Assessment of nitrogen hotspots induced by cropping systems in the Bohai Rim region in China by integrating DNDC modelling and the reactive nitrogen spatial intensity (NrSI) framework

Qingmei Wang1,2*, Xia Liang2,4*, Yingchun Wang, Ligang Wang1,4, Arvin R Mosier2 and Deli Chen2*

1 Institute of Agricultural Resources and Regional Planning, Chinese Academy of Agricultural Sciences, Beijing 100081, People's Republic of China
2 School of Agriculture and Food, The University of Melbourne, Victoria 3010, Australia
3 Development Center for Science and Technology, Ministry of Agriculture and Rural Affairs of the People's Republic of China, Beijing 100122, People's Republic of China

E-mail: liang.xia@unimelb.edu.au and wangligang@caas.cn

Keywords: cropping systems, DNDC, reactive nitrogen, spatial intensity, Bohai Rim region

Abstract

More than half of nitrogen (N) inputs to cropland are lost to the environment via denitrification, ammonia (NH₃) volatilization, nitrate leaching and surface runoff. Cropping systems are, therefore, a large contributor to reactive N (Nr, all species of N except N₂) losses. The Nr spatial intensity (NrSI) framework was developed to quantitively the environmental burdens due to Nr losses on a per area basis. However, the current application of the NrSI framework is limited by the development of virtual N factors (VNFs, Nr released to the environment per unit of Nr consumed) for agricultural products and it could not differentiate pathways of Nr losses linked to consequences in various environmental media. As the Denitrification-Decomposition (DNDC) model is capable of tracking N fluxes across cropping systems and regions, we integrated the DNDC model and the NrSI framework to identify hotspots of Nr losses induced by cropping systems, and illustrate the approach with a case study for the Bohai Rim region (BR) in China. Altogether 29 types of cropping systems (i.e. 16 mono, 10 double and 3 triple cropping systems) in 429 counties were simulated for the N balance, Nr losses and the NrSI associated with crop production. Regarding the total Nr losses in the BR, 45% of the total N input was lost to the environment during crop production with NH₃ volatilization and nitrate leaching the two main pathways, making up 24% and 19% of the total N input, respectively. Shandong province was the biggest contributor of the total Nr losses (45.6%) among regions, and winter wheat-summer maize, triple vegetable and spring maize cropping systems were the top three contributors among various cropping systems. For Nr loss hotspots, there are substantial variations of NrSI across cropping systems (41–1024 kg N ha⁻¹ y⁻¹) and counties (28–4782 kg N ha⁻¹ y⁻¹). Beijing had the highest NrSI associated with crop production (307 kg N ha⁻¹ y⁻¹) among regions, and vegetable systems had the highest NrSI of 355 kg N ha⁻¹ y⁻¹ among cropping systems. The application of this integrated method is useful to identify areas and/or cropping systems with particularly high Nr losses and NrSI to provide basic information for setting Nr mitigation priorities on a wide range of regions and cropping systems.

1. Introduction

Nitrogen (N) is an essential nutrient for plant growth, and its application in cropping systems has boosted crop yield to feed almost half of the world’s population (Erisman et al 2008, Galloway et al 2008). However, more than half of N inputs to cropland are lost to the environment via denitrification, ammonia (NH₃) volatilization, nitrate leaching and surface runoff (Erisman et al 2013, Lassaletta et al 2014, ...
Zhang et al. (2015), making cropping systems a large contributor to reactive N (Nr, all species of N except N\(_2\)) losses (Rockstrom et al. 2009, Bodirsky et al. 2014). Increasing losses of Nr could result in a cascade of impacts on the environment and human health. For instance, NH\(_3\) reacts readily with acid gases and aerosols to form particulate matter in the atmosphere and nitrate pollution of both groundwater and surface water risks human health and can lead to eutrophication (Erisman et al. 2013, Galloway and Leach 2016).

To quantify the environmental burdens due to Nr losses, the Nr spatial intensity (NrSI) framework was developed to map the geographical locations of anthropogenic Nr losses for both agricultural and settled systems to inform management decisions and help mitigate Nr pollution for sustainable development (Liang et al. 2018). For the calculations of NrSI of agricultural systems, a set of nation-/region-specific virtual N factors (VNFs, defined as the Nr released to the environment per unit of Nr consumed (Leach et al. 2012)) for various food products are needed. Thus, it is not applicable to those countries/regions without VNFs. The current NrSI framework does not differentiate pathways of Nr losses, which should be considered because the loss route and form (e.g. nitrous oxide (N\(_2\)O) and NH\(_3\) to the atmosphere, ammonium (NH\(_4^+\)) and nitrate to the ground and surface water) determine their environmental consequences (Erisman et al. 2013). Therefore, it is necessary to develop an alternative approach to fill these gaps.

The primary objective of this study is to develop a new approach by integrating the Denitrification-Decomposition (DNDC) model and the NrSI framework to identify hotspots of Nr losses induced by various cropping systems and through different pathways on regional scale. One advantage of using the DNDC model to more accurately estimate the multiple pathways of Nr losses is that it can simulate the N biogeochemistry in agroecosystems with the consideration of effects of local soil properties, meteorological conditions and conventional farming practices (Li 2009). In contrast, previous studies mainly relied on N input/activity data, transformation/partitioning coefficients and emission factors (Guo et al. 2012a, Wang et al. 2018). For example, they used N loss factors for nitrate leaching, NH\(_3\) and N\(_2\)O emissions during crop production to determine Nr losses, which may introduce uncertainties due to spatial variations among different agricultural regions. As the DNDC model is capable of tracking soil N dynamics, N gas fluxes and nitrate leaching across crops and their rotation regimes, it can help to identify Nr hotspots among various cropping systems within a specific region. In this study, we selected the Bohai Rim region (BR), a typical intensive crop production base in China, to illustrate the application of this new approach for identifying areas and/or cropping systems with particularly high Nr losses and NrSI to provide basic information for setting Nr mitigation priorities on a wide range of regions and cropping systems.
2. Materials and methods

