount of Nr emissions to the environment by Beijing increased during 2000–2007 and then slightly decreased during

Fig. 6 Graph showing environmental measures for Nr removal
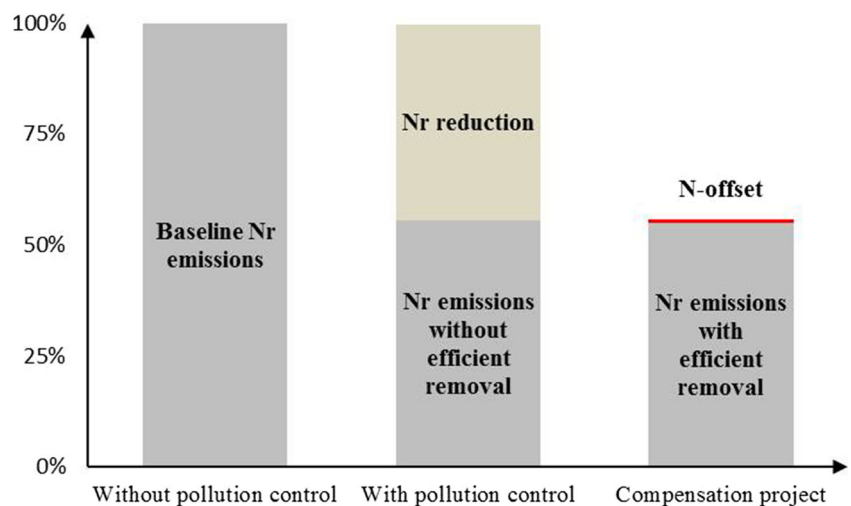
2008–2012 and were mainly due to fuel combustion; (ii) the Nr output intensity resulting from inhabitants' livelihoods and material production per unit decreased from 2000 to 2012; (iii) the environmental measures for Nr removal in Beijing were efficient in most years, indicating that progress on the mitigation of Nr load growth in this urban environment was significant especially during 2000–2006; and (iv) further measures based on N offset could provide a new approach to compensate for residual Nr emissions. Although this exploratory study focuses on the Beijing megacity as an example of an urban ecosystem undergoing rapid growth, the analysis framework for Nr estimations and removal efficiency evaluation method coupling with "N offset" concept might be suitable for use in case studies across other cities for exploring the relations between urbanization, environment protection, and sustainable development.

Compliance with ethical standards

Conflict of interest   The authors declare that they have no conflict of interest.

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