2.1. Bohai Rim region
The BR is located in north China around the Bohai Sea and includes two municipalities (Beijing and Tianjin) and three provinces (Hebei, Liaoning and Shandong) (figure 1). It covers an area of 520,000 km² (about 5.5% of the total land area in China) and is home to over 234 million people (amounting to 17.7% of the nation’s total population). With ~15.3% of the total arable land in China, the BR is an important crop production base. The production of wheat, maize, peanut, cotton and vegetables made up 29.8%, 28.3%, 36.7%, 24.9% and 31.0% of the national total production in 2008 (the year of interest for this study) (NBSC 2009). Such a high productivity level in the BR relies on the intensive use of synthetic N fertilizer (Cui et al 2006), leading to high Nr losses and environmental risks (Yu and Mao 2002, Liu et al 2011, Huang et al 2013). The annual mean concentration of atmospheric NH₃ at agricultural sites in the BR was around 10 µg N m⁻³ in 2009, while the regional background NH₃ concentrations in China were 1.5–3.4 µg N m⁻³ (Shen et al 2009, Meng et al 2010, Liu et al 2011). High nitrate concentrations in the shallow groundwater were also observed in the BR, which is associated with the nitrate leaching from intensive cropping systems (Ju et al 2006). As reported by the Marine Environment Quality Bulletin of Bohai Sea (SOA 2009), the coastal waters in BR were also heavily contaminated, with inorganic N being one of the most important pollutants, which is largely derived from crop production (Huang et al 2013).

2.2. Model description and validation
The DNDC model is a process-oriented model that simulates carbon (C) and N biogeochemistry in agroecosystems (Li 2009). It was originally developed to model N₂O, carbon dioxide (CO₂) and N₂ emissions from agricultural soils in the United States (Li et al 1992a, 1992b), and has been applied and expanded by researchers worldwide in a range of countries and cropping systems (Giltrap et al 2010). The model is comprised of two components with six modules. The first component, containing the soil climate, crop growth and decomposition modules, simulates environmental variables such as temperature, moisture, pH, redox potential (Eh) and substrate concentration profiles driven by primary ecological factors. The second component, including the nitrification, denitrification and fermentation modules, simulates the biogeochemical production, consumption and emissions of CO₂, methane (CH₄), NH₃, nitric oxide (NO), N₂O as well as nitrate leaching from soil, driven by the variables generated by the first component. The detailed information of DNDC model can be found in Li et al (1992a, 1992b, 2004, 2006). In the past two decades, the DNDC model has been tested with observations from numerous field measurements of crop yields, soil physical and chemical conditions, soil C/N dynamics, C/N gas fluxes, and nitrate leaching across the major cropping systems in China, and applied successfully to conduct filed and regional simulations (Xie et al 2017). All the crop parameters used for the DNDC model were recalibrated for major crop varieties grown in China (Li et al 2017a).

To validate the DNDC model for cropping systems in the BR, field experiments were conducted during 2008 to 2009 for the seven typical cropping systems (Qiu et al 2012), i.e. winter wheat-open-field vegetable in Zhangqiu county, winter wheat-summer maize in Huantai county, greenhouse vegetables in Shouguang county, winter wheat-summer maize in Qingxian county, spring maize in Luannan, Linghai and Wafangdian counties (figure 1, table S1). Specifically, the simulated soil temperature and moisture, daily net ecosystem exchanges of CO₂ and N₂O flux, crop yields, inorganic C content and nitrate leaching were validated against the observations of major cropping systems in the BR, and good agreements were found with statistically significant correlations (figures S1–S3) (available online at https://stacks.iop.org/ERL/15/105008/mmedia). The detailed information of model validation and simulation performance refer to previous work (Qiu et al 2012). Therefore, we assumed that the DNDC model would provide reliable simulation results to further analyze Nr losses and NrSI associated with crop production in the BR.

2.3. Input data for DNDC regional simulations
To conduct the DNDC simulation on regional scale, the region should be divided into polygons or grid cells with all the input data compiled in a Geographic Information System (GIS) database accompanied by a climate library for the target region. The GIS files include spatially differentiated information of location, climate file ID, soil properties, cropping systems and their areas, and farming management practices for each polygon/grid cell. The climate library contains the daily weather data (i.e. maximum and minimum air temperature, precipitation) (Li 2009). In this study, county was selected as the basic unit for the simulation, and the climate and soil conditions within one county were assumed uniform.

Input data for the DNDC model included: 1) meteorological variables, including daily maximum and minimum air temperature, and daily precipitation. They were obtained from 82 weather stations of China Meteorological Administration (http://data.cma.cn/en). For those counties without national weather stations, they shared the meteorological data from the nearest one. 2) soil properties, such as soil bulk density, clay fraction, soil organic C content and pH were derived from the Second National Soil Survey of China, and China Soil Records...
input and high quality of the county-level statistic datasets. Synthetic N fertilizer is the key driver of Nr loss (NH₃ volatilization, nitrate leaching and N₂O emission) (Bouwman et al 2002, Behera et al 2013, Li et al 2014), and the crop planting area, total synthetic N input, and per area synthetic N application rate did not change much from 2008 to 2015 in the BR (tables S8–10). Therefore, the 2008 results from this study were useful to identify historical Nr hotspots and to compare with current hotspot after the implementation of the national ‘Zero-growth Action Plan’ for synthetic fertilizer use since 2015 (MARA 2015).

2.4. Calculations of NrSI associated with crop production

The NrSI estimates the intensity of the Nr losses on a per area basis, expressed in the unit of kg N ha⁻¹ y⁻¹. In this study, NrSI associated with crop production was calculated based on the DNDC simulation results for each county/province and cropping system, and Nr losses via four pathways were considered during crop production—N₂O emission, NO emission, NH₃ volatilization and nitrate leaching. The NrSI associated with crop production for a specific county/province i and for a specific cropping system j was calculated as follows:

\[ NrSI_i = \left( \frac{\sum_{j=1}^{n} Nr_{ij}}{\sum_{j=1}^{n} S_{ij}} \right) \cdot \left( \frac{S_{ij}}{m} \right) \]

\[ NrSI_j = \left( \frac{\sum_{i=1}^{m} Nr_{ij}}{\sum_{i=1}^{m} S_{ij}} \right) \cdot \left( \frac{S_{ij}}{n} \right) \]

where \( Nr_{ij} \) and \( Nr_{ij} \) is the Nr losses from cropping system j in county i, in the unit of kg N; \( S_{ij} \) and \( S_{ij} \) is the planting area for cropping system j in county i, in the unit of ha; \( m \) is the total number of counties in the BR; \( n \) is the total types of cropping system in the BR.

3. Results and discussion

3.1. N balance in the BR

In 2008, the total N input (N from atmospheric deposition, fixation, mineralization, synthetic fertilizer, animal manure and crop residues) into the croplands was 8.1 Tg N y⁻¹ in the BR (tables S11 and S13). Synthetic N fertilizer was the largest N input to the croplands, amounting to 5.1 Tg N y⁻¹, which accounted for 22% of the national total input (NBSC 2009). The average application rate of synthetic N fertilizer for cropland in the BR was 311 kg N ha⁻¹ y⁻¹ (table 1), significantly higher than the national average of 233 kg N ha⁻¹ y⁻¹ (Yan et al 2014b). N from organic fertilizer (including animal manure and crop residues) was the second largest N input to the croplands (about 2.4 Tg N y⁻¹) with a mean application

(3) land use by crops, i.e. cropping systems and their areas. The county-level data of arable land, planting areas for all crops and their productivity were from Ministry of Agriculture and Rural Affairs, China (table S2). To determine the areas for each cropping system (table S3), we reanalyzed the original crop area and merged the census data with a prioritized list of most possible cropping systems on county scale in the BR (table S4) (Qiu et al 2003, Li et al 2017a). 4) farming management practices, e.g. sowing and harvest date, fertilization application time, irrigation and tilling method. These were obtained primarily from field surveys. When conducting the field survey, the BR was divided into seven sub-regions based on variations in planting regimes, soil types and climate conditions etc (table S5). Typical counties were selected to conduct the field surveys and represent each sub-region. 5) crop physiological/phenology parameters, i.e. maximum yield, biomass partitioning into and C/N ratios of grain, shoot and root, cumulative thermal degree days to maturity (TDD), water requirement, and N fixation index (see SI for detailed information). The crop parameter database was developed for 23 major crops in China (Li et al 2017a). 6) fertilizer and livestock data. The amount of fertilizer consumption and number of different types of livestock in each county were obtained from the Ministry of Agriculture and Rural Affairs, China. The livestock category considered in this study included beef cattle, pig and sheep based on the data availability on county level. We then determined the amount of manure produced in each county based on animal excreta parameter and associated N content (Wang et al 2006), and assumed that in each county, 20% of the manure produced was evenly applied to the cropland (Qiu et al 2008), i.e. each county had the same N input from manure application on a per area basis (equation S1). The DNDC model also included N input via atmospheric N deposition and mineralization, and from crop residue (the straw return ratios were set between 25%–60% in the BR (table S6)) (see SI for more detailed information). Input files for model simulation and main parameters in each file were provided in the SI (table S7).

Based on the above input data, the DNDC simulations were run for each cropping system in each county. Altogether, 29 types of cropping systems (figure 4) in 429 counties were simulated for the year 2008. Winter wheat-summer maize, triple vegetable and spring maize were the major cropping systems in the BR. The three major crops (wheat, maize and vegetable) made up 74.2% of the total planting area and 92.1% of the total crop productivity in the BR in 2008 (table S2). The year 2008 was selected for approach illustration because there were sufficient field measurements for model validation, comprehensive field surveys of farming practices for model
rate of 145 kg N ha\(^{-1}\) y\(^{-1}\), which is nearly three times as much as the national average (\(~50\) kg N ha\(^{-1}\) y\(^{-1}\)) (Yan et al. 2014b). Atmospheric deposition, biological fixation and mineralization made up the rest N inputs of 0.7 Tg N y\(^{-1}\). The total N output (crop uptake, gas emissions via N\(_2\)O, NO, N\(_2\)O, NH\(_3\), and nitrate leaching) was 6.5 Tg N y\(^{-1}\), resulting in a N surplus of 1.6 Tg N y\(^{-1}\) in the cropland in the BR. Among the total N output, about 2.7 Tg N y\(^{-1}\) was taken up by crops, accounting for 33% of the total N input. A large amount of Nr (45% of the total N input) was lost to the environment during crop production with NH\(_3\) volatilization and nitrate leaching the two main pathways, making up 24% and 19% of the total N input, respectively (table S11). The NH\(_3\) volatilization in the BR amounted to 2.0 Tg N y\(^{-1}\) with an average emission intensity of 120 kg N ha\(^{-1}\) y\(^{-1}\) for croplands, which contributed 24% of the national total NH\(_3\) emitted during crop production (Xu et al. 2016). Nitrate leaching totaled 1.5 Tg N y\(^{-1}\) with an average intensity of 93 kg N ha\(^{-1}\) y\(^{-1}\), N output via other gas emissions (i.e. N\(_2\)O, NO and N\(_2\)) was about 0.4 Tg N y\(^{-1}\). Notably, the total amount of N\(_2\)O emission in the BR accounted for 22% of the national total N\(_2\)O emission during crop production (Zhou et al. 2014) with a mean emission intensity of 6.5 kg N ha\(^{-1}\) y\(^{-1}\) (table 1).

The total amount of Nr losses associated with crop production in the BR was 3.6 Tg N y\(^{-1}\) with an area of 16.3 million ha of croplands (table S12). Among the four Nr loss pathways, NH\(_3\) volatilization and nitrate leaching were dominant forms, accounting for 53.6% and 41.8%, respectively; while N\(_2\)O and NO emission only made up 2.9% and 1.7% of the total on-farm Nr losses. The highest Nr losses were in Shandong province with a proportion of 45.6% to the total Nr losses in the BR, followed by Hebei province (30.6%) and Liaoning province (20.4%). Beijing and Tianjin had a similar share with a percentage of 1.6% and 1.8%, respectively. For the different cropping systems, 60.5% of the total Nr losses were derived from three major contributors, i.e. winter wheat-summer maize double cropping system (29.4%), triple vegetable cropping system (17.3%) and spring maize mono cropping system (13.8%) (table S13), with planted area accounted for 31.9%, 3.8% and 16.3% to the total cropland in the BR, respectively (table S3).

Overfertilization and poor nutrient management practices are the major reasons for the low N use efficiency and high Nr losses in China (Gu et al. 2015, Wang et al. 2018), especially for the regions with intensive agricultural activities. In Shandong province, the average N application rate was 470 kg N ha\(^{-1}\) in 2008 (table 1), which was more than doubled the threshold of safe N fertilization rate (225 kg N ha\(^{-1}\)) set by developed counties to avoid soil and water pollution (Cai et al. 2018). The overfertilization of N is even more common in greenhouse vegetable production. The results show the N application rate for triple vegetable system averaged 1360 kg N ha\(^{-1}\) y\(^{-1}\) in the BR in 2008, much higher than that required by vegetables.

The per area based N balance in the BR of our results was compared to a previous study that used a farmland N balance model (Guo et al. 2012a) (table 1). Results from both studies showed high N input, Nr losses and N surplus in the cropland in the BR. Per area based total N input and synthetic N fertilizer application rate were lower in our study compared with the results of Guo et al. (2012b) due primarily to the difference in data source. We applied the most reliable county-level dataset obtained

Table 1. Cropland N balance on a per area basis in the BR in 2008 (Unit: kg N ha\(^{-1}\) y\(^{-1}\)).

| Region          | This Study | Guo et al 2012a |
|-----------------|------------|-----------------|
| Input           |            |                 |
| Synthetic fertilizer | 658.6   | Beijing Tianjin Hebei Liaoning Shandong The BR The BR |
| Manure          | 369.1      | 282.0           | 287.9 | 254.6 | 353.4 | 310.6 | 481.8 |
| Crop residue    | 196.8      | 97.8            | 106.4 | 114.1 | 116.3 | 113.1 | 34.3  |
| N deposition    | 45.4       | 33.6            | 34.4  | 10.7  | 40.3  | 32.4  | 23.5  |
| N fixation      | 10.3       | 12.1            | 14.3  | 6.5   | 13.5  | 12.3  | 28.0  |
| N mineralization| 7.0        | 4.5             | 4.8   | 8.7   | 3.9   | 5.2   | 21.7  |
| Others (i.e. seeds, irrigation water) | 29.9 | 17.6  | 21.1  | 24.2  | 26.2  | 23.9  | -     |
| Output          |            |                 |
| N uptake by crops\(^a\) | 522.1   | 361.0           | 377.1 | 346.1 | 439.9 | 399.7 | 337.4 |
| Nitrate leaching\(^b\) | 147.4   | 72.2            | 81.7  | 130.1 | 85.1  | 93.4  | 38.2  |
| NH\(_3\) volatilization | 151.4  | 110.6           | 116.6 | 79.4  | 140.3 | 119.8 | 113.8 |
| N\(_2\)O emission | 5.1    | 0.8             | 4.3   | 16.7  | 3.9   | 6.5   | -     |
| NO emission     | 2.8        | 1.8             | 3.0   | 2.9   | 4.9   | 3.8   | 8.7   |
| N\(_2\) emission | 11.0   | 7.0             | 10.2  | 14.8  | 12.7  | 12.2  | -     |
| Net N balance   | 136.5      | 86.5            | 91.8  | 72.7  | 113.6 | 97.9  | 268.9 |

\(^a\)N uptake by crops refers to N uptake by whole crop plant.

\(^b\)Nitrate leaching in this study refers to nitrate leached out of a 0–50 cm soil profile.

\(^c\)This value was calculated based on information provided in Guo et al (2012b).
from the Ministry of Agriculture and Rural Affairs, China. The total amount of synthetic N fertilizer used in the BR in 2008 was 5.1 million tons in this study. While it was reported to be 9.1 million tons in Guo et al. (2012b), which is more than doubled that recorded on provincial level by the National Bureau of Statistics that reported a value of 4.1 million tons. Different estimation methods could be another possible reason for the differences in the results. Our estimated N taken up by crops, and NH$_3$ volatilization are comparable to those by Guo et al. (2012b), but we found higher nitrate leaching and lower N surplus rates. A likely explanation is that the DNDC model simulated the nitrate leached out of a 0–50 cm soil profile in this study, so nitrate deeper in the soil profile was included in the Nr loss via leaching rather than N surplus in the soil.

### 3.2. Spatial variations of cropland NrSI

The average cropland NrSI in the BR was 224 kg N ha$^{-1}$ y$^{-1}$. Although contributing the least to the total cropland Nr losses in the BR, Beijing had the highest NrSI of 307 kg N ha$^{-1}$ y$^{-1}$ due to its relatively small cropland area (the least among the five provinces) but high proportion of vegetable area (~17% of the total planting area in Beijing). Tianjin had the lowest NrSI of 185 kg N ha$^{-1}$ y$^{-1}$. Hebei, Liaoning, and Shandong had similar cropland NrSI (206, 229 and 234 kg N ha$^{-1}$ y$^{-1}$ respectively). Compared to the provincial level, the cropland NrSI of 429 counties varied greatly, ranging from 28 kg N ha$^{-1}$ y$^{-1}$ to 4782 kg N ha$^{-1}$ y$^{-1}$ (figure 2). Based on a national analysis, Wang et al. (2018) grouped all counties in China into four groups based on the average per area Nr losses, and defined the top 25% as the hotspots, corresponding to a critical value of 96 kg N ha$^{-1}$ y$^{-1}$. Their results showed that the Nr hotspots contributed to 52% of the national Nr losses with only 9% of the total area in China in 2012. The BR was part of the 9%. Based on this critical value, more than 360 counties, accounting for 84% of the croplands in the BR, were categorized as hotspot of Nr losses. Such a high NrSI in the BR has caused serious environmental pollution, including haze events (Ma et al. 2014, Miao and Liu 2019), surface- and ground-water nitrate contamination (Gu et al. 2013), and high eutrophication potential for the Bohai Sea. Note that Nr losses via surface runoff were not taken into account in this study, which may underestimate the cropland NrSI in the BR.

NH$_3$ volatilization and nitrate leaching were the two major Nr loss pathways from cropland in the BR. Beijing and Shandong province suffered more serious NH$_3$ pollution with mean emission intensities of 151 kg N ha$^{-1}$ y$^{-1}$ and 140 kg N ha$^{-1}$ y$^{-1}$ from cropland (figures 3(a) and 3(c)). The NH$_3$
emission is significantly correlated to the application rate of synthetic N fertilizer and manure ($r = 0.93$, $p < 0.01$). Volatilized NH$_3$ from fertilizers produces a substantial loss of N available for crops, causes economic losses to farmers, and poses detrimental impacts on air quality by the formation of fine particulate matter (PM$_{2.5}$) in the atmosphere (Galloway et al 2008, Sanz-Cobena et al 2014). Beijing and Liaoning province had relatively higher nitrate leaching intensities of 147 kg N ha$^{-1}$ y$^{-1}$ and 130 kg N ha$^{-1}$ y$^{-1}$, respectively (figures 3(b) and 3(d)). Croplands in these regions may lead to a high risk to water body contamination (e.g. Liaohe River watershed and coastal areas in south Liaoning province, Chaobaihe River watershed in Hebei province, and Xiaoqinghe River watershed in Shandong province), which should be prioritized for mitigation of nitrate leaching and control of non-point source pollution through both technical and policy approaches. Significant variations in cropland NrSI among counties in the BR were primarily associated with varieties in crops, cropland areas, and the NrSI of different cropping systems analyzed in the following section.

3.3. NrSI of different cropping systems

Altogether 29 types of cropping systems in the BR were analyzed in this study, including 16 mono cropping (figure 4(a)), 10 double cropping (figure 4(b)) and 3 triple cropping systems (figure 4(c)). Large variations in NrSI were found among different cropping systems. For the 16 mono cropping systems, vegetables had the highest NrSI of 355 kg N ha$^{-1}$ y$^{-1}$, and sugarcane had the lowest NrSI of 41 kg N ha$^{-1}$ y$^{-1}$ with the other cropping systems' NrSI ranged from 58 kg N ha$^{-1}$ y$^{-1}$ to 198 kg N ha$^{-1}$ y$^{-1}$ (figure 4(a)). Among the 10 double cropping systems, winter wheat-vegetable cropping system showed the highest NrSI of 554 kg N ha$^{-1}$ y$^{-1}$, while oat-rice cropping system presented the lowest NrSI of 52 kg N ha$^{-1}$ y$^{-1}$, and the rest ranged between 58 kg N ha$^{-1}$ y$^{-1}$ and 213 kg N ha$^{-1}$ y$^{-1}$ (figure 4(b)). For the three triple cropping systems, the NrSI of vegetable-vegetable-vegetable, potato-vegetable-vegetable, and rice-rice-vegetable cropping systems were 1024 kg N ha$^{-1}$ y$^{-1}$, 484 kg N ha$^{-1}$ y$^{-1}$ and 706 kg N ha$^{-1}$ y$^{-1}$, respectively (figure 4(c)). Comparable results of the NH$_3$ volatilization, nitrate leaching, and N$_2$O emission...
were found between our study and other published observations for major cropping systems in the BR except the N$_2$O emissions from spring maize cropping system (table 2). An exponential relationship between fertilizer N rate and N$_2$O emission, especially in cereal cropping systems, was reported by Shcherbak et al (2014), which indicates the higher fertilizer N application rate may lead to a larger N$_2$O emission from spring maize cropping system in the BR. Since there are significant differences across sites or years in Nr losses from a particular cropping system (table 2), this integration approach is able to provide an overall picture of Nr losses induced by various cropping systems simultaneously on regional level.

For all cropping systems, NH$_3$ volatilization and nitrate leaching dominated the Nr losses during crop production. Their contribution to the total on-farm Nr losses ranged from 62% to 99%. Except the over-use of fertilizers, the high level of NH$_3$ volatilization is...
### Table 2. Comparison of N inputs into and Nr losses from major cropping systems in the BR between our study and other published observations.

| Year | Region                | Cropping system               | N input (kg N ha\(^{-1}\) y\(^{-1}\)) | Nr loss intensity (kg N ha\(^{-1}\) y\(^{-1}\)) | NH\(_3\) volatilization | Nitrate leaching | N\(_2\)O emission | Studies          |
|------|-----------------------|--------------------------------|---------------------------------------|-----------------------------------------------|-------------------------|------------------|------------------|------------------|
| 2008 | The BR                | Winter wheat-summer maize     | 607                                   | 139.1                                         | 59.2                    | 3.5              |                  | This study       |
|      |                       | Vegetable-vegetable-vegetable | 1404                                  | 639.6                                         | 356.9                   | 13.8             |                  |                  |
|      |                       | Vegetables                    | 536                                   | 161.3                                         | 168.4                   | 10.3             |                  |                  |
|      |                       | Spring maize                  | 354                                   | 72.3                                          | 105.4                   | 10.7             |                  |                  |
| 2000s| Northern China Plain  | Winter wheat-summer maize     | 545                                   | 120                                           | 136                     | 16\(^a\)         |                  | Zhao et al 2009  |
| 2003–2004| Hebei             | Winter wheat-summer maize     | 368–968                               | 11–145                                        |                         |                  |                  | Li et al 2007    |
| 2008–2009| Shandong          | Winter wheat-summer maize     | 600                                   | 21.4–60.2                                     |                         |                  |                  | Cui et al 2012   |
| 2010–2013| Beijing           | Winter wheat-summer maize     | 560                                   | 6.5–51.8                                      | 16.3–77.2               | 2.02             |                  | Huang et al 2017 |
| 2012 | Shandong             | Summer maize                  | 100–200                               |                                               |                         |                  |                  |                  |
| 2012 | Beijing              | Summer maize                  | 216                                   |                                               |                         |                  |                  | Jia et al 2014   |
| 2012–2013| Beijing           | Summer maize                  | 300                                   |                                               |                         |                  |                  | Yan et al 2014b  |
| 2012–2013| Beijing           | Summer maize                  | 270                                   |                                               |                         |                  |                  | Li et al 2017a   |
| 2009 | Liaoning             | Spring maize                  | 270                                   |                                               |                         |                  |                  | Yang et al 2014  |
| 2010 | Liaoning             | Spring maize                  | 270                                   |                                               |                         |                  |                  | Li et al 2012    |
| 2010 | Liaoning             | Spring maize                  | 265                                   |                                               |                         |                  |                  | Yang et al 2014  |
| 2011–2012| Liaoning          | Spring maize                  | 229                                   |                                               |                         |                  |                  | Xu et al 2014    |
| 2005 | Shandong             | Vegetable                     | 493–1316                              |                                               |                         |                  |                  | Song et al 2009  |
| 2004 | Shandong             | Tomato                        | 870                                   |                                               |                         |                  |                  | He et al 2009    |
| 2005 | Shandong             | Tomato                        | 630                                   |                                               |                         |                  |                  |                  |
| 2009 | Beijing             | Romanesco broccoli            | 820                                   |                                               |                         |                  |                  | Guo et al 2012a  |
| 2009 | Shandong             | Onion                         | 466                                   |                                               |                         |                  |                  | Yao et al 2017   |
| 2010 | Shandong             | Onion                         | 487                                   |                                               |                         |                  |                  |                  |
| 2010–2011| Shandong           | Tomato                        | 895                                   |                                               |                         |                  |                  | Fan et al 2014   |
| 2010 | Hebei                | Tomato                        | 410                                   |                                               |                         |                  |                  | Guo et al 2012c  |
| 2012 | Beijing             | Cabbage-celery                | 703.5                                 |                                               |                         |                  |                  | Yan et al 2014b  |
| 2012 | Beijing             | Cucumber                      | 703.5                                 |                                               |                         |                  |                  |                  |
| 2017 | Hebei                | Tomato/cucumber-cabbage       | 390–780                               |                                               |                         |                  |                  | Zheng et al 2018 |

\(^a\)This value represents the total N loss through denitrification  
\(^b\)This value is the N losses through all pathways
also caused by the wide use of urea in China (accounting for over 50% of the total N fertilizer consumption) and the surface broadcasting of NH₃-based fertilizers without soil covering (Li et al. 2015). Among all the cropping systems, rice-based cropping systems, such as rice mono system and oat-rice rotations, showed relatively higher proportion of N losses via N₂O emission due to alternate anaerobic and aerobic cycling that could considerably enhance N₂O emission compared to constant aerobic and anaerobic conditions (Smith and Patrick 1983) as frequent dryness of the rice paddy after the first mid-season aeration is a widely adopted practice for rice cultivation in China (Cai et al. 1997).

The cropping systems involved with vegetable production had a relatively higher NrSI, primarily due to the continuous over-fertilization and shallow root system (Chen et al. 2004, Ju et al. 2004, Xiong et al. 2006). For example, the average synthetic N fertilizer inputs for vegetable mono-cropping in 116 counties and triple-vegetable cropping in 225 counties were 402 kg N ha⁻¹ y⁻¹ and 1241 kg N ha⁻¹ y⁻¹ in 2008. In contrast, the average synthetic N fertilizer input was only 100 kg N ha⁻¹ y⁻¹ for sugarcane, 90 kg N ha⁻¹ y⁻¹ for oat and 70 kg N ha⁻¹ y⁻¹ for flax mono-cropping systems. Considerable N was accumulated in the soil after the continuous over-fertilization, which could easily result in nitrate leaching, especially for vegetables with a shallow root system (FAO 2006). The NrSI of various cropping systems could help identify systems with particularly high N losses, thus providing opportunities for future sustainable agricultural production by adjusting and optimizing the temporal and spatial layout for different cropping systems.

3.4. Sources of uncertainty

Uncertainties in our analysis mainly originate from the quality of input data (Li et al. 2017a). Although the county-level datasets were highly reliable, the assumption of homogeneous soil properties and climate conditions will inevitably introduce uncertainties to some extent. In addition, the simplification of parameters, such as the ratios of crop residue returning and animal excreta utilized as manure, and the limited data on farming practices obtained through field surveys, might also result in potential uncertainties. Since the study area is flat overall, we did not consider surface runoff in the regional modeling, leading to an underestimation of Nr losses. However, treating the soil as a series of discrete horizontal layers and assuming some soil properties uniform within each layer/across all layers (0–50 cm soil profile), the DNDC model may overestimate nitrate leaching (2014). Future improvement of the DNDC model with fine input data and more field observations for model validation would benefit the application of this integration method for Nr hotspots assessment to other regions.

3.5. Significance and future application of the integrated approach

Integrating the DNDC model and the NrSI framework is a novel step forward for identifying Nr hotspots. Since the NrSI framework has been proposed to quantify the environmental burdens of Nr losses (Liang et al. 2018), its application is mainly limited by the development of VNFs for agricultural products. VNFs play an important role to accurately assess the Nr losses associated with crop production. Currently, however, few countries have developed their own VNFs (Shibata et al. 2017). The integration of the DNDC model resolves this problem as it can track soil N dynamics, N gas fluxes and nitrate leaching across crops and their rotation regimes. Meanwhile, with the consideration of local soil properties, meteorological conditions and conventional farming practices (Li 2009), it can more accurately estimate Nr losses and differentiate their multiple pathways from local to regional scale. This integrated N assessment method, therefore, provides a more comprehensive estimation of N balance, Nr losses and the NrSI associated with crop production on multiple levels (e.g. county, provincial, and regional), across various cropping systems and via different Nr loss pathways (i.e. NH₃ volatilization, nitrate leaching, N₂O and NO emissions). The DNDC model has been applied and expanded by researchers worldwide in a range of countries and cropping systems (Giltrap et al. 2010, Li et al. 2017a). The comprehensive database of 62 crops and 12 soil types embedded in the DNDC model (Li et al. 2017a) enables the application of this integrated N assessment method at a wide range of regions and cropping systems in the future.

4. Conclusion

This study develops a new approach by integrating the DNDC model and the NrSI framework to identify hotspots of Nr losses induced by various cropping systems and through different pathways on regional scale. We illustrate the approach with a case study of the BR, China. The analysis provides a comprehensive estimation of N balance, Nr losses and the NrSI associated with crop production on multiple levels (i.e. county, provincial and regional), across various cropping systems (i.e. mono, double and triple cropping) and via different Nr loss pathways (i.e. NH₃ volatilization, nitrate leaching, N₂O and NO emissions) in the BR. The application of this integrated N assessment method could be used to identify areas and/or cropping systems with particularly high Nr losses and NrSI to provide basic information for setting Nr mitigation priorities on a wide range of regions and cropping systems.
Acknowledgments

This research was supported by the National Key Research and Development Program of China (2017YFF0211700, 2016YFD0201204, 2017YFD0201801 and 2016YFF0101100), the Australia-China Joint Research Centre—Healthy soils for sustainable food production and environmental quality (ACSRF48165) and the China Scholarship Council (CSC).

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

ORCID iDs

Qingmei Wang https://orcid.org/0000-0002-9045-8749
Xia Liang https://orcid.org/0000-0001-6494-4885
Deli Chen https://orcid.org/0000-0001-6767-1376

References

Behera S N, Sharma M, Anuja V P and Balasubramanian R 2013 Ammonia in the atmosphere: A review on emission sources, atmospheric chemistry and deposition on terrestrial bodies Environ. Sci. Pollut. Res. 20 8092–131
Bodirsky B L et al 2014 Reactive nitrogen requirements to feed the world in 2050 and potential to mitigate nitrogen pollution Nat. Commun. 5 3858
Bouwman A F and Batjes N H 2002 Emissions of N2O and NO from fertilised fields: summary of available measurement data Glob. Biogeochem. Cycles 16 1038
Cai J, Xia X, Chen H, Wang T and Zhang H 2018 Decomposition of fertilizer use intensity and its environmental risk in China's grain production process Sustainability 10 498
Cai Z, Xing G, Yan X, Xu H, Tuuruta H, Yagi K and Minami K 1997 Methane and nitrous oxide emissions from rice paddy fields as affected by nitrogen fertilisers and water management Plant Soil 196 7–14
Chen Q, Zhang X, Zhang H, Christie P, Li X, Horlacher D and Liebig H-P 2004 Evaluation of current fertilizer practice and soil fertility in vegetable production in the Beijing region Nutr. Cycling Agroecosyst. 69 51–58
Cai F, Yan G, Zhou Z, Zheng X and Deng J 2012 Annual emissions of nitrous oxide and nitric oxide from a wheat–maize cropping system on a silt loam calcareous soil in the North China Plain Soil Biol. Biochem. 48 10–19
Cai Z et al 2008 Soil nitrate–N levels required for high yield maize production in the North China Plain Nutr. Cycling Agroecosyst. 82 187–96
Erisman J W, Galloway J N, Seitzinger S, Bleeker A, Dise N B, Petretsu A M R, Leach A M and de Vries W 2013 Consequences of human modification of the global nitrogen cycle Philos. Trans. R. Soc. B 368 20130116
Erisman J W, Sutton M A, Galloway J, Klimont Z and and Winjewarter W 2008 How a century of ammonia synthesis changed the world Nat. Geosci. 1 636–9
Fan Z, Liu S, Zhang X, Jiang Z, Yang K, Jian D, Chen Y, Li J, Chen Q and Wang J 2014 Conventional flooding irrigation causes an overuse of nitrogen fertilizer and low nitrogen use efficiency in intensively used solar greenhouse vegetable production Agric. Water Manage. 144 11–19
FAO 2006 Fertilizer and plant nutrition bulletin 16 Food and Agriculture Organization of the United Nations Rome
Galloway J N and Leach A M 2016 Your feet’s too big Nat. Geosci. 9 97–98
Galloway J N, Townsend A R, Erismann J W, Bekunda M, Cai Z, Freney J R, Martinelli L A, Seitzinger S P and Sutton M A 2008 Transformation of the nitrogen cycle: recent trends, questions, and potential solutions Science 320 889–92
Giltrap D L, Li C and Sagar S 2010 DNDC: A process-based model of greenhouse gas fluxes from agricultural soils Agric. Ecosyst. Environ. 136 292–300
Gu B, Ge Y, Chang S X, Luo W and Chang J 2013 Nitrate in groundwater of China: sources and driving forces Glob. Environ. Change 23 1112–21
Gu B, Xu X, Chang J, Ge Y and Vitousek P M 2015 Integrated reactive nitrogen budgets and future trends in China Proc. Natl Acad. Sci. 112 8792–7
Guo H N, Wu J X, Zuo Q, Xue S C, Zou G Y, Gu J L and and Zhang I. 2012a Effect of different fertilizer application countermeasures on yield, quality of Romanesco broccoli and nitrogen balance Northern Hortic. 15 (in Chinese with English abstract) 153–7
Guo L, Yang R and Wang D 2012b A study on the spatial difference of farmland nitrogen nutrient budget in the Bohai Rim region China J. Geogr. Sci. 22 761–8
Guo Y, Li B, Di H, Zhang L and Gao Z 2012c Effects of dicyandiamide (DCD) on nitrate leaching, gaseous emissions of ammonia and nitrous oxide in a greenhouse vegetable production system in northern China Soil Sci. Plant Nutr. 58 647–58
He F, Jiang R, Chen Q, Zhang F and Su F 2009 Nitrous oxide emissions from an intensively managed greenhouse vegetable cropping system in Northern China Environ. Pollut. 157 1666–72
Huang J, Li Q, Huang L, Zhang Z, Mu J and Huang Y 2013 Watershed-scale evaluation for land-based nonpoint source nutrients management in the Bohai Sea Bay, China Ocean Coastal Manage. 71 314–25
Huang T, Ju X and Yang H 2017 Nitrate leaching in a winter wheat-summer maize rotation on a calcareous soil as affected by nitrogen and straw management Sci. Rep. 7 42247
Jia X, Shao L, Liu P, Zhao B, Gu L, Dong S, Bing S H, Zhang J and Zhao B 2014 Effect of different nitrogen and irrigation treatments on yield and nitrate leaching of summer maize (Zea mays L.) under lysimeter conditions Agric. Water Manage. 137 92–103
Ju X T, Kou C L, Zhang F S and Christie P 2006 Nitrogen balance and groundwater nitrate contamination: comparison among three intensive cropping systems on the North China Plain Environ. Pollut. 143 117–25
Ju X, Liu X, Zhang F and Roelcke M 2004 Nitrogen fertilization, soil nitrate accumulation, and policy recommendations in several agricultural regions of China AMBIO J. Hum. Environ. 33 300–5
Lassalleta L, Billen G, Grizzetti B, Anglade J and Garnier J 2014 50 years in nitrogen use efficiency of world cropping systems: the relationship between yield and nitrogen input to cropland Environ. Res. Lett. 9 105011
Leach A M, Galloway J N, Bleeker A, Erismann J W, Kohn R and Kittes J 2012 A nitrogen footprint model to help consumers understand their role in nitrogen losses to the environment Environ. Dev. 1 40–66
Li C S, Farahbakhshazad N, Jaynes D B, Dinnes D L, Salas W and McLaughlin D 2006 Modeling nitrate leaching with a biogeochemical model modified based on observations in a row-crop field in Iowa Ecol. Model. 196 116–30
Li C S et al 2004 Modeling greenhouse gas emissions from rice-based production systems: sensitivity and upscaling Glob. Biogeochem. Cycles 18 GB1043
Li C S 2009 User’s guide for the DNDC model (version 9.3) Report of the Institute for the Study of Earth, Oceans and Space (Durham, NH) University of New Hampshire
Li C, Frolking S and Frolking T A1992a A model of nitrous oxide evolution from soil driven by rainfall events: 1. Model structure and sensitivity J. Geophys. Res. 97 9759–76
Li C, Frolking S and Frolking T A1992b A model of nitrous oxide evolution from soil driven by rainfall events: 2. Model applications J. Geophys. Res. 97 9777–83
Li H, Qiu J, Wang L, Xu M, Liu Z and Wang W2012 Estimates of NOx emissions and mitigation potential from a spring maize field based on DNDC model J. Integr. Agric. 11 2067–78
Li H, Wang L, Li J, Gao M, Zhang J, Zhang J, Qiu J, Deng J, Li C and Frolking S2017a The development of China-DNDC and review of its applications for sustaining Chinese agriculture Ecol. Model. 348 1–13
Li H, Wang L, Qiu J, Li C, Gao M and Gao C2014 Calibration of DNDC model for nitrate leaching from an intensively cultivated region of Northern China Geoderma 223–225 108–18
Li Q, Cui X, Liu X, Roelcke M, Pasga D, Zerullaa W, Wissemeiera A H, Chen X, Goulding K and Zhang F2017b A new urease-inhibiting formulation decreases ammonia volatilization and improves maize nitrogen utilization in North China Plain Sci. Rep. 7 43853
Li Q, Yang A, Wang Z, Roelcke M, Chen X, Zhang F, Pasga D, Zerullaa W, Wissemeera A H and Liu X2015 Effect of a new urease inhibitor on ammonia volatilization and nitrogen utilization in wheat in north and northwest China Field Crop. Res. 175 96–105
Li X, Hu C, Delgado J A, Zhang Y and Ouyang Z2007 Increased nitrogen use efficiencies as a key mitigation alternative to reduce nitrate leaching in North China Plain Agric. Water Manage. 89 137–47
Liang X, Lam S K, Gu B, Galloway J N, Leach A M and Chen D2018 Reactive nitrogen spatial intensity (NrSI): A new indicator for environmental sustainability Glob. Environ. Change 52 101–7
Liu X, Duan L, Mo J, Du E, Shen J, Lu X, Zhang Y, Zhou X, He C and Zhang F2011 Nitrogen deposition and its ecological impact in China: an overview Environ. Pollut. 159 2251–64
Ma L, Guo J, Veltsofo G L, Li Y, Chen Q, Ma W, Oenema O and Zhang F2014 Impacts of urban expansion on nitrogen and phosphorus flows in the food system of Beijing from 1978 to 2008 Glob. Environ. Change 28 192–204
Meng Z-Y, Xu X-B, Wang T, Zhang X-Y, Yu X-L, Wang S-F, Lin W-L, Chen Y-Z, Jiang Y-A and An X-Q2010 Ambient sulfur dioxide, nitrogen dioxide, and ammonia at ten background and rural sites in China during 2007–2008 Atmos. Environ. 44 2625–31
Miao Y and Liu S2019 Linkages between aerosol pollution and planetary boundary layer structure in China Sci. Total Environ. 650 288–96
MOA 2015 Ministry of agriculture. Zero increase action plan on fertilizer nitrogen recovery efficiencies in crop production China Field Crop. Res. 163 10–17
Yan H, Xie L, Guo L, Fan J, Diao T, Lin M, Zhang H and Lin Z2016 High-resolution inventory of ammonia emissions from agricultural fertilizer in China from 1978 to 2008 Atmos. Chem. Phys. 16 1207–18
Xu X, He P, Qiu S, Pampolino M F, Zhao S, Johnston A M and Zhou W2014 Estimating a new approach of fertilizer recommendation across small-holder farms in China Field Crop. Res. 163 10–17
Yan H, Xie L, Guo L, Fan J, Diao T, Lin M, Zhang H and Lin Z2016a Characteristics of nitrous oxide emissions and the affecting factors from vegetable fields on the North China Plain J. Environ. Manage. 144 316–21
Yan X, Ti C, Vitousek P, Chen D, Leip A, Cai Z and Zhu Z2014b Fertilizer nitrogen recovery efficiencies in crop production systems of China with and without consideration of the residual effect of nitrogen Environ. Res. Lett. 9 095002
Yang L, Wang L, Li H, Qiu J and Liu H2014 Impacts of fertilization alternatives and crop straw incorporation on N2O emissions from a spring maize field in northeastern China J. Integr. Agric. 13 881–92
Yao Z, Yan G, Zheng X, Wang R, Liu C and Butterbach-Bahl K2017 Reducing N2O and NO emissions while sustaining crop productivity in a Chinese vegetable–cereal double cropping system Environ. Pollut. 231 929–41
Yu D and Mao H2002 Regional carrying capacity: case studies of Bohai Rim area J. Geogr. Sci. 12 177–85
Zhang X, Davidson E A, Mauzerall D L, Searchinger T D, Dumas P and Shen Y2015 Managing nitrogen for sustainable development Nature 528 51–59
Zhao R, Chen X and Zhang F2009 Nitrogen cycling and balance in winter wheat–summer maize rotation system in Northern China J. Integr. Agric. 8 225–31
Shcherbak I, Millar N and Robertson G P2014 Global metaanalysis of the nonlinear response of soil nitrous oxide (N2O) emissions to fertilizer nitrogen Proc. Natl Acad. Sci. 111 1999–204
Shen J L, Tang A H, Liu X J, Fangmeier A, Goulding K T W and Zhang F2009 High concentrations and dry deposition of reactive nitrogen species at two sites in the North China Plain Environ. Pollut. 157 3106–13
Shihata H et al 2017 Nitrogen footprint: regional realities and options to reduce nitrogen loss to the environment Ambio 46 129–42
Smith C J and Patrick W H Jr 1983 Nitrous oxide emission as affected by alternate anaerobic and aerobic conditions from soil suspensions enriched with (NH4)2SO4 Soil Biol. Biochem. 15 693–7
China Plain Acta Pedologica Sin. 46 684–97 in Chinese with English abstract
Zheng L et al 2018 Impact of fertilization on ammonia volatilization and N2O emissions in an open vege-
table Chin. J. Appl. Ecol. 29 4063–70 in Chinese with English abstract
Zhou F et al 2014 A new high-resolution N2O emission inven-
tory for China in 2008 Environ. Sci. Technol. 48 8538–47